16539
NATIONAL LIBRARY
OTTAWA

BIBLIOTHÈQUE NATIONALE
OTTAWA

NAME OF AUTHOR... LALONDE, Jean-Pierre.....
TITLE OF THESIS... Fluorine and Other Vein Elements as Geochemical
... Indicators of Fluorite Deposits in the Madoc Area, Ontario
.....
UNIVERSITY... Carleton University, Ottawa, K1S 5B6.....
DEGREE FOR WHICH THESIS WAS PRESENTED. M. Sc.
YEAR THIS DEGREE GRANTED... 1973.....

Permission is hereby granted to THE NATIONAL LIBRARY
OF CANADA to microfilm this thesis and to lend or sell copies
of the film.

The author reserves other publication rights, and
neither the thesis nor extensive extracts from it may be
printed or otherwise reproduced without the author's
written permission.

(Signed)... *J.P. Lalonde*

PERMANENT ADDRESS:

.. Apt. 209, 30 De La Verendrye,
.. Hull, Quebec.....
.....

DATED... 31 May 19 73

NL-91 (10-68)

FLUORINE AND OTHER VEIN ELEMENTS
AS GEOCHEMICAL INDICATORS OF
FLUORITE DEPOSITS IN THE MADOC
AREA, ONTARIO

by

JEAN-PIERRE LALONDE, B.Sc. (HONOURS)

A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Master of Science.

Carleton University
Ottawa, Ontario.
March, 1973

The undersigned hereby recommend to the
Faculty of Graduate Studies acceptance of this
thesis, submitted by Jean-Pierre Lalonde, B.Sc.,
in partial fulfilment of the requirements for
the degree of Master of Science.

.....
Supervisor

.....
Chairman of Department

.....

.....

Carleton University

Ottawa, Ontario

April 11, 1973

ABSTRACT

The known fluorite deposits occur in Precambrian marbles and Paleozoic limestones as irregular and discontinuous veins in faults and fractures. The veins contain fluorite, calcite, barite, celestite, and minor amounts of sulphides such as pyrite, marcasite, and sphalerite.

The secondary dispersion of fluorine was studied regionally by sampling 45 soil profiles along two regional traverses, collecting approximately 60 stream sediment, 80 surface water, and 200 ground water samples. Soils were also collected along seven detailed traverses crossing known fluorite veins or their extension. Fluorine was determined by selective ion electrode, Zn by atomic absorption spectrophotometry, and Ba and Sr by X-ray fluorescence.

Most rock types of the Madoc area are fluorine rich and contain between 1000 and 2700 ppm. Several surface water anomalies associated with areas of fluorite occurrence were located and dispersion trains are traceable for several miles. The fluorine content of stream sediments is, however, of limited use in geochemical exploration because of the small contrast between background and anomalous concentrations. The fluorine content of ground waters clearly delineates areas containing known fluorite occurrences as well as other targets of

interest; a positive correlation exists between ground water anomalies and fluorine rich soils along the regional traverses. The lateral dispersion of fluorine in soils overlying subcropping fluorite veins is restricted and, therefore, can be used to pin-point such occurrences. The most favourable soil horizon to sample for all elements studied is the organic A horizon which accentuates the contrast between background and anomalous concentrations. Barium and zinc in soils are also good tracers of fluorite veins; but Sr proved to be ineffective. The water soluble fluorine content of the A soil horizon can be used as an inexpensive field test.

Geochemical exploration methods proved useful to re-evaluate the potential of the area and can help locate new deposits. The dispersion of fluorine in ground waters, soils, and vegetation requires careful examination from an environmental viewpoint.

ACKNOWLEDGEMENT

The author wishes to express his sincere appreciation to Dr. W.M. Tupper and to Dr. R.W. Boyle of the Geological Survey of Canada for their council and support throughout the project. The co-operation of Bondar-Clegg and Co. Ltd. who initially made available their analytical instrumentation for fluorine analysis and of the Geological Survey of Canada for providing analytical instrumentation is greatfully acknowledged. Financial support was obtained from N.R.C. grant No. 2056-28 and the Geological Survey of Canada. Special thanks are extended to my wife, Ginette, for her patience and assistance, to Calvin Murray, technologist at Carleton University, particularly for his help with the zinc analyses, and to Dr. D. Watkinson, Dr. R. Garrett, Dr. I. Jonasson, Mr. E.H. Hornbrook, Mr. C.C. Durham, and Mr. J. Lynch for having read and commented on parts of this thesis.

TABLE OF CONTENTS

ABSTRACT	iii
ACKNOWLEDGEMENTS	v
INTRODUCTION	1
FIELD AREA	3
Location and roads	3
Climate	3
Topography	3
Drainage	6
Soils	6
GEOLOGICAL SETTING	9
Rock types	9
Structure	11
Fluorite deposits	12
Vein mineralogy	14
Origin of deposits	15
Production of fluorspar	17
FIELD WORK	18
ANALYTICAL METHODS	19
PRIMARY GEOCHEMICAL DISPERSION	21
Objective	21
Results and discussion	21
SECONDARY GEOCHEMICAL DISPERSION	24
1. Surface waters	24
Objective	24
Background	24
Methods	25
Results and discussion	25
2. Stream sediments	33
Objective	33
Method	34
Results and discussion	34
3. Ground waters	45
Objective	45
Method	46
Results and discussion	47
4. Regional soil traverses	60
Objective	60
Method	60
Results and discussion	61
(1) Regional traverse A	61
(2) Regional traverse B	63

5.	Detailed soil traverses	64
	Objective	64
	Method	66
	(1) Noyes traverse	66
	description	66
	results and discussion	67
	(2) McBeath traverse	69
	description	69
	results and discussion	69
	(3) Bailey traverse	71
	description	71
	results and discussion	71
	(4) Blakely traverse	73
	description	73
	results and discussion	73
	(5) Lee traverse	75
	description	75
	results and discussion	75
	(6) Ponton traverse	77
	description	77
	results and discussion	77
6.	Water soluble soil fluorine	80
	Objective	80
	Method	80
	Results and discussion	81
7.	General results and discussion of soil surveys	85
	SUMMARY AND CONCLUSIONS	93
	APPENDICES	
A	FLUORSPAR AN IMPORTANT SOURCE OF FLUORINE	99
	Uses of fluorite	99
	Supply and demand	102
B	GEOCHEMISTRY OF FLUORINE	107
	Rocks	107
	Water	110
	Sediments	116
	Soils	117
	Biogeochemistry	122
C	INSTRUMENTATION AND ANALYTICAL METHODS	126
	DETERMINATION OF FLUORINE	126
	Instrumentation	126
	Theory	126
	Interferences	128
	Operational limits	129
	Problems	132

Determination of fluorine	
in waters	133
Equipment	133
Solutions	133
Preparation of standards . . .	135
Method	136
Discussion	136
Determination of fluorine in	
soils and sediments	138
Equipment	138
Reagents and solutions	138
Preparation of standards . . .	138
Method	139
Discussion	140
DETERMINATION OF pH	143
Equipment	143
Method	143
Discussion	144
DETERMINATION OF ZINC	144
Equipment	145
Method	145
Discussion	146
DETERMINATION OF BARIUM AND STRONTIUM .	146
REFERENCES	149

LIST OF FIGURES

1	Location map of the field area	5
2	Frequency distribution of fluorine in the surface waters of the Madoc area	27
3	Plot of the pH against the fluorine content of surface waters	27
4	Fluorine concentration in Jarvis Lake and immediate area	32
5	Frequency distribution of fluorine in stream sediments	35
6	Plot of the fluorine content of stream waters against the fluorine content of both populations of stream sediments	37
7	Frequency distribution of zinc in stream sediments	38
8	Plot of the fluorine content of stream sediments of different compositions against the pH of stream waters	40
9	Plot of the zinc content of stream sediments of different compositions against the pH of stream waters	41
10	Plot of the fluorine against the zinc content of stream sediments treated as two populations	42
11	Fluorine content of ground waters along the northern regional traverse	48
12	Fluorine content of ground waters along the southern regional traverse	49
13	Frequency distribution of fluorine in ground waters.	50
14	Frequency distribution of fluorine in ground waters from areas underlain by different rock types	52
15	Plot of the pH against the fluorine content of ground waters from areas underlain by limestone	54

16	Regional soil traverses	(in pocket)
17	Fluorite occurrences in the Madoc area and the location of detailed soil traverses . . .	65
18	Noyes and McBeath detailed traverses	(in pocket)
19A	Fluorine content of soils along the Bailey traverse	72
B	Zinc content of the B horizon along the Bailey traverse	72
20	Fluorine content of A horizons along the Blakely traverse	74
21	Fluorine content of the A horizon along the Lee traverse	76
22A	Fluorine content of soils along the Ponton traverse	78
B	Zinc content of the B horizon along the Ponton traverse	78
23A	Fluorine content of the A horizon along the detailed (10 feet interval) Ponton traverse	79
B	Water soluble fluorine in the A horizon along the detailed (10 feet interval) Ponton traverse	79
24	Frequency distribution of fluorine in the A, B, and C horizon of 68 complete soil profiles	86
25	Plot of the arithmetic mean and median values of the fluorine content of waters from deposits in acid magmatic rocks against pH	115
26	Comparison of the fluoride and glass pH electrodes	127
27	Fluoride electrode response in a 1 ppm fluoride standard solution.	131

LIST OF TABLES

1	Mean monthly and annual temperature and precipitation at Tweed averaged over 29 years .	4
2	Table of formations	8
3	Fluorine content of rocks from the Madoc area .	22
4	Fluorine content of various rock types	23
5	Seasonal variation in the fluorine content of surface waters	28
6	Comparison of results obtained in this survey with those obtained by Wright (1971) at equivalent sample locations	28
7	Water soluble fluorine and its percentage of the total soil fluorine	82
8	Comparison of fluorine soluble in buffered and non-buffered solutions and the reproducibility of water leaches	83
9	Fluorine content of different soil size fractions	89
10	Zinc content of different soil horizons . . .	90
11	Types of fluorspar and uses	101
12	World production of fluorspar by countries .	104
13	Fluorine content of crustal rocks	109
14	The solubility of fluorite in pure water according to various authors	113
15	Fluorine content of soils	118
16	Adsorption of fluoride by minerals, aluminum hydroxide, and soils	120
17	Fluorine content of replicate surface water samples related to the time of buffering . .	137
18	Analytical reproducibility and verification of the effect of the "in-erucible" residence time of sample solutions on reproducibility .	141

19	Reproducibility of zinc analyses	147
20	Reproducibility of Ba and Sr analyses by XRF	148

LIST OF MAPS
in pocket

- 1 Geological map of the Madoc area.
- 2 Fluorine in surface waters and fluorine and zinc in stream sediments.
- 3 Fluorine in ground waters.

INTRODUCTION

The industrial importance of fluorite in recent years has increased considerably, and this trend is expected to continue.* Total world reserves in 1971 were insufficient to supply the world's demand until the turn of the century (Readling, 1970; Cote, 1972). Therefore, it is important to locate new fluorite deposits and geochemical exploration methods could prove useful.

Limited research has been done to investigate the possibilities of using fluorine as a tracer of fluorite or other fluorite bearing deposits such as barite, tin, lead-zinc, and tungsten. A study of fluorine dispersion aureoles in soils over fluorite veins in the Kentucky-Illinois mining district indicated that the fluorine content was generally less than 1.5 times background (Nackowski, 1952). Nackowski concluded that fluorine was unsuitable as an indicator, and that Pb and Zn were more useful guides. Hawkes and Webb (1962) suggest that fluorine may be a useful indicator of fluorite deposits but not a pathfinder element for Pb-Zn deposits. These early results, combined with analytical problems, were sufficient to retard research on the use of fluorine as a geochemical guide to fluorite and related types of deposits.

* A summary of the uses and economics of the mineral commodity can be found in Appendix A.

The recent development of the fluoride selective ion electrode has greatly simplified fluorine analyses (Frant and Ross, 1966; Edmund, 1969; Ficklin, 1970). It was decided, therefore, to re-investigate the practicality of geochemical exploration methods using fluorine as a tracer of fluorite occurrences. The Madoc area of southeastern Ontario was selected for this study. This area contains fluorite-barite veins which were mined until 1960.

The objectives of this thesis are: to determine the dispersion of fluorine in surface and ground waters, stream sediments, and soils in the vicinity of fluorite deposits; to investigate and compare the dispersion of other vein elements such as Ba, Sr, and Zn in these soils; and to establish the feasibility of locating fluorite-barite veins by means of geochemical exploration methods. The study could also be useful in reappraising the potential of the Madoc fluorite mining area.

Because no satisfactory review paper was available on the geochemistry of fluorine oriented towards geochemical exploration, the pertinent literature up to October of 1972 was reviewed and is summarized in Appendix 3.

FIELD AREA

Location and roads

The field area, covering approximately 200 square miles, is located within a 10 mile radius of the town of Madoc in Hastings county of south-central Ontario (Figure 1). Most of the area is settled and is accessible by concession roads running in an east-west and north-south direction at one mile intervals. Three paved highways trend in a north-south direction. Highway 7, which passes immediately north of Madoc in an east-west direction, links Ottawa and Peterborough.

Climate

The regional climate is an important environmental factor affecting the mobilization of elements. The climate is temperate, the average temperature for the year being 44°F (Table 1). Precipitation over a period of 29 years averages between 32 to 35 inches (Gillespie, Wicklund, and Richards; 1962). The area is free of frost for approximately 130 days each year.

Topography

The Precambrian-Paleozoic contact that passes along the south side of Moira Lake divides the area into two parts. South of the lake, the terrain which is underlain by flat-lying Paleozoic limestone is flat to gently

Table 1: Mean monthly and annual temperature and precipitation at Tweed averaged over 29 years. (Gillespie, Wicklund and Richards, 1962)

	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Yearly
Mean Temp. (°F)	15	17	29	42	55	65	69	67	59	47	38	21	44
Mean Prec. (inches)	3.12	2.20	3.25	2.30	3.23	2.71	3.26	2.19	3.31	2.73	3.32	2.92	34.5

Figure 1: Location map of the field area.

rolling (see topography on maps in pocket). Local relief rarely exceeds 50 feet except along the south shore of Moira Lake and the Moira River valley. Directly north of the lake, the area is underlain by Paleozoic limestone and Precambrian marble and the topography is similar to that in the south. Precambrian granite and metavolcanic rocks underlie the area of rolling topography to the northwest and the mean elevation increases gradually from Madoc towards Malone. The surface expression of the metavolcanic rocks in the northeastern corner of the field area is also a rolling topography.

Drainage

The Madoc region is drained by the Moira River and its tributaries, the Skootamata and Black Rivers, which flow towards Lake Ontario. Moira Lake is the largest body of water, but a few other small lakes (approximately 10, none of which exceeds one mile in length) are present.

The drainage systems over the flat-lying limestone to the south are poorly developed and are interrupted by extensive swamps. Over the Precambrian rocks, streams are better developed.

Soils

The soils of Hastings County were studied by Gillespie, Wicklund and Richards (1962). They were classified into three great soil groups. Slightly

alkaline brown forest soils developed on glacial till predominate over the flat-lying limestone south of Highway 7 whereas acidic to neutral podzols developed on till are the most important soil type covering the Precambrian rocks. Organic soils occur in the numerous swamps distributed throughout the field area.

Table 2: Table of Formations

Cenozoic

Pleistocene: sand, gravel, clay, till

Great Unconformity

Paleozoic

Ordovician:	Trenton group	predominantly limestone
	Black River group	

Great Unconformity

Precambrian

Granite, syenite

Intrusive Contact

Marble, argillite, conglomerate

Mafic and felsic metavolcanic rocks

GEOLOGICAL SETTING

Rock types

The geology of the area has been studied by Wilson (1939) and Hewitt (1964 and 1968). A geological map of the Kingston area, compiled by MacDonald (1970), was used as the principal reference for the general geology because it is the only available map which covers all the field area.

The oldest rocks are the Precambrian Tudor mafic metavolcanics which lie in the northeastern corner of the area (see Table 2 and Map 1 in pocket). They are intruded on the east by the Elzevir granite and are overlain on the west by metasedimentary rocks which consist predominantly of marble. Northwest of the town of Madoc, the Madoc metavolcanics occupy an area of several square miles. They are predominantly black, grey-green, or pink and the most common facies consist of pillowed, massive, vesicular, and amygdaloidal lava, and agglomerate. A series of rhyolitic and felsic metavolcanic rocks locally overlies the mafic metavolcanic.

Precambrian metasediments consisting of undifferentiated marble, calcitic marble, and lime-silicate rocks overlie the metavolcanic rocks. Pelitic rocks, argillite, schist, and conglomerate locally lie between the metavolcanic rocks and marble.

Two granitic plutons of Precambrian age intrude the metamorphosed basement rocks. These are the Deloro

granite which lies northwest of Madoc and the Moira granite which extends east of Moira Lake.

The Deloro granite is overlain on the east by Paleozoic limestone, on the west by marble and pelitic rocks, and on the north and south by marble. The pluton is differentiated into three phases (Saha, 1959). The principal phase consists of a pink, medium to coarse grained granite. A syenite phase extends along the western margin of the pluton, while to the northeast of Jarvis Lake is a body of fine to medium grained, pink granophyric granite about 2.5 miles long by 1.5 miles wide. This granite contains fluorite as a minor accessory mineral. An average modal analysis of seven specimens of granophyric granite by Saha (1959) revealed that accessory muscovite, fluorite, and zircon compose no more than 0.5% of the rock.

The Moira granite is composed largely of albite and quartz as well as minor microcline. No accessory fluorite has been noted in this granite. The Noyes granite located south of Moira Lake has a similar composition and is probably an extension of the Moira granite.

The youngest rocks in the area belong to the flat-lying Black River and Trenton sedimentary Groups of Ordovician age and consist predominantly of limestone and argillaceous limestone. Minor occurrences of Trenton limestone locally overlie the Black River limestone to the south. The basal member of the Black River Group

consists of a reddish or chocolate-brown arkose which is overlain in some places by a cryptocrystalline to medium crystalline, "chocolate-brown" limestone. The Black River Formation of the Black River Group which predominates in the south overlies these members. This formation consists of a variably fossiliferous, cryptocrystalline to fine crystalline, medium to thick bedded, medium grey limestone.

The area was glaciated during Pleistocene time as witnessed by glacial deposits such as boulder moraines, kame moraines, eskers, and drumlin fields. The glaciers moved towards the southwest. Following glaciation, much of the area was inundated by a glacial lake approximately to the present elevation of 600 feet. This explains the occurrence of clay deposits below this elevation.

Structure

The principal structures of interest are a series of northwest trending faults that cut both the Precambrian and Paleozoic rocks. These contain the known fluorite veins.

The Moira fault trends northwesterly through the center of the field area. It is a nearly vertical and slightly sinuous fracture zone which has little surface expression except at its southeastern end. It has been traced for about 8 miles extending from immediately south of Highway 7 into lots 2 and 3 of concession VIII in Hungerford Township. The fault is either represented by a single break or by a zone of closely spaced narrow

fractures. A number of linear topographic features (e.g. the unusually straight arms along the Moira River) suggest the possible existence of other fault systems.

Fluorite deposits

Fluorite occurs in many different geological settings probably because it can be precipitated under a variety of different pressure-temperature conditions. Although commercial deposits are somewhat restricted in their geological occurrence, they occur in a variety of environments such as residual deposits (e.g. above veins in the Rosiclare district of southern Illinois), low temperature vein deposits in fracture or shear zones (e.g. Kentucky-Illinois district; Madoc, Ontario; Burin peninsula, Newfoundland), in collapse breccias and breccia pipes, as high temperature bedding replacements (e.g. central Mexico, Cave-in Rock area of southern Illinois), and as emplacements in intrusive contact zones. The most important deposits in North America have been of the vein type.

The fluorite deposits of the Madoc area, the Burin Peninsula, and the Kentucky-Illinois district have some marked geological similarities in their host rocks, shape of deposits, mineralogical composition, and banded texture. There are, however, some differences; those at Madoc and in the Kentucky-Illinois district occur mainly in limestone whereas the fluorite veins in Newfoundland occur in granite.

Fluorite veins at Madoc occur as fracture fillings along a northwest trending fault zone in rocks of Precambrian and Paleozoic age (Wilson, 1929; Guillet, 1964; Hewitt, 1968). Out of a total of 30 known fluorite occurrences in this area, 17 occur in the Black River limestone, 10 in marble, 2 in granite, and 1 occurs in both limestone and metavolcanics. If the importance of the wallrocks relative to the size of the known deposits is assessed, the order changes with marble being the most important, followed by granite, limestone, and metavolcanic rocks.

The fluorite deposits can be divided into two groups. Those occurring along the Moira fault, are referred to as the Moira Lake group (see Map 1 in pocket). These deposits occupy lenticular fault cavities that resulted from the horizontal displacement of undulating fault walls. Prospecting and drilling along the Moira fault revealed several deposits. Some fluorite lenses in the Moira Lake group vary up to 18 feet in width.

The Lee-Miller group includes all fluorite veins occurring in subsidiary fractures west and predominantly northwest of the Moira fault. These veins occupy narrow, isolated, vertical fissures mostly in Black River limestone. They occur either as connected or disconnected "en échelon" lenses and their mineralogy is similar to that of the Moira Lake group. Although some veins extend for several hundred feet, their width generally does not exceed three feet.

The cluster of Lee-Miller veins to the northwest of the Moira fault may represent the displaced northern extension of the Moira fault. However, this hypothesis is probably incorrect since the distribution of fluorine in ground waters, as we shall see later, indicates that the Lee-Miller group extends southwards, parallel to the Moira Lake group.

Almost all subsidiary deposits occur west of the Moira fault except for the Hill occurrence and a few small occurrences on lot 11, concession XIV of Huntington Township. One of the rare occurrences having a north-eastern trend is the Hill occurrence, located immediately southwest of Madoc (see Figure 17 on page 65).

Vein mineralogy

The vein material consists of fluorite, calcite, and barite with minor celestite, quartz, marcasite, pyrite, sphalerite, and bituminous material. As in many vein fluorite deposits, there is no consistent paragenesis. The banded distribution of fluorite, calcite, and barite indicates rhythmic deposition. Sulphides, celestite, and quartz tend to be more abundant in zones near the walls.

The fluorite is colourless, amber, or green, and cubic as well as octahedral crystals are common. The average mineral composition of the veins is summarized by Guillet (1964) as follows:

Composition of the vein-material is extremely variable, but run-of-mine averages indicate a fluorite content between 50 and 75 percent. Calcite is the next most common mineral often

approaching 50 percent of the ore but normally averaging perhaps 25 percent. Calcite tends to increase both with depth and with narrowing vein width at the Howard, Keene, and Bailey mines (see Figure 17 on page 65). Barite is present in amounts from 5 to 40 percent but averages perhaps 15 percent. Barite increases markedly to the south constituting perhaps one-third of the vein-material in the Noyes, Howard, and Johnston deposits; it is common also in small isolated occurrences along the Moira River, south of the main group of Lee-Miller deposits. The amount of celestite, quartz, and sulphide minerals rarely exceeds 5 percent in total.

Origin of deposits

The source and nature of the solutions from which the fluorite precipitated is debatable. The lack of evidence of post-Ordovician magmatic activity suggests that transport and deposition from magmatic hydrothermal solutions is improbable, although an igneous body such as a carbonatite or a granite may have formed at depth and liberated fluorine rich solutions which mixed with ground waters.

The transport and deposition of fluorine from low temperature (100°C to 150°C) meteoric waters or connate brines seems more probable (Durham, 1966 & 1970; Jackson and Beales, 1967; Brown, 1967; Tooms, 1970; and Heyl, 1969). Fluorine may have been concentrated in warm connate brines undersaturated with respect to carbonic acid. The Salton Sea brines which are 15 times richer in fluorine

than sea water and contain only 1/5 of the carbonic acid are a good example of such brines (White, 1968). The post depositional faulting and fracturing of the sedimentary rocks in the Madoc area could have provided convenient escape routes for connate brines from nearby sedimentary rocks as well as sites where changes in the physical and chemical parameters caused the precipitation of vein material.

The Madoc fluorite occurrences have several features in common with the Mississippi Valley fluorite deposits of Kentucky-Illinois. These are:

- (a) The fluorite veins occur in faults and fractures predominantly in carbonate rocks.
- (b) The major mineral associations are comparable. Iron and zinc sulphides are common in both areas but galena is rare at Madoc.
- (c) The ores are poor in precious metals.
- (d) The ores are coarsely crystalline in cavities.
- (e) There is no evidence of metamorphism or important alteration. At Madoc, the vein contacts are sharp and the only evidence of alteration is a thin bleached zone in the granite wallrock at the Noyes mine.
- (f) Igneous activity is apparently lacking in both areas although cryptovolcanic structures in the Kentucky-Illinois district make it impossible to completely disregard a contribution from magmatic solutions.

- (g) Bituminous vein material is common in both areas.
- (h) Both areas occur at the edge of basins.

Production of fluorspar

Fluorite veins were mined intermittently in the Madoc area between 1905 and 1960 and yielded most of the 122,000 tons of fluorspar concentrates produced to date in Ontario. The fluorite was hand sorted to obtain metallurgical grade fluorspar containing 70 to 75% CaF_2 . Operations were conducted by underground and open pit mining.

Several factors contributed to the cessation of operations. Most of the larger deposits are located near swamps, and hence water problems were encountered in the underground mine workings. The deposits, being relatively small, could not compete with the large stratiform deposits of Mexico and failure to find a very large deposit discouraged mining companies from doing extensive exploration. There is, however, no evidence that such a large deposit does not exist.

FIELD WORK

Field work started in September of 1971. The first samples consisted of 12 surface waters and 21 soil profiles sampled along three detailed traverses. This reconnaissance was followed later in the autumn by the collection of surface water and stream sediment samples over a broader area and additional soil samples from a number of profiles along traverses.

A few soil samples were collected away from known fluorite veins to obtain regional background contents of fluorine in soils. Using the latter results as a basis, it was decided to sample soil profiles along two twenty mile regional traverses.

Field work was discontinued at the beginning of December of 1971, and resumed again in April of 1972, when ground waters were collected along two regional traverses corresponding as closely as possible to the regional soil traverses. The results from both water traverses prompted a reconnaissance ground water survey to study the regional dispersion of fluorine. The surface water and stream sediment sampling programs were also continued. The regional and detailed soil traverses of the previous autumn were extended, and samples were obtained along additional traverses. When field work was terminated in mid July of 1972, a total of approximately 25 rock samples, 60 stream sediments, 110 surface waters, 200 ground waters, and over 450 soil samples had been collected.

ANALYTICAL METHODS

Geochemical exploration requires that a variety of different sample types (e.g. waters, soils, sediments, etc. ...) be analysed routinely for several elements. It is, therefore, important that the analytical methods be rapid, precise, and inexpensive in order to make geochemical prospecting economical and efficient. Portable analytical instruments and field tests are a major asset.

The quantitative analysis of fluorine in geological materials required until recently a lengthy distillation separation to eliminate interferences followed by a titrimetric or spectrophotometric determination. These methods are reliable but time consuming and are therefore not easily adaptable to geochemical exploration. Following the development of the fluoride selective ion electrode in the late 1960's, a number of researchers (Frant and Ross, 1966; Van Loon, 1968; Hall and Walsh, 1969; Edmond, 1969; and Ficklin, 1970) investigated the possibility of measuring fluorine concentrations in soils and rocks. This led to the development of precise and inexpensive methods that can be used in geochemical exploration.

The mineralogy of the fluorite veins in the Madoc area indicates that F, Ba, Sr, and Zn are the elements most likely to be dispersed in detectable amounts.

Fluorine, was determined by selective ion electrode, Zn by atomic absorption spectrophotometry, and Ba and Sr by x-ray fluorescence.

A description of the fluoride selective ion electrode theory and operational limits as well as a detailed description and discussion of all analytical methods (e.g., for F, Ba, Sr, Zn and pH determinations) used in this thesis can be found in Appendix C.

PRIMARY GEOCHEMICAL DISPERSION

Objective

The investigation of the geochemical dispersion of fluorine in the rock units near Madoc was not an original objective because a student from Queens University in Kingston was to investigate this problem. This project, however, was later abandoned.

Twenty-five rock samples were randomly collected from various rock types, especially the Black River limestone. Because a composite sample of Black River limestone (sample code: BR; Table 3) collected west of Banker Lake had an unusually large fluorine content, it was decided to analyse eight selected representative samples for fluorine to determine background concentrations and to obtain some clues on the possible origin of the Madoc fluorite deposits.

Results and discussion

The fluorine content of selected rock samples is shown in Table 3 and the sample locations are plotted on Map 1 in the pocket. The rocks appear enriched in fluorine when compared with concentrations in similar rocks cited in the literature (Table 4). The fluorine content of Black River limestone ranges from 1060 ppm to 2660 ppm, one order of magnitude greater than the crustal average of 220 ppm for limestone. A fluorine rich marble (sample number 8) which contains pyrite comes

Table 3: Fluorine content of rocks from the Madoc area.

Sample Number ⁺	Rock Name	F ppm	Notes
1	limestone	2660	massive, grey, fossiliferous
2	limestone	2170	massive, grey, fossiliferous
3	limestone	1750	massive, grey
4	limestone	1060	massive, grey
5	limestone	1300	chocolate brown
6	mafic metavolcanic	2200	composite sample
7	breccia	1440	abundant quartz fragments
8	marble	1750	trace of sulfides
BR [*]	limestone	2100	composite sample
Mar [*]	marble	200	composite sample
Noyes [*]	granite	200	fresh granite

⁺ Sample locations are plotted on the geological map

^{*} Unpublished data from Boyle, R.W. (analysed colorimetrically)

from an area not far removed from ground water, stream sediment, and soil fluorine anomalies. A composite sample of Madoc mafic metavolcanic rocks (sample number 6) is rich in fluorine. Further sampling and analyses could indicate the existence of a large fluorine enriched area.

The samples analysed are too few to base adequate conclusions about the nature and origin of the primary dispersion of fluorine in the rocks of the Madoc area. Fluorine enrichment of some of the rocks may have resulted from the deposition of fluorine from the same mineralizing solutions which gave rise to the fluorite deposits. On the other hand, the dispersion may be primary and the fluorine in the deposits could have come from the surrounding rocks such as the Black River limestone after having been mobilized and deposited by either connate brines or meteoric waters.

Table 4: Fluorine content of various rock types (from Fleischer and Robinson, 1963) (see Table 13 in Appendix B).

Rock Name	No. of Samples	F content in ppm	
		range	average
granite and granodiorite	93	20-2700	810
basalt	130	20-1060	360
limestone	98	0-1210	220

SECONDARY GEOCHEMICAL DISPERSION

1. SURFACE WATERS

Objective

The objective of the surface water survey was to determine the concentration and the mobility of fluorine in the regional surface waters in order to assess the usefulness of such surveys in geochemical exploration for fluorite deposits.

Background

The hydrogeochemistry of fluorine in the Madoc area was studied by Wright (1971). The calcium content of waters was found to vary between 10 and 136 ppm and from solubility product calculations, no inhibition of the mobility of fluorine is expected as the result of phosphate and fluorite precipitation. Because of the very low Al^{3+} and Fe^{3+} concentrations in the waters from Madoc, very little complexing may be expected (a conclusion also supported by Daniel R. Boyle who found no complexing in ground waters of the same area - personal communication). Replicate sampling led Wright to the conclusion that seasonal variations in the fluorine content of surface waters were negligible, and that all samples could be considered as one population.

Methods

Samples were collected from streams above their intersection with roads, and from most of the lakes. The sample coverage is better in the northern part of the area where the drainage is better developed. Samples were collected in 250 ml. polyethylene bottles with similar caps. Replicate samples were collected at every tenth sample location. Water temperature and pH readings were taken in the field, and the samples were buffered and analysed for fluorine in the evening. A series of 27 samples collected in the autumn of 1971 yielded high fluorine concentrations in Jarvis Lake, its outlet stream, and in a small lake along the Moira fault, south of Moira Lake. These areas were resampled and the survey extended to cover a larger area in the spring of 1972.

A summary of the hydrogeochemistry of fluorine can be found in Appendix B.

Results and Discussion

Surface waters were collected from 78 different locations (Map 2 in pocket). Eighteen are from lakes, 9 from swamps, and 51 from streams or rivers. The fluorine concentration varied from 60 to 420 ppb, the arithmetic mean ($\bar{x}$) being about 125 ppb (Figure 2). The standard deviation(s)* was calculated to be 45 ppb. If concentrat-

* N.B. The standard deviation may be expressed as:

$$\sqrt{\frac{\sum (\bar{x} - x)^2}{n}}$$

where: $\bar{x}$ is the arithmetic mean
 x is any element of a population
 n is the number of elements
in the population

ions greater than the mean plus three standard deviations are considered anomalous (Hawkes and Webb, 1962; p. 26-31) 260 ppb can be taken with confidence as the upper limit of threshold or the lower limit of anomalous concentrations. In calculating the mean and the standard deviation, all fluorine concentrations above 300 ppb which are part of a second mode of anomalous samples (Figure 2), were ignored.

The choice of 260 ppb as the lower limit of anomalous concentrations provides a minimum contrast of approximately 110% over the regional mean. This contrast could, however, be increased if the regional fluorine content of rainfall was subtracted from all results in order to obtain a more accurate measure of the true amount of fluorine dissolved from the rocks and soils of the area. The positive skew of the principal mode reflects a large number of high background and threshold concentrations as may be expected in an area containing fluorite mineralization.

The pH of 44 surface waters was measured with a portable pH meter (see Appendix C). These surface waters are alkaline and vary in pH from 7.10 to 8.30, the arithmetic mean ($\bar{x}$) being 7.65. A plot of pH against the fluorine concentration (Figure 3) suggests that high and low fluorine concentrations can occur at lower pH. If anomalous fluorine concentrations are ignored, the dispersion diagram is almost symmetrical about 150 ppb.

Figure 2: Frequency distribution of fluorine in the surface waters of the Madoc area.

Figure 3: Plot of the pH against the fluorine content of surface waters.

Table 5: Seasonal variations in the fluorine content of surface waters.

Sample location	F ppb (Oct. 1971)	F ppb (June, 1972)	Maximum % [*] difference
2	99	105	6.1
3	115	99	16.2
10	89	125	40.5
13	115	120	4.4
15	265	340	28.4
16	89	95	6.8
17	125	140	12.0
18	110	99	11.1
20	115	150	30.0
23	270	230	17.4
27	220	240	9.1

Table 6: Comparison of results obtained in this survey with those obtained by Wright (1971) at equivalent sample locations.

Sample location	F ppb (June, 1972)	F ppb (Wright, 1971)	Maximum % [*] difference
17	140	90	55.5
18	99	130	31.0
19	130	140	7.7
21	155	170	10.0
22	220	270	18.2
23	230	270	17.4
25	75	100	33.3
26	110	90	22.2
39	255	290	14.0
75	340	540	59.0

* $(\Delta F / \text{smaller concentration}) \times 100$

Another way of describing this peculiar distribution is that the pH and fluorine concentration tend to vary directly up to 150 ppb above which concentration they appear to vary indirectly. The reasons for this are not evident.

Wright (1971) claimed that no significant seasonal variation occurred in the fluorine concentration of surface waters of the Madoc area, and that all samples could be treated as one population. Two series of replicate samples demonstrate that significant seasonal variations up to 40% can occur (Table 5). Such variations are dependent on the seasonal rainfall and on the amount of fluorine dissolved by ground waters. During periods of increased rainfall, surface run off will increase and tend to dilute the fluorine concentration in certain streams while larger quantities of ground water flowing into streams in areas of fluorite occurrences will tend to increase the overall fluorine concentration.

Comparison of results obtained in this survey with those obtained by Wright at approximately the same sample location (Table 6) demonstrates that seasonal variations up to a maximum of 59% may occur and that results obtained in this study tend to be slightly lower. Nevertheless, a good correspondence generally exists between both series. Such observations lead to the conclusion that if samples collected at various times of the year are treated as one population, high threshold

concentrations between the second and third standard deviation may be considered as anomalous. Duplicate samples collected at every tenth location gave identical results on analysis.

Fluorine anomalies were found in 4 different areas (Map 2 in pocket).

One anomaly (340 ppb F) occurs in a small lake near the Moira fault, approximately 2 miles south of Moira Lake. It is possible that this anomaly reflects the presence of fluorite veins in the nearby Moira fault. This hypothesis is also supported by the dispersion of fluorine in ground waters along the Moira fault (Map 3). A more detailed sampling of surface waters in this small area should give an unequivocal answer.

A second anomaly is located in Banker Lake which has an anomalous fluorine concentration of 340 ppb that may be attributed to either the presence of the Lee Junior mine a few hundred feet northeast or to the fluorine rich limestones (sample BR in Table 3) to the west, or possibly to both. Another anomaly (340 ppb F) in the same area was found in a small stream 1 mile southwest of Banker Lake. This stream drains an area containing known fluorite veins.

A third group of anomalous samples was collected in the Jarvis Lake area. Fluorine concentrations were not quantitatively anomalous (230 ppb) but because of the size of the dispersion train, this area cannot be ignored.

High fluorine contents were found in Jarvis Lake, in an adjacent smaller lake to the east, in a stream paralleling Jarvis Lake on the west, and along the total length of the outlet stream that drains into the Moira River. Jarvis Lake was sampled at various locations to ascertain if variations in the fluorine content could be detected (Figure 4). All samples from the lake contained comparable concentrations and there was no indication of a possible source for the fluorine. The granophyric granite underlying the area may be the source of the fluorine. This granite contains fluorite as a minor accessory mineral. It should be noted, however, that streams draining the area underlain by this granite east of Jarvis Lake do not have high fluorine contents. Alternatively, since this anomaly lies along the northern extension of the Lee-Miller group of veins, it may be an indication of fluorite deposits in the Jarvis Lake area. Small fluorite veins are known north and southeast of this lake, and ground waters to the northeast were found to be highly anomalous in fluorine (Map 3).

The fluorine content is constant in the outlet stream of Jarvis Lake as far as the Moira River. This is evidence that fluorine in surface waters has a high mobility and can travel for several miles, provided there is no drastic change in environmental conditions.

A fourth anomaly (420 ppb F) occurs in a stream near Deloro which flows south, and parallels the Moira

Figure 4: Fluorine concentration in Jarvis Lake and immediate area.

River. Insufficient information is available to decide on the source of the fluorine. Old tailings at Deloro or the large area outlined by a ground water anomaly north of Deloro may be responsible for this anomalous dispersion.

Fluorine is removed from water when it is carried into a large lake or swamp. An example is Moira Lake. The fluorine content of water at the inlet was 150 ppb whereas at the outlet it had decreased to 86 ppb. Variations in fluorine content also occur in the lake. A small bay underlain by the Moira fault which contains fluorite deposits immediately to the north contained 125 ppb . A second example is the decrease of 185 ppb between samples 75 (340 ppb F) and 21 (155 ppb F) which are separated by a swamp in the area south of Banker Lake.

Results indicate that the fluorine content of surface waters is a useful reconnaissance tool since anomalies reflect areas of known mineralization or possible extensions. A line joining all three anomalous lakes trends roughly parallel to the Moira fault system and related fractures.

2. STREAM SEDIMENTS

Objective

Stream sediments were sampled to ascertain if any relationship exists between the fluorine content of stream water and sediments and to determine if the fluorine and zinc contents of sediments can be used advantageously in reconnaissance surveys for fluorite deposits.

Method

Stream sediments were collected, where possible, at the same location as the stream waters. The 53 sediments were collected below the water line and consisted of the finest material available. In the laboratory, the samples were oven dried at 90°C, sieved to minus 80 mesh, and analysed for fluorine and zinc. Data on the composition of sediment sample material and results of analyses can be found on file at Carleton University and on Map 2.

Results and discussion

The fluorine content of stream sediments ranges from 300 to 20,000 ppm. The arithmetic mean ($\bar{x}$) calculated after excluding three obviously anomalous concentrations above 1,000 ppm is 510 ppm. The frequency distribution diagram (Figure 5) indicates two separate populations. This is probably attributable to the fact that the entire survey was carried out in a small region containing a number of fluorite deposits and the abundant high threshold and anomalous concentrations constitute a separate population in themselves. With very few exceptions, the lower modal concentrations occur in the east while the high modal concentrations predominate in the northwest where most surface water anomalies are located.

It is difficult to determine the anomalous concentrations because of the clear bimodal distribution. If all samples with fluorine contents below 800 ppm are

Figure 5: Frequency distribution of fluorine in stream sediments.

considered, the arithmetic mean is 510 ppm. Because of the bimodality, the standard deviation for the background population was calculated. The arithmetic mean ($\bar{x}$), is 425 ppm and the standard deviation(s) is 55 ppm, making all fluorine contents above 590 ppm anomalous. However, this limit is probably too low because of the negative skew of the distribution. The most convenient method of finding the lower limit of anomalous concentrations may be to arbitrarily choose the mode of the second population. Therefore, by making 650 ppm the smallest anomalous concentration, meaningful patterns appear. Little contrast exists, however, between background and anomalous fluorine contents in stream sediments.

A plot of the fluorine content of stream waters against both populations of fluorine in sediments (Figure 6) indicates that the fluorine content of waters and sediments tends to vary directly but not proportionately. Generally, the adsorption of fluorine onto stream sediments appears to be limited in the alkaline stream waters of the Madoc area.

The zinc content of stream sediments varies from 25 to 650 ppm. The mode occurs between 40 and 50 ppm and the arithmetic mean is 50 ppm (Figure 7), provided only non-anomalous samples with Zn contents below 90 ppm are considered. The standard deviation is calculated to be 15 ppm and, therefore, all concentrations greater than 95 ppm (the mean plus three standard deviations) can be considered as anomalous. It should also be noted that the

Figure 6: Plot of the fluorine content of streams waters against the fluorine content of both populations of stream sediments.

Figure 7: Frequency distribution of zinc in stream sediments.

frequency distribution for Zn is distorted because of the number of large concentrations occurring in the small sample population.

No relationships were found between the composition of the sample (i.e.: proportions of sand, silt, clay and organic matter) and the F and Zn content. However, plots of the pH of the water against the concentrations of both elements in stream sediments (Figures 8 and 9) give nonlinear distributions and suggest that minimum concentrations tend to occur at pH 7.6 to 7.8. The reasons for this are obscure.

A plot of the F content against that of Zn in sediments (Figure 10) indicates that high Zn concentrations are usually associated with high F concentrations, but that the reverse is not necessarily true. The distribution of points becomes clearer when considered in the light of the two fluorine populations in sediments. Practically all samples from the first population are low in both F and Zn and plot as a well defined cluster of points. However, sediments which belong to the second population can have high or low Zn contents.

Six areas of interest are indicated by anomalous stream sediments (Map 2).

- (1) Sample 28, which is highly anomalous in both F (20,000 ppm) and Zn (650 ppm), was collected south of Moira Lake, in a small stream close to the Blakely mine. This stream flows near the base of mine tailings which contain abundant fluorite and sphalerite.

Figure 8: Plot of the fluorine content of stream sediments of different composition against the pH of stream water.

Figure 9: Plot of the zinc content of stream sediments of different compositions against the pH of stream water.

Figure 10: Plot of the fluorine against the zinc content of stream sediments treated as two populations.

- (2) Sediment sample number 29 was collected from a small stream about 1 mile east of Bend Bay and 2 miles west of White Lake. It contains slightly anomalous concentrations of F (660 ppm) and Zn (140 ppm) which are not related to known fluorite occurrences. This anomaly correlates with anomalous ground waters and fluorine-rich regional soils nearby.
- (3) Two sediment samples (numbers 42 and 43) collected about 2 miles northeast of Jarvis Lake are anomalous in fluorine. One sample contains a slightly anomalous amount of Zn. This anomaly is not associated with known fluorite mineralization but occurs close to the limestone-granophyric granite contact and also near a ground water anomaly (see Maps 1 and 3).
- (4) Sample number 75, collected about 1 mile southwest of Banker Lake is anomalous in Zn (180 ppm). It is associated with a surface water fluorine anomaly and occurs in an area containing several fluorite veins.
- (5) The largest area anomalous in Zn and containing high F occurs for several miles down the Moira River and its small tributary which flows south near the Deloro tailings. The Deloro tailings may be the source of this dispersion but a definite conclusion cannot be drawn because sediments were not sampled north of

Deloro and it is not known if the tailings are fluorine rich. However, it is doubtful that the highly anomalous F and Zn concentrations obtained for locations 17 and 18 are part of this same dispersion pattern because they indicate a sudden increase in the concentrations of these elements. These samples were collected along straight east-west trending arms of the Moira River which might be fault controlled and contain fluorite veins. A ground water sample collected 100 feet from location 17 was anomalous (see Maps).

- (6) Samples 36 and 64 from southern Marmora Township are highly anomalous in fluorine. Two explanations are possible. Firstly, a tributary to this stream drains the iron mine tailings southeast of Marmora; and secondly, the stream passes near two areas having anomalous ground water fluorine contents north and south of Deloro (Map 3).

No sediment anomaly was found in the stream draining the Jarvis Lake area. This may indicate that fluorine-bearing clastic particles are not being carried downstream but are deposited in the lake which acts as a settling basin. It is also possible that the one sediment sample collected along this stream is unrepresentative or that the alkaline pH conditions (pH 7.4 to 8.1) are unfavourable for the sorption of fluoride ions by the sediments.

Fluorine and zinc anomalies coincide in areas 2 and 5, areas that are not known to be contaminated. The three sample sites (17, 18 and 29) can be joined by a straight line suggested by a linear trend in the Moira River. This trend may indicate the presence of fractures which could contain fluorite vein mineralization.

All areas characterized by anomalous stream sediments occur over or close to ground water anomalies. This suggests that analysing stream sediments for F and Zn can be an effective reconnaissance exploration technique in the Madoc area. Careful interpretation is necessary, however, because of the low contrast between background and anomalous concentrations.

Fluoride ions are apparently poorly adsorbed by stream sediments in the alkaline surface waters of the Madoc area. Although the sampling density is insufficient to permit a strongly supported conclusion on the best sampling interval, that interval should not exceed 0.5 miles because the fluorine and zinc content of sediments may change rapidly.

3. GROUND WATERS

Objective

The Madoc area is in an agricultural district and numerous ground water sources exist either as wells or springs. It was decided in late April of 1972 to sample ground waters along regional traverses corresponding

as closely as possible to the regional soil traverses (Map 3) to verify if the areas containing known fluorite veins could be detected and to determine if any correlation exists between the fluorine content of ground waters and soils. From a geochemical prospecting viewpoint, significant results were obtained from the ground water fluorine traverses. It was therefore decided to sample the area systematically to study the regional dispersions.

Method

Forty-seven ground waters were collected along two regional traverses extending approximately 20 miles in an eastwest direction. Samples were collected either directly from wells or from cold water faucets inside farm houses after ensuring that no water softeners of any type were being used. A few checks indicated that no difference in fluorine concentration existed between the water collected directly from the well and that which went through pressure systems. No fixed sampling interval could be used, but an effort was made to collect samples at approximately $\frac{1}{2}$ to 1 mile intervals. Samples were collected in 250 ml. polyethylene bottles and the pH and temperature were accurately measured for all samples except those along the original traverses.

A total of 200 water samples were collected for the regional ground water reconnaissance survey, yielding

a sampling density of one sample per square mile. Duplicate sample pairs were collected at every tenth sample location, and as for surface waters, all sample pairs gave identical results.

A summary of fluorine hydrogeochemistry is given in Appendix B.

Results and discussion

The fluorine results for both ground water traverses are recorded in Figures 11 and 12. Samples collected in the areas of known fluorite mineralization, as well as in other areas, are clearly anomalous against a background of approximately 100 ppb. The northern traverse (Figure 11) crosses marble, granite, limestone, and metavolcanic rocks. The large ground water fluorine concentrations found in the area of known fluorite occurrences and in another area to the east (sample number 42) correlate with high regional soil fluorine concentrations in the A horizon. The area crossed by the southern traverse is predominantly underlain by Black River limestone, and a similar correlation between the soil and ground water regional traverses exists.

The concentration of fluorine in waters of the regional ground water survey ranged from 21 to 1,800 ppb, and the arithmetic mean ($\bar{x}$), calculated after neglecting

Figure 11: Fluorine content of ground water along the northern regional traverse.

Figure 12: Fluorine content of ground water along the southern regional traverse.

Figure 13: Frequency distribution of fluorine in ground waters.

all obviously anomalous concentrations above 300* ppb, is 105 ppb. The mode occurs between 50 and 75 ppb (Figure 13). The frequency distribution has a marked positive skew, an indication that fluorite occurs in the area and that the number of high background and threshold concentrations is greater than would normally be expected. The standard deviation(s) was calculated to be 58 ppb; fluorine concentrations greater than 280 ppb can, therefore, be considered anomalous. The contrast between the lower limit of anomalous concentrations and the arithmetic mean is 165%. The frequency distribution also indicates that at least two populations of anomalous fluorine concentrations exist between 300 and 325 ppb, and 600 and 625 ppb. The reasons for this are not clear.

Frequency distributions of the fluorine content of ground waters from various rock types were also plotted (Figure 14). The arithmetic means ($\bar{x}$) vary from 63 ppb in metavolcanic rocks to 115 ppb in limestone. The modal concentrations in marble, granite and metavolcanic rocks are roughly comparable. However, ground waters in limestone are slightly richer in fluorine. The frequency distribution for ground water fluorine in metavolcanic rocks is negatively skewed reflecting the low fluorine concentration in waters within this rock type.

* N.B. Fluorine concentrations above 300 ppm were omitted from most calculations because they are clearly anomalous and would distort statistical analysis (e.g. arithmetic mean and standard deviation).

Figure 14: Frequency distribution of fluorine in ground water from areas underlain by different rock types.

Ground waters in the Madoc area are neutral to slightly alkaline, the pH varying from 6.05 to 7.89. Mean pH values were calculated for each rock type to ascertain if any major differences occurred; but all arithmetic means are roughly the same.

Mean pH values in:

limestone	7.15
metavolcanic rocks .	7.06
marble	7.00
granite	7.17

Plots of pH against the fluorine concentration failed to reveal any patterns of interest (Figure 15).

A regional ground water fluorine map was compiled (Map 3) and contoured using the concentrations of 70, 140, 280, 560, and 1,100 ppb as contour intervals. However, gaps occur in the sample distribution making interpolation and some subjective interpretations necessary. The interpreted contours are shown as dashed lines. The dispersion patterns obtained are revealing. The areas which contain fluorite veins (i.e. Moira Lake group and the northern Lee-Miller group) are clearly anomalous and a host of satellitic anomalies was also detected.

Observations from the distribution of known fluorite veins makes it possible on geological grounds to project a second fault that strikes southwesterly and passes through or near Banker Lake causing an offset

Figure 15: Plot of the pH against the fluorine content of ground water from areas underlain by limestone.

of the Moira fault to the southwest. This offset portion would then explain the northern group of Lee-Miller veins, and the failure to trace the Moira fault north of Highway 7. Unfortunately, the distribution of fluorine in ground waters tends to negate this theory. A more likely interpretation suggested by the fluorine dispersion is that two, almost parallel, systems of faults containing fluorite veins cut across the area and extend further south than previously thought (Map 3).

Two smaller systems trending parallel to the major systems may also exist. The largest underlies the town of Madoc and may possibly join up with the anomaly located 2 miles to the northwest. The second system is located 1 mile east of Springbrook. It consists of one highly anomalous fluorine concentration (990 ppb) which appears to be related to a northwest trending group of threshold concentrations. This pattern may be reflecting rocks containing fluorine or fluorine rich ground waters being dispersed from the area containing the highly anomalous concentration into an area of limestone fractured predominantly in a NW-SE direction.

The two isolated single point anomalies west of the major central fluorine anomaly probably indicate that a number of small isolated groups of fluorite and barite veins are dispersed throughout this area. The point anomaly near the Moira River correlates with a sediment anomaly.

Another group of anomalies occurs near Deloro. The large anomalous area to the north may be the source of the high F and Zn concentrations found in the sediments along the Moira River and the small tributary draining the area east of the tailings dump. The predominant rock types are limestone and marble which are favourable for fluorite vein mineralization. It is also possible that this large anomaly reflects the dispersion of fluorine from the Deloro tailings into the ground water system. However, it is not known if the tailings are rich in fluorine. The anomaly to the south is smaller and trends northwest. The extension of this anomaly south of Highway 7 crosses an area where a regional soil was found to be rich in both F and Zn. Sediments in the stream which drains the area west of Deloro are also anomalous in fluorine.

Highly anomalous well waters (1700 and 1800 ppb F) were found northeast of Jarvis Lake. These wells are in limestone that overlies the granophyric phase of the Deloro granite. This anomaly may be caused by the dispersion of fluorine from fluorite veins or from the granite. According to Saha (1959), the minor accessory minerals muscovite, fluorite, and zircon make up no more than 0.5% of this granitic rock. Even if this total was all fluorite, the granophyric granite would then contain approximately 2,500 ppm fluorine. This fluorine concentration, however, is similar to the average for the Black

River limestone. The granite is, therefore, probably not the main source of the fluorine. On the other hand, this anomaly may represent the northern extension of the major anomalous trends into the Jarvis Lake area. Minor fluorite veins have already been located north and southeast of Jarvis Lake.

Two other single point anomalies were found. The first (620 ppb F) occurs in basic metavolcanic rocks in the northeastern corner of the field area. It is difficult to speculate on what this fluorine concentration indicates since ground waters in these metavolcanic rocks are generally fluorine poor. The second anomalous water sample (1700 ppb F) was collected about 1 mile south of Tweed. The area is underlain by granite, and the fluorine content of samples collected to the north, south, and west is normal. Other areas of interest are designated by isolated high threshold fluorine concentrations.

All ground waters were collected in the spring of 1972 between April 28th and June 11th. On completion of the survey, replicate samples were collected from four locations to ascertain the significance of seasonal variations. The fluorine content had increased only slightly during one and a half months, and the variation probably did not exceed 10%. Therefore, all data can safely be treated as one population. However, in September of 1972, some of the anomalous locations were resampled by Daniel R. Boyle (personal communication)

and the fluorine content was found to have increased from 2 to 5 times. All concentrations, however, were relative (i.e. the waters highest in fluorine in April were still highest in September). A marked change occurred in the fluorine content of ground water from location 147. This water which contained 57 ppb in June contained over 10 times that amount in September.

A considerable seasonal variation, therefore, occurred in the fluorine content of ground waters between spring and late summer of 1972. One reason for this variation may be the unusually high amount of precipitation which fell over most of eastern Canada during the months of July and August, 1972. This abnormal rainfall caused a marked rise in the water table which may have influenced the chemistry of ground water and may also have locally affected the direction of ground water flow. Samples collected at different times of the year cannot, therefore, be treated as one population. The best time to sample well waters is probably during the winter months when precipitation has the least effect on the ground water system.

The sample density for the ground water survey averaged 1 sample per square mile. This density proved useful in outlining the major trends. However, a number of small areas containing fluorite were probably not detected because the fluorine content of ground waters can, in places, change drastically within a few hundred feet. This is illustrated by the sudden change in fluorine concentration in the anomalous areas northeast and south

of Jarvis Lake and around the point anomaly south of Tweed. From these considerations, it follows that a comprehensive ground water survey should include data from as many sample locations as possible, even if some locations are only a few hundred feet apart. However, for geochemical reconnaissance a density of 1 sample per half mile square is probably ideal.

Hydrological studies of the ground water flow throughout the area would be useful to interpret and assess the importance of certain anomalous dispersions. The fluorine content of ground waters in the Madoc area is a useful exploration tool. Important areas containing known fluorite veins are clearly outlined. The dispersion of fluorine in ground waters suggests that the major areas can be extended and that several new locations are worthy of further investigation.

The fluorine content of three ground water samples reached concentrations of 1700 to 1800 ppb. These concentrations are almost double the recommended content for human consumption. Humans drinking these waters can easily exceed the average daily intake of 2 milligrams above which fluorosis may occur (Marier and Rose, 1971). The significant seasonal variation registered between spring and late summer of 1972 suggests that the fluorine concentration in these three wells increased even more and that other ground waters near fluorite veins probably exceeded 1 ppm. It is therefore suggested that ground waters should be carefully examined

at several locations because they can be detrimental to the health of humans and animals that drink them daily.

4. REGIONAL SOIL TRAVERSES

Objective

The fluorine content of four regional soil profiles collected in the fall of 1971, indicated that significant differences existed between the fluorine content of soils collected in the neighbourhood of fluorite veins and those collected several miles away. It was decided, therefore, to determine the regional dispersion of fluorine in soils along two 20 mile traverses: one across an area of variable rock and soil types, the other across an area with more uniform geological conditions.

Method

The field work was carried out in early December of 1971, after the first snowfall. Samples were collected at 1 mile intervals except near areas of known fluorite occurrences where the spacing was reduced to 0.5 miles. The sample sites were at least 200 feet removed from roads and were chosen in such a way as to avoid cultivated fields contaminated by fertilizers. Each of the three principal soil horizons (A, B, and C) was sampled where possible. The samples were oven dried at 90°C and sieved to -80 mesh. Descriptions of sample locations and soil

characteristics are on file at Carleton University, and the sample locations are plotted on Map 3 to indicate the correspondence between soil and ground water sample sites.

Results and discussion

(1) Regional Traverse A

The fluorine content varies between 140 and 1450 ppm (Figure 16 in pocket). From a regional background lower than 200 ppm over the Tudor metavolcanic rocks in the northeast, the fluorine content of the A soil horizon increases to almost 600 ppm near known fluorite veins and then decreases. Farther west, the fluorine content of soils again increases to outline another broad area of fluorine rich soils with a markedly anomalous sample at its center. The fluorine content of the B and C horizon soils is too erratic to separate these two broad regional dispersions. The C horizon could not be sampled at all sites, and hence, the data along the traverse are not complete. However, the response of the C horizon appears to be slightly less erratic than that of the B. The A horizon results can be interpreted with greater facility because a greater contrast is present.

A good correspondence can be established between the eastern high fluorine concentrations in soils and the major ground water anomalies along the Moira fault. Both indicate that fluorine rich areas probably exist east of the Moira fault near Madoc. The second group of high

concentrations coincides with the extension of the northwest trending ground water anomaly south of Deloro. A marble from this area was also found to contain 1,750 ppm of fluorine (see Table 3).

No clear correlation exists between the rock type and the fluorine content of the overlying soils except that soils over the Tudor metavolcanic rocks are low in fluorine, as are also the local ground waters. Regional variations in the fluorine content of soils in the Madoc area reflect firstly the fluorine content of underlying rocks, and secondly, the dispersion of fluorine from fluorite veins.

The Zn content in the B soil horizon along the regional traverse is markedly erratic, ranging from 20 to 190 ppm. No relationship to the known fluorite veins can be discerned except that the concentration increases westward. The high Zn content at location 13 correlates with a high fluorine content. Background for Zn ranges up to 70 ppm.

The Ba content of these soils varies between 100 and 1,100 ppm and tends to increase with depth in the soil profile. The B horizon is extremely erratic, whereas the A horizon clearly exhibits a broad anomaly embracing the zones of known fluorite occurrences and corresponding to the major ground water anomalous trends. Contrary to fluorine, the Ba content of soils increases eastward towards the Tudor metavolcanic rocks.

Variations in the Sr content of these soils are negligible. The content ranges between 200 and 450 ppm, averaging approximately 300 ppm, and increases slightly with depth in the top few feet.

(2) Regional Traverse B

The fluorine content varies from 170 to 790 ppm (Figure 16). It is immediately evident that the fluorine content is not as erratic as along traverse A, and that fluorine enriched soils are well contrasted against an average background of 300 to 400 ppm. One reason for this feature is that the rock and soil types are more uniform along this traverse. A good correspondence exists between the fluorine content of the A and B soil horizons. However, the B horizon along this traverse tends to be slightly richer. The only marked exception occurs at sample location 1 where the concentration in the organic horizon is notably lower.

The area of known fluorite occurrence is clearly outlined. The three western high fluorine concentrations at locations 1, 7, and 12 occur in or near areas of fluorine-rich ground waters while the eastern regional anomaly occurs over an area with background ground water fluorine contents. However, the latter anomaly overlaps the Moira granite and is also not far removed from a major scarp.

Zinc concentrations vary from 15 to 150 ppm and average at approximately 50 ppm. The zinc content

of the B horizon is constant and does not correlate with the three western fluorine anomalies. However, a Zn anomaly correlates with the broad eastern fluorine anomaly.

Barium and Sr in the B soil horizon both indicate one large and poorly contrasted area slightly enriched in these elements. This area does however correlate with the two central soil fluorine anomalies.

Regional soil sampling in the Madoc area is effective in outlining areas of known fluorite veins. Most of the areas indicated by fluorine-rich soils also have fluorine-rich ground waters. A regional soil reconnaissance survey of the fluorine content in either the A or B soil horizon with samples taken on a half mile square grid, would yield a useful two dimensional picture of fluorine dispersion in the Madoc area. Such information would be important in areas where no ground waters are available.

5. DETAILED SOIL TRAVERSES

Objective

Detailed soil sampling was carried out along traverses crossing fluorite veins or their extension. The aim was to study the secondary dispersion of fluorine and other vein elements (e.g. Ba, Sr, and Zn) in soils near fluorite veins and to obtain information on the usefulness of detailed soil sampling programs as a method of locating fluorite deposits.

Figure 17: Fluorite occurrences in the Madoc area and location of detailed soil traverses.

Method

A major problem was locating appropriate sites where undisturbed and uncontaminated soils were present. Because of this, most soil traverses cross the extension of veins. The thickness of overburden in areas sampled varied from one inch to about twenty feet. The A, B, and C soil horizons were sampled where possible; however, after noting that the A horizon was the most useful, only this horizon was sampled in later traverses. The samples were generally collected at 100 feet paced intervals and were oven dried at 90°C and sieved to -80 mesh.

Field work was started in early October, 1971, and was completed by mid July, 1972. Soils were sampled along a total of 9 traverses, but only 7 were completed and included in this report. The description of the various veins over which soils were collected are taken from Guillet (1964). Traverse locations are indicated on Figure 17.

Summaries of the biogeochemistry and soil geochemistry of fluorine are given in Appendix B.

(1) Noyes Traverse

Description

Soils were collected across the Noyes occurrence located along the Moira fault, south of Moira Lake. The vein was mined intermittently from 1917 until 1941 and

total production is estimated at 25,000 tons. The deposits apparently occupy lenticular fault cavities trending N 50° W along a single break in pink Noyes granite. The lenses vary from a few feet to over 200 feet in length and from a few inches to 17 feet in width. The granite near the vein contact is altered and is enriched in the vein elements (Boyle, R.W., personal communication).

The traverse crosses the vein near shaft number 1, on a bearing of N 40° E. At this point, the vein mineralization is located about 50 feet below the surface and no contamination was apparent. The soil type is an acidic, brown forest soil (Gillespie, Wicklund and Richards, 1962). Samples were collected at 100 foot intervals. Descriptions of the soil samples and sample sites for this and other traverses are on file at Carleton University.

Results and discussion

The fluorine content varies from 240 to 1000 ppm (Figure 18) with background between 300 and 400 ppm and increasing directly with sample depth in the top few feet. About 900 feet south of the Noyes vein, the fluorine concentration in the A and B horizons increases and outlines a broad dispersion pattern about 1,200 feet wide. A marked fluorine enrichment in the A horizon occurs about 275 feet north of the known vein at sample location 11. This anomalous condition is not reflected in underlying B and C horizons. However, an enrichment in the latter occurs 200 feet farther north. Therefore, either the

fluorine dispersed from the vein was mobilized northwards or this anomaly indicates the presence of undiscovered fluorite occurrences. Since no anomaly was found near the vein and shaft opening, the possibility of contamination along the traverse is minimal.

The C horizon yields an erratic pattern which does not help interpretation. The B horizon traverse is more stable and indicates two anomalous areas: one at either end of the wide dispersion pattern. The A horizon exhibits the greatest contrast (100 to 200%) between background and anomalies and is therefore the most useful horizon to sample.

No significant variation in the Sr content of soils occurs anywhere along this traverse. A slight increase in the Zn content over a very broad area correlates with the dispersion of fluorine, but the contrast is poor and does not exceed 100% over an average background of 30 ppm.

An anomalous Ba dispersion occurs in the A horizon for a distance of 200 feet north of the vein. The contrast obtained is of the order of 100% above a generally high background of about 900 ppm. The B and C horizons are not useful in geochemical prospecting for fluorite veins at this location.

(2) McBeath Traverse

Description

This traverse trends N 45° E across the northern end of the Moira fault about 1,000 feet south of Highway 7. Fragments of vein material are exposed in a number of small pits, and a few hundred feet farther south, a small fluorite and barite vein about 1 foot wide and 50 feet long was mined by open pitting. The wall rock consists of Black River limestone; the overburden varies in thickness from a few inches to a few feet; the relief is negligible except for a scarp near Highway 7 at the northern end of the traverse; and the soils are acidic to neutral podzols. Samples were collected at 50 feet intervals across the fault and at 100 feet intervals elsewhere.

Results and discussion

The fluorine content of soils varies from 100 to 5,000 ppm with the upper limit of background estimated at 400 ppm (Figure 18). Three fluorine rich areas were located and all are supported by Ba and Zn enrichments. The central anomaly on the traverse occurs over a known possible fluorite vein in the Moira fault. The A horizon is markedly enriched in fluorine over the fault whereas variations in the B horizon are insignificant. Across the western anomaly, the B horizon, however, gives the higher results, but it is not known if this dispersion is related to a fluorite occurrence. Since the fluorine anomaly is also supported by Zn and Ba, it is possible that it may

indicate the presence of fluorite mineralization. The third anomaly at the northern end of the traverse coincides with the limestone scarp near Highway 7.

The Ba content of these soils varies from a non detectable amount (e.g. below 150 ppm) up to 1,520 ppm. Background appears to increase southwards from 600 up to 1,000 ppm. A good correspondence exists between the A and the B horizon. The contrast of anomalies against background is almost the same for two anomalies (85%), but the B horizon responds markedly better over the fault (a 150% increase in the B as compared to a 65% increase in the A horizon).

The Zn content of the B horizon varies from 40 to 560 ppm, and the upper limit of background is estimated at 80 ppm. The anomalous contrast is greater than 150%. Zinc is dispersed 200 feet westward of the fault zone. However, the cause of this displacement is not understood since the land is relatively flat and the overburden very thin. This anomaly may not be related to vein mineralization in the fault.

The Sr content of the A and B horizons is similar but the dispersion patterns cannot be interpreted. Strontium varies from 100 to 375 ppm, averaging about 275 ppm.

(3) Bailey Traverse

Description

This traverse crosses the southern end of the vein about 200 feet south of the Bailey mine escapeway (see Guillet, 1964). The vein strikes 315° , varies in width from 2 to 12 feet over a distance of 375 feet, and has been mined to a depth of 179 feet. Over 25,000 tons of fluorspar were produced from the mine until 1950. The country rock consists of grey-black argillite and banded marble. This location was chosen because of the thick clay overburden and cultivated field covering the vein. Samples were collected at 50 feet intervals across the vein and at 100 feet intervals elsewhere.

Results and discussion

The fluorine concentration in the three horizons varies from 370 to 1160 ppm, with the upper limit of background estimated at 550 ppm (Figure 19). This high fluorine background may reflect the high clay content of these soils. The A and B horizon traverses agree remarkably well, with the A horizon displaying the greater contrast. No fluorine enrichment was detected in the clay soils over the vein. It is possible that the clay may have acted as a barrier to the upward migration of fluoride ions. However, an anomaly was located on the slope at the southwestern end of the traverse. This

Figure 19: A - Fluorine content of soils along the Bailey Traverse.
 B - Zinc content of the B horizon along the Bailey Traverse.

anomaly may be attributable to contamination from the road which is located uphill, about 50 feet away.

Zinc concentrations in the B horizon are so erratic that it is impossible to estimate background. Concentrations range from 35 to 135 ppm. No anomalous Zn concentrations occur in the clay soils over the vein extension but a series of enriched samples occurs to the east where the overburden is thinner and marble containing numerous calcite veins outcrops.

(4) Blakely Traverse

Description

Only the A horizon was sampled over the southern extension of the Blakely vein, about 200 feet southeast of the mine tailings. The vein strikes 315° along the base of a northeasterly facing escarpment of Black River limestone and persists for 750 feet, varying in width from 0.5 to 6 feet. It was mined at intervals from 1918 until 1947. No vein mineralization is reported to occur as far south as the traverse.

Results and discussion

The fluorine content of the slightly alkaline brown forest soils varies from 375 to 690 ppm (Figure 20). The upper limit of background is difficult to estimate but is probably in the range from 450 to 500 ppm. Samples collected across a small valley are slightly rich in fluorine with the exception of one sample, collected near

Figure 20: Fluorine content of A horizons along the Blakely traverse.

the stream, which may have been leached of its fluorine content.

The fluorine content of water logged organic soils occurring in a marsh at the top of the slope is low. Most of the fluorine mobilized by vegetation has probably been leached. On the other side of the marsh, the fluorine content rapidly increases again. No identifiable pattern in the fluorine dispersion that can be related to the known fluorite mineralization was found. A cultivated field and a highway made it impossible to extend this traverse northwards.

(5) Lee Traverse

Description

This traverse crosses the southern extension of the eastern Lee Senior vein about 400 feet south of a small beaver pond, and close to a small pit in Black River limestone. The area was mined intermittently from 1916 until 1943, but fluorspar production was minor. Only the A horizon was sampled. The local topography is flat, the overburden is thin, and the soil type is a slightly alkaline brown forest soil

Results and discussion

The fluorine content ranges from 340 to 750 ppm and background is estimated at 400 ppm (Figure 21). An anomaly exhibiting a contrast of 85% occurs over the extension of the vein.

Figure 21: Fluorine content of the A horizon along the Lee traverse.

(6) Ponton Traverse

Description

This traverse trends N 45° E across the southern end of the vein. The area is underlain by flat-lying Black River limestone, the relief is negligible, the overburden is thin (1 to 2 feet at most) and the podzolic soil is neutral to weakly alkaline. The vein which trends N 45° W is over 400 feet long and up to 2.5 feet wide. It was mined intermittently by open pitting from 1917 until 1942, and the total fluorspar production is estimated at 1,500 tons.

Results

The fluorine concentration in the A and B soil horizons varies from 250 to 800 ppm (Figure 22). The upper limits of background are estimated at 400 ppm for the A horizon and 500 ppm for the B. The B horizon displays no particular pattern except that it is erratic near the vein. The anomaly in the A horizon displays a contrast of 100% above background. The main vein is indicated by one anomalous sample only while the second smaller vein about 100 feet west is not reflected.

The sampling interval was shortened from 100 to 10 feet and a 200 feet long traverse was extended 100 feet on either side of the vein to study the true extent of the fluorine dispersion near the vein (Figure 23A). Only the

Figure 22: A - Fluorine content of soils along the Ponton traverse.
B - Zinc content of the B horizon along the Ponton traverse.

Figure 23: A - Fluorine content of the A horizon along the detailed (10 feet interval) Ponton traverse.
 B - Water soluble fluorine in the A horizon along the detailed (10 feet interval) Ponton traverse.

A horizon was sampled. The results indicate that the major anomalous dispersion can be dissected into two anomalies, and that the fluorine is mainly dispersed in the soils east of the vein. The anomalous dispersion is about 70 feet wide, and the maximum contrast above background is 270%. The second, smaller vein is also reflected. Therefore, a 100 feet sampling interval is too large and fluorine dispersions from subcropping fluorite veins could easily be missed. The sampling interval, for best results, should be shortened at least to 50 feet or less.

6. WATER SOLUBLE SOIL FLUORINE

Objective

Samples from a few representative soil profiles were leached to obtain information on the form and mobility of fluorine in soils and on its availability to plants. Although the results were informative, the experimental work was not pursued at length because it was not an original objective.

Method

To 0.5 g. portions of dried and sieved soil in a polystyrene vial, add 36 ml. of distilled-deionized water and shake for 24 hours. Add 4 ml. of sodium acetate buffer (see Appendix C) and analyse with the selective ion electrode. As shown below and in Table 8 sodium

acetate does not help remove fluorine from soils but suppresses the results when used during leaching.

Results and discussion

The proportion of exchangeable fluorine decreases markedly from the A to the C horizon (Table 7). This observation is true when considering the results either as the total exchangeable fluorine or as a percentage of the total soil fluorine. The amount of exchangeable soil fluorine commonly varies from 1 to 10 ppm, or 0.2 to greater than 3% of the total soil fluorine content, depending on the soil type.

In clay soils, the amount of water leachable fluorine does not decrease as sharply from the A to the C horizon as in silty or sandy soil profiles and the percentage of exchangeable fluorine is generally lower. The fluorine in clay soils is, therefore, more firmly held probably as an ion pair type bond or by specific adsorption and is not easily released by the weak polar attraction of water molecules.

Leaches with pure ethanol were used, but this organic solvent did not release detectable amounts of fluorine from the soils. Water-containing the Na-acetate buffer was also used but smaller quantities of fluorine were leached. Duplicate water leaches were also tested, and the results were reproducible with 20% (Table 8). A possible explanation as to why the A horizon

Table 7: Water-soluble fluorine and its percentage of the total soil fluorine.

Sample number		Water soluble fluorine in ppm	Total soil fluorine in ppm	Percentage of soluble fluorine	Notes *
1S6	A	10.0	530	1.9	brown forest
	B	5.6	480	1.2	sand & silt
	C	2.9	460	0.6	acid
8S2	A	9.6	560	1.7	podzol
	B	3.5	510	0.7	silt & clay
	C	2.2	535	0.4	acid
8S13	A	2.2	1,500	0.2	brown forest
	B	1.8	1,000	0.2	clay
	C	2.4	1,100	0.2	neutral to alk.
8S16	A	2.5	585	0.4	podzol
	B	2.9	640	0.5	clay
	C	2.2	495	0.4	acid
8S17	A	2.2	335	0.7	podzol
	B	1.2	350	0.3	clay
	C	1.2	575	0.2	acid
8S21	A	1.4	200	0.7	podzol
	B	1.0	160	0.6	silt & clay
	C	0.8	180	0.4	acid
8S22	A	2.3	150	1.6	podzolic
	B	2.6	170	1.5	silt & clay
	C	2.4	250	1.0	acid
9S4	A	3.1	400	0.8	brown forest
	B	2.7	390	0.7	clay
	C	3.9	430	0.9	alkaline
9S14	A	5.0	200	2.5	brown forest
	B	2.6	240	1.1	silt & clay
	C	2.2	225	1.0	alkaline
9S15	A	5.6	170	3.3	podzol
	B	3.5	230	1.5	sand, silt
	C	2.6	240	1.1	acid

* Notes: soil type, clastic fraction, and pH reaction.

Table 8: Comparison of fluorine soluble in buffered and non-buffered solutions and the reproducibility of water leaches.

Sample number	Soil fluorine soluble in a buffered solution (ppm)	Water soluble fluorine (ppm)	Water soluble fluorine replicate (ppm)	Maximum % Difference
9S14 A	3.6	6.0	5.0	20
B	2.0	3.0	2.6	15
C	ND	2.4	2.2	9
9S15 A	4.8	6.2	5.6	11
B	3.0	4.0	3.5	14
C	2.2	2.8	2.5	12

contains more water extractable fluorine is that plants take up fluorine from the soil and concentrate it in intercellular spaces along the edges and tips of leaves (Bovay, 1969; Romney, 1969; Chapman, 1966). Part of this fluorine is excreted to the leaf surface where it can be carried into the atmosphere or washed into the soil by rain. The rest is carried down with the leaves and dying vegetation in the autumn. Once in the soil, it is initially held loosely by the decaying organic matter or adsorbed onto centers of positive charge on organic or clay-organic micelles. Research on optimum conditions for the study of exchangeable soil fluorine was done by Larsen and Widdowson (1971) (see Appendix B).

Provided that certain parameters such as soil type, pH, drainage, and vegetation cover are relatively constant, the amount of water leachable fluorine in the A horizon could be used to locate fluorite occurrences. Such tests are easily and inexpensively done in a field laboratory, and results would be available shortly after sampling. Field tests as simple as washing the leaves of certain plants or trees on grids or traverses in uncontaminated areas could also yield data useful in the search for fluorite deposits.

Water leaches were done on the soils of the detailed (10 foot interval) Ponton traverse (Figure 23B). The water extractable fluorine varied from 5 to 50 ppm and the anomalous areas were clearly outlined. The water leachable fluorine anomaly is broader and the contrast

between background and anomaly is marked. This experiment confirms the supposition that the exchangeable fluorine of organic soil horizons can be used to prospect for fluorite veins because it reflects the total fluorine content of soils.

7. GENERAL RESULTS AND DISCUSSION OF SOIL SURVEYS

The fluorine content along the detailed traverses ranges from 120 to 5,000 ppm, and the average background lies approximately between 400 and 450 ppm.

On compiling 68 complete soil profiles, the arithmetic means ($\bar{x}$) indicate that the fluorine content increases from the A horizon to the C (Figure 24). This statement is, however, not entirely correct because the higher mean in the C horizon is probably due to a small number of erratic, high fluorine concentrations. This is suggested from the frequency distribution diagrams which show the distributions for the A and C horizons as clearly bimodal. The modes also correspond closely.

The soil pH is variable. The soils tend to be acidic over most rock types except limestone where the trend is slightly alkaline. However, there are numerous exceptions. An expected trend was for the pH to increase with depth (see Appendix B).

The fluorine content varies indirectly with the clastic size fraction (Table 9) (e.g. the smaller the soil particles the greater the fluorine content). This indicates

Figure 24: Frequency distribution of fluorine in the A, B, and C horizons of 68 complete soil profiles.

that much of the soil fluorine cannot be attributed to fluorine containing minerals such as apatite, fluorite, and micas, but is probably present as an adsorbed phase on the surface of small particles such as silts, clays, and soil colloids. The minus 80 mesh soil fraction is suitable and convenient to use. Smaller size fractions of the A horizon would probably not increase the contrast between background and anomalies.

The secondary dispersion of fluorine in soils around subcropping fluorite veins is restricted to a zone of about 50 feet on either side of the veins. The reasons for these narrow and sharp dispersion patterns are: the narrow width of the veins in the Black River limestone, the planar topography which prevents the dispersion of fluorine by mass wastage (soil creep), surface run off, and percolating ground waters, and the inhibiting effect of calcium ions on fluoride ion mobility (Gisinger, 1968). The fluorine anomalies are superjacent, and the most suitable horizon to sample is the A horizon for three reasons:

- (1) It gives the largest contrast between background and anomalies.
- (2) It is easy to sample.
- (3) Samples can be quickly analysed for water leachable fluorine in a field lab, if required.

The dispersion of fluorine in soils over the Noyes granite is broad, and the A horizon also exhibits

the largest contrast. The largest fluorine concentrations are found a few hundred feet northeast of the mined vein.

Over the thick clay covered Bailey vein, no anomalous fluorine contents were detected. However, because of the clay soil, the background was slightly higher than usual. The clay may also have acted as a barrier to the upward migration of fluoride ions.

The sampling interval should be less than 100 feet to detect the narrow fluorine dispersion haloes. An interval of 25 to 50 feet is recommended for detailed soil surveys. Over known occurrences, the fluorine content increased by 85% or more above the local background.

A number of unexplained fluorine anomalies supported by Ba and Zn anomalies were located along some of the traverses. These may indicate the presence of still undiscovered veins.

The Zn content varies from 15 to 560 ppm, with a background between 40 and 60 ppm. The contrast over fluorite veins is variable but usually exceeds 100%. The B soil horizon was routinely analysed for Zn; however, examination of the Zn content of the various horizons at a few localities indicates that this element is also concentrated in the A horizon (Table 10). Zinc and fluorine correlations are an asset in the interpretative procedure.

The Ba content varies from 200 to 1,600 ppm and the upper limit of background lies between 800 and

Table 9: Fluorine content of different soil size fractions.

Sample number	Size fraction (mesh)	Fluorine content (ppm)	Fluorine content in the minus 80 mesh fraction (ppm)
B-14 A	50 $\geq$ X $\geq$ 100	230	200
	100 $\geq$ X $\geq$ 200	280	
	200 $\geq$ X	300	
B-14 B	"	220	240
		340	
		370	
B-14 C	"	250	230
		370	
		430	
A-13 A	"	1040	1500
		1280	
		1440	
A-13 B	"	750	1000
		1000	
		1160	
A-13 C	"	960	1100
		1120	
		1400	

Table 10: Zinc content of different soil horizons.

Sample Number	Horizon	Zinc ppm
1S6	A	85
	B	80
	C	35
1S11	A	160
	B	80
	C	75
A-8	A	90
	B	70
	C	40
A-13	A	260
	B	220
	C	75
B-7	A	75
	B	70
	C	35

1,000 ppm. Barium anomalies correlate well with fluorine. Barium has a greater mobility than fluorine in the limestone environments and gives broader dispersion haloes which are easier to detect. The A and B horizons give approximately equivalent results.

The Sr content varies from 100 to 500 ppm, the upper limit of background lying between 350 and 450 ppm. Strontium dispersion haloes did not reflect the fluorite veins.

Geochemical surveys utilizing soil grids should be useful in the Madoc area to locate new fluorite deposits. Soil sampling programs are simple because the A horizon consistently yields useful dispersion haloes of F, Ba, and Zn over fluorite veins. Other authors have also observed the greater effectiveness of A horizon sampling in other areas (Boyle and Dass, 1967).

Vegetation grown on fluorine rich soils near subcropping fluorite veins will contain more inorganic fluorine. If this vegetation is consumed by humans or animals, an excessive fluorine intake can result. Nearby well waters would also probably contain high fluorine concentrations, therefore, increasing the possibility of fluorosis. Extremely toxic organofluorides (e.g. fluoroacetate and fluorocitrate) have been detected in vegetation such as forage crops, soybeans, and wheatgrass grown in areas containing high concentrations of industrial atmospheric fluoride (Marier, 1971). It would be wise to

bear in mind that vegetation growing on fluorine rich soils may have the ability to convert some of the fluorine into organic forms. Even if this transformation was minor, it would remain a very real danger since organofluorides are estimated to be about 500 times more toxic than inorganic fluoride. A detailed study of the organic and inorganic fluorine content in vegetation and livestock in the Madoc area could determine the importance of the above considerations.

SUMMARY AND CONCLUSIONS

The secondary dispersion of fluorine in surface and ground waters, stream sediments, and soils was examined in an area containing fluorite veins. The usefulness of Ba, Sr, and Zn as tracers for fluorite-barite mineralization in soils was also examined.

- (a) The fluorine analyses were performed using an Orion selective ion electrode and ionalyser meter. These instruments make possible precise, quick, and inexpensive analyses for fluorine. The electrode and meter are easily transported and can be used directly in the field or in a field laboratory. The precision and accuracy are dependent on the sample preparation. Water analyses were almost perfectly duplicated while soil and sediment analyses were reproducible within 5%. The fluoride ion electrode is a useful analytical tool in geochemical exploration for fluorite and associated deposits.
- (b) Most rock types in the Madoc area are enriched in fluorine. The fluorine content of limestone is reported in the literature as varying from 0 to 1,210 ppm, averaging 220 ppm. The fluorine content of six samples of Black River limestone collected near Madoc varies from 1,060 to 2,660 ppm, averaging 1,840 ppm. Samples of mafic metavolcanic rocks, marble, and breccia are also rich in fluorine.

- (c) The fluorine content of alkaline surface waters varies from 60 to 420 ppb, averaging 125 ppb. Several anomalies were found which correlate with anomalies in ground waters, sediments, and soils. Fluorine is mobile in stream waters and can migrate for several miles. Areas containing known fluorite deposits were indicated by larger fluorine concentrations in surface waters, and a number of anomalous areas in which there are no known deposits were also indicated. One can conclude therefore that the fluorine content of surface waters can yield important geochemical data that may help to locate new areas containing fluorite deposits.
- (d) Stream sediments were analysed for F and Zn. The fluorine content of stream sediments varies from 300 to 20,000 ppm, averaging 510 ppm. The contrast between anomalous and background concentrations is low. The Zn content of stream sediments varies from 25 to 650 ppm, averaging 60 ppm. High Zn contents are usually associated with high F contents, but the reverse is not true. All areas indicated by anomalous stream sediments occur over or near to ground water anomalies. Stream sediments are useful in prospecting for fluorite veins but because of the limited contrast between background and anomalous concentrations, interpretation is difficult, and stream sediment surveys should be supported by some

other type of reconnaissance survey. The sampling interval should not exceed 0.5 miles.

- (e) The fluorine concentration in the neutral to slightly alkaline ground waters varies from 21 to 1,800 ppb, averaging 105 ppb. Samples were collected at an approximate density of one per square mile. The areas of known fluorite occurrences as well as other areas are clearly outlined by anomalous ground water fluorine concentrations. The fluorine content of ground waters in limestone is significantly higher than in other rock types, especially the Tudor metavolcanic rocks. This reflects the lower fluorine content of the latter rock type. The sampling density used was appropriate for outlining the known groups of fluorite veins; however, because the fluorine content of ground water can drastically change, even within a few hundred feet, it is important to sample as many wells and springs as possible when detailed information is required. An optimum sampling density for reconnaissance would consist in one sample per half mile square.

Important seasonal variations occur in the fluorine content of ground waters, a feature that dictates that ground water surveys should be carried out in as short a time as possible. It is suggested that the most appropriate time to conduct such surveys is during winter when precipitation least affects the

ground water systems. Ground water reconnaissance surveys are particularly useful methods in the search for fluorite deposits.

- (f) Soil samples were collected along two 20 mile regional traverses using a sampling interval varying from 0.5 to 1.5 miles. Along one traverse, the A horizon exhibits a greater contrast over areas of known fluorite mineralization while in the second, both the A and B horizons respond equally well. The C horizon was not sampled at all locations but the available results from this horizon tend to be erratic. The regional soil fluorine traverses are marked by anomalies that should receive further investigation. These higher fluorine contents occur over or near ground water anomalies, strongly suggesting that a positive correlation exists between the two. The investigation indicates that regional soil sampling surveys are a useful geochemical reconnaissance method for locating zones containing fluorite deposits. The regional dispersions of Ba and Zn are helpful in interpreting regional surveys, but these elements generally display less contrast than fluorine.
- (g) Soil samples were collected along traverses across fluorite veins or their extension to study the dispersion of fluorine in soils. The fluorine content was found to vary from 130 to 5,000 ppm and

and average between 350 and 450 ppm. The secondary dispersion of fluorine in soils over subcropping fluorite veins in limestone is restricted to a narrow zone about 50 feet on either side of the veins. This is probably due to a combination of three factors: the narrow width of the veins, the lack of topographical relief, and the inhibiting effect of calcium on the mobility of fluoride ions in soils. The fluorine anomalies are usually superjacent and the most favourable soil horizon for sampling is the organic A horizon because it accentuates the contrast between background and anomalous fluorine contents.

A sampling interval less than 100 feet is necessary so as not to miss the narrow fluorine dispersion haloes and to increase the chances of getting more than one anomalous station over the vein. The Ba and Zn contents of soils are useful tracers for fluorite veins, and their contents correlate closely with those of fluorine. Strontium, however, is of little use for locating fluorite veins. The A horizon also appears to give the best results for Ba and Zn.

- (h) The water soluble fluorine in soils, expressed either as an absolute amount or a percentage of the total soil fluorine, is greatest in the A horizon and decreases downwards into the C horizon. The uptake and subsequent release of free fluoride by plants

is probably responsible for this increase in the A horizon.

The amount of water leachable fluorine varies from 0.2% to about 6% of the total amount of fluorine present. Smaller amounts of leachable fluorine as well as less differentiation in the leachable fluorine content of the different soil horizons occurs in clay rich soils. The good correlation of water soluble fluorine with the total fluorine along a detailed soil traverse indicates that this simple leaching method can be used as a rapid and inexpensive test in geochemical exploration for fluorite deposits.

- (i) In conclusion, geochemical exploration methods using F, Ba, and Zn as tracers are applicable to the search for new fluorite deposits. The information obtained from the various reconnaissance surveys indicates that the area still contains yet undiscovered fluorite veins. Natural fluorine dispersions in vegetation and, especially, in ground waters of the Madoc area should be carefully studied to determine if they are a health hazard.

APPENDIX A

FLUORSPAR: AN IMPORTANT SOURCE OF FLUORINEUses of fluorite

Fluorite (CaF_2), the most common fluorine mineral, has been known since antiquity when transparent crystals in various colours were used as semi-precious stones. Components for high quality optical systems are still cut from clear colourless crystals of natural or synthetic fluorite.

Agricola in his *Bermanus* (1529) reports its use as a flux in the smelting of metals. Heinrich Schwanhard of Nuremberg, a famous glass cutter, discovered in 1670 that glass could be etched when fluorite was treated with strong acids. Many investigators in trying to isolate fluorine were disabled or met with premature death because of continuous exposure to toxic fluorine or fluorine compounds. Elemental fluorine was finally isolated and identified in 1886 by Professor Henry Moissan at the "Ecole Supérieure de Pharmacie" in Paris using an electric furnace process (Week and Leicester, 1968).

Fluorite, commercially known as fluorspar, is industry's principal source of fluorine. In recent years, fluorspar has become an increasingly important mineral commodity upon which a broad spectrum of industrial processes are dependent.

General reviews on the uses and status of fluorspar are provided by Guillet (1964), Readling (1970), Cote (1972).

Fluorspar is marketed in three grades according to its prospective use (Table 11). These are: ceramic grade containing 88 to 97% CaF_2 ; metallurgical grade containing 60 to 80% CaF_2 ; and acid grade containing over 97% CaF_2 .

Ceramic grade fluorspar, the least important of the three, is used mostly as an opacifier of glass and enamels, and as a glaze constituent for face brick.

Metallurgical grade fluorspar is employed in a number of smelting processes, the most important being in the steel industry where it is used to remove impurities and to improve the separation of metal and slag by increasing slag fluidity. Because of the ever growing demand for steel and the introduction of technological changes in furnace processes, the consumption of metallurgical grade fluorspar is increasing yearly. Steel makers are changing from the basic open hearth process which consumes 3 to 5 lbs. of fluorspar per ton of steel produced to the electric furnace process and recently, to the basic oxygen process which require 8 to 10 lbs. and 10 to 15 lbs. of fluorspar, respectively .

The production of hydrofluoric acid utilizes more than half of the world's current fluorspar output (Cote, 1972). The aluminum industry alone consumes

Table 11: Types of fluorspar and uses

Classification	Uses	Approximate % of total CaF_2 production used
Transparent crystals	gemstones optical components	--
Ceramic grade 88 - 97% CaF_2	opalescent glass enamels brick glazing	less than 5%
Metallurgical grade 60 - 80% CaF_2	steel production smelting of metals	45 to 50%
Acid grade 97% CaF_2	production of magnesium and beryllium synthetic cryolite for the aluminum industry fluorine salts rocket fuel fluorocarbons: solvents, resins, films, refriger- ants, aerosol propellants, plastics petroleum alkylation uranium refining water fluoridation	50 to 55%

approximately 40% of all HF produced. This HF is reacted with sodium salts and aluminum fluoride to obtain artificial cryolite which is essential for fluxing in the electrolytic cell reduction of aluminum oxide from bauxite to aluminum. Approximately 45 lbs. of cryolite and 40 lbs. of aluminum fluoride are required to produce one ton of aluminum in the process. This is equal to slightly more than 125 lbs. of acid grade fluorspar per ton. Roughly 35% of the HF produced is used to synthesize fluorocarbons such as solvents, resins, plastics, films, refrigerants, and aerosol propellants. It is also important in the uranium hexafluoride diffusion process for refining uranium. Each ton of uranium that is converted into uranium hexafluoride requires an equivalent amount of fluorspar. Fluorine is also used in the production of magnesium, in rocket fuels, in petroleum alkylation, in water fluoridation, and in the production of some portland cements.

The amount of fluorine that a country uses could possibly be used as an index of its industrial development.

Supply and demand

The world's total fluorspar consumption in 1970 is estimated at 4.1 million tons. The most important source is Mexico's extensive bedded deposits which supply approximately one quarter of the world's demand (Table 12). The United States is the largest consumer; roughly 85% of its total fluorspar requirement is imported. The Kentucky-

Illinois district supplies the greater part of the U.S. home production.

The rapid growth of the world's fluorspar demand is expected to continue primarily because of the increasing consumption in the steel industry as a result of the wider use of basic oxygen steel furnaces. It is anticipated that the demand for fluorspar in this industry alone will reach 3 million tons in 1975, more than double the 1968 figure. Therefore, the steel industry is faced with a possible shortage of metallurgical grade fluorspar and will thus be forced either to use expensive, higher grade fluorite concentrates, to reduce consumption, or to discover new sources. During the 1960's, aluminum production increased at an annual rate of 8%. This growth is expected to persist throughout the 70's, and by 1975 the aluminum industry may require the equivalent of 1 million metric tons of acid grade fluorspar yearly. The fluorocarbons industry is also expected to continue growing at the yearly average rate of 8%. All considered, the world demand for fluorspar may vary from 5 to 6.5 million tons yearly by 1975.

Prices are increasing for all grades of fluorspar. The maximum price quoted in 1971 for acid grade fluorspar in the United States was \$93.50 a metric ton as compared with \$70 to \$80 in 1970. Metallurgical grade fluorspar is lower priced because of inexpensive concentration processes such as hand sorting. Prices in 1970 ranged from \$45 to \$50 a short ton and are still increasing.

Table 12: World production of fluorspar, by countries (Short tons).

Country	1967	1968	1969
North America:			
Canada	72,752	105,000	110,000
Mexico	865,439	1,021,000	1,089,417
United States (shipments)	295,643	252,411	182,567
South America:			
Argentina	21,225	21,853	22,000
Chile	502	--	--
Europe:			
France (marketable)	269,000	297,600	830,693
Germany: East	88,000	88,000	88,000
West (marketable)	108,063	110,000	101,743
Italy	226,190	247,944	284,490
Spain (marketable)	268,000	282,000	353,000
United Kingdom	163,142	218,000	220,000
U.S.S.R.	420,000	420,000	440,000
Africa:			
Rhodesia, Southern	165	165	165
South Africa, Republic of	105,058	119,667	165,650
Tunisia	2,756	6,003	6,000
Asia:			
China, mainland	275,000	275,000	275,000
India	1,778	1,305	2,385
Japan	16,871	17,335	13,133
Korea: North	33,000	33,000	33,000
South	62,796	51,372	43,000
Mongolia	55,000	66,000	83,000
Thailand	146,775	270,173	328,000
Turkey	1,600	2,209	2,308
Total	3,498,755	3,906,042	4,173,551

(adapted from Readling, 1970)

Although the demand for hydrofluoric acid will continue to rise, the use of acid grade fluorspar as a source of fluorine may not continue to increase as rapidly as in the late 1960's. This suppression may be brought about indirectly by pollution control policies which will prevent phosphate fertilizer refining companies from releasing toxic fluorine pollutants into the environment. This fluorine which is easily removable as fluosilicic acid, is marketable. Considering that natural phosphates on the average contain 3 to 4% fluorine, it is possible to extract from the 16 million tons of phosphate fertilizers treated yearly in the United States alone, an amount of fluorine equivalent to 1.2 million tons of acid grade fluorspar.

Present Canadian fluorspar production comes from two mines on the Burin Peninsula in Newfoundland. All production is utilized in the Alcan plants at Arvida, Quebec. Production in 1970 was estimated at 158,000 short tons, making Canada the tenth largest world producer of fluorspar. Almost all fluorspar consumed outside the aluminum industry in Canada is imported mainly from Mexico.

Steadily increasing demand and prices will undoubtedly provide sufficient incentive to re-assess known fluorspar occurrences in Canada. One of these occurrences is located near the town of Madoc in southeastern Ontario.

The world's fluorspar reserves are unknown but are often quoted to range from 70 to 150 million tons. An imminent shortage will develop before the turn of the century if no additional reserves are located. Therefore, extensive exploration programs will be initiated to discover new sources. Geochemical exploration methods may be of great help in this task especially since geophysical methods are of little use in locating fluorite deposits.

APPENDIX B

GEOCHEMISTRY OF FLUORINE

Fluorine, the lightest halogen, is the most electronegative element and one of the most reactive. Its ionic radius ($1.36 \text{ \AA}$) is comparable to that of the hydroxyl ion ($1.40 \text{ \AA}$). Since the electric charges are also similar, F^- ions can isomorphously replace OH^- ions in some crystal lattices. To a lesser degree, F^- also replaces Cl^- ($1.81 \text{ \AA}$) and O^{2-} ($1.40 \text{ \AA}$).

Reviews of fluorine geochemistry are given by Rankama and Sahama (1950), Goldschmidt (1954), Correns (1956), Fleischer and Robinson (1963), Gulyaeva and Itkina (1967), Marier and Rose (1971), and Koritnig (1972).

Rocks

Fluorine is the 14th most abundant element in the earth's crust. In igneous rocks it ranks twelfth in abundance and averages 800 ppm (Rankama and Sahama, 1950), while in continental rocks, it averages 650 ppm (Fleischer and Robinson, 1963). It is the most abundant of the halogens and it is widespread in the lithosphere, hydrosphere, and atmosphere.

Fluorine is strongly lithophilic and is commonly concentrated in the last magmatic fractions. It is abundant in granitic and alkalic rocks and their extrusive equivalents (Table 13). Granites that have undergone

greisenization are generally strongly enriched in fluorine.

Limestones are usually poor in fluorine.

Excluding phosphorites, only shales and pelites in the sedimentary rock suite contain substantial amounts of fluorine. This is attributable to certain clay minerals which readily accept fluoride ions in their lattice.

Data on the fluorine content of metamorphic rocks are scarce. However, it is reasonable that the fluorine content of metamorphic rocks is dependent on the rock's original content. It also follows that the metamorphic rocks richest in fluorine are those that contain the large proportions of micas and amphiboles.

Fluorine occurs not only in the fluorite and apatite phase of silicate rocks but also in the lattices of silicates such as micas, amphiboles, tourmaline, and sphene as well as in liquid inclusions. Koritnig (1972) lists the most important fluorine minerals as follows:

Fluorite	47.81 to 48.80%
Apatite	1.35 to 3.36%
Phlogopite	0.05 to 6.74%
Biotite	0.08 to 3.50%
Muscovite	0.02 to 1.95%
Sphene	0.03 to 1.36%
Tourmaline	0.07 to 1.27%

Table 13: Fluorine content of crustal rocks. (Adapted from a literature compilation by Fleischer and Robinson, 1963)

ROCK TYPE	ROCK NAME	NO. OF SAMPLES	F CONTENT PPM	
			RANGE	AVERAGE
Intrusive igneous rocks	gabbro, diabase	26	50-1100	420
	granite, granodiorite	93	20-2700	810
	alkalic rock (syenite and nepheline syenite)	65	200-2250	1000
Extrusive igneous rocks	basalt	130	20-1060	360
	andesite	77	0-780	210
	rhyolite, obsidian, liparite	78	0-1700	480
	phonolite	14	860-1490	930
Sedimentary rocks	limestone	98	0-1210	220
	dolomite	14	110-400	260
	sandstone and greywacke	49	10-880	180
	shale	79	10-7600	800
	evaporite	30	10-890	200
	phosphorite		up to 40,000	
Unconsolidated materials	oceanic sediment	79	100-1600	730
	volcanic ash and bentonite	270	100-2900	750
	soil	327	10-7070	285
N.B.: All rocks considered to contain anomalous amounts of fluorine were omitted.				

Waters

Fluorine occurs in surface and ground waters, in the oceans, and in precipitation (rainwater and snow). The average fluorine content in Russian fresh water basins was found to vary between 200 ppb and 500 ppb (Kazakov, and Sokolova, 1950). They postulated that such factors as the commonly low pH of the natural waters in the basins and the negligible amount of dissolved phosphate have little effect on fluorine hydrogeochemistry. The average fluorine concentration in river and lake waters is reported to be 260 ppb and 100 ppb by ~~Correns~~ (1956) and Carpenter (1968) respectively. The latter figure is probably closer to the world average for the fluorine content of fresh water.

The fluorine content of ground waters is variable. Concentrations from 0 ppm to 67.2 ppm have been reported, the highest concentrations having been found in the Rustenburg district of South Africa (Bond, 1945). In North America, most naturally fluoridated waters are hard waters, and these can contain up to 27 ppm fluorine (Marier and Rose, 1971). However, very few ground waters, even in terraines containing fluorite deposits, have a fluorine concentration exceeding 10 ppm, the maximum allowed by the solubility product of fluorite in pure water. Very little is known about the fluorine content of ground waters in relation to their host rock; but as may be expected,

waters derived from alkalic and granitic rocks are generally rich in fluorine. High fluorine contents in the ground waters of the Moscow area were found to coincide with high sulfate contents up to 50 to 70 ppm sulfate above which, the concentration of fluorine no longer increases but appears to be stabilized by calcium (Voroshilov, 1966). Although host rocks may contain little fluorite, ground waters can be enriched in fluorine as a result of extended contact with host rocks containing other fluorine minerals.

The oceans are reported to contain between 0.77 and 1.40 ppm of total fluorine (Marier and Rose, 1971), but the concentration most commonly falls between 1.0 and 1.2 ppm. The solubility of fluorite in sea water was found by Kazakov and Sokolova (1950) to vary from 7 ppm at 0°C. to 12 ppm at 15°C. The oceans are, therefore, greatly undersaturated with respect to fluorite and precipitation of the mineral is not expected. The oceans are closer to saturation with respect to apatite. Fifty per cent of the total sea water fluorine is bound as the double ion MgF^+ while the rest occurs as the free fluoride ion (Robertson, 1966). The fluorine content of total dissolved salts in river waters was calculated to be 280 times greater than the fluorine content of ocean salts (Kazakov and Sokolova, 1950). This points to the existence of efficient mechanisms for the removal of fluorine in the oceans.

Fluorine is released naturally to the atmosphere from the oceans and continents primarily by evaporation and transpiration and secondly as spray aerosols and gaseous escape. With the expansion of industry and the growing importance of fluorine technology, man is also contributing significant amounts of fluorine to the atmosphere. This fluorine is dissolved and carried down by rain water.

The fluorine concentration in rain water has been theoretically investigated (Bewers, 1972). The natural range of fluorine can be expected to vary from 24 ppb to 49 ppb. The fluorine content of rain water from isolated areas with good atmospheric mixing confirms the theoretical values. However, much higher concentrations are reported for industrial areas. Rain water in the industrial areas of Germany (Garber, 1970) is reported to contain between 280 ppb and 14,100 ppb depending on the type of industry and the distance from the emitting source.

The fluorine content of natural waters is dependent on the solubility of fluorine minerals. Although over 30 minerals are known to contain fluorine, only apatite and fluorite can possibly exert some control on the fluorine content of waters. Fluorite is the least soluble of the fluorine minerals. Its solubility in pure water increases directly with temperature and has been calculated by various investigators to be about 16.5 ppm CaF_2 which is equivalent to 8 ppm of fluorine at room temperature

(Table 14). Daniel R. Boyle (personal communication) has tested the solubility of fluorite in doubly distilled water and found it to yield closer to 10 ppm fluorine. The compounds of fluorine with metalloids and metals such as Na, K, and Si are more soluble and favour the mobilization of fluorine. Calcium salts reduce the solubility of CaF_2 in water because of the common ion effect. An increase in the CO_2 content of water raises the solubility of fluorite.

Table 14: The solubility of fluorite in pure water according to various authors.

Author and year of investigation	T°C	Solubility of CaF_2 mg/l.	F ppm
Kohlrausch 1908	0.05	13.1	6.37
	26.6	16.0	7.79
Aumeras 1927	25.0	18.0	8.77
Mougnard 1931	18.0	18.3	8.91
Jensen 1937	-	14.3	7.20
Kazakov 1950	20.0	15	7.3
Boyle*	1972	20.6	10

* Personal communication

The highest ground water fluorine concentrations in areas containing ore deposits in acid magmatic rocks occur either in acidic or alkaline waters (Figure 25), the lowest concentrations occurring at pH 6.7 (Krainov et al., 1967). They attribute this phenomenon firstly to the increased stability of negative fluoride complexes and a greater concentration of Na in alkaline waters, and secondly to the common occurrence of large amounts of complex-forming elements in acidic waters from sulfide deposits coupled with the attack of sulfuric acid on fluorite which liberates hydrofluoric acid.

According to Krainov, the hydrogeochemistry of fluorine in sedimentary rocks and in acid magmatic rocks is essentially similar.

Fluorine has the capacity to form complex compounds with the elements of Groups III and IV of the periodic table. Acid salts of the quadrivalent metals are known and these are of the general type H_2MF_6 , where M can for example be Si, Ti, and Zr, and where the two hydrogens can be replaced by the metals of Groups I or II (Carter, 1928). These salts are all more soluble than fluorite.

Fluoride ions in water commonly form complexes with Al, Fe, B, and Si. Aluminum fluoride complexes form when the fluoride content of water exceeds 2 ppm (Kleyner, 1950). The possible series of complexes is:

Figure 25: Plot of the arithmetic means (□) and median values (•) of the fluorine content of waters from deposits of acid magmatic rocks against pH. (Krainov et al., 1967)

Hydroxyl ions can also partly replace fluorine in these complexes. Similar complexes can form with Fe^{3+} , but they are approximately 10 times less stable than the corresponding aluminum complexes (Krainov et.al., 1967); furthermore, the positive complexes are at least 1,000 times more stable than the negative ones. Experimentally, the addition of Ca decomposes the negative fluoride complexes while the addition of Na, which forms highly soluble fluorine salts, stabilizes the complexes and hence maintains fluorine in solution (Savchenko, 1957). Boron was also observed by Krainov to increase the mobility of fluorine in ground waters. Every high fluorine concentration coupled with high Ca was accompanied by high B contents. Complexes of the type $[\text{BF}_4]^-$, $[\text{BF}_3(\text{OH})]^-$, and $[\text{BF}_2(\text{OH})_2]^-$ were probably responsible for maintaining the mobility of fluorine.

Fluorine is very mobile in ground waters and forms detectable dispersion aureoles around deposits (Krainov et.al., 1967). The dispersion of fluorine in stream waters in Germany was found useful in prospecting for fluorite deposits (Friedrick and Plugger, 1971).

Sediments

Little is known about the geochemistry of fluorine in sediments. The normal fluorine content of freshwater

sediments varies from 400 to 1,000 ppm, averaging 670 ppm (Mun et.al., 1966). The range of fluorine concentrations in ocean sediments is almost identical even though sea water normally contains more fluorine. They also pointed out that sapropels from four lakes averaged 960 ppm fluorine (1.5 times higher than the sediments), and that the organic fraction of the sediments contained from 1,200 to 5,000 ppm, averaging 3,000 ppm F. Organic matter, therefore, appears to play an important role in concentrating fluorine in some sediments. An indication of this phenomenon between fluorine and organic matter in certain bitumens and coals of Russia was also found by Gulyayeva and Itkina (1963). Consequently, fluoride ions may be adsorbed by certain organic materials as well as clay minerals in stream and lake sediments. The downstream dispersion of resistant clastic fluorine bearing minerals can also produce dispersion patterns useful in geochemical exploration.

Soils

Fluorine is a constituent of all soils. Normal soil fluorine concentrations average between 200 and 350 ppm (Table 15). The world average of 285 ppm quoted by Fleischer and Robinson (1963) for fluorine in soil is probably the best approximation. They omitted phosphatic soils from their compilation.

Fluorine increases with depth in virgin soils (Robinson and Edgington, 1946). Therefore, fluorine is not

Table 15: Fluorine content of soils

Reference	Number of Samples	F ⁻ content in ppm Range	Average
Steinkoenig (1919)	16	trace - 1500	240
Robinson and Edgington (1946)	137	trace - 7070	290
Vinogradov (1957)	46	30 - 320	200
Nackowski (1952)	-	170 - 510	340
Fleischer and Robinson (1963)	341	10 - 7070	285

* Compilation of data from 10 authors.

N.B. Phosphate rich soils were omitted.

only related to the colloids, clays, and organic matter of the upper soil horizons but is also present in unweathered clastic minerals such as micas in the C soil horizon. Micas and clays are marked adsorbers of fluoride ions. This phenomenon is attributed to the exchange of adsorbed hydroxyl ions for fluoride ions at centers of positive charge on clay mineral surfaces.

An increasing fluorine content is frequently accompanied by a corresponding increase in CaCO_3 which inhibits fluoride ion mobility (Gisinger, 1968). The

availability of fluorine in soils is dependent on its form. Less than 10% of the total soil fluorine is usually water soluble. Gisinger experimentally added complex, soluble fluorine salts to soils and found that most of the fluorine was not firmly bound even after two years.

Plants can increase the amount of exchangeable fluorine in soils. The highly acidic root tips can release Ca from apatite thereby mobilizing phosphate and fluoride ions (Johnston, 1972). Other minerals such as micas and clays are also attacked by enzymes from root tips with a consequent release of fluorine.

Fluorine in soils can form insoluble aluminum silicofluorides of the type $\text{Al}_2(\text{SiF}_6)_3$ (MacIntire et.al., 1955). Experimental work by Huang and Jackson (1965) indicated that fluoride ions bring lattice Al^{3+} and Fe^{3+} ions into solution with a stoichiometric release of OH^- . However, this reaction is of minor significance. The quantity of colloidal soil material and the abundance of aluminum hydroxides are by far the most important factors influencing the retention of fluorine in soils.

Various materials were tested for their capacity to adsorb fluoride ions (Table 16) (Bower and Hatcher, 1967). Aluminum hydroxides were at least 20 times more efficient than clays. Three out of the four soils analysed by Romney et.al. (1969) had a high fluorine content and the most important factor affecting the fluorine concentration was the clay mineral composition of the soil and not the pH.

Table 16: Adsorption of fluoride by minerals, aluminum hydroxide, and soils. (Adapted from Bower and Hatcher, 1967)

Material	pH of Sat. Paste	F Adsorbed at Indicated Equil. Solu. Conc.	
		2 ppm	16 ppm
Gibbsite, Brazil	7.0	80	190
Goethite, Ironton, Minn.	7.0	trace	30
Kaolinite, Bath, S.C.	6.2	100	295
Kaolinite, Dry Branch, Ga.	5.0	70	200
Dehydrated halloysite, Bedford, Ind.	6.1	580	1400
Hydrated halloysite, Bedford Ind..	7.0	420	1777
Bentonite (montmorillonite) Wyo. .	8.7	trace	trace
Vermiculite, Mont.	8.5	trace	trace
Aluminum hydroxide, freshly ppt. .	6.3	21,800	32,600
Aluminum hydroxide, ppt. on wyo. bentonite (18 me Al(OH) ₃ /g. bent.)	6.3	26,900	47,900

The use of commercial fertilizers increases the soil fluorine content. The addition of 1,000 lbs. per acre of superphosphate can locally increase the soil fluorine content by 7.5 ppm. Only 5 to 6% of the fluorine increment added yearly by fertilizers was removed by seepage water and the fluorine lost by harvest was negligible (Oelschlager and Hohenheim, 1971). Therefore, the content of agricultural soils increases every time phosphate fertilizers are added, and after several years this accumulates to significant amounts. The mobility of fluorine in soils and its availability to plants is greatly dependent on the solubility of the fluorine compounds as well as the lime and alumina content (MacIntire et.al., 1951).

The exchangeable soil fluorine in fertilized agricultural soils was studied by leaching with a 0.1 M CaCl_2 solution (Larsen and Widdowson, 1971) and it was found that:

- (a) the soil to solution ratio giving optimum results was 16 g. per 50 ml.
- (b) the fluorine concentration in soil extracts was stabilized after 16 hours of shaking.
- (c) the addition of superphosphate fertilizers greatly increases the amount of water leachable fluorine.
- (d) the greatest amount of water soluble fluorine in agricultural soils was found in the top 20 inches.
- (e) there was a definite pH effect on the soluble soil fluorine, a minimum occurring at pH 6.

Little serious research has been done on the use of fluorine dispersions in soils as applied to geochemical exploration. Only two papers, one by Nackowski (1952) and the other by Cachau-Herreillat and Prouhet (1971), were available for reference.

The usefulness of F, Ba, Sr, Cu, Pb, and Zn as tracers in soils over fluorite deposits was tested in three areas of the Kentucky-Illinois fluorite district (Nackowski, 1952). In two areas, the fluorine content of soils varied from 170 to 510 ppm, averaging 340 ppm. Anomalous concentrations were only 21% higher than the mean. In the third area, the fluorine content of soils ranged from 340 to 1,400 ppm, averaging 650 ppm. Anomalous concentrations were at best only 54% higher than the mean. Nackowski concluded from this that the use of the fluorine content of soils as an indicator of fluorite-barite deposits was unsuitable and that Pb and Zn which also occur in the Kentucky-Illinois deposits should be used.

The practicality of fluorine as an indicator of skarn tungsten deposits was tested in the Pyrénées (Cachau-Herreillat and Prouhet, 1971). A soil fluorine anomaly was found which considerably enlarged the target area but was displaced laterally from the tungsten anomaly.

Biogeochemistry

Fluorine plays a more basic role in animal life than had been formerly thought (Frieden, 1972; Messer, 1972)

and is not only present as a constituent of bone phosphates. Reviews on the biogeochemistry of fluorine are given by Hegsted (1967) and Marier and Rose (1971).

Although fluorine is a minor constituent of all vegetable matter, its metabolic function in plants is still unknown. Fluorine contents of 10 ppm or less (air dried basis) are considered normal for vegetation. The amount of fluorine taken up by vegetation is largely dependent on the plant type as well as the available fluorine in soils. Some, like the tea plant, are fluorine accumulators. The average fluorine content of commercial tea is about 100 ppm, of which 90% is water soluble (Fleischer and Robinson, 1963). Some types of British tea have been found to contain as much as 400 ppm. In industrially contaminated regions, the fluorine content of leaves can increase by factors varying from 2 to 260.

Fluorine occurs in vegetation in at least two forms. Some plants indigenous to Africa, Australia, and Brazil synthesize organofluorides such as fluoroacetates which mammalian species convert to fluorocitrate, a potent inhibitor of aconitase which controls the blood citrate levels. Fluoroacetate is approximately 500 times more toxic than free fluoride. Recent data (Marier, 1971) indicate that this process may be more widespread than was considered some years ago.

Vegetation can also accumulate fluorine in inorganic forms (Bovay, 1969; Romney, 1969; Brewer, 1966).

This fluorine is concentrated in intercellular spaces, especially at the leaf margins and tips. Varying amounts of fluorine (up to 40%) can be mobilized towards the outer leaf surfaces where it can be removed by washing. In industrially polluted areas, large quantities of atmospheric fluorine can be absorbed through plant leaves. This fluorine is concentrated in the same leaf parts.

The amount of fluorine taken up by plants is often unrelated to the soil's total fluorine content. Other factors such as the soil type, the soil pH reaction, and the total calcium and phosphate contents play important roles. Fluoride ions are not taken up by crops on soils that contain sufficient calcium (MacIntire et.al., 1969); however, greater fluoride uptakes can occur in acidic soils. The presence of certain elements like Al, Fe, and B, which form complexes with fluoride ions may have a favourable effect on the uptake of fluorine by vegetation. The presence of only 110 ppb of available boron in soils can double the fluorine uptake of vegetation, and this effect is expected to increase in acidic soils (Collet et.al., 1969). This phenomenon was attributed to a synergistic effect of unbound boron on fluorine uptake.

Although an extensive literature exists on the biogeochemistry of fluorine oriented towards agriculture and environmental pollution, the literature on its use in mineral exploration is nil, although there are indications that it could possibly be useful. Provided

such factors as soil type, pH, drainage, and vegetation cover are kept as constant as possible, the fluorine content of vegetation will reflect the fluorine content of the soil. Field tests as simple as washing the leaves of certain plants or trees in unpolluted areas could yield data useful in the search for deposits.

APPENDIX C

INSTRUMENTATION AND ANALYTICAL METHODS

DETERMINATION OF FLUORINE

Instrumentation

Theory

The success of the fluoride selective ion electrode, developed by Orion Research in the late 60's, is dependent on the crystal membrane property of a lanthanum fluoride crystal. Just as the conventional glass pH electrode responds to the activity of hydrogen ions in solution, the fluoride electrode responds to fluoride ion activity. Both types of electrodes develop a potential across a thin layer of ionically conducting material (Orion Research Manual). The pH electrode employs a thin glass membrane whereas the fluoride electrode uses a rare earth fluoride single crystal (Figure 26). Sealed inside the electrode is an internal Ag/AgCl reference which is immersed in a filling solution containing both fluoride and chloride ions. These respectively ensure a stable potential between the crystal and internal solution as well as between the internal solution and the internal reference. Changes in the fluoride ion activity cause changes in potential. However, when the fluoride ion concentration is low (ie. 0.02 to 10,000 ppm) the difference between the activity and concentration is negligible.

Figure 26: Comparison of the fluoride and glass pH electrodes.

As long as only one ionic species affects the electrode potential, the fluoride electrode responds according to the Nernst equation (Fluoride electrode manual):

$$E = E^{\circ} - 2.3 \frac{RT}{F} \log A_{F^{-}}$$

where:

E = the measured total potential of the system.

E° = potential characteristic of the particular electrode reaction.

R = the gas constant

T = the absolute temperature

F = the Faraday constant (96,493 coulombs)

$A_{F^{-}}$ = the fluoride ion activity in the sample solution

(for a singly charged species at constant temperature (25°C) $2.3 \frac{RT}{F} = 0.059$)

Interferences

Provided the analytical conditions are constant within certain limits, the fluoride ion electrode is practically interference free. The hydroxyl ion, which has a charge and ionic radius similar to the fluoride ion, is the only ionic species that can seriously interfere with the electrode. However, the electrode is ten times more sensitive to the fluoride ion. Therefore, interference by hydroxyl ions is only important in highly basic solutions with low fluoride concentrations. To minimize

this effect, the solutions to be analysed are usually buffered at a pH lower than 7.

Below pH 4.5, hydrogen ions complex fluoride ions in the form of HF and HF_2^- , and since the electrode responds only to free fluoride, the activity or concentration reading will be low. To minimize this effect, the pH of the solutions to be analysed is buffered within the pH range of 5.0 to 6.5.

The magnitude of the electrode's response changes with variations in the total ionic strength of solutions. It is, therefore, important to minimize the effect of natural variations in the total ionic strength of sample solutions by using a total ionic strength buffer.

Activity measurements are also temperature dependent. The temperature of sample solutions should not vary by more than a few degrees.

Operational limits

Quantitative determinations of fluoride ion concentrations varying from 10^{-6} molar (20 ppb) to 10^0 molar or more are possible with the fluoride electrode. The Orion model 407 selective ion meter used in the analyses has a logarithmic scale which permits after calibration the direct readout of fluoride concentrations. This instrument proved to be stable over extended periods and seldom required recalibration until after 4 to 5 hours of operation. A small amount of drift from center scale

was attributable to the coarseness of the meter's center scale calibration control. This drifting commonly occurred towards the upper end of the scale and was found to average about half a division (e.g., 0.05 units). The upper or lower end of the calibrated scale was not affected and, therefore, the drifting was a significant source of error for only those readings near center scale. For solutions containing similar fluoride concentrations (within one order of magnitude), the potential difference between the electrode and solution equilibrates after a few minutes. The electrode's response was verified under optimum conditions (Figure 27) and it was found that reliable readings could be taken after 3 minutes. However, before calibrating, it is important that the instrument's circuits be allowed to reach a stable temperature. This preliminary warm-up commonly required 15 to 30 minutes.

Reproducibility under constant analytical conditions is perfect and identical readings are repeatedly obtained. However, replicate readings after a new calibration can differ by as much as 2%. The reproducibility of readings for duplicate sample preparations (i.e., soils and sediments) can vary by greater amounts because of the heterogeneity of samples. This will be discussed later.

The fluoride electrode responds to small concentration changes in very dilute fluoride solutions but, because it is a logarithmic device, it cannot detect small differences in concentrated solutions.

Figure 27: Fluoride electrode response in a 1 ppm fluoride standard solution.

Problems

A correct pH of sample solutions is not only necessary to prevent interferences. While leaching soils with 0.1 M Na_2CO_3 solutions, the electrode was too hastily dipped into the highly alkaline solution with the subsequent effect that the fluoride electrode lost much of its sensitivity. The response dropped to about 50% of the theoretical and it became impossible to calibrate the ion meter. This effect was counteracted by soaking the electrodes for a few days in a mildly acidic solution containing 10 ppm fluoride and gently buffing the LaF_3 crystal.

A problem also developed with the Orion model 90-01 liquid junction, reference electrode. A thin shield coating inside the electrode disintegrated causing an erratic response. The electrode was replaced by an Orion model 90-01-00 reference electrode which is shielded differently.

Minor electrode instability also resulted from air bubbles adhering to the inside surface of the sealed fluoride electrode. These bubbles were usually dislodged by shaking the electrode.

The fluoride electrode's response is temperature dependent. The magnetic stirrer utilised during analyses developed sufficient heat to significantly increase the temperature of sample solutions after a few minutes. It was therefore important to isolate the magnetic stirrer from the solutions with an asbestos plate.

Determination of fluorine in waters

Equipment

- Orion model 407 selective ion meter
- Orion model 94-09, lanthanum fluoride solid crystal, fluoride electrode
- Orion model 90-01-00 single junction reference electrode and 90-00-00 internal filling solution
- a magnetic stirrer: Fisher Scientific cat. no. 14-511-1V2
- a plastic coated magnetic bead
- a .5 inch thick asbestos plate
- a thermometer
- an automatic timer
- polyethylene beakers: 250 ml.
- polyethylene wash bottles
- graduated cylinders: 100 ml.
- volumetric flasks: 100 ml.
- an abundant supply of absorbant tissues

Solutions

- Total ionic strength adjustment buffer (TISAB):
Dissolve 400 gm of sodium acetate in distilled deionized water; add 30 ml. of glacial acetic acid and make up to 2 litres.
- Canlab's methyl purple indicator which changes colour from purple to green in the pH range of 4.8 to 5.4

- Distilled deionized water for all dilutions and washings

The method for the preparation of the total ionic strength buffer was obtained from Bondar and Clegg Laboratories in Ottawa. The sodium acetate serves to increase the total ionic strength of sample solutions making natural variations in ionic strength negligible. The pH of sample solutions is simultaneously adjusted within the recommended working range, and the acetic acid minimizes the complexing of free fluoride with Al and Fe. Many other types of buffers exist (Frant and Ross, 1968; Ke and Regier, 1970; Wright, 1971). The most effective buffer to release complexed fluoride ions contains CDTA (cyclohexylene dinitrilo tetraacetic acid) which complexes dissolved Al, Fe, Be, Zr, etc. Wright (1971) found that, for practical purposes, a one to one relationship existed between the fluorine results of CDTA-TISAB buffered and TISAB buffered surface waters and mine waters from the Madoc area. D.R. Boyle (personal communication) was unable to detect any complexing in ground waters from the vicinity of fluorite veins at Madoc. Therefore, any appropriate TISAB solution can be used with confidence in the Madoc area.

It is important to use either doubly distilled or distilled-deionized water to make all solutions, dilutions, and washings since ordinary distilled water is often not fluorine free. Blanks of distilled water

contained detectable fluorine concentrations up to 20 ppb. However, no fluorine was detected in blanks of distilled-deionized water.

Preparation of standards

A 1,000 $\mu\text{g./ml.}$ fluorine master standard solution was prepared by dissolving 2.21 g. of pure, dry NaF in distilled-deionized water and diluting to 1 litre. This standard solution and all others were then stored in polyethylene bottles.

A 10 $\mu\text{g./ml.}$ standard solution was prepared by diluting 10 ml. of the 1,000 $\mu\text{g./ml.}$ solution to 1 litre. Daily working standards were prepared by diluting this standard (e.g., 1 ml. of 10 $\mu\text{g./ml.}$ solution diluted to 100 ml. gives a 0.1 $\mu\text{g./ml.}$ or 100 ppb standard). In preparing the daily standards, 10 ml. of TISAB should either be added before diluting to the final volume or added to 90 ml. of the standard solution. This step is necessary to make the total ionic strength of the standards similar to that of the buffered unknowns. The addition of buffer as in the latter case permits the direct reading of unknown fluoride ion concentrations on the logarithmic scale of the ion meter.

Two standards are required to calibrate the ion meter: one to adjust the center scale and one to calibrate the upper or lower working limit. Detailed calibration instructions are included in the Orion meter manual.

If readings are made in millivolts with an expanded scale pH meter, a blank standard is given an arbitrary millivolt value and the subsequent readings for a series of standards are plotted against the fluoride concentration on semi-logarithmic paper. A standard working curve is thus obtained.

Method

Measure 90 ml. of sample solution in a 100 ml. graduated cylinder. Add 10 ml. of TISAB and pour into a polyethylene beaker. Lower the electrodes while stirring at low speed with the magnetic stirrer. Allow the electrodes to stabilize (no less than 3 minutes) and take a reading. Rinse the electrodes with distilled-deionized water and gently wipe dry with absorbent tissue. It is then possible to go on to the next unknown.

Discussion

The water samples should be buffered as soon as possible to prevent sample deterioration. No difference was found between duplicate samples buffered either directly in the field or 24 hours later. However, variations in the fluorine content were detected in the same samples buffered and analysed 2 months later (Table 17). The greatest variations occurred in two samples that also contained algae.

Table 17: Fluorine content of replicate surface water samples as related to the time of buffering.

Sample number	Fluorine content in parts per billion			note
	sample buffered in the field	sample buffered after 24 hours	sample buffered after 2 months	
7	115	115	124	algae
10	99	99	96	
16	89	89	74	algae

If the fluoride ion content of some water samples is outside the calibrated range, the ion meter should be recalibrated with the appropriate standards or the samples can be diluted with distilled-deionized water and TISAB.

Fluorine measurements can be made directly in the field if the temperature does not vary by more than a few degrees from sample to sample; otherwise, the instrument has to be recalibrated. This temperature condition is difficult to satisfy when doing hydrogeochemical reconnaissance. Vehicle vibrations were also found to affect the instrument's center scale calibration, making frequent, time consuming readjustments necessary. Therefore, field tests were abandoned and water samples were analysed in the evenings after they had reached ambient temperature.

Determination of fluorine in soils and sediments

Equipment

- the same analytical equipment as for water analyses.
- plastic measuring spoons.
- an analytical balance capable of measuring to the nearest milligram.
- a muffle furnace capable of reaching 700 to 750°C and containing five or more crucibles.
- about 30 nickel crucibles of 100 ml. capacity with covers.
- an abundant supply of 250 ml. polyethylene bottles.

Reagents and solutions

- flux: KNO_3 and Na_2CO_3 in a 1:2 ratio by weight.
- citric acid: dissolve 250 g. of citric acid monohydrate crystals in distilled water and dilute to 1 litre.
- Can labs methyl purple indicator solution (as received).

Preparation of standards

Standards are made with a similar matrix and ionic strength as the unknowns. To 4 g. of flux, (approximately 3/4 tablespoon), add a known quantity of fluoride standard.

Add 25 ml. of distilled-deionized water followed by 25 ml. of citric acid. Dissolve and make up the volume to 200 ml. and check the pH with 10 drops of methyl purple indicator. (The pH should be within the correct range; however, if it needs adjusting, add dropwise either concentrated base or acid). It is not necessary to fuse the standards since no difference in fluoride content was found between equivalent fused and unfused standards. The working standards can be kept for several days under constant conditions before any deterioration occurs. At least 2 standards are required to calibrate the upper and lower limit of the working range on the logarithmic scale. (i.e., 2 ml. of 100 $\mu\text{g./ml.}$ standard solution diluted to 200 ml. gives a 1 $\mu\text{g./ml.}$ standard which is equivalent to an 800 ppm fluorine content in an unknown analysed by the following method.)

Method

Weigh exactly 0.250 g. of -80 mesh sample and transfer to a 100 ml. nickel crucible. Add 3 g. of Na_2CO_3 - KNO_3 fluxing mixture and blend thoroughly with the sample. Cover this mixture with 1 g. of flux and fuse in a muffle furnace at 700°C to 750°C for 10 minutes. Let cool from a quiescent melt to a solid fusion cake. Add 25 ml. of distilled-deionized water followed by 25 ml. of citric acid. The citric acid should be added slowly to prevent excessive effervescence and spillage. Let stand

for several hours (overnight) to allow the fusion cake to dissolve and loosen. Transfer to a clean 250 ml. polyethylene bottle that has been calibrated and dilute to 200 ml. with distilled-deionized water. Add 10 drops of methyl purple indicator which should give the solution a steel grey to blue-green colour. Analyse with the fluoride electrode as for water samples.

Discussion

The sample preparation used in this study is an adaptation of Ficklin's (1970) method by Bondar-Clegg Laboratories Ltd. The method uses more flux to ensure a better sample decomposition. Consequently, more acid is also required to neutralize the fluxing material. The larger final volume (200 ml. as compared to 100 ml.) is also convenient because is not necessary to control carefully the volume of water used in washings.

The method developed by Ficklin is simple and free from notable interferences. The complexing of aluminum and iron ions with fluoride is prevented by the addition of citric acid. Ficklin reports that results obtained with this method of sample preparation agree within 20% with the USGS rock standards analysed by older methods and that analytical results can be replicated within 15%. A verification of analytical replication in this study gave significantly better results, of the order of 5% (Table 18).

Table 18: Analytical reproducibility and verification of the effect of the in-crucible residence time of sample solutions on reproducibility.

Sample Number and Horizon	In-crucible residence time in hours	ppm F
B-6 (A)	2	440
"	12	400
"	24	390
"	48	415
B-6 (B)	2	390
"	12	410
"	24	430
"	48	415
B-6 (C)	2	310
"	12	305
"	24	320
"	48	305
"	(6 days)	305

Since it was not always possible to transfer the solutions from the crucibles at regular intervals, the residence time of the sample solutions in the nickel crucibles was investigated to determine if it had an effect on the fluoride ion concentration; but none was detected (Table 18). Soil samples were also analysed to ascertain which particle size fraction gives the best fluorine results (Table 9 on page 89). The -80 mesh fraction was found to be

suitable. The positioning of crucibles in the muffle furnace was also investigated because the temperature at the front of the furnace was notably lower than at the back. Replicate samples fused at different temperatures gave quite comparable results; from this, it appears that small variations in fusion temperature have no significant effect on the amount of fluorine liberated from the sample.

The major drawback of the $\text{Na}_2\text{CO}_3\text{-KNO}_3$ sample fusion as compared to using NaOH , KOH , or Na_2O_2 attacks is that the resulting fusion cake does not dissolve readily and can only be freed from the crucible after much time and effort. It was convenient to let the crucibles stand overnight allowing the citric acid to dissolve and neutralize the fusion products. If a routine is set up, this delay becomes an asset. It is possible for one man to routinely prepare 30 samples per day.

If methyl purple is used as an indicator, sample solutions having an improper pH should be noted as soon as possible because the colour deteriorates to blue-green after a few hours.

Samples containing a large concentration of fluorine (e.g. 10% or more fluorite) attacked the nickel crucibles during fusion. This attack usually resulted in serious pitting of the crucible inner surface, and in one case, the base of the crucible completely deteriorated. This phenomenon is possibly attributable to the production of a strongly corrosive substance such as HF or NaF .

DETERMINATION OF pH

The pH of most water samples and of selected soil profiles was determined.

Equipment

- a model GSC portable pH meter and battery charger
- a Beckman model 39149 combination pH electrode
- Fisher Scientific, pH 4, 7, and 10 standard buffers
- 100 ml. polyethylene beakers
- distilled-deionized water and absorbant tissue

Method

The dried electrode was dipped into a 30 to 40 ml. volume of water sample contained in a 100 ml. beaker. The sample was agitated periodically and pH readings were taken after one minute.

The pH of soils was determined in the laboratory on water saturated preparations of undried soil samples according to a method described by Jackson (1958). A volume of approximately 40 ml. of soil was placed in a small beaker and distilled-deionized water was added to the soil in increments from a wash bottle until the entire soil mass was just saturated. A few drops were then added until the surface glistened slightly. At this point, the soil was stirred with a glass rod and drops of water were

added until a slow flowing paste was obtained. This mixture was allowed to stand for several hours to permit equilibrium and the pH was taken by gently inserting the electrode in a hole made with the glass rod and allowing the mixture to close around it.

Discussion

The model GSC, battery operated, portable pH meter used in this study was developed in 1972 by Q. Bristow and G. Gaumont at the Geological Survey of Canada. The meter is coupled with a Beckman combination electrode which is stored in a tube inside the meter. The instrument is calibrated with a pH 7 buffer solution and is verified against two other known buffers.

The instrument remained calibrated for 3 to 4 hour intervals with only a negligible amount of drift and could be used for over 18 hours before the batteries required recharging. Readings could accurately be taken to 0.02 pH units within two minutes by zeroing the 10 turn potentiometer equipped with a calibrated dial. The instrument was effective for taking pH measurements directly in the field.

DETERMINATION OF ZINC

Soils and stream sediments were analysed for zinc by atomic absorption spectrophotometry after a hot nitric acid leach.

Equipment

- a Jarrel-Ash model 82-270 Atomsorb spectrophotometer connected to a strip chart recorder
- an analytical balance
- an abundant supply of 16 mm. x 150 mm. test tubes
- a hot sand bath

Method

Zinc was taken into solution by a hot nitric acid attack on soil and stream sediment samples (Gilbert, 1959).

Weigh 0.200 g. portions of -80 mesh soil or sediment and transfer to a test tube. Add 3 ml. of 30% nitric acid and set on a hot sand bath at a temperature of about 80°C for 3 hours; shake at half hour intervals. Allow the tubes to cool and dilute to 10 ml. with distilled-deionized water and analyse spectrophotometrically. The instrumental working conditions were:

burner height: 15

burner position: parallel

air: 15 psi.

acetylene: 3 psi.

slits: 50 & 75

gain: 5.2

cathode current: 6-7 milliamps

damping: 4

wavelength: 213.2 mμ

Discussion

Samples were prepared in batches of 50. The detection limit was approximately $0.2 \mu\text{g./ml.}$ which is equivalent to 10 ppm in the samples. One out of ten analyses were duplicated to verify the reproducibility of the data (Table 19). Eight duplicates out of 11 were reproduced within 5%, and all 11 duplicates within 15%. This last figure is an indication of the maximum uncertainty. The major factor limiting the precision of analyses is probably the heterogeneous nature (size and mineral composition) of the -80 mesh fraction analysed. Better precision may have been obtained if the samples had been thoroughly mixed and crushed to -200 mesh. Standards were prepared by diluting appropriate amounts of 1,000 ppm standard stock solution in 10% nitric acid to obtain 0.5, 1, 2, 4, 6, 8, and $10 \mu\text{g./ml.}$ standards.

DETERMINATION OF BARIUM AND STRONTIUM

Selected soils were analysed for Ba and Sr by X-ray fluorescence at Bondar-Clegg Laboratories in Ottawa. The instrument used was a Siemens, multichannel, instant read-out XRF spectrometer. During analysis, the soil pulps were rotated to expose them as uniformly as possible to the incident X-rays. This procedure reduces considerably any matrix effect.

Table 19: Reproducibility of Zn analyses.

Sample number	Zn ppm		% difference*
	(1)	(2)	
A-8	69	68	1.4
A-13	190	213	12
B-7	71	68	4.2
B-21	64	64	-
S-32	44	45	2.3
S-37	103	107	4.0
S-44	50	44	12
1S19	27	25	7.4
3S17	64	64	-
5S18	79	68	14
6S26	40	39	2.5

* the percent difference is calculated on the smallest concentration.

Analyses were carried out on -80 mesh soil fractions and were reproducible within 13% for Ba and 7% for Sr (Table 20). The sample size fraction was also investigated to see if it had any effect on the final results. Indications are that if such an effect exists, it is negligible. The amount of sample used for analysis is also important. If too thin a sample is used, a portion of the incident X-rays will pass through the sample and give rise to low results.

Table 20: Reproducibility of Ba and Sr analyses by XRF.

Sample number	(1)		(2)		% difference	
	Ba ppm	Sr ppm	Ba ppm	Sr ppm	Ba	Sr
1S12	1000	385	900	360	11.1	7.0
1S15	925	375	925	360	-	4.2
5S12	900	340	925	340	2.8	-
5S17	900	330	875	335	2.9	1.5
A-13	950	310	975	295	2.6	5.1
A-27	850	435	950*	420*	13.0	3.6
B-22	800	405	(825) 800*	(400) 400*	3.1	1.3

* Samples were crushed to -200 mesh

N.B. The percentage was calculated on the smallest concentration.

REFERENCES

- Aumeras, M., 1927, Journal de Chim. Phys., v. 24, p. 548-571.
- Bovay, E., 1969, Fluoride accumulation in leaves due to boron-containing fertilizers; Fluoride, v. 2, p. 222-228.
- Bewers, J.M., 1972, The global circulation of halogens in nature: 24th Session of the International Geological Congress, held in Montreal, 1972; Section 10, Geochemistry, p. 273-271.
- Bond, G.W., 1945, A geochemical survey of the underground water supplies of the Union of South Africa; Geol. Surv. South Africa, Memoir 41, 208 p.
- Bower, C.A., and Hatcher, J.T., 1967, Adsorption of fluoride by soils and minerals: Soil Sci., v. 103, p. 151-154.
- Boyle, R.W., and Dass, A.S., 1967, Geochemical prospecting - Use of the A horizon in soil surveys: Econ. Geol., v. 62, p. 274-286.
- Brewer, R.F., 1966, Fluorine: Diagnostic criteria for plants and soils, Chapman, H.D. editor, Univ. of Calif., Div. of Agricultural Sci., p. 180-196.
- Brown, J.S., 1967, Genesis of stratiform lead-zinc-fluorite-barite deposits (Mississippi Valley Type); Econ. Geol., monograph 3, 443 p.
- Cachau-Hereillat, F., and Prouhet, J.P., 1971, The utilization of metalloids (As, P, F) as pathfinders for skarn tungsten deposits in the Pyrénées, France: 3rd International Geochemical Symposium, Can. Inst. Mining and Metallurgy, special v. 11, p. 116-120.
- Carpenter, R., 1969, Factors controlling the marine geochemistry of fluorine: Geochim. et Cosmochim. Acta, v. 33, p. 1153-1167.
- Collet, G.F., 1969, Fluoride, v. 2, p. 229.
- Correns, G.W., 1956, Geochemistry of the halogens: Phys. and Chem. of the Earth, v. 1, p. 181-233, Pergamon Press, London.
- Cote, P.R., 1972, Fluorspar: Canadian Minerals Yearbook, 1970, Mineral Report 20, p. 227-233.

- Dunham, K.C., 1966, Role of juvenile solutions, connate waters, and evaporitic brines in the genesis of Pb-Zn-F-Ba deposits: Inst. of Mining and Metallurgy Trans. B, v. 75, p. 226.
- Dunham, K.C., 1970, Mineralization by deep formation waters - A review, Inst. of Mining and Metallurgy Trans. B, v. 79, p. 127-136.
- Edmond, C.R., 1969, Direct determination of fluoride in phosphate rock samples using the specific ion electrode: Anal. Chem., v. 41, p. 1327-1328.
- Ficklin, W.H., 1970, A rapid method for the determination of fluoride in rocks and soils using an ion selective electrode: U.S. Geol. Survey Prof. Paper 700-C, p. 186-188.
- Fleischer, M., and Robinson, W.O., 1962, Some problems in the geochemistry of fluorine: Programme of the Royal Society of Canada, p. 58-75.
- Frant, M.S., and Ross, J.W., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Anal. Chem., v. 40, p. 1169.
- Frieden, E., 1972, The chemical elements of life: Scientific American, July, p. 52-60.
- Friedrich, G.H., and Plugger, W.L., 1971, Geochemical prospecting for barite and fluorite deposits: 3rd International Geochemical Symposium, Can. Inst. of Mining and Metallurgy, special v. 11, p. 151-156.
- Gilbert, M.A., 1959, Field and laboratory methods used by the Geological Survey of Canada in geochemical surveys, No. 1, Laboratory methods for the determination of Cu, Zn, and Pb: Geol. Survey of Canada paper 59-3.
- Gillespie, J.E., Wicklund, R.E., and Richards, N.R., 1962, Soil survey of Hastings County, Ontario: Report No. 27 of the Ontario Soil Survey, 72 p.
- Gisinger, L., 1968, The solution of various fluorine compounds in soil: Fluoride, v. 1, p. 21-26.
- Goldschmidt, V.M., 1954, Geochemistry: Clarendon Press, p. 568-583.

- Guillet, G.R., 1964, Fluorspar in Ontario: Ont. Dept. of Mines, Industrial Mineral Report No. 12, 68 p.
- Gulyayeva, L.A., and Itkina, E.S., 1963, Migration of the halogens in sedimentary rocks: Chemistry of the Earth's Crust, Izd. Akad. Nauk SSSR, II, p. 472-486.
- Hall, J., and Walsh, J.N., 1969, A rapid method for the determination of fluorine in silicate rocks and minerals: Anal. Chim. Acta, v. 45, p. 341-342.
- Hawkes, H.E., and Webb, J.S., 1962, Geochemistry in mineral exploration, Harper and Row, 365 p.
- Hegstead, D.M., 1967, The beneficial and detrimental effect of fluoride in the environment: Proceedings of the Univ. of Missouri's 1st annual conference on Trace Substances and Environmental Health, p. 105-113.
- Hewitt, D.F., 1964, Geological notes for Maps No. 2053 and 2054, Madoc-Gananoque Area: Ont. Dept. of Mines Geological Circular No. 12, 33 p.
- Hewitt, D.F., 1968, Geology of Madoc Township and the northern part of Huntington Township: Ont. Dept. of Mines, Geological Report No. 73, 45 p.
- Heyl, A.V., 1969, Some aspects of the genesis of zinc-lead-barite-fluorite deposits in the Mississippi Valley, U.S.A.: Inst. of Mining and Metallurgy Trans. B, v. 78, p. 148-160.
- Huang, P.M., and Jackson, M.L., 1965, Mechanism of reaction of neutral fluoride solution with layer silicates and oxides of soil: Soil Science Society of America Proceedings No. 29, p. 661-665.
- Jackson, S.A., and Beales, F.W., 1967, An aspect of sedimentary basin evolution - The concentration of Mississippi Valley type ores during late stages of diagenesis: Bull. of Canadian Petroleum Geology, v. 14, p. 383-433.
- Jacson, M.L., 1958, Soil Chemical Analysis, Prentice-Hall.
- Johnston, W.B., and Olsen, R.A., 1972, Dissolution of fluorapatite by plant roots: Soil Sci., v. 114, p. 29-36.
- Kazakov, A.V., and Sokolova, E.I., 1950, Conditions of the formation of fluorite in sedimentary rocks: Akad. Nauk SSSR, Inst. Geol. Nauk, Trudy vyp. 114, Geol. Serii No. 40, p. 22-64.

- Ke, P.J., and Regier, L.W., 1971, Direct potentiometric determination of fluoride in water after 8-hydroxyquinoline extraction: *Anal. Chim. Acta*, v. 53, p. 23-28.
- Kleyner, K.E., 1950, Aluminum fluoride complexes in solution (Russian): *Jour. of General Chem.*, Tom 20.
- Kohlrauch, F., 1909, Concerning the solubility of CaF_2 (German): *Zs. Phys. Chem.*, v. 64, p. 121-169.
- Koritnig, S., 1972, Fluorine: *Handbook of Geochemistry*, v. 11/3, Wedepohl, K.H. editor, Springer Verlag-Heidelberg, New York.
- Krainov, S.R., Rubeikin, V.Z., Kapranov, S.D., and Petrova, N.G., 1967, Fundamental features of the hydro-geochemistry of fluorine in regions of fluorine bearing deposits: (Russian) *University Reports, Geology and Prospecting*, No. 12, p. 30-40.
- Larsen, S., and Widdowson, A.E., 1971, Soil fluorine: *Jour. of Soil Sci.*, v. 22, p. 210-221.
- MacIntire, W.H., Shaw, W.M., and Robinson, B., 1955, Behaviour of incorporations of potassium and calcium fluorides in a six-year lysimeter study: *Jour. of Agricultural and Food Chem.*, v. 3, p. 772-777.
- McDonald, G., 1970, Geology of the Kingston Area - A compilation Carleton Univ. Geological Paper 70-2.
- Marier, J.R., 1971, Fluoride in the environment: *International Symposium on the Identification and Measurement of Environmental Pollutants*, Ottawa, June 1971, p. 404-406.
- Marier, J.R., and Rose, D., 1971, Environmental fluoride: *National Research Council of Canada, publication no. 12*, 226, 39 p.
- Messer, H.H., Armstrong, W.D., and Singer, L., 1972, Fertility impairment in mice on a low fluoride intake: *Science*, v. 177, p. 873.
- Mougnaud, P., 1931, Sur le dosage du fluor: *Comptes Rendus*, v. 192, p. 1733.
- Mun, A.I., Bazilevich, Z.A., and Budeyeva, K.P., 1966, Geochemical behaviour of fluorine in the bottom sediments of continental bassins: *Geochem. International*, v. 3, p. 678-703.

- Nackowski, M.P., 1952, Geochemical prospecting applied to the Illinois-Kentucky fluorspar area: unpublished Ph.D. thesis, Univ. of Missouri.
- Oelschlager, W., and Hohenheim, D.D.R., 1971, Fluoride uptake in soils and its depletion: Fluoride, v. 4, p. 80-84.
- Pluger, W.L., and Friedrich, G.H., 1972, Determination of total and cold extractable fluoride in soil and stream sediments with an ion selective fluoride electrode: Handbook of the 4th International Geochemical Exploration Symposium, London, p. 44.
- Rankama, K., and Sahama, T.G., 1950, Geochemistry: The Univ. of Chicago Press, p. 756-762.
- Readling, C.L., 1970, Fluorspar and cryolite: Bureau of Mines, Minerals Yearbook for 1969, U.S. Dept. of Interior, p. 505-513.
- Robertson, C.E., 1966, Solubility implication of apatite in sea water: U.S. Geol. Survey Prof. Paper 550-D, p. 178-185.
- Robinson, W.O., and Edgington, G., 1946, Fluorine in soils: Soil Sci., v. 61, p. 341-353.
- Romney, E.M., Wool, R.A., and Wieland, P.A.T., 1969, Radioactive fluorine 18 in soil and plants: Soil Sci., v. 108, p. 419-423.
- Saha, A.K., 1959, Emplacement of 3 granitic plutons in southeastern Ontario: Geol. Soc. Am. Bull., v. 70, p. 1293-1326.
- Savchenko, G.S., and Tamanayev, E.V., 1951, On the formation of aluminum and fluorine complexes in water solution (Russian): Jour. of General Chem., v. 21, No. 12.
- Steinkoenig, L.A., 1919, Relation of fluorine in soils, plants, and animals: Ind. Eng. Chem., v. 11, p. 463-465.
- Tooms, J.S., 1970, Review of knowledge of metalliferous brines and related deposits: Inst. of Mining and Metallurgy Trans. B, v. 79, p. 116-126.
- Van Loon, J.C., 1968, The rapid determination of fluorides in mineral fluorides using a specific ion electrode: Analytical Letters, v. 1, p. 393-398.

- Vinogradov, A.P., and Danilove, V.V., 1948, Fluorine in the soils of U.S.S.R.: Akad. Nauk SSSR Doklady, v. 59, no. 7.
- Voroshilov, Yu I., 1966, The geochemical behaviour of fluorine in ground waters of the Moscow region: Geochem. International, v. 3, p. 261.
- Weeks, M.E., and Leicester, H.M., 1968, Discovery of the elements: published by the Jour. of Chem. Education, p. 727-742.
- White, D.E., 1968, Environment of generation of some base metal ore deposits: Econ. Geol., v. 63, p. 301-331.
- Wilson, M.E., 1929, Fluorspar deposits of Canada: Geol. Survey of Canada, Econ. Geol. series No. 6.
- Wilson, M.E., 1940, Geological maps: Madoc sheet map no. 559A, Marmora sheet map no. 560A, Geol. Survey of Canada.
- Wright, G.R., 1971, An evaluation of the fluoride selective ion electrode's use in geochemical exploration and pollution studies: unpublished M.Sc. thesis, Univ. of Toronto.

SYMBOLS

- Provincial highway
- Road, all weather
- Secondary road
- Cell back
- Stream
- Swamp
- Geological contact
- Fault
- Fault extended
- Fluvial bearing faults & fractures
- Rock sample location

LEGEND

Precambrian

VIII, sand, gravel, clay, marl

Paleozoic

Ordovician

- S. Black River Group
- SA. Trenton Group

UNCONFORMITY

Precambrian

- 1. Granite
- 2A. Gneiss
- 2B. Diabase and gabbro

INTRUSIVE CONTACT

- 3. Differentiated mafic and fine silicate rocks
- 2. Pelitic rocks, argillite, graywacke, schist, conglomerate
- 1. Mafic and intermediate and felsic rocks

The base map was prepared by the GSC cartographic services

REFERENCES:

- MacDonald, G. (1970)
- Howell, D.E. (1968)
- Wilson, M.E. (1968)

MAP 1

GEOLOGICAL MAP

MADOC AREA

ONTARIO

SCALE 1:50,000

CONTOUR INTERVAL 50 FEET

National Geographic System reference

1041

LEGEND

- Road, all weather.....
- Other roads.....
- Civil track.....
- Stream.....
- Swamp.....
- Fluoride occurrence.....
- Sample location.....

Analysis and compilation by J. P. LACROIX (101)

The base map was prepared by the G.S.C. cartographic services

MAP 2

FLUORINE IN SURFACE WATERS
AND
FLUORINE AND ZINC IN STREAM SEDIMENTS

MADOC AREA

ONTARIO

Canadian Geographic System reference

CONTOUR INTERVAL 50 FEET

10/1

LEGEND

- Provincial highway
- Road, all weather
- Secondary road
- Cart track
- Stream
- Swamp
- Regional soil sample location
- Regional ground water sample location
- Ground water sample location
- Fluorine content in ppb
- Fluorine contour
- Fluorine contour interpolated
- Contour interval at 10 ppb

Analysis and compilation
by J-P. LAROCHE (1972)

This map was prepared by the OSC
cartographic section

MAP-3
FLUORINE IN GROUND WATERS
IN ppb
MADOC AREA
ONTARIO

Sr

ppm

Sr

ppm

Ba

ppm

Ba

ppm

Zn

ppm

Zn

ppm

2 of 2

LEGEND

TRAVERSE 'A'

TRAVERSE 'B'

REGIONAL SOIL TRAVERSES

FIGURE 16

2 of 2

SAMPLE NUMBER and DISTANCE

SAMPLE NUMBER and DISTANCE

LEGEND

SCALE: 1 CM = 100 FEET

NOYES

Mc BEATH

FIGURE-18

DETAILED TRAVERSES