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RESEARCH IN GEOCHEMICAL PROSPECTING METHODS FOR FLUORITE DEPOSITS, MADOC AREA, ONTARIO

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ABSTRACT

The known fluorite deposits occur in Precambrian marble and Paleozoic limestone as irregular and discontinuous veins in faults and fractures. The veins contain fluorite, calcite, barite, celestite, and minor amounts of sulphides including 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 groundwater samples. Soils were also collected along seven detailed traverses crossing known fluorite veins or their extensions. Fluorine was determined by selective ion electrode, zinc by atomic absorption spectrophotometry, and barium and strontium by X-ray fluorescence.

Most rock types of the Madoc area are fluorine-rich and contain between 1,000 and 2,700 ppm F. Several surface water anomalies associated with areas of fluorite occurrences 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 groundwaters clearly delineates areas containing known fluorite occurrences as well as other targets of interest; a positive correlation exists between groundwater 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 for fluorite veins; but strontium 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.

RÉSUMÉ

Les gisements connus de fluorine se trouvent dans les marbres précambriens et les roches calcaire paléozoïques sous forme de veines irrégulières et discontinues dans des failles et des fractures. Ces veines contiennent de la fluorine, de la calcite, de la barytine, de la célestine et un peu de sulfures, tel que de la pyrite, de la marcassite, et de la blende.

A l'échelle régionale la dispersion secondaire du fluor fut étudiée en échantillonnant 45 coupes pédologiques le long de deux cheminements, en recueillant environ 60 échantillons de sédiments de ruisseaux, 80 échantillons d'eaux superficielles et 200 d'eaux souterraines. Des échantillons de sols furent également recueillis le long de sept cheminements détaillés traversant des filons de fluorine ou leur prolongation. La présence du fluor fut déterminée par électrode sélective, du zinc par spectrophotométrie d'absorption atomique, du baryum et du strontium par radiographie fluorescente.

Les roches de la région de Madoc sont riches en fluor et contiennent de 1000 à 2700 ppm de F. Dans les eaux superficielles, plusieurs anomalies associées aux régions productrices de fluorine furent localisées. Toutefois,

la teneur en fluor des alluvions fut d'une utilité douteuse en exploration géochimique à cause du peu de différence qui existe entre les concentrations anormales et la concentration régionale. La teneur en fluor des eaux souterraines indique clairement les régions où se trouvent les gisements connus ainsi que d'autres endroits prometteurs. Il existe une corrélation positive entre les anomalies des eaux souterraines et les sols riches en fluor le long des cheminements régionaux. La dispersion latérale du fluor dans les sols recouvrant les veines de fluorine est limitée et peut alors servir à localiser les veines. L'horizon du sol qui se prête le mieux à l'échantillonnage de tous les éléments étudiés est l'horizon organique "A" qui accentue le contraste entre les concentrations anormales et la concentration normale. Le baryum et le zinc dans le sol sont aussi de bons indicateurs de filons de fluorine; cependant, le strontium ne l'est pas. Il est possible d'utiliser la fraction du fluor de l'horizon "A" qui est soluble dans l'eau pour des essaies à peu de frais sur le terrain.

Les méthodes d'exploration géochimique se sont avérées utiles dans la réévaluation du potentiel de la région et peuvent aider à localiser de nouveaux gîtes.

RESEARCH IN GEOCHEMICAL PROSPECTING METHODS FOR FLUORITE DEPOSITS, MADOC AREA, ONTARIO

INTRODUCTION

The industrial importance of fluorite has increased considerably in recent years, and this trend is expected to continue. It has been estimated that the total world reserves in 1971 are hardly sufficient to supply the world's demand until the turn of the century. Therefore, it is of prime importance to locate new fluorite deposits, and geochemical exploration methods could prove useful in accomplishing this task.

Only a limited amount of research has been done to investigate the possibilities of using fluorine as a tracer for fluorite or other fluorite-bearing deposits such as barite, apatite, tin, lead-zinc, uranium, and tungsten. A study of fluorine dispersion aureoles in soils over fluorite veins in the Kentucky-Illinois mining district indicated that the fluorine content over veins was generally less than 1.5 times background (Nackowski, 1952). From this Nackowski concluded that fluorine was unsuitable as an indicator, and that Pb and Zn were more useful guides. Hawkes and Webb (1962) state that fluorine may be a useful indicator of fluorite deposits but is not a good pathfinder for Pb-Zn deposits. These early statements, combined with analytical problems, were sufficient to retard research on the use of fluorine as a guide to fluorite and related types of deposits until relatively recently when the development of the fluoride selective ion electrode has greatly simplified fluorine analyses, and Friedrich and Pluger (1971) have shown that the fluoride content of stream waters and stream sediments can be used effectively for locating fluorite deposits in Germany and Spain.

It was, therefore, decided to investigate the practicality of geochemical exploration methods using fluorine as a pathfinder for fluorite mineralization. The Madoc area of southeastern Ontario was selected for this study. This area contains fluorite-barite veins which were mined as late as 1960.

The objectives of the research described in this paper were: to determine the dispersion of fluorine in surface and groundwaters, 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. It was also thought that the study would be useful in reappraising the potential of the Madoc fluorite mining area.

Location, topography, climate, drainage, soil

The field area, covering approximately 200 square miles, is located within a 10-mile-radius of the town of Madoc in Hastings County, south-central Ontario (Fig. 1). The climate is temperate, the average yearly temperature being 44°F, and the average precipitation being between 32 and 35 inches (Gillespie *et al.*, 1962).

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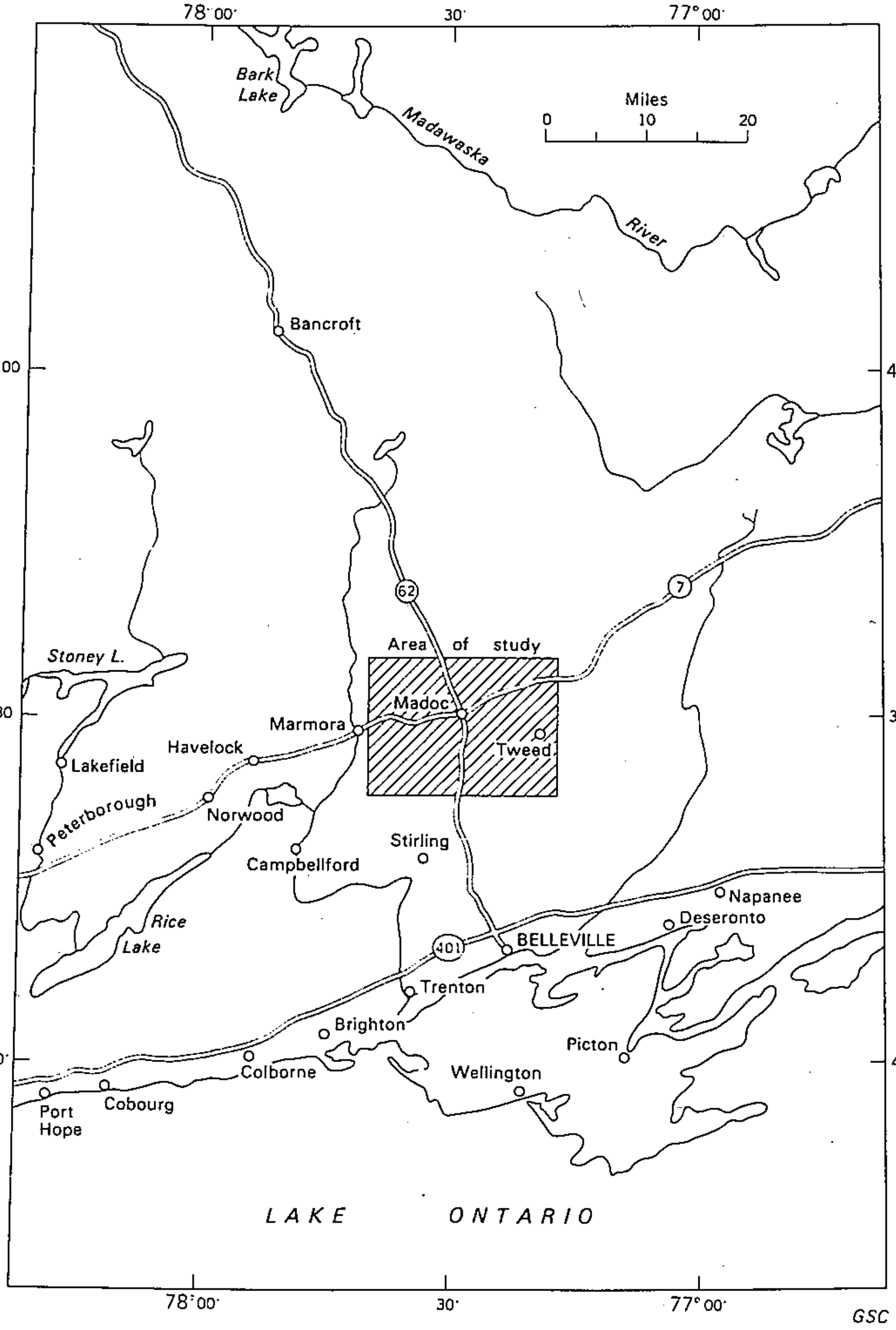

Figure 1. Index map.

The Precambrian-Paleozoic contact that runs along the south side of Moira Lake divides the area into two parts. In the south, the area is underlain by flat-lying Paleozoic limestone. Excluding a few sharply incised valleys, the terrain is flat to gently rolling. Precambrian granites, metavolcanics, and marbles underlie the areas of rolling topography to the north.

The Madoc area is drained by the Moira River, and Moira Lake is the largest body of water. The drainage systems over the flat-lying limestone to the south are poorly developed and are interrupted by extensive swamps.

The soils of Hastings County were studied by Gillespie et al. (1962). In the field area, they can be classified into three great soil groups. Slightly alkaline brown forest soils developed on glacial till predominate over the flat-lying limestones, 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.

Acknowledgments

The author wishes to express his appreciation to Dr. R.W. Boyle of the Geological Survey of Canada who suggested the study, supplied instrumentation for fluorine analysis, made outside arrangements for certain rock and soil analyses and critically read the present report. Thanks are extended to Dr. W.M. Tupper for his supervision and helpful suggestions during the preparation of the thesis on which the present report is based. Thanks are also expressed to all those who assisted in the sample analysis in the laboratories of Carleton University, at Bondar and Clegg Co. Ltd., Ottawa, and at the Geological Survey of Canada, Ottawa. The author is also grateful to Bondar and Clegg Laboratories for making their fluorine analytical methods and instrumentation available at the start of the project.

GEOLOGICAL SETTING

The geology of the area has been studied by Wilson (1929) and Hewitt (1964, 1968), and a geological map of the Kingston area was recently compiled by McDonald (1970).

Rock types

The consolidated rocks of the area are of Precambrian and Paleozoic age (Table 1). The oldest rocks are Precambrian basic metavolcanics which lie in the northeastern corner of the field area (Fig. 20A). These are intruded on the east by the Elzevir granite and are overlain on the west by metasedimentary rocks which are chiefly marbles. 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 rhyolite and felsite volcanics locally overlies the basic volcanics.

Precambrian metasediments consisting of undifferentiated marbles, calcitic marbles, and lime-silicate rocks overlie the volcanic rocks. Pelitic rocks, argillites, schists, and conglomerates locally lie between the metavolcanics and marbles.

TABLE 1
Table of formations

CENOZOIC

Pleistocene: sand, gravel, clay, till

Great Unconformity

PALEOZOIC

Ordovician:	Trenton Group	predominantly limestone
	Black River Group	

Great Unconformity

PRECAMBRIAN (Grenville)

Granite, syenite

Intrusive Contact

Marble, argillite, conglomerate

Basic and acidic metavolcanics

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 from Moira Lake.

The Deloro granite is overlain on the east by Paleozoic limestones, on the west by marbles and pelitic rocks, and on the north and south by marbles. 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, there 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) indicated that accessory muscovite, fluorite, and zircon compose no more than 0.5 per cent of the rock.

The second granite intrusion is the Moira granite which is composed largely of albite and quartz in addition to minor microcline. No accessory fluorite has been reported 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. Overlying these rocks are 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 general ice movement was towards the southwest.

Structure

The principal structures of interest in the area are a series of northwest-trending faults that cut both the Precambrian and Paleozoic rocks. These contain the known fluorite veins which are concentrated mainly in the Madoc area.

The Moira fault trends northwest across the central part of the field area. It is a nearly vertical and slightly sinuous fracture zone which has little surface expression except at its southeastern end. The fault has been traced for about 8 miles extending from a point 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 in which the largest deposits are found or by a zone of closely-spaced narrow fractures. A number of linear topographic features (e.g. the unusually straight stretches along the Moira River) suggest the possible existence of other fault systems.

Fluorite Deposits

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 one occurs in both limestone and metavolcanics. If the importance of the wall-rocks relative to the size of the known deposits is assessed, the order changes: marble become the most important, followed by granite, limestone, and metavolcanics.

The fluorite deposits can be divided into two groups. Those occurring along the Moira fault, or the main break, are referred to as the Moira Lake group. These deposits occupy lenticular fault cavities that resulted from the horizontal displacement of undulating fault walls. Prospecting and drilling along the Moira fault revealed the most important deposits in the area. Some fluorite lenses in the Moira Lake group were 18 feet wide.

The Lee-Miller group includes all fluorite veins occurring in subsidiary fractures to the west and predominantly to the northwest of the Moira fault. These veins occupy narrow, isolated, vertical fissures mostly in Black River limestone. They occur either as connected or disconnected <u>en échelon</u> 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 vein material in the Madoc deposits consists of fluorite, calcite, and barite with minor celestite, quartz, marcasite, pyrite, sphalerite, and bituminous material. As with many vein fluorite deposits, there is no consistent paragenesis. The banded distribution of fluorite, calcite, and barite indicates a rhythmic deposition. Sulphides, celestite, and quartz tend to be more abundant in the zones nearest to 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 per cent. Calcite is the next most common mineral often approaching 50 per cent of the ore but normally averaging perhaps 25 per cent. Calcite tends to increase both with depth and with narrowing vein width at the Howard, Keene, and Bailey mines. Barite is present in amounts from 5 to 40 per cent but averages perhaps 15 per cent. 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 per cent in total.

SAMPLING AND ANALYTICAL PROCEDURES

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 fall by the collection of surface water and stream sediments over a broader area, and additional soil samples from a number of profiles were obtained.

A few soil samples were collected well away from known fluorite veins to obtain regional background concentrations 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 1971, and resumed again in April 1972, at which time groundwaters were collected along two twenty-mile long regional traverses, corresponding as closely as possible to the regional soil traverses. The results from both water traverses prompted a reconnaissance groundwater 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 run during the previous fall 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 groundwater, and over 450 soil samples had been collected.

The surface waters and groundwaters were collected in 250 ml polyethylene bottles with similar caps and their pH and temperature determined in situ. The pH measurements were made with a Model GSC[1] portable pH meter fitted with a Beckman combination electrode. Before sampling, the sample bottles were thoroughly cleaned with acid- and metal-free water and rinsed twice with the water to be sampled. Duplicate samples were collected at every tenth sample location.

Soil samples were obtained with a shovel or mattock, and care was taken to avoid contamination from one horizon to the other. Soil and stream

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[1] The Model GSC portable pH meter was developed in 1972 by Q. Bristow and G. Gaumont at the Geological Survey of Canada.

sediment samples were collected in water-resistant paper sample bags. Bagged sediment samples were separated from one another by storing them in water-proof bags.

The soil and sediment samples were brought back to Ottawa where soil pH measurements were made. The samples were then oven dried in their bags at approximately 70°C for 48 hours and then sieved to minus 80 mesh.

The rock samples were sent to Bondar and Clegg laboratories where they were crushed, ground, and analyzed for fluorine by Orion Research selective ion electrode following a fusion and distillation procedure to avoid interferences due to complexing.

The fluorine content of waters was determined by selective ion electrode in a field laboratory after the samples had reached room temperature. The water samples were buffered with a solution containing sodium acetate and acetic acid at pH 6.0.

For fluorine determination using the selective ion electrode, soils and sediments were fused with a KNO_3-Na_2CO_3 flux and dissolved with citric acid according to a method adapted from Ficklin (1970). The zinc content of soils and sediments was determined by atomic absorption spectrophotometry after a hot nitric acid leach (Gilbert, 1959). The barium and strontium contents of the soils were determined by X-ray fluorescence[1].

PRIMARY GEOCHEMICAL DISPERSION OF FLUORINE

Objective

Twenty-five representative rock samples were randomly collected from various rock types, especially the Black River limestone, during the sampling program. Since a composite sample of unmineralized Black River limestone (sample code: BR; Table 2) collected west of Banker Lake had an unusually large fluorine content, it was decided to analyze a number of the rocks for fluorine to determine the background content in the rocks.

Results and Discussion

The fluorine contents of a few random rock samples from the Madoc area are shown in Table 2 and the sample locations are plotted on Figure 20A.

A number of the rocks appear to be considerably enriched in fluorine when compared with analyses of similar rocks stated in the literature (Table 3). The fluorine content of unmineralized limestone ranges from 1,060 ppm to 2,660 ppm, one order of magnitude greater than the crustal average of 220 ppm for limestone. A fluorine enriched marble (sample number 8) which contains a trace of sulphides (pyrite) comes from an area not far removed from the point where groundwater, stream sediment, and soil fluorine anomalies occur.

Extended sampling could indicate the existence of a large fluorine-enriched area.

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[1] The interested reader will find a complete description and discussion of the analytical methods in appendix C of a thesis by the writer (Lalonde, 1973).

TABLE 2
Fluorine Content of Various Rocks from the Madoc area

Sample Number[+]	Rock Name	F ppm	Notes
BR[★]	limestone	2,100	composite sample
Mar[★]	marble	200	composite sample
Noyes[★]	granite	200	fresh granite
1	limestone	2,660	massive, grey, fossiliferous
2	limestone	2,170	massive, grey, fossiliferous
3	limestone	1,750	massive, grey
4	limestone	1,060	massive, grey
5	limestone	1,300	chocolate brown
6	basic metavolcanic	2,200	composite sample
7	breccia	1,440	abundant quartz fragments
8	marble	1,750	trace of sulphides

[+] Sample locations are plotted on Figure 20A
[★] Unpublished data from R. W. Boyle

TABLE 3
Fluorine Content of Various Rock Types
(after Fleischer and Robinson, 1963)

Rock Name	No. of samples	F content in ppm	
		range	average
granite and granodiorite	93	20 - 2,700	810
basalt	130	20 - 1,060	360
limestone	98	0 - 1,210	220

SECONDARY GEOCHEMICAL DISPERSION

Surface Waters

Objective

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

The hydrogeochemistry of fluorine in the Madoc area was studied by Wright (1971), who found the calcium content of waters around Madoc to vary between 10 and 136 ppm. From solubility-product calculations no inhibition of the fluorine mobility was noted as the results of fluorite of fluorapatite precipitation. Because of the very low Al^{3+} and Fe^{3+} concentrations in the waters at Madoc, very little complexing can be anticipated, a feature also supported by the results of D. R. Boyle who found no complexed fluorine in groundwaters from the same area (pers. comm.).

Results and Discussion

Surface waters were collected from 78 different locations (Fig. 20B). The concentration of fluorine in surface waters of the area varied from 60 to 420 ppb, and the arithmetic mean calculated after neglecting obviously anomalous concentrations above 300 ppb, was 125 ppb. The standard deviation was calculated to be 45 ppb. Since any concentration greater than the mean plus three standard deviations is certainly anomalous, 260 ppb can be taken with confidence as the lower limit of anomalous concentrations. This provides a minimum contrast of 110 per cent over the regional mean. This contrast could, however, be increased if the regional fluorine content of rain or snow 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, a feature to be expected in an area containing fluorite mineralization (Fig. 2).

The surface waters of the Madoc area are alkaline and were found to vary in pH from 7.10 to 8.30, the arithmetic mean being 7.65.

Significant seasonal variations up to 40 per cent can occur in the fluorine concentration at certain locations (Table 4). Such variations are dependent on the amount of rainfall within a certain period and on the amount of fluorine dissolved in groundwaters. During periods of increased rainfall the amount of surface run-off will also increase and tend to dilute the fluorine concentration in certain stream waters while the larger amounts of groundwater also being poured into the streams in areas of fluorite mineralization would tend to increase the over-all fluorine concentration.

The comparison of results obtained in this survey with those obtained by Wright (1971) at approximately the same sample locations demonstrated that seasonal variations up to a maximum of 59 per cent can occur. 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 should also possibly be considered as anomalous. Sample pairs collected at every tenth location gave identical results on analysis.

Anomalies in the surface water fluorine concentrations were found in four different areas (Fig. 20B, in pocket).

One anomaly (Sample 15-340 ppb) occurs in a small lake along the Moira fault, approximately two miles south of Moira Lake. It is possible that this anomaly indicates the presence of fluorite veins in the nearby Moira fault. This hypothesis is also supported by the dispersion of fluorine in groundwaters along the Moira fault (Fig. 20C). A more detailed sampling of surface waters in this small area should give a more definite answer.

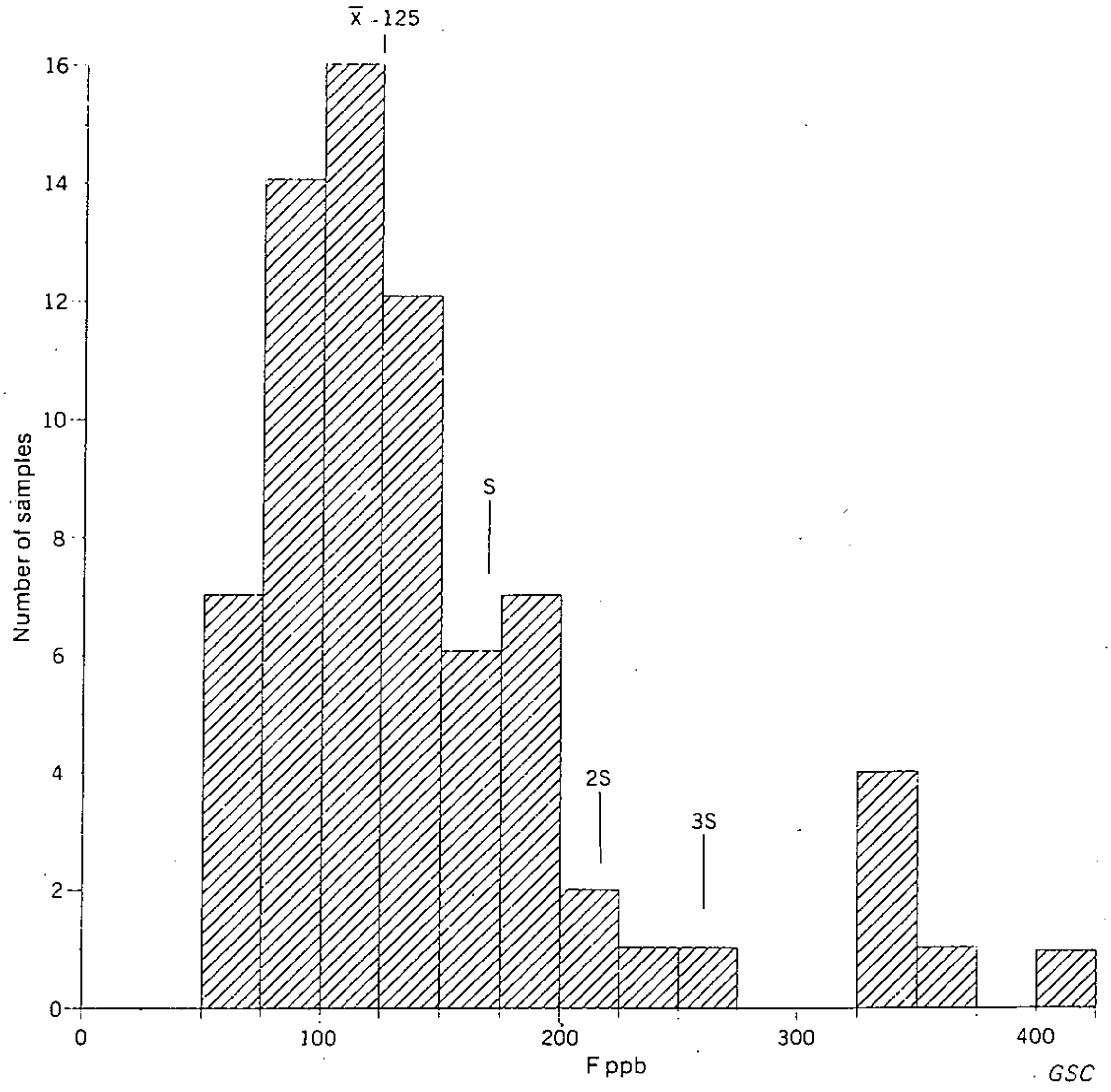

Figure 2. Frequency distribution of fluorine in the surface waters of the Madoc area.

TABLE 4
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

A second anomaly is located in Banker Lake (Sample 53). This lake has an anomalous fluorine concentration of 340 ppb which may be attributed to either the presence of the Lee Junior mines a few hundred feet northeast or to the fluorine-rich limestone (Sample BR in Table 3) to the west, or possibly to both. Another anomaly (Sample 75-340 ppb) in the same area was found in a small stream one mile southwest of Banker Lake. This stream drains an area containing a number of known fluorite veins.

A third group of samples collected in the Jarvis Lake area has a high threshold (230 ppb), but because of the size of the dispersion train the samples are considered noteworthy. 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 see if any variations in the fluorine content could be detected (Fig. 3). All samples from the lake were comparable, and there was no indication of the possible source of the fluorine. An explanation for this anomaly may be the presence of the granophyric granite underlying the area. 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, 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 groundwater to the northeast was found to be highly anomalous in fluorine (Fig. 20C).

The fluorine content in the outlet stream of Jarvis Lake is constant 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 are no drastic changes in the environmental conditions.

A fourth anomaly (Sample 38-420 ppb) was detected near Deloro in a stream which flows south, and parallels the Moira River. Insufficient information is available to decide on the source of the fluorine. Old tailings at Deloro or the large area outlined by a groundwater anomaly north of Deloro may be responsible for this anomalous dispersion of fluorine.

The results indicate that the fluorine content of surface waters is a useful reconnaissance tool in the Madoc area since anomalies reflect areas of known mineralization and possible extensions. It should be noted that a line joining all three anomalous lakes trends roughly parallel to the Moira fault system and related fractures.

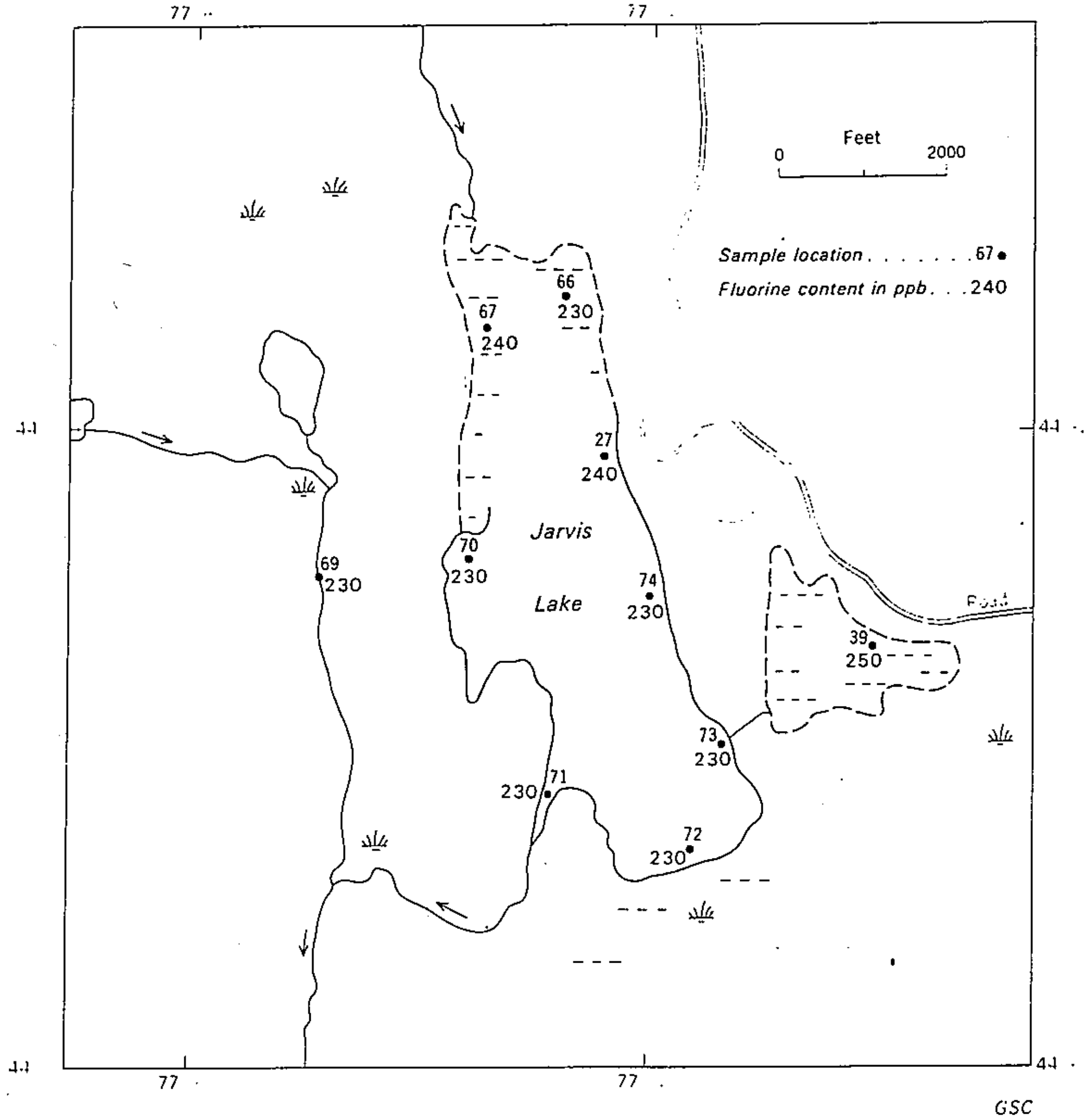

Figure 3. Fluorine concentration in Jarvis Lake and immediate area.

Stream Sediments

Objective

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

Results and Discussion

The stream sediments were collected from below water level at stream water sample sites and consisted of the finest material available.

The fluorine content of stream sediments ranges from 300 to 20,000 ppm. The frequency distribution diagram (Fig. 4) indicates two separate populations. This is probably attributable to the fact that the whole survey was carried out in a small mineralized region and that abundant high threshold and anomalous concentrations constitute a separate population in themselves.

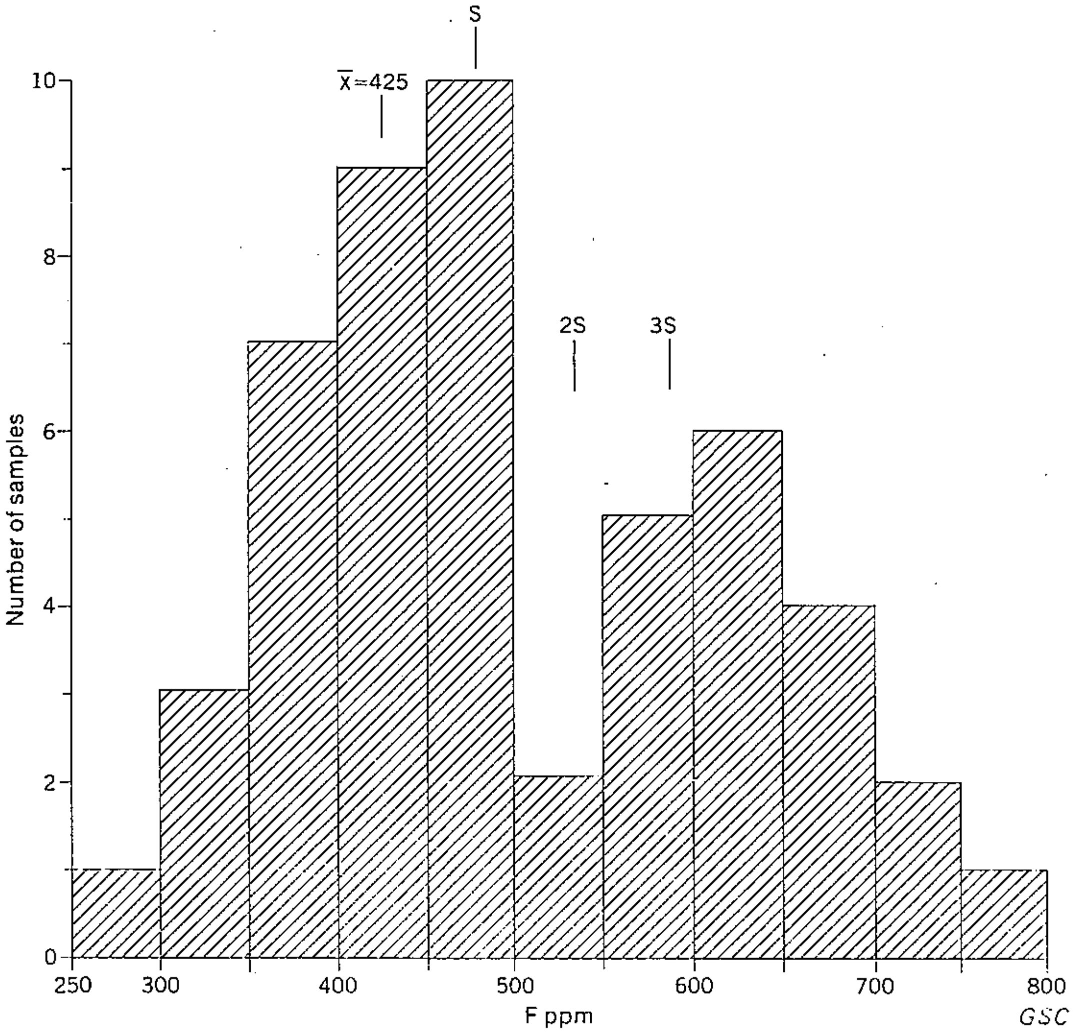

Figure 4. Frequency distribution of fluorine in stream sediments.

With few exceptions, the lower modal concentrations occur in the east while the high modal concentrations predominate in the northwest where most of the surface water anomalies are located.

It is difficult to determine what are the anomalous concentrations because of the clear bimodal distribution. Because of the bimodality, it was decided to calculate the standard deviation for the lower background population. The arithmetic mean is 425 ppm and the standard deviation, 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 take all concentrations greater than the mode of the second population as anomalous. Therefore, by making 650 ppm the smallest anomalous concentration, meaningful patterns become apparent. Little contrast exists between background and anomalous fluorine contents in stream sediments.

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 (Fig. 5) provided only the nonanomalous samples with Zn contents below 90 ppm are considered. The standard deviation is calculated to be 15 ppm and, therefore, all concentrations greater than the mean plus three standard deviations (95 ppm) can be considered as anomalous. It should also be noted that the frequency distribution for Zn is distorted because of the number of large concentrations occurring in a small population.

No relationships were found between the composition of the sample (e.g. with respect to proportions of sand, silt, clay and organic matter) and the fluorine and Zn content.

A plot of the fluorine content against that of Zn in sediments (Fig. 6) indicates that high Zn concentrations are usually associated with high fluorine concentration, 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 fluorine 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 (Fig. 20B).

(1) Sample 28, which is highly anomalous in both fluorine (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.

(2) Sediment sample number 29 was collected from a small stream about one mile east of Bend Bay and two miles west of White Lake. It contains slightly anomalous concentrations of fluorine (460 ppm) and Zn (140 ppm) which are not related to known mineralization. This anomaly correlates with anomalous groundwaters and fluorine-rich soils nearby.

(3) The third area anomalous in fluorine is indicated by two sediment samples (numbers 42 and 43) collected about two miles northeast of Jarvis Lake. This anomaly is not associated with known mineralization but occurs close to the limestone-granophyric granite contact and near a groundwater anomaly (see Fig. 20A, C).

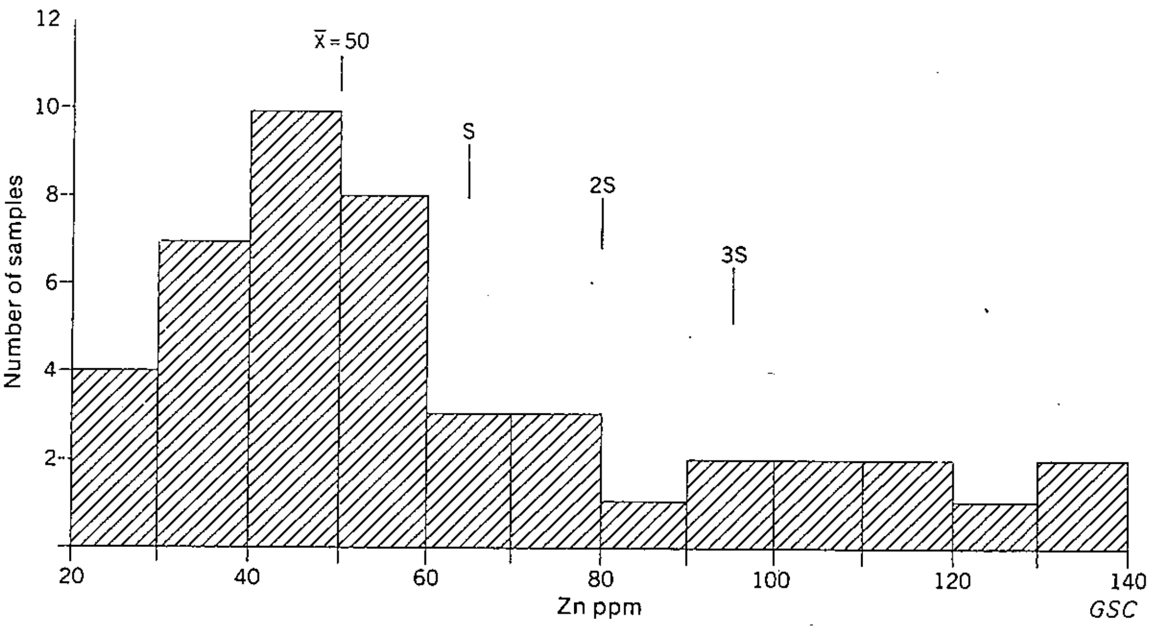

Figure 5. Frequency distribution of zinc in stream sediments.

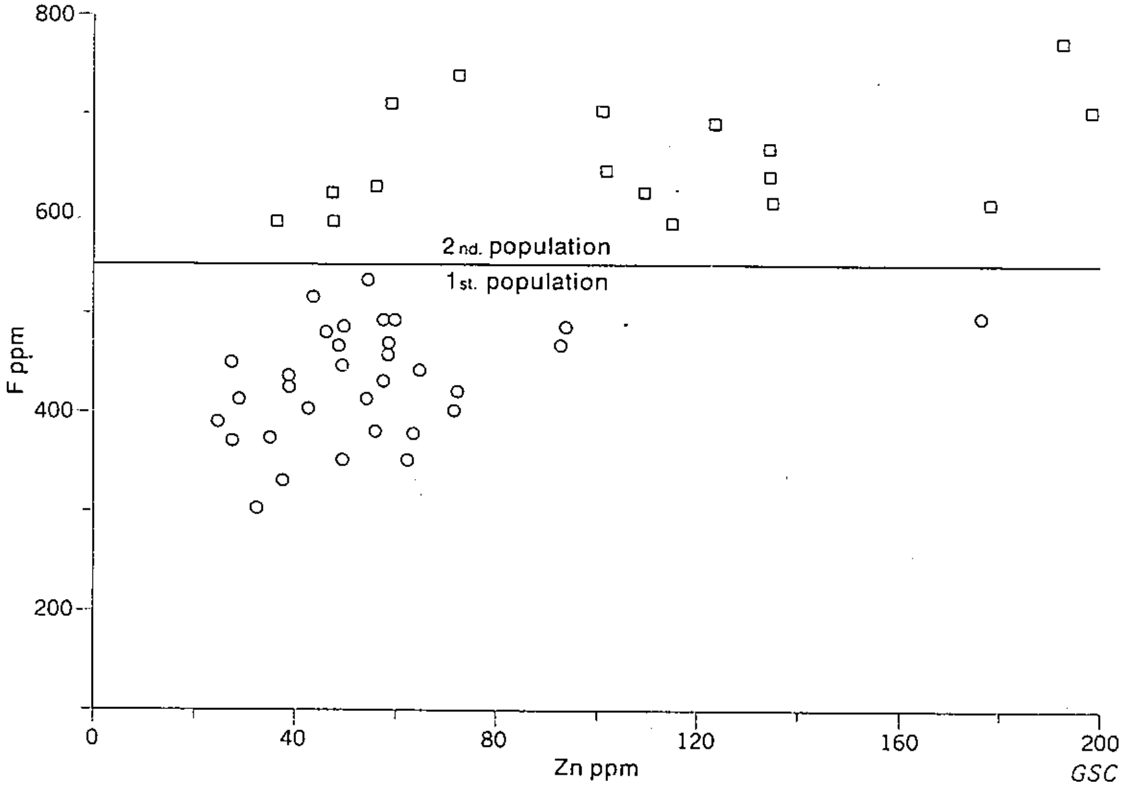

Figure 6. Correlation between the two fluorine populations and zinc content of stream sediments.

(4) The fourth anomaly is indicated by one high Zn concentration (180 ppm) at sample location 75, about one mile southwest of Banker Lake. It is associated with a surface water fluorine anomaly and occurs in an area containing several fluorite veins.

(5) The fifth area is the largest; anomalous Zn and high fluorine concentrations occur 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 fluorine and Zn concentrations obtained for locations 17 and 18 are part of this same dispersion pattern because they show a sudden increase in the concentrations of these elements. These samples were collected along straight east-west trending stretches of the Moira River which might be structurally controlled. A groundwater sample collected 100 feet from location 17 was anomalous (Fig. 20C).

(6) The last area of interest is outlined by samples 36 and 64 in a stream in concessions VII and VIII of southern Marmora Township. These sediments 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 groundwater fluorine contents north and south of Deloro (Fig. 20C).

Fluorine and zinc anomalies coincide in the second and fifth areas of interest which are believed to be free from contamination. The three sample sites (17, 18, and 29) can be joined by a straight line suggested by a linear trend in the Moira River. The trend may indicate the presence of faults which could contain fluorite vein mineralization.

All areas characterized by anomalous stream sediments occur over or close to groundwater anomalies. This suggests that analyzing stream sediments for fluorine and zinc can be an effective reconnaissance exploration technique in the Madoc area. Careful interpretation is necessary, however, because of the poor contrast of anomalous fluorine contents in stream sediments which may not exceed the regional mean by more than 27 per cent. 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, it is safe to say that this interval should not exceed 0.5 mile because the fluorine and zinc content of sediments may change rapidly.

Groundwater

Objective

Since the Madoc area is in an agricultural district, there are numerous groundwater sources either in wells or springs. It was decided in late April of 1972 to sample groundwaters along regional traverses corresponding as closely as possible to the regional soil traverses (Fig. 20C) to verify if the areas containing known fluorite veins could be detected and to see if any correlation exists between the fluorine content of regional groundwaters and soils. From a geochemical prospecting viewpoint, excellent results were obtained from the groundwater fluorine traverses, and it was decided to sample the whole area systematically in order to study the regional dispersion.

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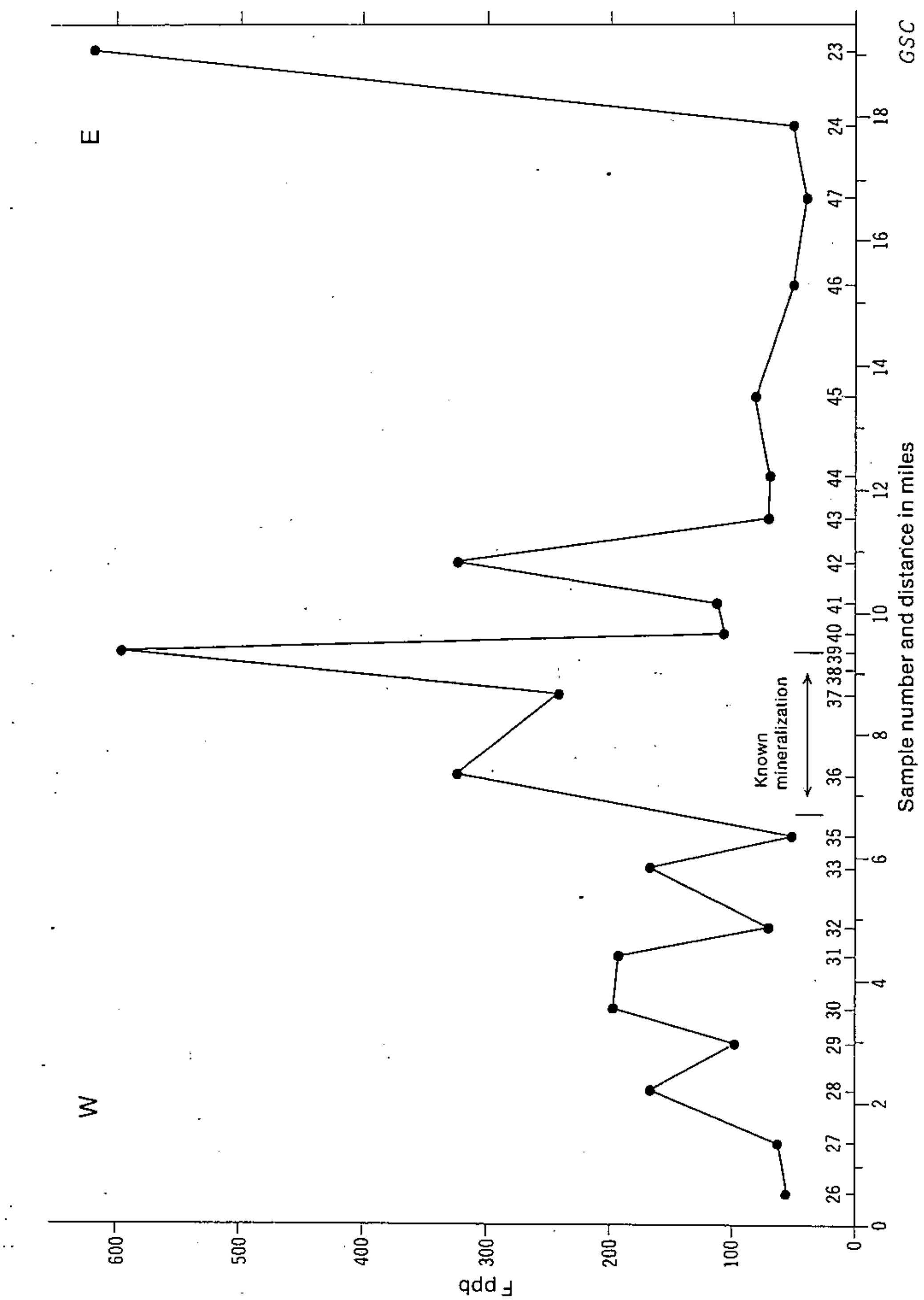

Figure 7. Fluorine content of groundwater along the northern regional traverse.

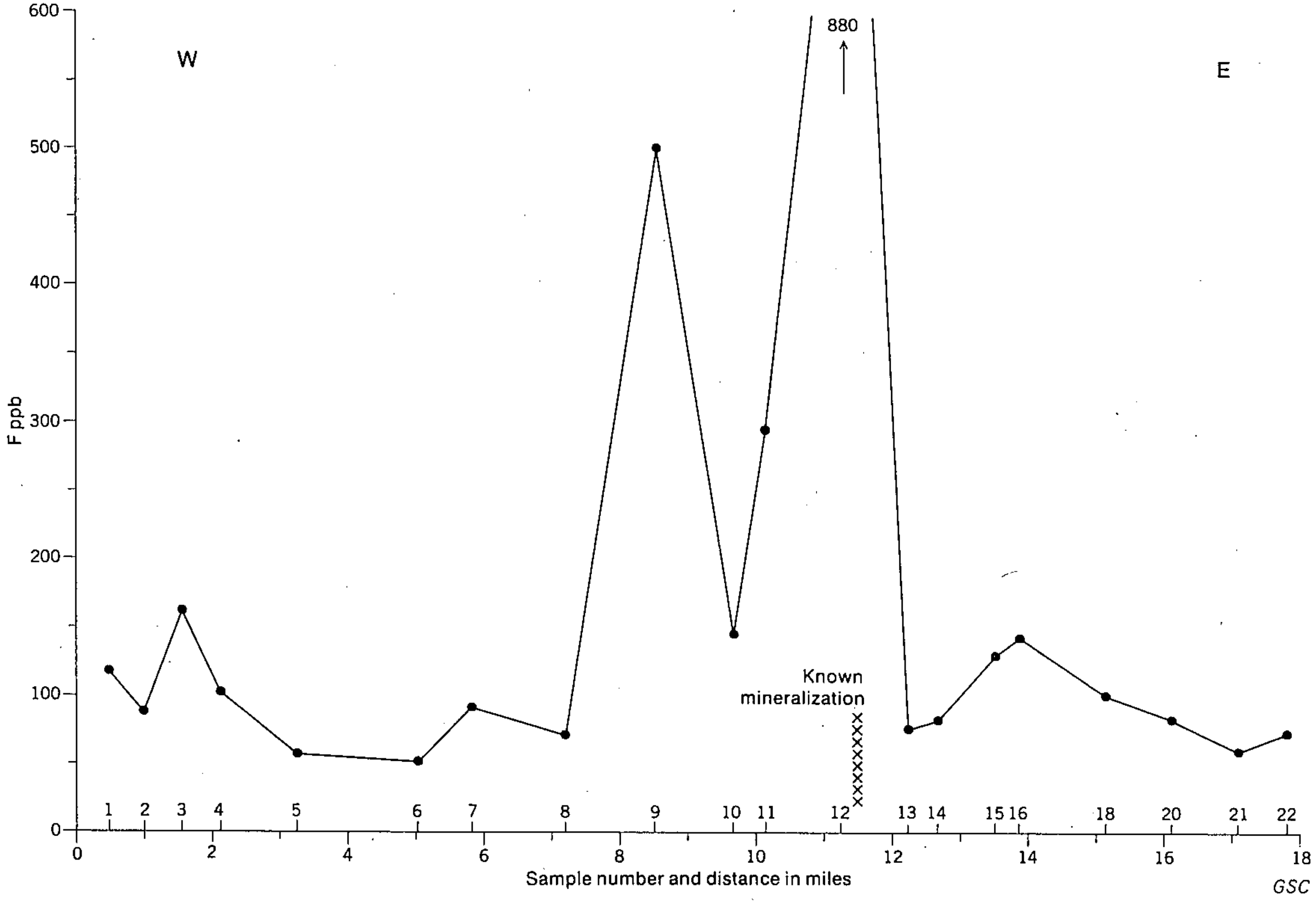

Figure 8. Fluorine content of groundwater along the southern regional traverse.

Method

Forty-seven groundwaters were collected along two regional traverses each of which extended approximately 20 miles in an east-west direction.

Samples were collected either directly from wells or from cold water faucets inside farm houses after making sure 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 one half to 1 mile intervals.

Results and Discussion

The fluorine results for both groundwater traverses are shown in Figures 7 and 8. Samples collected in the areas of known mineralization, as well as in other areas, are clearly anomalous against a background of approximately 100 ppb. The northern traverse (Fig. 7) crosses various rock types such as marble, granite, limestone, and metavolcanics. The large groundwater fluoride concentrations found in the area of known fluorite mineralization and the adjacent area to the east correlate with high soil fluorine concentrations in the A horizon (Fig. 11). The area crossed by the southern traverse is predominantly underlain by Black River limestone, and a similar correlation between the soil and groundwater traverses exist.

The concentration of fluorine in waters of the regional groundwater survey ranged from 21 to 1,800 ppb, and the arithmetic mean calculated after neglecting all obviously anomalous concentrations above 300 ppb, is 105 ppb. The mode occurs between 50 and 75 ppb (Fig. 9). The frequency distribution has a marked positive skew, an indication that mineralization occurs in the area and that the number of high background and threshold concentrations is greater than would normally be expected. The standard deviation 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 per cent.

Frequency distributions of the fluorine content of groundwaters in various rock types were also plotted (Fig. 10). The arithmetic means 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, groundwaters in limestone are slightly richer in fluorine. The frequency distribution for groundwater fluorine in metavolcanic rocks is negatively skewed reflecting the low fluorine concentration in waters within this rock type.

The pH of groundwaters varied from 6.05 to 7.89. Mean pH values were calculated for each rock type to ascertain if any major differences occurred; but all the arithmetic means are similar. Therefore, the groundwaters in the Madoc area are neutral to slightly alkaline.

Mean pH values

limestone	7.15
metavolcanics	7.06
marble	7.00
granite	7.17

Figure 8. Fluorine content of groundwater along the southern regional traverse.

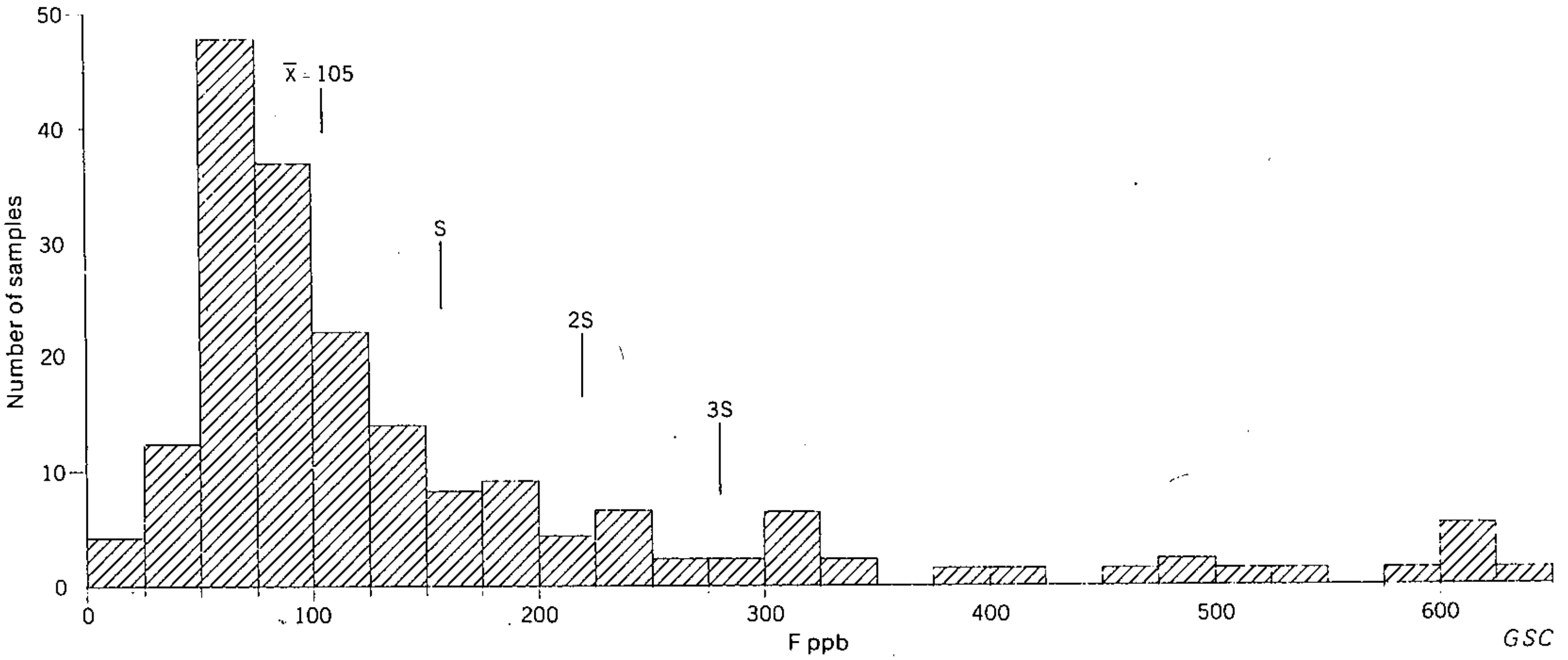

Figure 9. Frequency distribution of fluorine in groundwaters.

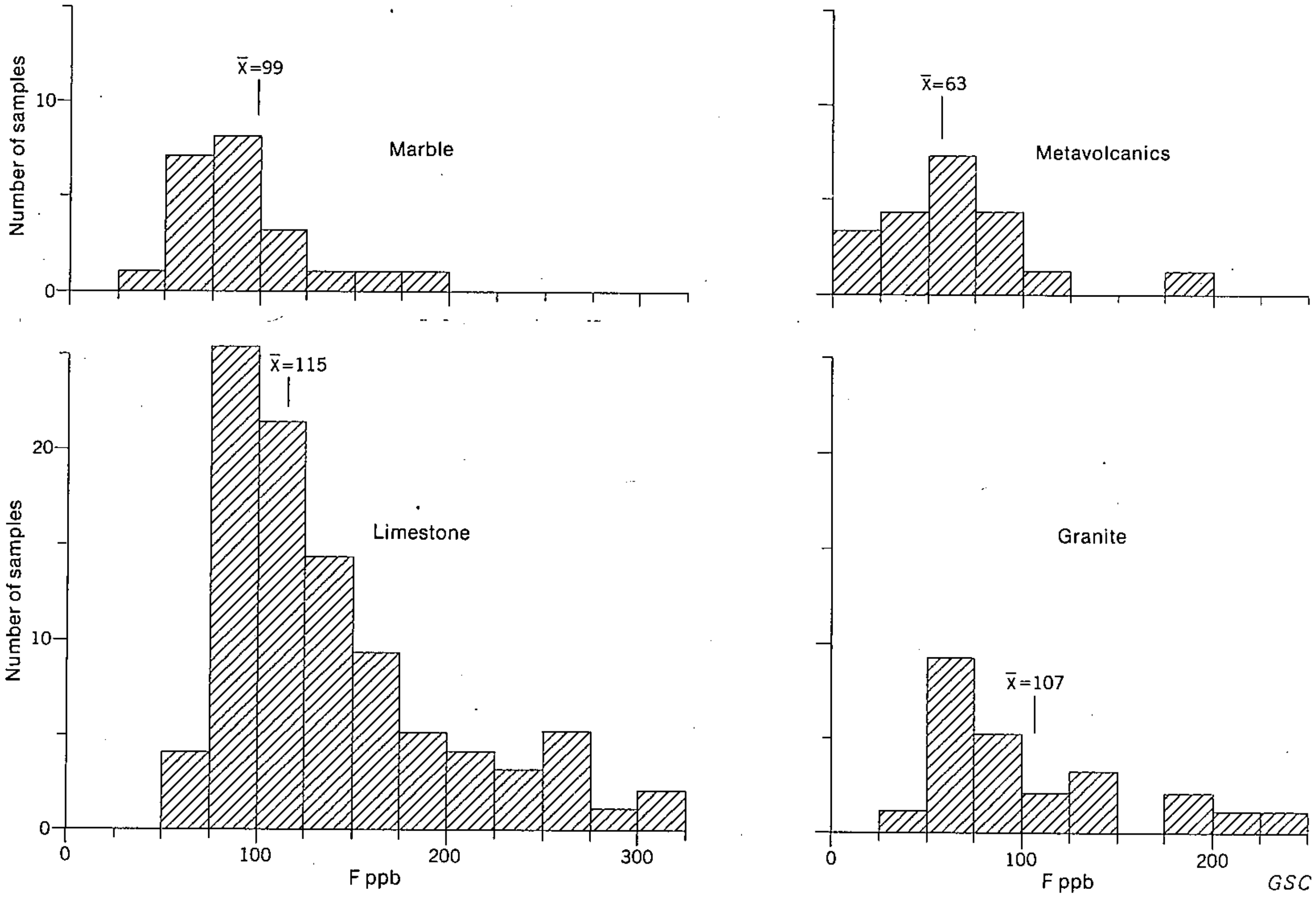

Figure 10. Frequency distribution of fluorine in groundwater from areas underlain by different rock types.

Plots of the pH against the fluorine concentration failed to reveal any patterns of interest.

A regional groundwater fluorine map was compiled (Fig. 20C) and contoured. However, gaps occur in the regional sample coverage making interpolation and some subjective interpretation 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) stand out as clearly anomalous. A host of satellitic anomalies were also detected.

Observations of the distribution of known fluorite veins makes it possible on geological grounds to project a second fault that strikes southwest and passes through or near Banker Lake causing an offset 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 groundwaters tends to negate this theory. A more likely interpretation suggested by the dispersion of fluorine in groundwaters, is that two, almost parallel, systems of mineralized faults cut across the area and extend farther south than had previously been thought (Fig. 20C).

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 two miles northwest. The second is located one 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.

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

Another group of anomalies occurs near Deloro. The large anomalous area to the north may be the source of the high fluorine and zinc contents 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 groundwater system. However, it is not known if the tailings are rich in fluorine. The anomaly to the south is smaller and trends in a northwest direction. The extension of this anomaly south of Highway 7 crosses an area where the soil was found to be rich in both fluorine and zinc. Sediments in the stream which drains the area west of Deloro are also anomalous in fluorine.

Highly anomalous well waters (1,700 and 1,800 ppb) were found northeast of Jarvis Lake. These wells are in limestone that overlie the granophyric phase of the Deloro granite. This anomaly could be caused by the dispersion of fluorine from mineralized veins or the granite body. According to Saha (1959), the minor accessory minerals muscovite, fluorite, and zircon make up no more than 0.5 per cent of the granitic rock. Even if this total were 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 limestones analyzed. 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 are known in the area north and southeast of Jarvis Lake.

Two other single-point anomalies were found. The first (620 ppb) occurs in basic metavolcanic rocks in the northeast corner of the field area. It is difficult to speculate as to what this fluorine concentration may indicate since the groundwaters in the metavolcanic rocks are generally fluorine-poor. The second anomalous water sample (1,700 ppb) is located about one mile south of Tweed. The area is underlain by granite, and the fluorine content of groundwaters collected to the north, south, and west is normal. Other areas of interest are designated by isolated high threshold fluorine contents.

All groundwaters 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 of the groundwaters had increased only slightly during one and a half months, and the variation did not exceed 10 per cent. Therefore, all data collected during this study can safely be treated as one population. However, in September 1972, some of the anomalous locations were resampled by D.R. Boyle (pers. comm.), 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 groundwater from location 147. This water which contained 57 ppb in June contained well over 10 times that amount in September.

A considerable seasonal variation, therefore, occurred in the fluorine content of groundwaters 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 July and August, 1972. This abnormal rainfall caused a marked rise in the water table which may have influenced the chemistry of the groundwater and may also have locally affected the direction of the groundwater flow. Samples collected at different times of the year cannot, therefore, be treated as one population. The best time to sample well waters may be during the winter months when precipitation has the least effect on the groundwater system.

The sampling density of the groundwater survey averaged one sample per square mile. This sampling density proved useful in outlining the major trends. However, a number of smaller mineralized areas were probably not detected because the fluorine content of groundwaters in places, can change drastically within hundreds of feet. This is illustrated by the sudden change in fluorine concentration in the anomalous areas northeast and south of Jarvis Lake and around the single-point anomaly south of Tweed. From these considerations, it follows that a comprehensive groundwater survey should include data from as many sample sites as possible, even if some sites are only a few hundred feet apart.

Hydrological studies of the groundwater flow throughout the area would be useful to interpret and assess the importance of certain anomalous dispersions.

The fluorine concentration of groundwaters in the Madoc area is a useful exploration tool. The most important areas containing fluorite veins are clearly outlined. The dispersion of fluorine in groundwaters suggests that the major areas can be extended and that several new areas are worthy of further investigation.

Regional Soil Traverses

Objective

The fluorine content of four regional soil profiles sampled 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 one-mile intervals except near areas of known mineralization where the spacing was reduced to 0.5 mile.

The sample sites were at least 200 feet removed from roads and were chosen in such a way as to avoid cultivated fields possibly contaminated by fertilizers. Each of the three principal soil horizons (A, B, and C) were sampled where possible. The samples were oven dried at 90°C and sieved to -80 mesh. The sample locations are plotted on Figure 20C to show the correspondence between soil and groundwater sample sites.

Results and Discussion

Regional traverse A. The fluorine content of soils along traverse A varies between 140 and 1,450 ppm (Fig. 11, in pocket). From a regional background of less than 200 ppm over the metavolcanics in the northeast, the fluorine content of the A soil horizons increases to concentrations between 500 and 600 ppm near the known fluorite veins. 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 centre. The fluorine content of B and C horizon soils is too erratic to separate these two broad regional features.

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 also be established between the eastern high fluorine concentrations in soils and the major groundwater anomalies along the Moira fault. Both indicate that a fluorine-rich area exists east of the Moira fault near Madoc. The second group of high concentrations coincides with the extension of a northwest-trending groundwater anomaly south of Deloro. A marble from this area was also found to contain 1,750 ppm of fluorine (see Table 2).

No clear correlation exists between the rock type and the fluorine content of the overlying soils except that soils over the metavolcanics are low in fluorine, as are also the local groundwaters. The regional variations in the fluorine content of soils in the Madoc area probably reflect firstly the fluorine content of underlying rocks, and secondly, the dispersion of fluorine from fluorite veins.

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

The barium content of the soils varies between 100 and 1,000 ppm and tends to increase with depth in the soil profile. The B horizon traverse is erratic and correlates poorly with the presence of fluorite veins, whereas the 'A' horizon traverse clearly exhibits a broad anomaly embracing the zone of known mineralization and corresponding to the major groundwater anomaly. Contrary to fluorine, the barium content of soils increases eastward towards the metavolcanic rocks.

The strontium content of soils shows almost no variation. The content ranges between 200 and 450 ppm and averages approximately 300 ppm. The concentration of Sr in soils increases slightly with depth in the top few feet.

Regional traverse B. Along traverse B, the fluorine content of the soils varies from 170 to 790 ppm (Fig. 11). 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 is that the rock and soil types are relatively uniform along this traverse. A good correspondence exists at most locations along this traverse between the fluorine content of the A and B soil horizons. The only exception occurs at sample location 1 where the concentration in the organic horizon is notably lower.

The area of known mineralization is clearly outlined. The three western high fluorine concentrations at locations 1, 7, and 12 occur in or near areas of fluorine-rich groundwaters whereas the eastern regional anomaly occurs over an area with background groundwater fluorine contents. However, the latter anomaly overlaps the Moira granite and is also not far from a major scarp. The B soil horizon along this traverse is slightly richer in fluorine than the A horizon.

The zinc content of the B horizons is monotonous and does not correlate with the three western fluorine anomalies. However, a Zn regional anomaly correlates with the broad eastern fluorine anomaly. Zinc concentrations vary from 15 to 150 ppm and average approximately 50 ppm.

Barium and strontium in the B soil horizons both indicate only one large and poorly contrasted area slightly enriched in these metals. However, this area does correlate with the two central soil fluorine anomalies.

Regional soil sampling in the Madoc area appears to be an effective method of geochemical prospecting reconnaissance provided that variables such as rock and soil type are kept as constant as possible. Most of the areas indicated by fluorine-rich soils also have fluorine-rich groundwaters. A regional soil reconnaissance survey based on the fluorine content of either the A or B soil horizons with samples taken on a half mile square grid, would probably yield a useful two dimensional picture of the fluorine dispersion in the Madoc area. Such information would be important in areas where no groundwaters are available.

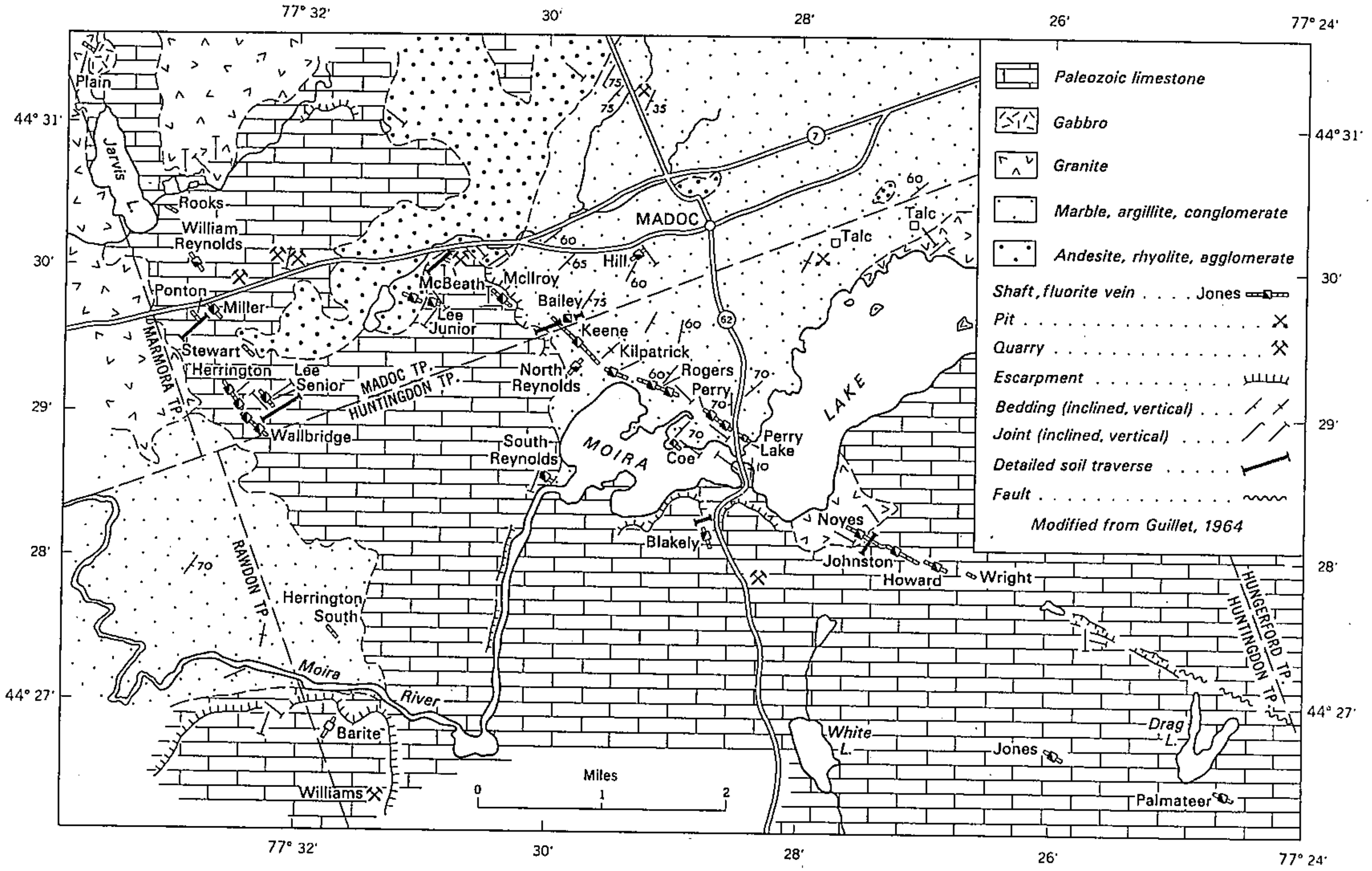

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Figure 12. Fluorite occurrences in the Madoc area and location of detailed soil traverses.

Detailed Soil Traverses

Objective

Detailed soil sampling was carried out along several traverses crossing fluorite veins or their extensions. 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 in the Madoc area.

Method

A major problem was locating suitable traverse sites where undisturbed and uncontaminated soils were present. Because of this, most traverses were run across the extension of veins. The overburden thickness in areas sampled varied from one inch up 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 responsive, only this horizon was sampled in later traverses. The samples were generally collected at 100-foot intervals. The major reference for the description of fluorite veins is Guillet (1964). Traverse locations are indicated on Figure 12.

I - Noyes traverse

Description. The first traverse was run across the Noyes property 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 N50°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., pers. comm.).

The traverse was run near shaft number 1, on a bearing of N40°E. At this point, the fluorite mineralization is about 50 feet below ground level, and no contamination was apparent. The soil type is an acidic, brown forest soil (Gillespie *et al.*, 1962). Samples were collected at 100-foot intervals.

Results and Discussion. The fluorine content of the soils along the traverse varies from 240 to 1,000 ppm (Fig. 13). The background apparently lies between 300 and 400 ppm and increases 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 with a width of some 1,200 feet. 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 the underlying B or 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 unsuspected mineralization. Since no anomaly was found near the vein and shaft opening, the possibility of contamination along the traverse appears considerably reduced.

Figure 12. Fluorite occurrences in the Madoc area and location of detailed soil traverses.

The C horizon yields an erratic pattern in which it is impossible to discern an anomalous area. The B horizon traverse is more stable and displays two anomalous parts, one at either end of the broad dispersion pattern. The A horizon exhibits the greatest contrast (100% to 200%) between background and anomalies and, therefore, appears to be the most useful horizon to sample.

Strontium and zinc did not outline an anomalous area. A slight increase in the Zn content over a very broad area correlates with the fluorine patterns north of the vein, but the contrast is poor and does not exceed 100 per cent 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 per cent above a generally high background of about 900 ppm. The B and C horizons again appear to be of little use in geochemical prospecting for fluorite veins in the area.

II - McBeath traverse

Description. This traverse followed a trend of N45°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 one foot wide and 50 feet long was mined by open pitting. The wall-rock consists of Black River limestone; the overburden varies from a few inches to a few feet thick; 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-foot intervals across the fault and at 100-foot intervals, or more, elsewhere.

Results and Discussion. The fluorine content of soils along this traverse varies from 100 to 5,000 ppm, the upper limit of the background being estimated at 400 ppm (Fig. 13). Three fluorine-rich areas were located and all are supported by Ba and Zn enrichments. The central anomaly on the traverse occurs over the Moira fault. The A horizon is markedly high in fluorine over the fault, whereas variations in the B horizon are insignificant. Across the western anomaly on the traverse, the B horizon, however, gives the higher results, but it is not known if this dispersion is related to a fluorite source. Since the fluorine anomaly is also supported by Zn and Ba, it is possible that it may indicate the presence of fluorine mineralization. The third anomaly at the northern end of the traverse coincides with the limestone scarp near Highway 7.

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

The zinc content of the B horizon varies from 40 ppm to 560 ppm, and the upper limit of the background is estimated at 80 ppm. The anomalous contrast is greater than 150 per cent. Zinc appears to have been dispersed 200 feet westward of the fault zone. However, the cause of this displacement

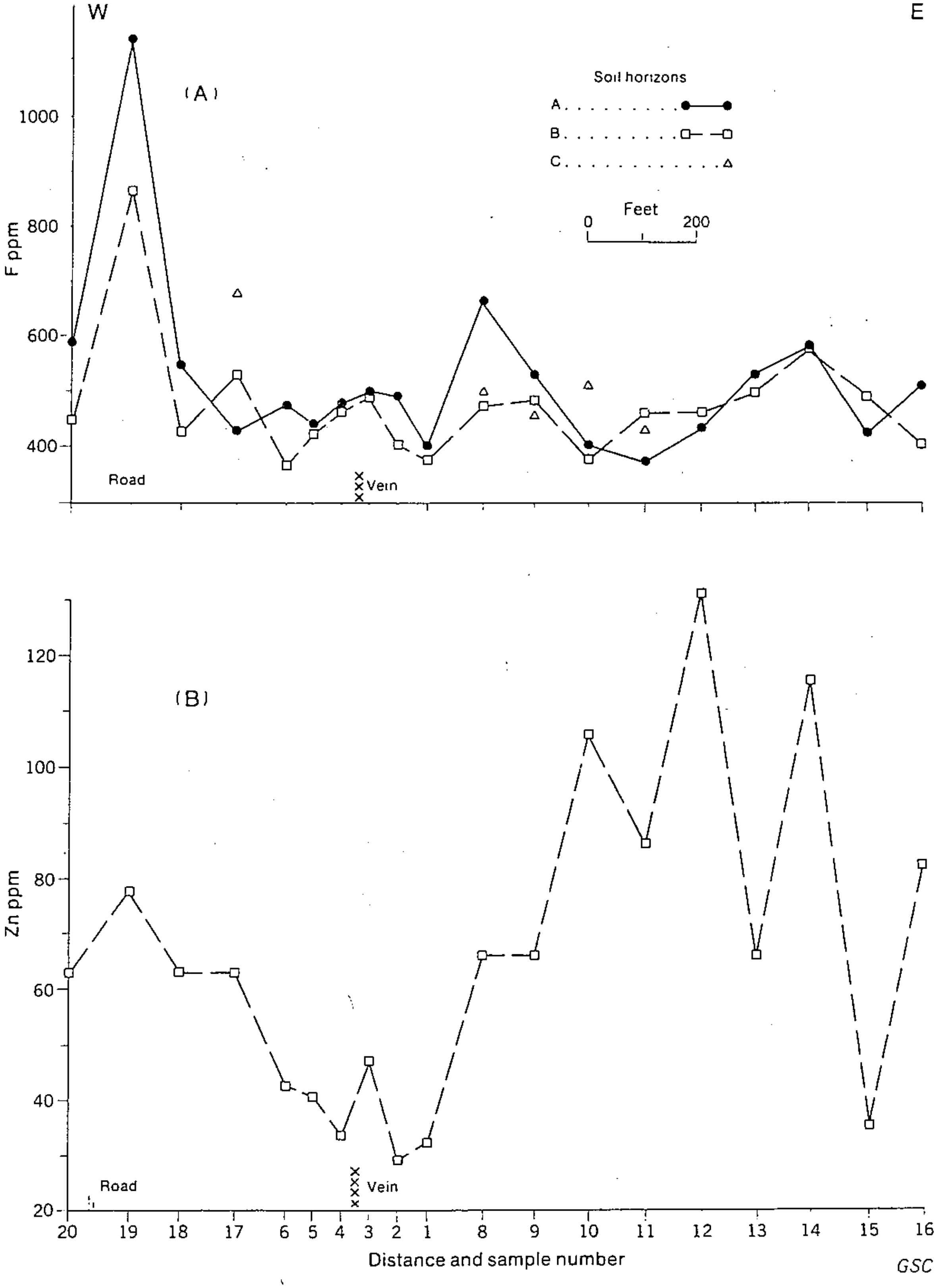

Figure 14. A – Fluorine content of soils along the Bailey traverse.
B – Zinc content of the B horizon along the Bailey traverse.

is not clearly understood since the land is relatively flat and the overburden very thin. It is possible that this anomaly is not related to mineralization in the fault.

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

III - Bailey traverse

Description. This traverse was run across the south end of the vein about 200 feet south of the Bailey mine's escapeway (see Guillet, 1964). The vein which strikes 315°, varies in width from 2 to 12 feet over a distance of 375 feet and has been mined to a depth of 170 feet. Over 25,000 tons of fluorspar were produced from the mine up to 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-foot intervals across the vein and at 100-foot intervals elsewhere.

Results and Discussion. The fluorine concentration in the three horizons varies from 370 to 1,160 ppm, the upper limit of the background being estimated at 550 ppm (Fig. 14). This high fluorine background probably reflects the high clay content of these soils. The A and B horizon traverses agree remarkably well, but the A horizon displays the greater contrast. No fluorine enrichment was detected in the clay soils over the vein; however, an anomaly was located on the slope at the southwestern end of the traverse, but it could be attributed to contamination from the road which is located about 50 feet uphill.

The B horizon Zn traverse is so erratic that it is impossible to estimate the 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 marbles containing numerous calcite veins outcrop.

IV - Lee traverse

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

Results and Discussion. The fluorine content ranges from 340 to 750 ppm and the background is estimated at 400 ppm (Fig. 15). An anomaly exhibiting a contrast of 85 per cent occurs over the extension of the vein.

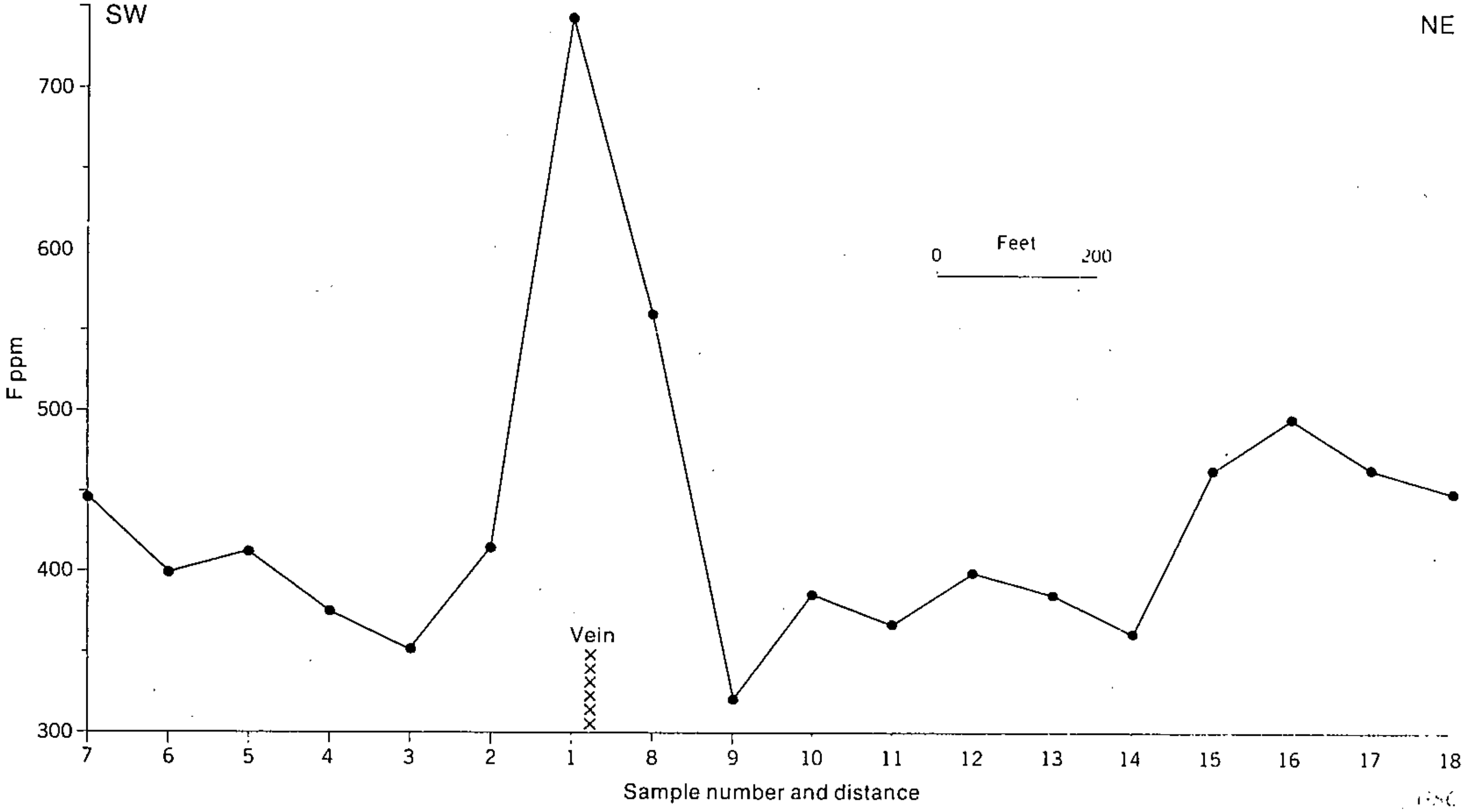

Figure 15. Fluorine content of the A horizon along the Lee traverse.

V - Ponton traverse

Description. This traverse was run on a bearing of N45°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 the most), and the podzolic soils are neutral to weakly alkaline. The vein which trends N45°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 A and B soil horizons along this traverse varies from 250 to 800 ppm (Fig. 16). The upper limit of the background is estimated at 400 ppm for the A horizon and at 500 ppm for the B. The B horizon traverse shows no particular pattern except that it is erratic near the vein. The anomaly in the A horizon displays a contrast of 100 per cent above the background. The main vein is indicated by one anomalous sample only while the second smaller vein about 100 feet to the west is not reflected.

The sampling interval was shortened from 100 to 10 feet and a 200-foot-long traverse was run across the vein 100 feet on either side of the vein. This operation was carried out to study the true extent of the fluorine dispersion near the vein (Fig. 17A). Only the A horizon was sampled. The results show that the major anomalous dispersion can be dissected into two anomalies, and that the fluorine is mostly dispersed into the soils east of the vein. The anomalous dispersion is about 700 feet wide, and the maximum contrast above the background is 270 per cent. The second, smaller vein is also reflected. Therefore, it is clear that a 100-foot sampling interval is probably too large, and that fluorine dispersions from subcropping fluorite veins could easily be missed. The sampling interval, for best results, should be shortened to 50 feet or less.

Water Soluble Soil Fluorine

Objective

A few representative soil profiles were leached with distilled-deionized water to obtain information on the form and mobility of fluorine in soils and on its availability to plants.

Results and Discussion

The results (Table 5) clearly indicate that the proportion of water soluble fluorine decreases markedly from the A to the C horizon. This observation is true when considering the results either as the total water soluble fluorine or as a percentage of the total soil fluorine. The amount of exchangeable soil fluorine in the Madoc area commonly varies from 1 to 10 ppm, or 0.2 to greater than 3 per cent 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. Therefore, the

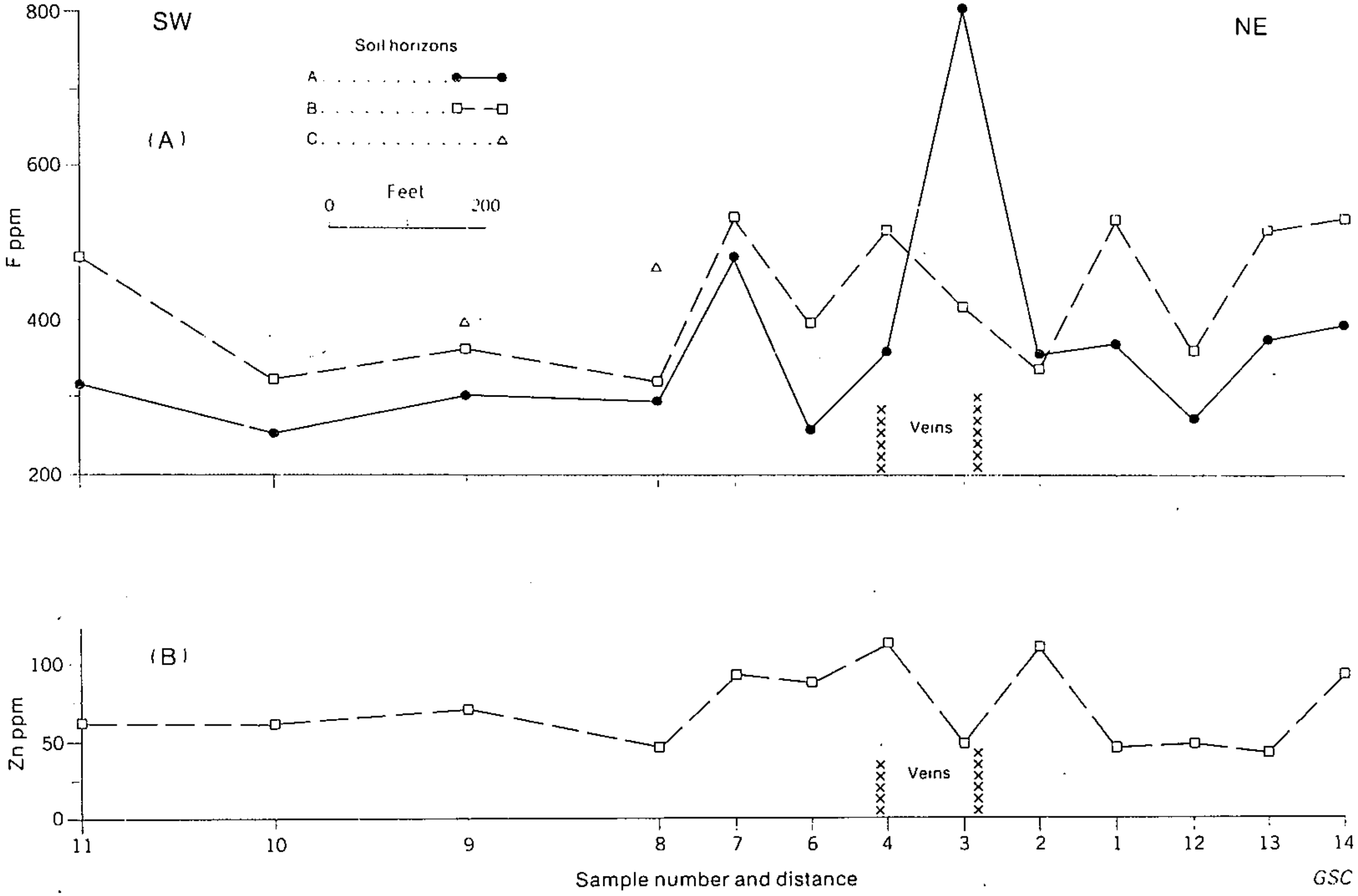

Figure 16. A - Fluorine content of soils along the Ponton traverse.
B - Zinc content of the B horizon along the Ponton traverse.

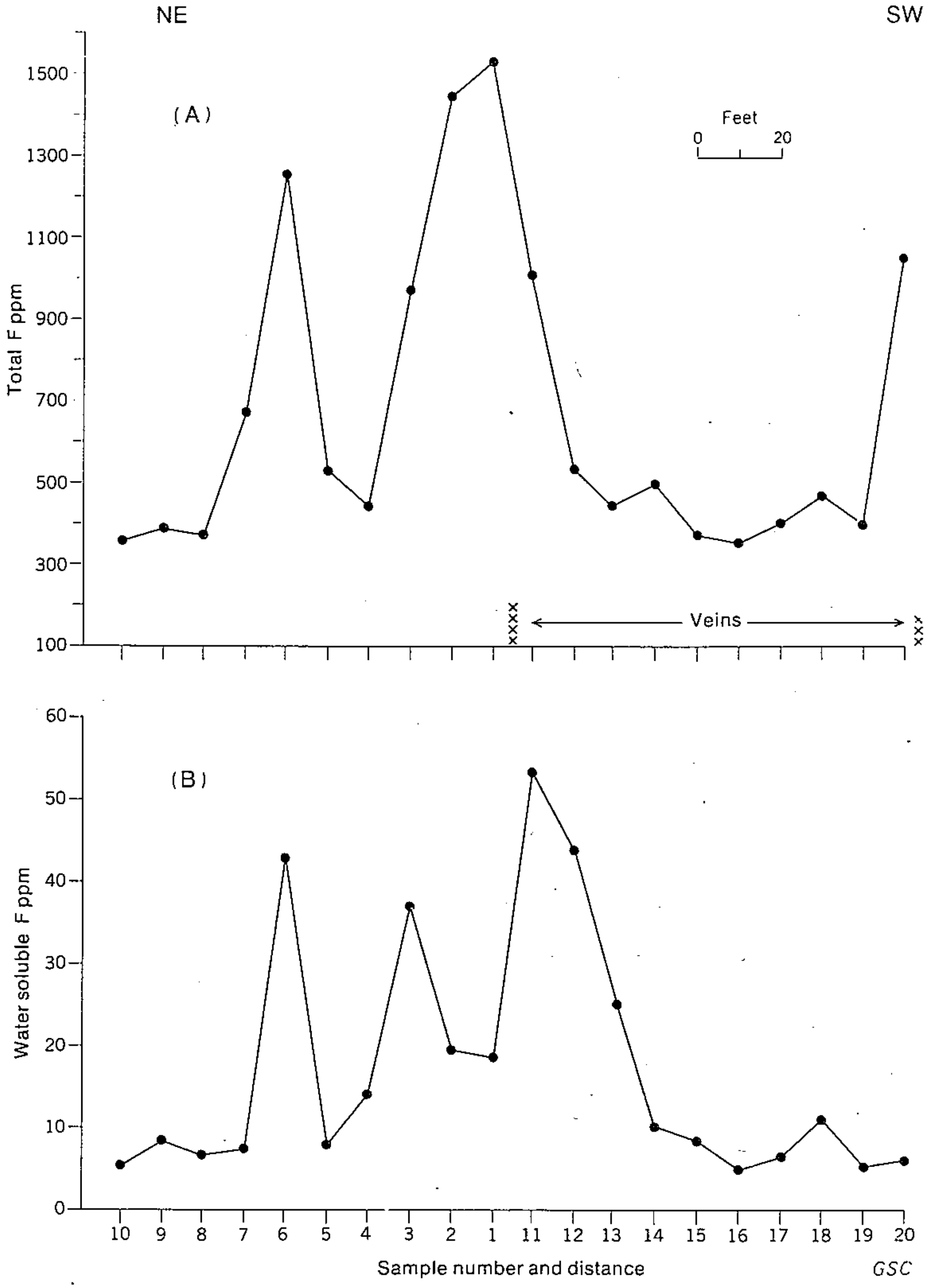

Figure 17. A – Fluorine content of the A horizon along the detailed (10-foot interval) Ponton traverse.
B – Water soluble fluorine in the A horizon along the detailed (10-foot interval) Ponton traverse.

fluorine in clay soils is 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.

Duplicate water leaches were also carried out and the results were found to be reproducible within 20 per cent. A possible explanation as to why the A horizon 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 et al., 1969). 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 dead vegetation in the fall. Once in the soil, the fluorine is initially held loosely by the decaying organic matter or adsorbed onto

TABLE 5

Water-soluble Fluorine and its Percentage of the Total Soil Fluorine Content

Sample number and soil horizon	Water-soluble fluorine in ppm	Total soil fluorine in ppm	Percentage of water-soluble fluorine	Soil type, clastic fraction, pH.
Noyes A 475 ft.	10.0	530	1.9	brown forest
B SW of vein	5.6	480	1.2	sand and silt
C	2.9	460	0.6	acid
A-2 A	9.6	560	1.7	podzol
B	3.5	510	0.7	silt and clay
C	2.2	535	0.4	acid
A-13 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 alkaline
A-16 A	2.5	585	0.4	podzol
B	2.9	640	0.5	clay
C	2.2	495	0.4	acid
A-17 A	2.2	335	0.7	podzol
B	1.2	350	0.3	clay
C	1.2	575	0.2	acid
A-21 A	1.4	200	0.7	podzol
B	1.0	160	0.6	silt and clay
C	0.8	180	0.4	acid
A-22 A	2.3	150	1.6	podzolic
B	2.6	170	1.5	silt and clay
C	2.4	250	1.0	acid
B-4 A	3.1	400	0.8	brown forest
B	2.7	390	0.7	clay
C	3.9	430	0.9	alkaline
B-14 A	5.0	200	2.5	brown forest
B	2.6	240	1.1	silt and clay
C	2.2	225	1.0	alkaline
B-15 A	5.6	170	3.3	podzol
B	3.5	230	1.5	sand and silt
C	2.6	240	1.1	acid

centres of positive charge associated with organic or clay-organic micelles. Research on the optimum conditions for exchangeable soil fluorine was done by Larsen and Widdowson (1971).

Provided that certain parameters such as soil type, pH, drainage, and vegetation cover are relatively constant, it seems probable that the amount of water-leachable fluorine in the A horizon could be used to locate fluorite mineralization. Such tests are easily and inexpensively done in a field laboratory, and the results are available shortly after sampling.

Water leaches were carried out on the soils of the detailed (10-foot interval) traverse over the Ponton property (Fig. 17). 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 of the good results obtained consistently with the A horizon, it is evident that vegetation plays an important role in the soil geochemistry of fluorine. Therefore, provided that such factors as the soil type, pH, drainage, and vegetation cover are kept as constant as possible, the fluorine content of the vegetation will reflect the fluorine content of the soils. Field tests as simple as washing the leaves of certain plants or trees on grids or traverses in uncontaminated areas could yield data useful in the search for fluorite deposits.

GENERAL RESULTS AND DISCUSSION OF SOIL SURVEYS

The fluorine content of soils in the detailed traverses ranges from 120 to 5,000 ppm, and the average background lies approximately between 400 and 450 ppm. The fluorine content in soil profiles varies in different ways depending on a number of variables. On compiling 68 complete soil profiles from the Madoc area, the arithmetic means indicate that the fluorine content increases from the A to the C horizon (Fig. 18). 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 reaction is variable. The soils tend to be acidic over most rock types except limestone where they tend to be slightly alkaline.

The fluorine content varies inversely with the clastic size fraction (Table 6), i.e., the smaller the soil particles the greater the fluorine content. This indicates that much of the soil fluorine is probably not solely attributable to fluorine-containing minerals such as apatite, fluorite, sphene, and micas, but is probably also 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, and 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 in limestone appears restricted to a zone of about 50 feet on either side of the veins. The reasons for these narrow and sharp dispersion

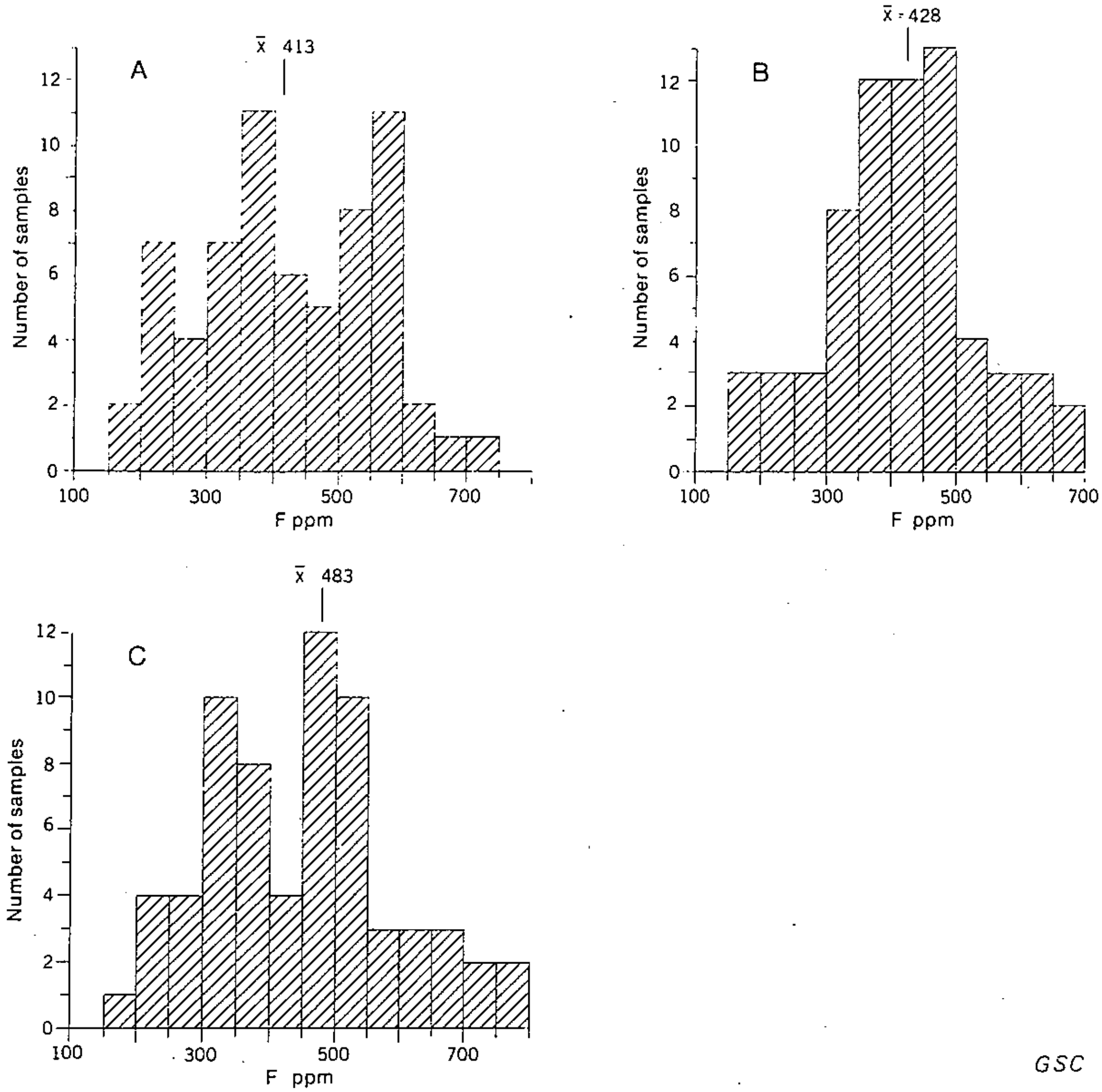

Figure 18. Frequency distribution of fluorine in the A, B, and C horizons of 68 complete soil profiles.

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 groundwaters, and the inhibiting effect of calcium ions on fluoride ion mobility (Gisinger, 1968). The fluorine anomalies are commonly directly over the veins, and the best horizon to sample appears to be the A horizon for three reasons:

(1) it gives the best contrast between background and anomalous conditions;
(2) it is easy to sample;
(3) samples can be quickly analyzed for water-leachable fluorine in a field laboratory if required.

The dispersion of fluorine in soils over the Noyes granite is broad, and the A horizon also exhibits the best contrast. The highest fluorine concentrations are found slightly to the northeast of the vein.

TABLE 6
Fluorine Content of Various Soil Size Fractions

Sample No. and horizon	Size fraction (mesh)	Fluorine content (ppm)	Fluorine content in the minus 80 mesh fraction (ppm)
B-14A	50 to 100	230	200
	100 to 200	280	
	-200	300	
B-14B	50 to 100	220	240
	100 to 200	340	
	-200	370	
B-14C	50 to 100	250	230
	100 to 200	370	
	-200	430	
A-13A	50 to 100	1,040	1,500
	100 to 200	1,280	
	-200	1,440	
A-13B	50 to 100	750	1,000
	100 to 200	1,000	
	-200	1,160	
A-13C	50 to 100	960	1,100
	100 to 200	1,120	
	-200	1,400	

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 probably be less than 100 feet to detect the narrow fluorine dispersion haloes. An interval of 25 to 50 feet is recommended for the best results in detailed soil surveys. Over known occurrences, the fluorine content was found to increase by 85 per cent or more above the local background.

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

The zinc content of soils varies from 15 to 560 ppm, and the general background is estimated between 40 and 60 ppm. The contrast over mineralized areas is variable but usually exceeds 100 per cent. The B soil horizons exclusively were routinely analyzed for Zn; however, an examination of the Zn content of the various horizons in a few places indicates that this element is also concentrated in the A horizon (Table 7). Zinc and fluorine correlations are an asset in the interpretative procedure.

TABLE 7
Zinc Content of the Minus 80 mesh Fraction of Various Soil Horizons

Sample No.	Horizon	Zinc ppm
Noyes 6	A	85
	B	80
	C	35
Noyes 11	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

The barium content of soils in the Madoc area varies from 200 to 1,600 ppm and the upper limit of the background lies between 800 and 1,000 ppm. Barium anomalies correlate well with fluorine. Barium appears to have a greater mobility than fluorine in a limestone environment and gives broader dispersion haloes which are easier to detect. The A and B horizons give approximately equivalent results.

The strontium content of soils varies from 100 to 500 ppm, the upper limit of the background lying between 350 and 450 ppm. Strontium dispersal haloes in the soils 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 around fluorite veins. Other authors have also observed the greater effectiveness of A horizon sampling in other areas (Boyle and Dass, 1967).

SUMMARY AND CONCLUSIONS

The secondary dispersion of fluorine in surface and groundwaters, 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 was also examined.

(a) The fluorine analyses were performed using an Orion Research selective fluoride ion electrode and ionanalyser 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 set up 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 per cent. The fluoride electrode is a useful analytical tool in geochemical prospecting for fluorite deposits and other types of 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 varied from 1,060 to 2,660 ppm, averaging 1,840 ppm.

(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 groundwaters, sediments, and soils. Fluorine is mobile in stream waters and can migrate for several miles. Areas containing known fluorite deposits were indicated by the fluorine content of 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 analyzed for fluorine and zinc. 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. Fluorine concentrations 27 per cent higher than the mean were considered as anomalous to make meaningful interpretations. The zinc content of stream sediments varies from 25 to 650 ppm, averaging 60 ppm. High zinc contents are usually associated with high fluorine contents, but the reverse is not necessarily true. All areas indicated by anomalous stream sediments occur over or very near to groundwater anomalies. From this it follows that stream sediments can be useful in prospecting for fluorite veins; but because of the limited contrast between background and anomalous concentrations, interpretation can be difficult, and stream sediment surveys should be supported by some other type of reconnaissance survey such as surface waters, groundwaters or regional soils. The sampling interval should not exceed 0.5 mile.

(e) The fluorine concentration in the neutral to slightly alkaline groundwaters 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 mineralization as well as several other areas of interest are clearly outlined by anomalous groundwater fluorine concentrations. The fluorine content of groundwaters in limestone is significantly higher than in other rock types, especially the Tudor basic metavolcanics. This probably reflects the lower fluorine content of the latter rocks. Although the sampling density used was appropriate for outlining the known groups of fluorite veins, in a comprehensive survey it is important to sample as many wells and springs as possible since the fluorine content of groundwater can change drastically from one well to another.

Important seasonal variations can occur in the fluorine content of groundwaters, a feature that dictates that groundwater surveys be carried out in as short a time as possible in a single season. It is suggested that the best time to conduct such surveys is during winter when precipitation least affects the groundwater systems. Groundwater reconnaissance surveys are particularly useful methods in the search for fluorite veins.

The fluorine content of three groundwater samples reached concentrations of 1,700 to 1,800 ppb. These concentrations are almost double the recommended content for fluoridated water.

People drinking these waters can easily exceed the average daily intake of 2 milligrams above which fluorosis may occur (Marier and Rose, 1971). It is suggested, therefore, that groundwaters at several locations be carefully studied because they may be detrimental to the public health.

(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 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 groundwater anomalies, strongly suggesting that a positive correlation exists between the two. The investigation suggests that regional soil sampling surveys in the Madoc area are a useful geochemical reconnaissance method for locating zones containing fluorite deposits. The regional dispersion of Ba and Zn is an aid in interpreting regional surveys, but these elements generally display less contrast than fluorine.

(g) Soil samples were collected at short intervals on lines across fluorite veins or their extension to study the dispersion of fluorine in detail. The fluorine content in these areas varied from 130 to 5,000 ppm and averaged 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. Over the Noyes granite where calcium levels are much lower, the dispersion was broader. The fluorine anomalies are usually directly over the veins, 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 barium and zinc 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 in the Madoc area. 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 organic horizon and decreases downwards to 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 per cent 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 fluorine, barium, and zinc as tracers are applicable to the search for new fluorite deposits in the Madoc area. The information obtained from the various reconnaissance surveys indicates that the area may still contain yet undiscovered fluorite veins.

APPENDIX

GEOCHEMISTRY OF FLUORINE

Fluorine, the lightest of the halogens, is the most electronegative of the elements and one of the most reactive. Its ionic radius (1.36 Å) is comparable to that of the hydroxyl ion (1.40 Å). 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 Å) and O^{-2} (1.40 Å).

Reviews of fluorine geochemistry are given by Rankama and Sahama (1950), Goldschmidt (1954), Correns (1956), Fleischer and Robinson (1963), Gulyaeva and Itkina (1964), and Marier and Rose (1971).

Rocks

Fluorine is the fourteenth 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 8). 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 into their lattices.

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

TABLE 8
Fluorine Content of Various Rocks

(adapted from a literature compilation
by Fleischer and Robinson, 1963)

Rock type	Rock name	F content ppm		
		no. of samples	range	average
Intrusive	gabbro, diabase	26	50-1,100	420
	granite, grano-diorite	93	20-2,700	810
	alkalic rock (syenite and nepheline syenite)	65	200-2,250	1,000
Extrusive	basalt	130	20-1,060	360
	andesite	77	0- 780	210
	rhyolite, obsidian, liparite	78	0-1,700	480
	phonolite	14	860-1,490	930
Sedimentary	limestone	98	0-1,210	220
	dolomite	14	110- 400	260
	sandstone	49	10- 880	180
	shale	79	10-7,600	800
	evaporite	30	10- 890	200
	phosphorite		up to 40,000	
Unconsolidated materials	oceanic sediments	79	100-1,600	730
	volcanic ash and bentonite	270	100-2,900	750
	soil	327	10-7,070	285

N. B. All rocks considered to contain anomalous amounts of fluorine were omitted.

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 3.36%
Muscovite	0.02 to 1.95%
Sphene	0.03 to 1.36%
Tourmaline	0.07 to 1.27%

Waters

Fluorine occurs in surface and groundwaters, in the oceans, and in precipitates. In the aqueous phase, fluorine is most commonly present as the fluoride ion. The average fluorine content in some Russian freshwater 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 of river and lake waters is reported to be 260 ppb and 100 ppb respectively (Correns, 1956; Carpenter, 1969). The latter figure is probably closer to the world average for the fluorine content of freshwater.

The fluorine content of groundwaters is variable. Concentrations from 0 to 67.2 ppm have been reported, the highest concentrations having been found in the Rustenburg district of South Africa (Bond, 1946). 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 groundwaters, even in terranes 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 groundwaters 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 groundwaters of the Moscow area coincide with high sulphate contents up to 50 or 70 ppm sulphate 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, groundwaters can be enriched in fluorine as a result of extended contact with host rocks containing other fluoriferous 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 complex ion MgF^+ while the rest occurs as the free fluoride ion (Robertson, 1966). The fluorine content of the 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 rainwater.

The concentration of fluorine in rainwater has been theoretically investigated (Bewers, 1972). The natural range of fluorine can be expected to vary from 24 to 49 ppb. The fluorine concentration of rainwater 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 0.28 and 14.1 ppm 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 fluorapatite and fluorite exert a major influence 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 researchers to be about 16.5 ppm CaF_2 which is equivalent to 8 ppm of fluorine at room temperature (Table 9). D.R. Boyle (pers. comm.) has tested the solubility of fluorite in doubly distilled water and found it to be 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 9
The Solubility of Fluorite in Pure Water According to Various Authors

Author and year of investigation	T°C	Solubility of CaF_2 mg/1	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	9.91
Kazakov 1950	20.0	15	7.3
Boyle* 1972	20.0	20.6	10

*Personal communication.

The highest fluorine concentrations in groundwaters in areas containing ore deposits in acid magmatic rocks occur either in acidic or alkaline waters (Fig. 19), the lowest concentrations occurring at pH 6.7 (Krainov et al., 1967). He attributes 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 sulphide deposits coupled with the attack of sulphuric acid on fluorite which liberates hydrofluoric acid.

$$CaF_2 + H_2SO_4 \rightleftharpoons CaSO_4 + 2HF$$

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

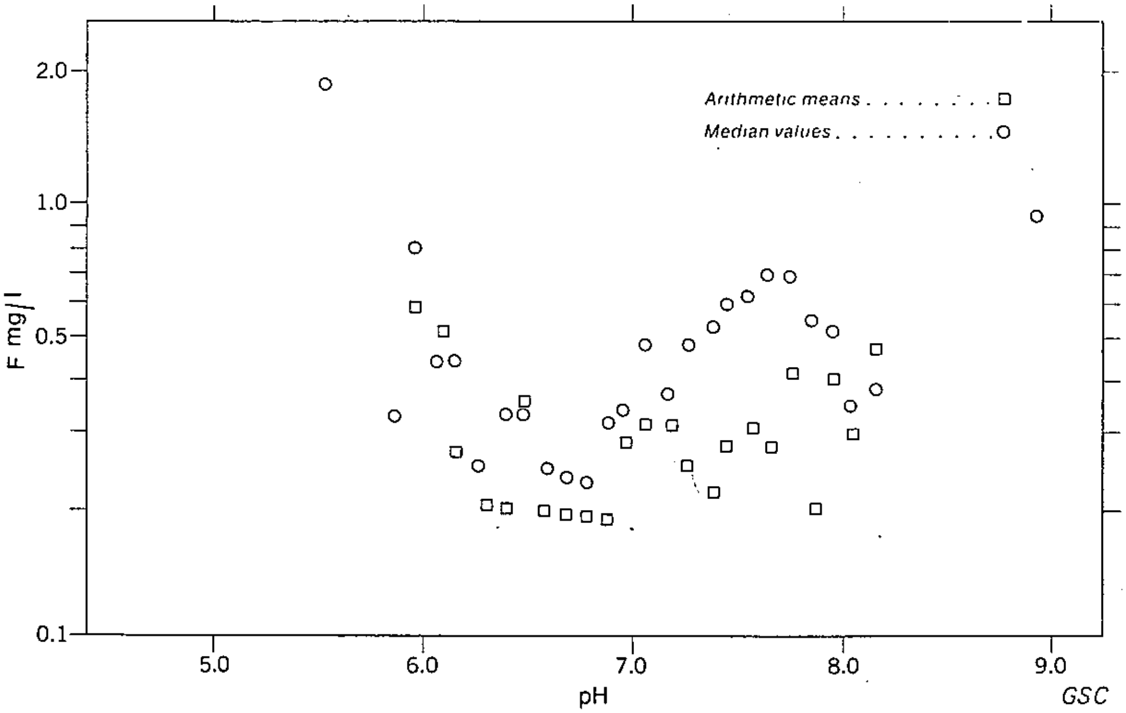

Figure 19. Correlation of the arithmetic means and median values of the fluorine content of waters from deposits in acid magmatic rocks with the pH (Krainov et al., 1967).

Fluorine readily forms complex compounds with the elements of Groups III and IV of the periodic table, examples being the acid salts of Si, Ti, and Zr. These salts are all more soluble than fluorite.

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

$$Al^{3+} + F^- \rightleftharpoons AlF^{2+} + F^- \rightleftharpoons AlF_2^+ + F^- \rightleftharpoons AlF_3 + F^- \rightleftharpoons AlF_4^- + F^- \rightleftharpoons$$

$$AlF_5^{2-} + F^- \rightleftharpoons AlF_6^{3-}$$

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 complexes. Experimentally, the addition of Ca^{2+} 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, 1951). Boron was also observed by Krainov to increase the mobility of fluorine in groundwaters. Every high fluorine concentration coupled with high Ca was accompanied by high B contents. Complexes of the type $[BF_4]^-$, $[BF_3(OH)]^-$, and $[BF_2(OH)_2]^-$ were probably responsible for maintaining the mobility of fluorine.

Fluorine is relatively mobile in groundwaters 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 (Friedrich and Pluger, 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 Gulyaeva 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 10). The world average of 285 ppm quoted by Fleischer and Robinson (1963) for fluorine in soil is probably the best approximation. They omitted phosphate-rich soils from their compilation.

Fluorine increases with depth in virgin soils (Robinson and Edgington, 1946). Therefore, fluorine is not 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. Micaceous clays are marked adsorbers of fluoride ions. This phenomenon is attributed to the exchange of adsorbed hydroxyl ions for fluoride ions at centres 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 per cent 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 and Olson, 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 $Al_2(SiF_6)_3$ (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 very 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.

TABLE 10
Fluorine Content of Soils[1]

Reference	Number of Samples	F content in ppm	
		Range	Average
Steinkoenig (1919)	16	trace - 1,500	240
Robinson and Edgington (1946)	137	trace - 7,070	290
Vinogradov (1957)	46	30 - 320	200
Nackowski (1952)	—	170 - 510	340
Fleischer and Robinson[2] (1963)	341	10 - 7,070	285

Notes: [1] Phosphate rich soils have been omitted.
[2] Compilation of data from 10 authors.

Various materials were tested for their capacity to adsorb fluorine ions (Table 11) by Bower and Hatcher (1967). Aluminum hydroxides were at least 20 times more efficient than clays.

Three out of the four soils analyzed by Romney et al. (1969) had a high fluorine content, and the most important factor affecting the fluorine was the clay mineral composition of the soil and not the pH.

The use of commercial fertilizers increases the soil's fluorine content. The addition of 1,000 pounds per acre of superphosphate can locally increase the soil fluorine content by 7.5 ppm. Only 5 to 6 per cent 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 fluorine 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., 1955).

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

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

TABLE 11

Adsorption of Fluorine by Minerals, Aluminum Hydroxide, and Soils

(adapted from Bower and Hatcher, 1967)

Material	pH of saturated paste	F adsorbed at indicated solution concentration	
		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	1,400
Hydrated halloysite, Bedford, Ind.	7.0	420	1,777
Bentonite (montmorillonite), Wyo.	8.7	trace	trace
Vermiculite, Mont.	8.5	trace	trace
Aluminum hydroxide, freshly precipitated	6.3	21,800	32,000

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 per cent 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 per cent 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 in minute quantities plays a more basic role in animal life than had been formerly thought (Frieden, 1972; Messer et al., 1972) and is not restricted to being a constituent of bone phosphates. Reviews on the biochemistry 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 per cent 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 et al., 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 grown on soils that contain sufficient calcium (MacIntire et al., 1955); 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, 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 western literature on its use in mineral exploration is for all practical purposes nonexistent. Provided such factors as soil type, pH, drainage, and vegetation cover are kept as constant as possible, the fluorine content of the 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 containing fluorine-bearing minerals.

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