A

THESIS

entitled

THE GEOCHEMISTRY OF FLUORINE AND ITS APPLICATIONS IN MINERAL EXPLORATION

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ABSTRACT

A detailed description of the geochemistry of fluorine is given, followed by investigations on the analytical geochemistry of the element and its applications in mineral exploration.

The role of fluorine in the formation of rocks and minerals and its concentration in these media has been described. Fluorine is concentrated in those minerals in which it is an essential element (e.g. fluorite, topaz, bastnaesite, amblygonite, humites) or in which it can easily substitute for the OH^- ion (e.g. micas, amphiboles, apatite, tourmaline) or O^{2-} ion (e.g. pyrochlore). In igneous rocks, fluorine is concentrated in the more acidic and/or alkalic members; ultrabasic rocks exhibiting the lowest concentrations of fluorine and alkali granites the highest. In sedimentary rocks, the element is concentrated in phosphatic and/or highly micaceous rocks. During regional metamorphism, fluorine is remobilized and rocks formed as a result of this process contain much less fluorine than their original igneous and sedimentary counterparts. Rocks formed as a result of pneumatolytic-hydrothermal alteration, such as greisens, skarns, fenites, serpentinized basics and kaolinized granites are invariably fluoriferous. The role of fluorine in the formation of mineral deposits has been discussed with emphasis being placed on elemental associations, controls to mineralization (chiefly chemical) and alteration. In the pedosphere fluorine is concentrated in rocks having a high phosphate and/or micaceous content. Calcium, phosphate, humic matter and clay composition all have a controlling effect on the fixation of fluorine in soils. In natural waters, fluorine is present largely in the ionic state but may form complexes with elements such as Al and Fe under certain conditions. Calcium and sodium greatly affect the concentration of fluorine in natural waters; the former supressing it and the latter enhancing it. On a dry weight basis, fluorine exhibits a large concentration range in vegetation (10 to 8, 000 ppm) but there appears to be no plants which specifically seek out areas of high fluorine concentration in their substrate. Factors affecting the concentration of fluorine in atmospheric and soil air are discussed.

Cold extractable (0.01M HCl), acid diffusible and total methods of fluorine analysis have been developed for use in mineral exploration. The procedure for each of these methods, based on the use of the fluorine ion electrode, are described together with discussions of the factors affecting determination. An understanding of the ability of these methods to extract fluorine from various fluoriferous minerals, as well as colloid and adsorbed phases, was found to be essential for their effective application in geochemical exploration.

Fluorine is concentrated in a large variety of mineral deposits: namely, carbonatites; kimberlites; pegmatites; greisen (Sn, W, Be, Mo, Bi) deposits; skarn deposits; many types of hypo-, meso- and epithermal mineral deposits containing tourmaline, topaz and fluorite; disseminated deposits (Sn, Nb, Ta, fluorite) in granitic, syenitic and rhyo-dacitic intrusions the alteration haloes of certain volcanogenic sulphide deposits in rhyo-dacitic intrusions; serpentinized ultrabasic and basic bodies possibly containing Ni, Cu, Cr, and Co mineralization;

sedimentary phosphate deposits; and many types of placer deposits (e. g. Nb, Ta, Sn). The element is therefore an ideal pathfinder in all types and stages of geochemical exploration aimed at the detection of these deposits. Detailed descriptions of the application of fluorine in prospecting for the mineral deposits mentioned above are given. These include lithogeochemical methods for detecting primary haloes, favourable mineral environments and fault zones; hydrogeochemical methods utilizing groundwaters and drainage sediments; and pedogeochemical surveys for detailed follow-up. Results of preliminary studies on the use of fluorine in vapour geochemical surveys indicate the need for more sensitive instrumentation before this technique can be fully assessed.

Finally, conclusions are drawn concerning the efficacy of fluorine in geochemical exploration.

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INTRODUCTION

When prospecting for mineral deposits the exploration geochemist must often consider the use of elements which, although not of economic value, are excellent 'pathfinders' for many types of deposits. These pathfinders (e.g. Hg and As) are chosen in preference to the major 'indicator' elements for a number of reasons:-

a) they may be more mobile in the secondary environment than the ore elements and will therefore form larger target anomalies,

b) they may be characteristic of certain types of deposits within a metallogenic province and can therefore be used to differentiate between types of ore, and

c) they may be more easily determined analytically than the ore elements.

Although fluorine is quite mobile in the secondary environment and is also associated, both as a minor and major consitituent, with a variety of mineral deposits (hydrothermal deposits, pegmatites, skarns, carbonatites, kimberlites, etc.) it has not been studied in as much detail as other pathfinder and indicator elements.

Research on the application of fluorine in mineral exploration was, therefore initiated by the author to assess the potential of fluorine as a pathfinder and indicator element in geochemical exploration. An initial appraisal of this research topic indicated the existence of three main problems:-

a) the general lack of analytical methods acceptable to the exploration geochemist,

b) the absence of an adequate account of the geochemistry of fluorine, which would be of benefit to the exploration geochemist, and

c) limited descriptions of the application of fluorine in mineral exploration which would allow a comprehensive assessment of the efficacy of fluorine as a pathfinder element.

The present research was carried out in an attempt to remedy these problems. Specifically, the objectives were:-

1. To develop partial (cold extractable and acid diffusible) and total methods of analysing geochemical media for fluorine which would be rapid, inexpensive, and of sufficient precision to be used in geochemical exploration.
2. To investigate any interferences which may affect the application of the analytical methods developed in (1) above.
3. To investigate the effectiveness of the methods in (1) in mineral exploration.
4. To collect data on the geochemistry of fluorine and present these in a form useful to the exploration geochemist.
5. To study the primary and secondary dispersion characteristics of fluorine in the vicinity of various types of mineralization with which the element is known to be associated.
6. To give a comprehensive assessment of the efficacy of fluorine as a pathfinder and indicator element in mineral exploration.

No work can ever be considered complete, and the author readily admits that many gaps regarding the geochemistry of fluorine and its application in mineral exploration still exist despite the present research. It is hoped that the reader will recognize these gaps as avenues for further research.

CHAPTER 1

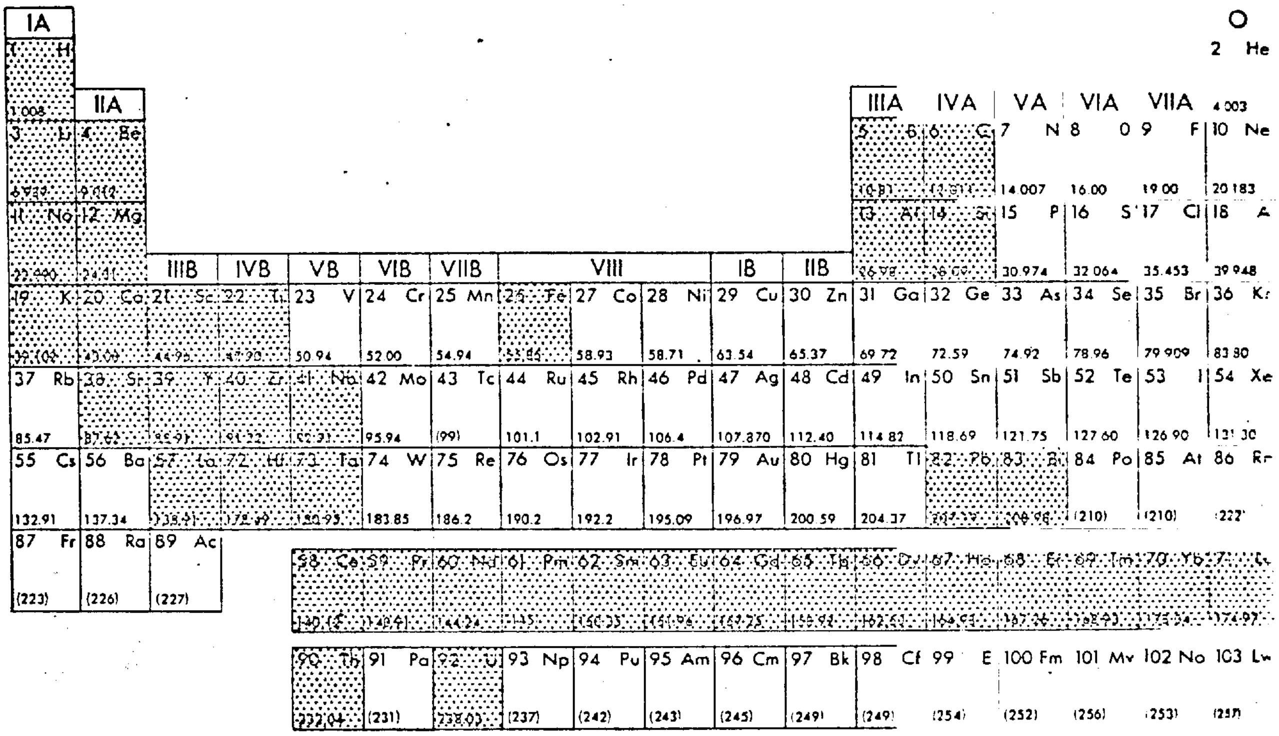
GEOCHEMISTRY OF FLUORINE

1.1 INTRODUCTION

Fluorine is the ninth element in the periodic table and has an electronic configuration of $1s^2\ 2s^2\ 2p^5$. It is the lightest element of the halogen group and consists of a single natural isotope of mass number 19.00. Fluorine is monovalent and is the most electronegative and chemically reactive element known. It occurs only rarely in the elemental state. In fact, the only documented occurrence of elemental fluorine is from the fluorite (antozonite) deposits of Wolsendorf, Bavaria where F_2 is produced in the lattice of fluorite as the result of radioactive bombardment from adjacent uranium minerals. In nature fluorine is characterized by ionic bonding and forms stable bonds only with the elements outlined in Figure 1.1. A number of elements (Be, Sc, Y, REE, Th, U, Zr, Nb, Ta, W, Sn, Ga, In, Tl, Ge) may, however, form complexes with fluorine under magmatic pegmatitic, pneumatolytic and hydrothermal conditions. Fluorine shows no bonding tendencies for the elements characteristic of basic rocks (V, Cr, Mn, Co, Ni, Cn, Platinoids) and, due to its high electronegativity, bonding with the anions of Groups VA, VIA and VIIA of the periodic table (with the exception perhaps of the metalloids P, As, Sb and Bi) is precluded.

The ionic radius of F^{-1} is 1.33 Å, a circumstance which allows the element to substitute for the OH^- (1.40 Å) and O^{2-} (1.40 Å) ions during the formation of minerals.

The geochemical cycle of fluorine is illustrated in Figure 1.2.



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
▨ 1 H 1.008																	2 He 4.003
▨ 3 Li 6.939	▨ 4 Be 9.012											▨ 5 B 10.81	▨ 6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.183
▨ 11 Na 22.990	▨ 12 Mg 24.31											▨ 13 Al 26.98	▨ 14 Si 28.09	15 P 30.974	16 S 32.064	17 Cl 35.453	18 A 39.948
▨ 19 K 39.102	▨ 20 Ca 40.08	▨ 21 Sc 44.96	▨ 22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	▨ 26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	▨ 38 Sr 87.62	▨ 39 Y 88.91	▨ 40 Zr 91.22	▨ 41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	▨ 57 La 138.91	▨ 72 Hf 178.49	▨ 73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	▨ 82 Pb 207.19	▨ 83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)															

▨ 58 Ce 140.12	▨ 59 Pr 140.91	▨ 60 Nd 144.24	▨ 61 Pm 145	▨ 62 Sm 150.35	▨ 63 Eu 151.96	▨ 64 Gd 157.25	▨ 65 Tb 158.92	▨ 66 Dy 162.50	▨ 67 Ho 164.93	▨ 68 Er 167.26	▨ 69 Tm 168.93	▨ 70 Yb 173.04	▨ 71 Lu 174.97
▨ 90 Th 232.04	91 Pa (231)	▨ 92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (245)	97 Bk (249)	98 Cf (249)	99 E (254)	100 Fm (252)	101 Mv (256)	102 No (253)	103 Lw (257)

Figure 1.1

Elements which bond Fluorine in Nature

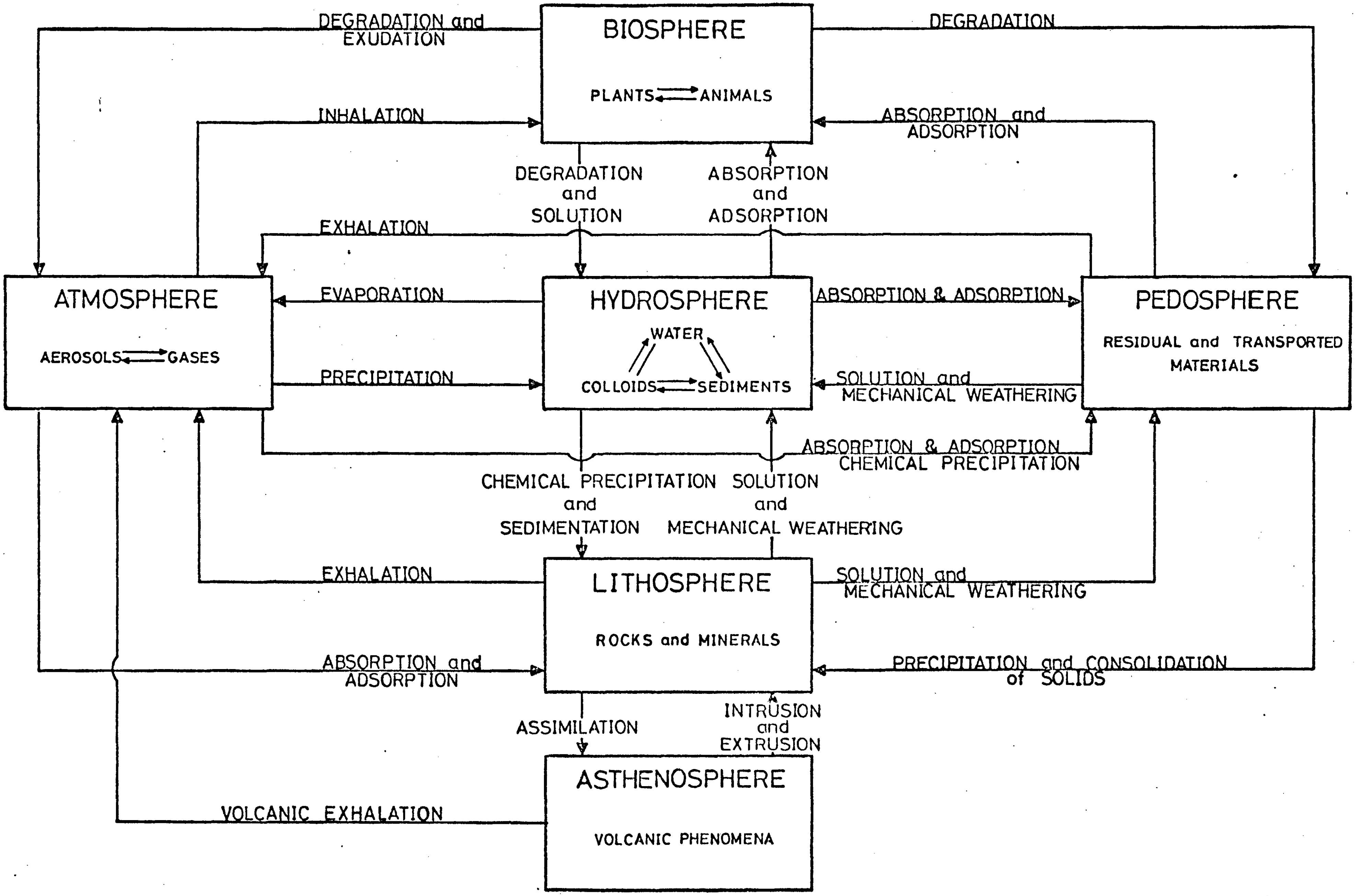


Fig. 1.2 The Geochemical Cycle of Fluorine

In the lithosphere fluorine is the fourteenth most abundant element superceded by O_2, H_2, C, Al, Fe, Ca, Mg, Si, Na, K, Ti, P and Mn in that order. It is apparent from this fact that fluorine forms an integral part of the composition of all types of rocks. In the system lithosphere-asthenosphere, fluorine exhibits both lithophilic and atmophilic characteristics. During the intrusion of magmas it tends to accumulate in the residual fractions of the melt as well as in the aqueous and vapour phases. Fluorine is, therefore, strongly associated with the pegmatitic, hydrothermal and pneumatolytic stages as well as with the main stage of magmatic differentiation. Fluorine reaches its highest concentration in magmatic rocks rich in silica and alkalies; in some of these the element may reach concentrations as high as 3%. In sedimentary rocks the concentration of fluorine is largely dependent upon the presence of micaceous and phosphatic constituents. In the metamorphi environment fluroine is remobilized and acts as a mineralizing flux. Because of the unique role fluorine plays in all of the phases of igneous activity, it is an important constituent of a number of different types of ore deposits, including pegmatites, carbonatites, kimberlites, hydrothermal deposits, greisens and skarns. It is thus a useful pathfinder and indicator element which can be employed in a number of geochemical prospecting methods in the search for these deposits.

In the pedosphere fluorine accumulates in surficial materials rich in colloids, clay minerals and phosphates. Surficial deposits poor in these constituents contain only minor amounts of fluorine. The fluorine content of residual soils is generally in the range 10 to 7,000 ppm, depending on the type of bedrock; some of these soils may report as much as 2% fluorine.

In the hydrosphere fluorine is present mainly in the ionic form (F^-) but may form complexes of the type $MF_n(x-n)$ (x = valence of M) with a number of cations under certain conditions. The fluorine content of waters is generally less than 8 ppm, but concentrations as high as 1 percent have been reported for some saline waters (Kraynov et al, 1969). Calcium and sodium are the major parameters limiting the concentration of fluorine in natural waters; calcium suppresses the fluorine content and sodium enhances it. Fluorine is extracted from natural waters by precipitation as fluorite (CaF_2) or apatite, $Ca_5(PO_4)_3$ (F, OH) or as a result of adsorption by clay and organic-rich sediments.

In the biosphere fluorine generally accumulates in plants as fluorapatite. There are a few plants, however, which accumulate fluorine as fluoracetate, fluor-oleic acid or fluor-palmitic acid. Such plants are extremely toxic to mammals. On a dry weight basis the fluorine content of plants is generally in the range 10 to 100 ppm, but a number of plants, of which the tea plant is one, may accumulate much higher concentrations of fluorine (up to 8,000 ppm). In animals fluorine is generally concentrated in the skeletal tissues as fluorapatite.

The atmosphere receives fluorine as a result of the evaporation of water, especially sea water, from volcanic exhalation, and as a result of exhalation and exudation from the lithosphere and biosphere respectively. The fluorine content of volcanic gases may comprise as much as 1 or 2 percent of the total gases expelled. It is not known how much fluorine is added to the atmosphere through evaporation processes, but investigations on the global circulation of fluorine (Bewers, 1972) indicate that this is probably the chief source of atmospheric fluorine. The contribution of fluorine to the atmosphere by exhalation and exudation processes is probably minimal when compared to other sources. The fluorine content of atmospheric gases varies from a trace to as much as 1.0 ug/m^3; in industrial areas it may be higher by an order of magnitude or more.

Comprehensive reviews on the geochemistry of fluorine are lacking, the works by Fleischer and Robinson (1963) and Allman and Koriting (1972) being the only notable articles in this respect apart from earlier writings by Fersman (1939) and Goldschmidt (1954). General papers of interest on the lithogeochemistry of fluorine have been published by Barth (1947), Seraphim (1951), Koritnig (1951, 1955, 1963), Borchert (1952), Kokubu (1956) and Correns (1956, 1957). The global circulation of fluorine has been discussed by Carpenter (1969) and Bewers (1972). An informative review on environmenta fluorine has been presented by Marier and Rose (1971).

1.2 LITHOGEOCHEMISTRY

In this section the fluorine content of minerals and igneous, metamorphic and sedimentary rocks is presented, followed by a description of fluoriferous mineral deposits and a discussion of the role of fluorine in the formation of these deposits.

1.2.1 Fluorine in Minerals

Apart from the physico-chemical conditions which prevail during the formation of minerals, the major factor governing the concentration of fluorine in minerals is its ionic radius (1.33 Å). Under favourable conditions F^- may substitute for the OH^- ion (1.40 Å) or the O^{2-} ion (1.32 Å) in various minerals.

The fluorine-bearing minerals can be divided into three main groups:

a) those in which fluorine is an essential anion (fluorides, complex halides, carbonates and sulphates);

b) those in which F^- substitutes for the OH^- ion (phosphates and silicates); and

c) those in which F^- replaces the O^{2-} ion (oxides and certain silicates).

Although the word 'essential' cannot be included in the latter two categories many of the minerals in these two groups will not form in the absence of a significant amount of fluorine (e.g. topaz) while the formation of others may be severely restricted if fluorine is absent.

The ability of the F^- ion to substitute for either the OH^- or O^{2-} ions depends mainly upon the co-ordination and kind of ligand that the OH^- or O^{2-} ion forms within the lattice of a given mineral. The reason for this arises from the differences in polarizability and electronegativity of F^-, OH^- and O^{2-}. In addition, those minerals in which fluorine substitutes for O^{2-} tend to be formed under high temperature and pressure conditions (e.g. sphene, pyrochlore, etc.). No secondary low-temperature minerals are known in which F^- substitutes for the O^{2-} ion.

The preference for fluorine to show greater isomorphism with the OH^- ion rather than the O^{2-} ion may be due to the ease with which the OH^- ion may escape from mineral lattices as H_2O by combining with an H^+ ion from a nearby OH^- ion (Bloss et al, 1959). Foster (1964) has also suggested that the oxygen fugacity of the magmatic system may also be a controlling factor. It is more probable, however, that the difference in valencies, electronegativities, bonding energies and co-ordination characteristics between the O^{2-} and OH^- ions are the chief controlling factors governing this preferential substitution. Moreover, it is clear, that regardless of the constraints on the system, the F^- ion will substitute for the OH^- ion to a much greater degree than for the O^{2-} ion.

The isomorphic relationship between F^- and OH^- for layered silicates has been discussed by Romo and Roy (1954), Rimsaite (1967) and Hubner (1969).

TABLE 1.1

FLUORINE IN ROCK-FORMING MINERALS

1

Mineral Group	Rock Type	Fluorine %			References*
		Observed Range	Range of Means	Mean or Weighted Mean	
Halides:					
Fluorspar	All rock types	47.81-48.80	-	48.67(?)	1
Villiaumite	Alkaline rocks	44.20-45.28	-	45.24(?)	1
Cryolite	Alkalic pegmatites	53.48-54.37	-	54.29(?)	1
Oxides:					
Pyrochlore	Carbonatites	0.60- 4.61	2.60-3.32(2)	2.93(11)	15
	Alkalic pegmatites	3.70	-	-	102
Perovskite	Ultrabasics and Alkalic pegmatites	Tr. - 0.08	-	0.03(11)	27
Magnetite	Volcanic rocks	0.020-0.096	-	0.058(2)	48
Carbonates:					
Bastnaesite	Granitoids and Acidic pegmatites	6.23- 9.94	-	8.54(?)	1
Phosphates:					
Fluor-Apatite	Acidic Intrusive rocks	0.80- 3.31	1.94-2.48(2)	2.35(8)	47,85,97
	Alkalic intrusive rocks	1.70- 3.49	2.02-2.82(3)	2.70(27)	29,47,72
	Carbonatites	1.50- 4.10	2.37-3.06(12)	2.74(15)	15,71
	Metamorphic rocks	1.05	-	-	13
	Phosphorites	2.47- 4.20	-	3.30(31)	2,18,36
Amblygonite-Montebrasite	Acidic pegmatites	1.40-11.80	4.61-5.13(2)	4.87(2)	9,10,73
Silicates:					
Silica Group:					
-Opal	Ocean sediments	8-120 ppm	-	50 ppm(22)	90
Feldspar Group:					
-Plagioclase	Volcanic rocks	0.069-0.089	-	0.079(2)	48
-Microcline	Acidic pegmatites	0.03	-	-	
Scapolite	Regional metamorphic skarns	Tr. - 0.11	-	0.03(6)	91
Feldspathoid Group:					
-Cancrinite	Alkaline rocks	0.04	-	-	26
Micacious Group:					
-Biotite	Acidic intrusive rocks	0.02- 3.80	0.20-3.09(15)	0.71(242)	16,19,25,35,38, 40,43,50,51,52, 54,57,58,60,63, 70,84,90
	Acidic pegmatites	0.23- 5.00	0.27-1.32(2)	0.88(12)	55,65,84,90,101
	Greisen	2.03-5.02	-	3.53(2)	17
	Metamorphic rocks	0.06- 3.33	0.23-1.36(3)	0.76(33)	22,39,43,45,56, 66,70,84,96

2

Mineral Group	Rock Type	Fluorine %			References*
		Observed Range	Range of Means	Mean or Weighted Mean	
Silicates contd.					
-Biotite contd.	Charnockites	1.22- 3.99	-	2.14(10)	61
	Regional metamorphic skarns	0.30- 1.25	-	0.61(12)	77
-Phlogopite	Acidic pegmatites	2.70- 3.70	-	3.20(2)	41
	Regional metamorphic skarns	0.66- 4.19	-	2.17(3)	92
	Metasomatic skarns	2.28- 4.30	-	3.75(4)	84
	Fluorite vein	5.70	-	-	84
	Volcanic Ejecta	2.57	-	-	84
	Lamprophyre	0.74	-	-	14
	Kimberlite/	0.12- 1.24	-	0.42(7)	84,106,107,108
	Unspecified rock types	0.56- 9.20	-	2.96(8)	17
-Muscovite	Acidic intrusive rocks	0.02- 0.77	0.17-0.20(2)	0.195(39)	78,90
	Acidic pegmatites	0.03- 2.18	0.19-0.93(4)	0.47(161)	55,75,78
	Unspecified rock types	0.10- 1.48	-	0.24(168)	41
-Lepidolite	Acidic pegmatites	0.64- 9.19	3.75-6.53(4)	5.73(57)	17,28,41,84(a), 95,101,104
-Zinnwaldite	Acidic pegmatites	3.82- 7.67	6.13-6.42(2)	6.25(7)	17,101
-Vermiculite	Serpentinite	0.05	-	-	67
-Apophyllite	Granitoids	3.20- 2.57	-	3.38(2)	46
-Kaolinite	Altered granite	0.026-0.15	-	-	34,49
-Glauconite	Terrestrial	0.0714-0.253	-	0.156(?)	90
-Phillipsite	Pacific ocean	0.020-0.100	-	0.0485(13)	7
-Chlorite	Metamorphic rocks	0.02-0.13	-	0.058(4)	65,90
Amphibole Group:					
-Amphibole (general)	Acidic intrusive rocks	0.01- 1.44	0.03-0.82(2)	0.58(26)	31,54
	Alkalic intrusive rocks	1.43- 2.95	2.11-2.16(3)	2.13(26)	17,29,76,94,103
	Metamorphic rocks	0.01- 0.91	0.01-0.43(3)	0.14(15)	5,12,23,24
	Regional metamorphic skarn	0.13- 1.53	-	0.47(24)	77
	Extrusive rocks	-	-	0.10(100)	40,100
-Anthophyllite series	Metamorphic rocks	Tr. - 0.52	-	0.17(12)	81,89

Continued

TABLE 1.1 contd.

FLUORINE IN ROCK FORMING MINERALS

3

Mineral Group	Rock Type	Fluorine %			References*
		Observed Range	Range of Means	Mean or Weighted Mean	
Silicates contd.					
-Calcium Amphiboles (non-alkalic)	All rock types	Tr. - 3.09	-	0.42(376)	59
-Tremolite	Metamorphic rocks	Tr. - 0.90	-	0.42(27)	59
-Actinolite	Metamorphic rocks	Tr. - 1.32	-	0.42(27)	59
	Acidic Pegmatite	2.18	-	-	59
	Alkalic rocks	0.35- 1.42	-	0.79(3)	59
-Hornblende	Acidic Intrusive Rocks	0.08- 2.90	0.23-1.03(4)	0.55(24)	6, 21, 58, 90
	Alkalic Intrusive Rocks	1.0- 1.10	-	1.05(2)	58, 90
	Metamorphic rocks	0.16- 0.73	-	0.30(8)	37, 86, 98
	Charnockites	0.40- 1.50	-	1.06(9)	42, 62
	Lamprophyre	0.16- 1.43	-	0.59(3)	74
-Alkali-Amphiboles	Alkalic Intrusive Rocks	0.14- 2.95	-	1.39(8)	17, 65(a)
	Alkalic pegmatites	2.05- 2.11	-	2.08(2)	17
	Metamorphosed limestones	0.20- 2.14	-	0.77(5)	17
	Ultramafic rocks	0.09- 1.30	-	0.89(3)	59
Pyroxene Group:					
-Pyroxene	Volcanic rocks	0.034	-	-	48
-Augite	Unspecified Rock Types	0.01- 0.10	-	-	99
-Aegirine	Alkaline Rocks	0.30	-	-	102
-Hypersthene	Metamorphic rocks	0.030	-	-	65

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Mineral Group	Rock Type	Fluorine %			References*
		Observed Range	Range of Means	Mean or Weighted Mean	
Silicates contd.					
Olivine Series:	Volcanic rocks	0.045	-	-	48
Tourmaline Group:					
-Schorlites and Dravites	Acidic pegmatites	Tr. - 0.95	-	0.285(165)	76
-Elbaites	Acidic pegmatites	0.10- 2.10	-	0.97(41)	76
Topaz:	Acidic pegmatites and greisens	15.7-20.5	-	18.7(13)	83
Sphene:	Acidic intrusive rocks	0.14- 1.36	-	0.62(26)	52, 53, 105
	Alkalic intrusive rocks	0.41- 1.36	-	0.95(12)	29, 105
	Acidic pegmatites	0.11- 1.15	-	0.45(5)	10, 105
	Alkalic pegmatites	0.33- 0.47	-	0.38(3)	24, 105
	Basic pegmatites	0.05	-	-	105
	Metasomatic skarns	0.20	-	-	105
	Metamorphic rocks	0.60- 1.40	-	1.0(2)	87, 105
Humite Group:					
-Humite	Metamsomatic limestone	2.77- 5.43	-	3.61(3)	28, 82, 88
-Clinohumite	"	0.60- 5.00	-	1.36(4)	3, 69, 88
-Norbergite	"	13.49-13.55	-	13.52(2)	82, 88
-Chondrodite	"	6.61- 7.11	-	6.90(3)	82, 88
Epidote Group:					
-Allanite	Acidic intrusive rocks	0.05- 0.60	-	0.32(8)	30
Vesuvianite (Idocrase)	Acidic pegmatites	3.07- 0.91	-	1.99(2)	44
Lamprophyllite	Alkalic intrusive rocks	1.10- 1.80	-	1.46(4)	29
	Alkalic pegmatites	1.65- 1.90	-	1.79(3)	29

* See Appendix I for reference list

Studies of the partitioning of fluorine between co-existing OH^--dominated minerals have shown that under certain conditions fluorine may be enriched in one mineral as opposed to the others. Thus, in pegmatites Gillberg (1964) has shown that biotites co-existing with muscovites contain more fluorine. Dodge and Ross (1971) have shown that biotites co-existing with hornblendes in some of the granitic rocks of California have much higher fluorine contents while Larsen and Draisin (1950) and Butler (1954) have shown that reversals of this situation may occur. This suggests that more detailed studies are required in order to fully understand the partitioning characteristics of fluorine during magmatic processes.

At the time of writing no general article on the distribution of fluorine in minerals exists. A large number of fluorine analyses of minerals are, however, scattered throughout the literature, and the author has attempted to present these data in a meaningful form (Table 1.1). All the important fluorine-bearing minerals have been classified under the main mineral groups and their analyses corresponding to the different rock types have been presented as ranges, range of means and means (arithmetic). In all, 105 references have been consulted.

It is apparent from the resume of analyses in Table 1.1 that considerable basic data are still lacking. This can best be seen by the lack of entries in the 'range of means' column.

These data exemplify to a marked degree the isomorphic relationship between the F^- and OH^- ions. Those minerals in which the OH^- ion is a prominent constituent (i.e. the mica, amphibole and tourmaline groups) show great diversity in their fluorine content.

The significance of the fluorine content of the various minerals can be described under the following groups. Concentrations mentioned in the description are taken from Table 1.1.

Halides: There are 34 fluoride minerals known of which fluorite (CaF_2), villiaumite (NaF) and cryolite (Na_3AlF_6) are the most important; the rest are rare Na, K, Ca, rare earth, alumino-fluorides. Fluorite is the most common fluoride mineral known and may occur in practically all rock types with the exception of the ultrabasics. Together with topaz it is the only major rock-forming mineral in which fluorine is an essential element. Fluorite is most abundant in acidic igneous rocks and hydrothermal deposits. Villiaumite is found only in highly alkaline igneous rocks (e.g. Lovozero Massif, USSR) and in certain salt pans (e.g. Rift Valley of Africa). Cryolite may occur as an accessory in igneous rocks, but is predominantly confined to pegmatites, occasionally in economic amounts (e.g. Ivigtut, Greenland and Miask, USSR). The remainder of the halide minerals occur mainly in acidic and alkaline pegmatites and occasionally in hydrothermal deposits.

Oxides: Only three oxide minerals contain fluorine as a significant constituent. Pyrochlore, (Nb, Ta)-oxy-fluoride, is the most important mineral of this group. It occurs almost entirely in carbonatites (0.60-4.61%F) and alkalic pegmatites (3.70%F). Fluorine may, however, substitute for the O^{2-} ion in a number of oxide minerals formed at high temperatures. Examples are perovskite (in certain ultrabasics and alkalic pegmatites) which may contain up to 800 ppm fluorine, and magnetite which may carry up to 960 ppm fluorine.

Carbonates: There are some ten fluor-carbonate minerals of which most are rare earth fluor-carbonates. The most important member of this group is bastnaesite (Ce(Fe/CO_3)) which occurs in significant concentrations (6.23-9.94% F) in granitoids, acidic pegmatites and certain carbonate veins and lenses (e.g. Mountain Pass deposit, San Bernardino County, California). The other fluor-carbonate minerals occur in pegmatites and hydrothermal Pb-Zn-fluorspar deposits.

Borates: Only two fluor-borate minerals are known, and these occur only in borax deposits.

Sulphates: Only three fluor-sulphates are known and these are extremely rare.

Phosphates: Fluorine occurs in significant quantities in twenty two phosphate minerals, but plays a major role in the formation of only eight; of these apatite and amblygonite-montebrasite are the most common. The role of fluorine in apatite has been thoroughly studied (McConnell, 1973). A tri-ionic relationship exists between F^-, OH^- and Cl^- in this mineral. Although hydroxy-apatites and chlor-apatites exist, they are generally rare and form only in the absence of fluorine. The average content of apatite varies from 0.80 to 4.10% fluorine. For acidic intrusive rocks, the fluorine content of apatite (0.80-3.31%) has been shown to possess a sympathetic correlation with the SiO_2 content (Taborszky, 1962). The mean fluorine content of apatite is slightly higher in alkalic intrusive rocks (2.70%) than for acidic intrusive rocks (2.35%). This is in keeping with the higher fluorine content of alkaline igneous rocks as compared with acidic igneous rocks. Apatites from acidic and alkalic pegmatites have similar mean fluorine contents (2.07% and 2.90% respectively). For carbonatites the fluorine of apatites exhibits a large range (1.50-4.10%), but the average content (2.74%) is similar to that for alkalic igneous rocks (2.70%). For metamorphic rocks, little is known of the fluorine content of apatite. It seems probable, however, that apatites from metamorphic rocks are greatly undersaturated with respect to fluorine since much of the fluorine is remobilized and migrates during metamorphic processes. Fluorine reaches its highest concentrations in phosphorites (2.47-4.20%), and although these deposits are not pure apatite deposits it is interesting to compare their fluorine content with other apatite analyses. Theoretically, the maximum amount which can be accommodated in the apatite structure is approximately 3.8% fluorine. Although the average content in phosphorites (3.30%) is below this figure, many analyses greater than 3.8% have been reported. This excess fluorine can perhaps be accounted for by coprecipitation of fluorite with the apatite. Similarly the excess of fluorine in some of the apatites from carbonatites can be explained by the occlusion of fluorite grains in the apatite crystals. The possibility of excess CaF_2 occurring in fluorapatite has been discussed by Mann and Turner (1972).

The stability of fluorapatite over large pressure and temperature ranges is exemplified by its ability to form in silicate magmas as well as in the marine environment.

The second most important fluor-phosphate mineral is amblygonite which together with montebrasite forms a $(LiNa)AlPO_4(F,OH)$ series. The two end-members of this series are found exclusively in acidic pegmatites, and their fluorine content may vary from 1.40 - 11.80%. The low fluorine-bearing minerals of this group signify a lack of fluorine in the residual melts during their formation.

Arsenates: Only three fluor-arsenate minerals are known (durangite, tilasite and svabite). They are extremely rare, occurring mainly in hydrotherm vein deposits.

Silicates: Since all silicate minerals contain OH^- and/or O^{2-} ions, fluorine may occur in all of the minerals in this group either in trace amounts or as a major constituent, but as mentioned previously there is a strong preference for it to concentrate in the hydroxyl-bearing minerals. The amount of fluorine which may enter a given silicate mineral will of course depend on the conditions under which the mineral was formed. Silicates which form under pegmatitic, pneumatalytic, hydrothermal and metasomatic conditions generally contain more fluorine than their rock-forming counterparts.

The fluorine present in the quartz and feldspar mineral groups is most probably the result of occluded material either in the form of fluid inclusions or as CaF_2. Roedder (1972) has noted the occurrence of fluorine in fluid inclusions of quartz from many different settings. There is good reason to assume, however, that the fluorine found in most other silicate minerals is the result of isomorphous substitution. This is certainly the case for silicates listed in Table 1.1 with the exception of the quartz, feldspar and feldspathoid groups.

The micaceous group of minerals are perhaps the greatest 'absorbers' of fluorine both during primary magmatic activity and secondary weathering processes. The most important members of this group are biotite, phlogopite, muscovite, lepidolite and the many secondary clay minerals.

The fluorine content in biotites has been extensively studied mainly as a result of attempts to correlate the trace element content of biotites to the ore potential of magmatic intrusions. (See also the Introduction in Chapter III). Fluorine reaches its highest levels in biotites from greisen zones (3.53%) and charnockitic intrusions (2.14%). The average fluorine content of biotites is significantly higher for acidic pegmatites (0.88%) than for acidic intrusive rocks (0.71%). It is also interesting to note that the fluorine content (range and mean) of biotites from metamorphic rocks is remarkably similar to that for acidic intrusive rocks. For regional metamorphic skarns, however, the fluorine content of biotites is low (0.61%).

Phlogopites may contain as much as 5% fluorine. This mica occurs in practically all rock types but is most often found in ultrabasic rocks such as peridotites, kimberlites (0.42%) and lamprophyres (0.74%). In places it may occur in acidic pegmatites (3.20%), contact metamorphic skarns (3.75%), regional metamorphic skarns (2.17%) and fluorspar veins (5.70%). Phlogopite rarely if ever occurs in rocks which have a very low fluorine content.

Muscovite also contains high concentrations of fluorine (up to 2.18%), but in general it has less ability to concentrate fluorine than do biotite and phlogopite. The largest concentrations occur in muscovites from pegmatitic deposits (0.47% F), while muscovites from acidic intrusive rocks generally contain less (0.195%).

The two pegmatite micas, lepidolite and zinnwaldite, are well known concentrators of fluorine. Both minerals show large ranges of 0.64 - 9.19% and 3.82 - 7.67% fluorine respectively, and are thus generally good indicators of the presence of large quantities of fluorine having been present during the pegmatitic stage of magmatic intrusion.

Other micaceous minerals which may concentrate fluorine are kaolinite in hydrothermally or pneumatolytically altered granites (0.026-0.15%), apophyllite in granitoids (3.38%), vermiculite in serpentinized ultrabasics (0.05%) and chlorite in certain metamorphic rocks (0.058%).

Many of the clay minerals in the secondary environment contain significantly high levels of fluorine (Table 2.12, Chapter II). The fluorine content of these minerals depends largely on the origin of the clay and the secondary processes to which it has been subjected. The total range of values observed for clay minerals is 204 to 22,400 ppm fluorine.

The second largest group of OH-bearing silicate minerals capable of concentrating fluorine is the amphibole group. The classification of amphiboles in Table 1.1 for the purpose of studying their fluorine content has been confounded by lack of proper description by the authors concerned. For instance, some authors describe amphiboles as a general group or as alkaline or non-alkaline whereas others use specific names such as hornblende, actinolite, etc. No attempt has been made by the present author to merge data from these various groups for obvious reasons of bias. We can, however, make a number of significant generalizations concerning the fluorine content of the amphibole minerals. Generally speaking the more alkaline the amphibole the greater its fluorine content. Amphiboles from alkalic intrusive rocks have a much higher fluorine content (2.13%) than those from acidic intrusive rocks (0.58%). Probably the same holds true for alkalic and acid pegmatites. The fluorine content of amphiboles from metamorphic rocks (0.14% and 0.30% for hornblende) with the exception of skarn deposits (0.47%) is considerably lower than for acidic intrusive rocks while amphiboles from extrusive rocks appear to be severely depleted in fluorine (0.10%). Low fluorine values for amphiboles from metamorphic terrains may be due to the remobilization and migration of volatile elements during regional metamorphic processes.

This would also appear to be the case for apatite but does not apply to biotite. The defficiency of fluorine in amphiboles from effusive rocks can be explained by degassing of volcanic rocks during extrusion and cooling (Noble et al, 1967).

Of the remaining major rock-forming minerals only aegirine (0.30%) and augite (0.01 - 0.10%) have been shown to accumulate significant amounts of fluorine.

A number of the accessory silicate minerals may possess high levels of fluorine. Of these, topaz, tourmaline, sphene, the humite group, epidote (allanite), vesuvianite (idocrase) and lamprophyllite are the most important.

Although both topaz and tourmaline may occur as disseminations in acidic igneous rocks they are chiefly confined to acidic pegmatites, greisen zones and occasionally high temperature hydrothermal veins. The fluorine content of topaz may vary between relatively large limits (15.7 - 20.5%), but it should be remembered that the presence of fluorine is essential to the formation of this mineral. The occurrence of topaz is, therefore, indicative of the presence of fluorine. Fluorine in the tourmaline group minerals (schorlite, dravite, elbaite) exhibits a very large concentration range (trace -2.10%) with elbaites (0.97%) containing much higher concentrations than schorlites and dravites (0.285%). The ability of tourmaline to take up fluorine is strongly dependent on the chemical activity of fluorine in the pegmatitic, hydrothermal or pneumatalytic fluids (Nemec, 1969).

Sphene may also be a sensitive indicator of the presence of fluorine during rock-forming and mineralizing processes. As with most other minerals it shows a much greater enrichment of fluorine in alkalic intrusive rocks

(0.95%) as compared to acidic intrusive rocks (0.62%). For acidic and alkalic pegmatites the average contents in sphene are similar (0.45% and 0.38% fluorine, respectively) but much lower than for the parent intrusive rocks. Although more analytical data are required, sphene would appear to be the only mineral which shows a depletion of fluorine in pegmatite deposits as compared with intrusive rocks.

The only member of the epidote group which has been shown to accumulate significant amounts of fluorine is allanite. It is most often found in acidic intrusive rocks where the content may range from 0.05 to 0.60% fluorine.

The two accessory minerals, vesuvianite (idocrase)) and lamprophyllite occur mainly in skarn deposits and alkalic pegmatites respectively. Both may accumulate large amounts of fluorine (1.99% and 1.79% respectively).

The last important fluorine-bearing silicate group which should be mentioned is the humite group (humite, clinohumite, norbergite, chondrodite). These minerals are entirely confined to metasomatic skarn zones but generally do not constitute an important percentage of the composition of these deposits. Of the four members of this group, norbergite (13.52%) contains the highest levels of fluorine with lesser amounts occurring in chondrodite (6.90%), humite (3.61%) and clinohumite (1.36%).

Having regard to the content of fluorine in the minerals described above a number of generalizations about the abundance of fluorine in rock-forming minerals and its association with other elements can be made.

1) The ease with which the F^- ion can substitute for the OH^- ion during the formation of minerals is demonstrated by the great number of hydroxyl-bearing minerals in which fluorine is concentrated. To a lesser extent, fluorine will substitute for the O^{2-} ion in oxide and silicate minerals.

2) Although topaz is the only major silicate mineral for which fluorine is essential, many of the other silicate minerals probably require some minimum amount of fluorine to be present before they will form. Often the formation of one mineral as opposed to another may be encouraged by the presence of fluorine in the magma or mineralizing solutions.

3) The amount of fluorine concentrated in a particular mineral depends on the physico-chemical conditions under which the mineral was formed and the chemical activity of F^{-1} in the solutions or melts at the time of formation. Minerals which are formed under pegmatitic, pneumatolytic, hydrothermal and metasomatic conditions possess much higher fluorine concentrations than corresponding minerals in associated igneous rocks. For intrusive rocks the higher concentrations are observed in those minerals formed from alkalic melts; this is probably also the case for extrusive rocks.

4) There is a strong association between the abundance of fluorine and the rare earth elements in minerals. This is demonstrated by the large number of REE-halide and REE-fluor-carbonate minerals which occur in nature. In aqueous solutions fluorine forms strong complexes with the REE elements, and it seems probable that their distribution in endogenic deposits is strongly governed by the activity of fluorine. The rare earth elements also occur in significant amounts in both apatite (Denisov et al 1961; and Lyaklovich and Barinskii, 1961) and fluorite (Kozlova, 1957, and others).

Other elements which possess a close genetic association with fluorine are Al (e. g. in cryolite and other alumino-fluorides), Be, Sc, Y, Zr, Nb, Ta, Th, U, B and Sn. All of these elements form strong fluoride complexes in solution. In addition B and Sn also form highly volatile fluorides (BF_3 and SnF_4).

In summary, fluorine occurs in a wide variety of minerals either as an essential constituent or camouflaged by isomorphic substitution. The concentration range for some of these minerals is significantly large. Finally, since fluorine occurs in many of the minerals in economic mineral deposits, the element should prove to be a most useful pathfinder in geochemical exploration.

1.2.2 Fluorine in the Igneous Intrusive Environment

In the magmatic environment fluorine possesses both lithophilic and atmophilic characteristics, hence the strong association between fluorine and silica content in igneous rocks and the common enrichment of the element in metasomatic deposits such as greisens and skarns.

Magmatism may be considered as consisting of a number of phases, viz. the intrusive, pegmatitic, pneumatalytic, hydrothermal and volcanic or extrusive phases. This section is concerned with the intrusive and pegmatitic phases and is followed by a discussion of the volcanic or extrusive phase. The pneumatolytic and hydrothermal phases are discussed in the sections on the metamorphic environment and ore genesis. These phases have been separated for descriptive purposes with the full knowledge that they are in no way independent of one another. The various phases are subjectively included in the appropriate sections in which they are felt to be most important. The relationship between type of magmatic intrusion and depth (viz. hypabyssal, epixzonal,etc.) is still not clearly understood;

TABLE 1.2

FLUORINE IN IGNEOUS INTRUSIVE ROCKS (all values in ppm)

ROCK TYPE	RANGE	MEAN	REFERENCE*
A. ACID-BASIC GROUP			
Ultramafic rocks	Tr. - 2,000	130(37)	11,23,48
Gabbros	50 - 11,000	430(47	16,28,29,44,49
Diorites	300 - 1,300	665(20	16,23,44
Granites & granodiorites	20 - 30,000	810(182)	15,16,52,28,29,44
B. TRANSITIONAL GROUP			
Syenites & monzonites	200 - 4,000	1,360(26)	23,43,44
C. ALKALINE GROUP			
Alkali-ultramafics	Tr. - 3,800	1,400(41)	6,12,23
Alkali-syenites	100 - 25,800	1,800(249)	10,21,24,29,43, 50,51
Alkali-granites	670 - 12,400	5,500(20)	2,3,23,34,49
D. LATE DIFFERENTIATES AND DYKE ROCKS			
Carbonatites	200 - 24,000	8,100(96)	6,12,13,20,38, 41,53
Kimberlites	520 - 2,500	1,310(42)	46,62,63,64,65,66
Diabase(Dolerite)	198 - 500	420(14)	18,23,44
Lamprophyres**	Tr. - 3,700	1,500(63)	6,7,12,34
Pegmatites	800 - 9,000	4,320(6)	36,47,52

* See Appendix II for reference list

** Includes alkali-lamprophyres

Tr. = trace

for this reason the author has not further subdivided the magmatic environments on the basis of depth.

Three types of magmas are significant in the formation of the different igneous rock types - granitic, basaltic and alkalic magmas. The last type has only recently been recognized mainly as the result of the strong evidence supporting a magmatic origin for carbonatites. Some believe that alkalic magmas are late differentiates of basaltic magmas. For descriptive purposes the author has accepted this concept and has included carbonatites in the section on late differentiates in Table 1.2. It should, however, be recognized that the evidence for suggesting that alkalic magmas are differentiates of basaltic magmas is still tenuous. A similar problem arises when trying to classify kimberlites. These rocks may be considered as differentiates of eclogitic mantle material. Their composition suggests that they are not as divorced from their parent as carbonatites, but their mode of emplacement and high volatile (F, CO_2 etc.) content makes them unique. They have been placed with carbonatites in the section on late differentiates in Table 1.2. As with carbonatites, their formation is far from one of simple differentiation.

The range and mean (arithmetic) fluorine content of the various igneous intrusive rocks are given in Table 1.2 where the rock types have been classified according to their acid-basic, transitional, alkaline, late differentiate and morphological character. The analytical data have been taken from sources considered by the author to be the most reliable. A number of the means would appear to be representative of the rock types (e.g. granites, granodiorites, alkali-syenites), but those for other types will undoubtedly change slightly as more analyses become available. The most striking overall characteristic of this data is the distinct increase in fluorine content with increasing SiO_2 content and increasing alkali content. The relationship between fluorine and SiO_2 can be seen in both the acid-basic and alkaline groups, and the relationship between fluorine and increasing alkali (Na, K) content is apparent when one compares the high fluorine content of the alkaline group of rocks with their acid-basic equivalents. The transitional group represents rocks having above normal SiO_2 and alkali compositions, and hence their fluorine content is likewise transitional between the acid-basic and the alkaline groups.

It should be noted that the ranges of fluorine content for the rock types in each of these three groups are not distinct and that there is much overlap in the data. This is a reflection of the various physico-chemical constraints under which these rock types were formed and the consequent behaviour of fluorine under these constraints.

Considering the ranges for the three groups it is apparent from the relationship between fluorine and SiO_2 that rocks having a low SiO_2 content are almost invariably low in fluorine whereas rocks with high SiO_2 contents generally have a high content but may occasionally be depleted in fluorine. This depletion is most probably the result of the release of volatiles during differentiation before the gaseous constituents reach equilibrium with the melt (pneumatotylic stage).

In magmatic systems the correlation between fluorine and SiO_2 is enhanced by the depolymerizing effect of F^{-1} on Si^{4+} to form Si-F bonds. Thus, as magmas become enriched in SiO_2 through differentiation the fluorine content will increase in the residual melt (Tauson, 1967; Greenland and Lovering, 1966). This process of enrichment is further augmented as a result of the inability of most rock-forming minerals to accept appreciable amounts of fluorine in their lattices (limited F^{-1} -O^{2-} substitution). Often, however, considerable amounts of fluorine are left over and take part in later magmatic stages. Experimental investigations by Wyllie and

Tuttle (1961) have shown that HF, being more soluble in silicate melts than water, depresses the melting temperature and hence accumulates to a higher degree in the residual melts (pegmatites, etc.). With increasing alkalinity the solubility of fluorine in melts is greatly increased, and its concentration in the gaseous phase is decreased (Kogarko et al, 1968; Delitsyna and Melent'yev, 1969). The increase in fluorine with increasing alkalinity shown in Table 1.2 bears this out.

The increase of fluorine with increasing SiO_2 and alkali content culminates with the highest concentrations in alkali-granites (5,500 ppm F).

Apart from the distinct overall relationship between fluorine, SiO_2 and alkali content, individual rock types have certain notable characteristics as regards fluorine concentration.

Ultramafic rocks have an average fluorine content of 130 ppm. Dunites and pyroxinites diverge from this average by having much lower concentrations (8-20 ppm), whereas peridotites and eclogites (100-300 ppm) have higher concentrations, and serpentinites have the highest fluorine content of all normal ultramafics (up to 2,000 ppm). The process of serpentinization is, therefore, one that favours fluorine concentration, probably as the result of a greater opportunity for F-OH substitution in the serpentine minerals. For mica-bearing ultramafics (mica-peridotite, mica-pyroxenite), the fluorine content is considerably higher (1,000-2,000 ppm) than for the non-mica bearing equivalents. The highest concentrations for all types of ultramafics are found in the alkali-ultramafics, rocks (alnoite, damjernite, etc.) that are most often found in alkaline massifs, especially in the vicinity of carbonatite intrusions. The main fluorine-bearing minerals in ultramafic and basic rocks are phlogopite, biotite, serpentine, augite and hornblende. Phlogopite for instance may contain up to 5% fluorine.

Gabbros have an average content of 430 ppm fluorine and a relatively large range (50-11,000 ppm). It is interesting to note that the average concentration for diabase and dolerite (420 ppm) is similar to that for gabbros, which is further evidence that these predominantly dyke rocks were originally derived from magmas of gabbroic composition.

Diorites have a mean fluorine content of 665 ppm and their range, compared to other rock types, is relatively narrow (300-1,300 ppm). The highest concentrations occur in hornblende-diorites.

Syenites and monzonites invariably contain higher concentrations of the alkali elements (minerals) than do granites. Their average fluorine content is consequently higher (1,300 ppm), although the range is not greater than that for granites and granodiorites. Syenites and monzonites form a transitional group between rocks of high alkali and low alkali content. Their alkali equivalents (alkali-syenites) have an average content of 1,800 ppm fluorine and the largest range of the alkaline group of rocks.

Granites and granodiorites have the highest fluorine concentrations in the acid-basic group (810 ppm). They also have the largest range for all rock types, a feature that is due largely to their variable mineralogy and mode of formation. The principle fluorine-bearing minerals in granitic rocks are biotite, muscovite, hornblende, apatite, topaz, fluorite and tourmaline. With the exception of biotite and possibly hornblende all of these can be considered as accessory minerals. Granitic rocks having greater than normal concentrations of these minerals can be expected to contain very high concentrations of fluorine (e. g. the fluorite granites of Cornwall and the topaz granites of Nigeria). On the other hand granitic rocks having an abnormally low concentration of accessory minerals will exhibit very low fluorine contents due mainly to the limited $F-O^{2-}$ substitution which can take place. The alkali equivalents of acid- granitic rocks (alkali-granites) normally contain the highest fluorine concentrations (5, 500 ppm), the largest concentrations being found in the riebeckite granites.

At present it is not clearly understood why granitic rocks with the same mineralogy and bulk chemical composition have widely different fluorine contents. From his studies of some of the granite complexes in the USSR, Tauson (1967) has postulated that the distribution of volatile elements, and in particular fluorine, is determined by the size of the intrusive, depth of its formation and composition. For intrusives of the same composition this leaves only depth and size as the controlling parameters.

During the last stages of intrusion the residual fraction of an acidic or alkalic melt will be concentrated in the apical parts of the intrusive. These residual melts will be rich in volatiles (F, H_2O, etc.) and rare elements, and their subsequent intrusion generally results in the formation of pegmatites of acid or alkalic composition. No data are available on the fluorine content of alkalic pegmatites per se, but from the analysis of various minerals (see Table 1. 1) that occur in these deposits and their modal percent (Vlasov et al, 1966) the average fluorine concentration can be expected to be well within the range given for the acidic pegmatites in Table 1. 2. For acidic pegmatites the average content is of the order of 4, 000 ppm, but considerable variation (800-9,000) is notable. This is primarily due to the mineralized and non-mineralized nature of these deposits in addition to their complex and simple structures. Barren (simple) pegmatites generally contain much less fluorine than rare metal pegmatites. As an example of this, an average content of 620 ppm fluorine characterizes the barren pegmatites of the Caucasian granitoids whereas the rare metal pegmatites yield an average of 1,400 ppm (Okikadze, 1971). Complex pegmatites contain a much greater variety of fluorine-bearing minerals than simple pegmatites, and higher fluorine contents can be expected in these deposits. The main fluorine-bearing minerals in pegmatites are the various micaceous minerals, apatite, fluorite, topaz and pyrochlore (alkali pegmatites only).

Lamprophyres contain variable amounts of fluorine (trace - 3,700). The mean of 1,500 ppm given in Table 1.2 is tentative since the term lamprophyre is given to a diverse group of dyke rocks which may differ significantly both in their composition and relationship to parental magmas. Thus, minettes and vogesites are generally associated with granites; kersantites and spessartites-malchites with diorites; and alnoites, camptonites and monchiquites with deep-seated ultramafic rocks of alkaline composition (Carbonatites and kimberlites). Most lamprophyres are alkaline, higher fluorine concentrations occurring in the more alkaline members (Tee Table 3.5 in the section on kimberlite exploration). However, the occurrence of large quantities of phlogopite (up to 5% fluorine) in these rocks may tend to obscure the relationship between fluorine and alkalinity. The principle fluorine-bearing minerals in lamprophyres are phlogopite, augite and hornblende. The origin of lamprophyres is enigmatic and controversial. Recently, Nemec (1968b), basing his evidence on the fluorine content of these rocks, has suggested that they are late differentiates. His investigations confirm that lamprophyres, like pegmatites, are richer in fluorine than their parent rocks.

Carbonatites and kimberlites can be considered as deep-seated, late differentiates. Their mode of emplacement in stable shield terrains and their chemical composition, which differs markedly from both basalts or granites, certainly suggest this. Both types of rocks are often closely associated spatially, and the occurrence of carbonatites within kimberlites has been noted (Tuttle and Gittins, 1967). The occurrence of eclogitic xenoliths in kimberlites suggest a mantle origin for these rocks. It is improbable, however, that the fluorine is of mantle origin, but it is apparent that fluorine and other volatiles (CO_2, H_2O, etc.) have had a modifying effect on the emplacement, structure and composition of these rocks, possibly as a result of fluidization process. Two types of kimberlite are recognized - micaceous and basaltic. These types are, however, arbitrary and transitions between them exist. The micaceous kimberlites generally have higher fluorine concentrations, mainly because of the greater percentage of phlogopite present in them. The average fluorine content (1,410 ppm) in Table 1.2 is based on the author's analyses of 24 different kimberlites (see Table 3.4 in the section on kimberlite exploration). The range for kimberlites is relatively narrow (520-2,400 ppm), and the lowest level of this range is much greater than the average of ultramafic rocks (130 ppm). The principle fluorine-bearing minerals in kimberlites are phlogopite, serpentine apatite and perovskite.

Carbonatites exhibit a relatively large range of fluorine concentrations (200-24,000 ppm). This is due primarily to the occurrence of fluorine in discrete minerals such as fluorite, apatite and pyrochlore which may be concentrated in different phases of carbonatites. The mean (8,100 ppm fluorine) is probably representative of most carbonatite complexes. Carbonatites appear to represent the last residual alkali-rich fraction of magmas that have virtually undergone complete differentiation. Their setting and relationship to present and past volcanism in stable shield environments suggest that their parent magma was basaltic in composition. Their high alkalinity normally implies an increase in the fluorine solubility in the melt.

It has long been known that a marked correlation exists between the fluorine content of igneous rocks and their rare element content (RE, Sn, Ta, Nb, Be, Li, Cs, Tb, U, B), a feature that is discussed in greater detail in the section on ore genesis. For granitoids, Odikadze (1971) has shown that an increase in fluorine concentration is accompanied by an increase in the concentration of Li, Rb, Cs, Ta, Nb, Sn and other rare elements. Similarly, there is a marked correlation between fluorine and the rare elements in pegmatites. Kimberlites and carbonatites have high rare earth and niobium-tantalum contents in addition to their high fluorine content. On the other hand, ultrabasic and basic rocks which are generally low in all of the above mentioned elements are also low in fluorine.

1.2.3 Fluorine in the Volcanic Extrusive Environment

During the volcanic or extrusive phase of igneous activity, fluorine is partitioned between the melt and the vapour phase. As a result of the degassing of effusive melts and rocks in the surface and near-surface environments, many of the minerals which normally would be hydrated in the deep intrusive environment occur in dehydrated form, and hence much fluorine moves into the vapour phase since there is restricted F-OH substitution. Noble et al (1967) have discussed the loss of halogens from crystallized and glassy silicic volcanic rocks, noting that up to half of the fluorine originally present is lost through degassing. Much of this leaves the system by way of volcanic fumaroles, either as HF or H_2SiF_6. The gasses of present day fumaroles generally contain between 1 and 2 volume percent of HF (White and Waring, 1963). Of the active gases (volume of gas minus H_2O

TABLE 1.3

FLUORINE IN IGNEOUS EXTRUSIVE ROCKS (all values in ppm)

ROCK TYPE	RANGE	MEAN	REFERENCE*
	A. ACID-BASIC GROUP		
Basalts	20 - 2,400	375(317)	16,32,60
Andesites	Tr. - 1,200	250(97)	16,60
Rhyolites and dacites	Tr. - 6,850	610(151)	16,60
	B. TRANSITIONAL GROUP		
Trachytes and latites	200 - 2,250	750(9)	23,29,60
	C. ALKALINE GROUP		
Alkali-ultramafics	200 - 4,900	2,015(7)	23
Alkali-basalts	500 - 1,700	925(6)	9,28,60
Phonolites	860 - 1,490	950(14)	23,29

* See Appendix II for list of references

vapour) the HF content may be as much as 30 percent. Rocks which are extruded at the surface normally lose fluorine by direct degassing into the atmosphere.

Considering the above processes one would anticipate a much lower mean fluorine content for the volcanic rocks than for their intrusive equivalents, and such is the case as shown in Table 1.3. The alkali-ultramafic volcanics do not conform to this rule, probably because the small number of analyses for these rocks represent phenomenological varietes, and hence the mean fluorine content is not truly representative. Clearly more data for this group of rocks are required.

Following the scheme for the intrusive rocks, the extrusive rocks are divided into acid-basic, transitional and alkaline groups. Excepting the alkali-ultramafics, the fluorine content of volcanic rocks exhibits, with one exception, the same relationship to the SiO_2 and alkali contents as that shown by intrusive rocks. For both the acid-basic and alkaline groups the average content increases with increasing SiO_2 content. Basalts deviate slightly from this rule in having a noticeably higher mean value than andesites. While andesites tend to be relatively uniform in composition, basalts may vary greatly in their alkali content, to the point where they are called alkali-basalts. It is possible, therefore, that a number of the fluorine analyses for basalts included in the acid-basic group represent sub-alkaline basalts. Alternatively, many andesitic rocks have undergone propylitization with concomitant leaching and remobilization of the fluorine. Inclusion of data for such propylitic rocks may have resulted in a lower mean for the andesite group. It should also be noted that the range for andesites (trace - 780 ppm fluorine) is much smaller than for basalts (20-2,400 ppm).

Taking the volcanic rocks as a whole it can be seen that the mean fluorine content increases with increasing alkalinity. Omitting the data for the alkali-ultramafics for reasons described above, the highest mean content is observed for the phonolites (950 ppm fluorine) which have both a high SiO_2 and alkali content. Trachytes and latites form a transitional group between rhyolites and phonolites in terms of SiO_2 and alkali content. Their mean fluorine content (900 ppm) falls between the mean values for these two groups.

The fluorine content of volcanic rocks only rarely exceeds 2,000 ppm in contrast to intrusive rocks, varieties of which commonly contain significantly more of the element. Certain rhyolites and alkali-ultramafics may contain in excess of 2,000 ppm fluorine.

Studies of the abundance of fluorine in volcanic rocks indicate that the element exhibits log-normal distribution (Fleischer and Robinson, 1963; Coats _et al_, 1963; Yoshida _et al_ 1971). The range and mean content may also vary significantly from one volcanic province to another (Coats _et al_ 1963; Gerasimovskii _et al_ 1969).

1.2.4 Fluorine in the Sedimentary Environment

Both chemical and mechanical weathering of rocks results in the release of fluorine and its subsequent deposition in sedimentary basins. Fluorine enters the sedimentary environment in a number of ways:-

a) as a constituent of resistate minerals such as topaz or tourmaline and to a lesser extent apatite, fluorite and the micas;

b) as an adsorbed ion on virtually any particle or colloidal anion acceptor; and

TABLE 1.4

FLUORINE IN SEDIMENTARY ROCKS (all values in ppm)

ROCK TYPE	RANGE	MEAN	REFERENCE*
	A. CLASTIC SEDIMENTS		
Shales, siltstones & mudstones	10 - 11,660	790(141)	1,16,27
Sandstones and greywackes	10 - 880	180(49)	16
Oceanic sediments	100 - 1,600	640(151)	16,45
Volcanic ash	100 - 2,900	725(168)	16
	B. BIOGENIC AND CHEMICAL SEDIMENTS		
Limestones	Tr. - 1,210	220(98)	16
Dolomites	110 - 400	260(14)	16
Phosphate rock	10,400 - 42,000	30,500(74)	55,56,57,59,67
Anhydrite and Gypsum	130 - 890	600(6)	29
Rock salt	2 - 6	5(4)	29
Coal	40 - 1,200	130(12)	5
Chert	210 - 830	515(3)	29

* See Appendix II for list of references

c) as an aqueous ion or as Fe, Al, Mg etc. complexes.

Most of the fluorine in the sedimentary cycle is water-born, but small amounts are added as a result of wind transport and atmospheric precipitation.

Little information on the distribution of fluorine is available for recent sediments (i.e. ocean, lake and alluvial sediments). In the marine environment, fluorine may be removed from sea water as a result of the precipitation of $CaCO_3$ and phosphate, but Carpenter (1969) has calculated that only 10 to 20 percent of the dissolved fluorine reaching the oceans in rivers can be accounted for by carbonate and apatite precipitation. Furthermore, very little of the remaining fluorine is removed by absorption on clay particles. These facts suggest that large quantities of fluorine must be lost to the atmosphere through evaporation. The data available on oceanic sediments (Table 1.4) indicate that their average fluorine content (640 ppm) is similar to that for shales (790 ppm). No data are yet available on the fluorine content of lake and river sediments.

Consolidated sediments can be divided into two main groups:

a) clastic sediments and

b) biogenic and chemical sediments.

The range and average fluorine contents for the rock types in each of these two groups is given in Table 1.4. Among the clastic sediments the fluorine content is greatest for the clay-bearing rocks (shales, siltstones and mudstones). Koritnig (1951) finds that the majority of fluorine in these rocks is tied up in sedimentary micas with smaller amounts occurring in apatite. The relatively wide range of fluorine observed for the shales, silststones and mudstones (10-11,660 ppm) is due largely to variations in the clay and apatite content of the rocks. The high concentrations in this range represent phosphatic shales. Sandstones and greywackes have fluorine contents (180 ppm) significantly lower than those for shales, siltstones and mudstones (790 ppm). This is to be expected mainly because of the low clay content in these rocks. Fluorite-cemented sandstones occur in West Cumberland, England (Lewis, 1931) and Colorado, USA (Boyer, 1961). The sandstones in Colorado are also uraniferous. The origin of the fluorine in these sandstones would not seem to be the result of chemical (sedimentary) precipitation and diagenesis but rather the element appears to have been introduced through the agencies of groundwater or hydrothermal solutions.

The precipitation of calcium compounds ($CaCO_3$, $CaSO_4$ and $Ca_3(F, OH)(PO_4)_3$ in sea water is often accompanied by the precipitation of fluorine. The element will precipitate with these compounds in one or a combination of three ways:-

a) as an elemental constituent e.g. in apatite, a major component of phosphorites;

b) as a coprecipitate (CaF_2 or MgF_2); and

c) indirectly as a constituent of skeletal tissues of various marine organisms.

Of the compounds mentioned above apatite or collophane in phosphorites contains the highest concentration of fluorine. The mean content of phosphate rock (3.10%, is less than that of saturated apatite (3.8%), but the observed range (1.40 - 4.2%) indicates that sedimentary phosphorites may occasionally be oversaturated with respect to fluorine, the excess being most probably due to coprecipitation of CaF_2 with the apatite.

In the case of anhydrite and gypsum, fluorine probably coprecipitates directly with the $CaSO_4$ as CaF_2. The range for these evaporites is 130 to 890 ppm fluorine; the mean concentration is of the order of 600 ppm.

During the formation of limestone deposits a small amount of fluorine may coprecipitate with the $CaCO_3$ as CaF_2 or MgF_2, but most appears to be combined in these sediments as a constituent of skeletal remains of marine organisms. The fluorine in these skeletal structures occurs mainly as fluorapatite or in some cases as fluorapatite with minor amounts of CaF_2. Limestones exhibit a wide concentration range (Tr. - 1,210 ppm fluorine) and the mean content for these rocks is of the order of 220 ppm. For dolomites the range (110 - 400 ppm) is much smaller than for limestones, but the mean (260 ppm) is similar to that for limestones.

The ability of fluorine to coprecipitate with calcium compounds can be contrasted with its inability to precipitate with Na and K compounds. Rock salt (NaCl) contains only trace amounts of fluorine (2-6 ppm), and although no data are as yet available it is probable that potash deposits containing KCl and other potassium salts will report only insignificant amounts of fluorine.

The high concentration of fluorine in certain cherts (210-830 ppm) suggests that it also coprecipitates with silica, although the exact mechanism for precipitation is not known.

The fluorine content of coal varies widely, from 40 to 1,200 ppm. Some of this is present in fluorite or apatite in certain coals. More generally, however, the element is largely present in the hydrocarbon (coaly) substance in an unknown form. Some of the fluorine in coals may be added by groundwaters, but much of the element appears to have been an original constituent of the coal plants. As noted above most plants contain between 10 and 100 ppm fluorine (dry weight); mainly as fluorapatite.

During decomposition, compaction and coalification processes fluorine is enriched much above the normal concentrations observed for plants.

1.2.5 Fluorine in the Metamorphic Environment

Two predominant processes of metamorphism can be recognized in geologic terrain - regional metamorphism and metasomatic-pneumatolytic alteration. Fluorine plays a major role in both these processes, especially the latter. The range and mean fluorine contents for the various metamorphic rock types resulting from these two processes are given in Table 1.5.

During regional metamorphism fluorine is a relatively mobile element. In regional metamorphic environments fluorine-bearing minerals are unstable due to high temperature-pressure conditions and the presence of water which promotes the hydrolysis of fluorine and its migration as HF. Fluorine moves along the chemical potential gradient until it encounters a chemical potential sink (i.e. a zone of low pressure, low concentration, low temperature etc.) such as reactive rocks (e.g. limestone) or until it escapes entirely from the metamorphic system, that is to the surface hydrosphere, atmosphere, etc. Korzinsky (1955) considers that the mobility of fluorine during regional metamorphism is surpassed only by that of H_2O, CO_2, S, SO_3, Cl, K_2O and Na_2O. The high mobility of fluorine during regional metamorphism has also been commented on by Nemec (1968) and Gavrilin *et al* (1972). The loss of fluorine from rocks due to increased mobility during regional metamorphism is best illustrated by comparing the mean fluorine content of schists (250 ppm) with that for shales, siltstones and mudstones (790 ppm). More than half of the fluorine has been lost during the formation of schists from their original equivalents.

TABLE 1.5

FLUORINE IN METAMORPHIC ROCKS (all values in ppm)

ROCK TYPE	RANGE	MEAN	REFERENCE*
	A. REGIONAL METAMORPHIC ROCKS		
Meta-Gabbro	99 - 140	120(2)	28
Schists	60 - 580	250(48)	28, 37, 44
Hornblende hybrid	400 - 930	620(4)	28
Amphibolite	140 - 1,400	740(10)	28, 33, 44
Gneiss	240 - 2,800	1,030(14)	28, 33, 44
	B. METASOMATIC ROCKS		
Hornfels	260 - 7,800	1,630(57)	2, 4, 17, 18
Skarns (Regional metamorphic origin	90 - 4,500	1,200(10)	33
Skarns (contact origin)	700 - 43,500	9,780(28)	30, 54
Greisens and greisenized granites	1,600 - 20,400	9,800(26)	14, 19, 25, 29, 31, 36, 39
Kaolinized granites	800 - 7,400	2,800(21)	19, 39, 58, 61
Fenites	Tr. - 600	400(3)	6, 12

* See Appendix II for list of references

Data on fluorine in regionally metamorphosed rocks are sparse, and the mean contents given in Table 1.5 are, therefore, at best only approximations. At present, with the exception of schists, the emphasis should be placed on the range of fluorine contents rather than on the mean when comparing its abundance in regionally metamorphosed rocks.

The principal mineral carriers of fluorine in regionally metamorphosed rocks are biotite, amphibole and apatite. The last mineral plays only a minor concentrating role in these rocks as compared to its major role in igneous and sedimentary rocks.

During regional metamorphic processes and igneous intrusive processes fluorine may be concentrated in the mobile fluid phase. Active gases (CO_2, HF, HCl, SO_3, etc.) form the largest percentage of this phase, the remainder being composed of water in either the vapour or liquid state. Reactions of this active gas-H_2O-liquid phase with the surrounding country rocks commonly gives rise to metasomatic-pneumatolytic alteration zones such as hornfels, skarns, greisens, kaolinized granites and fenites. The author prefers to use the combined term metasomatic-pneumatolytic to describe these reaction products since it is uncertain whether the fluid phase is entirely gaseous or composed of gaseous, aqueous and melt phases. Nevertheless, it is evident that gases predominate in these fluids in many geological situations.

Most metasomatic rocks are formed as the result of the emplacement of igneous intrusive bodies into the country rocks, as in the case of hornfels, skarns and fenites, or subsequently, as the result of escape of volatiles and solutions from the crystallizing igneous bodies into the country rocks or into the cupolas of the solidified igneous rocks themselves, as in the case of greisens, greisenized granites and kaolinized granites. Regional metamorphic skarns are the only metasomatic rocks which do not fit this pattern. These skarns possess much more fluorine (90-4,500 ppm) than other regional metamorphic rocks, but have much lower fluorine levels than contact skarns 700-43,500 ppm. This is merely a reflection of the availability and source of fluorine during the formation of the two types of skarns, the former deriving its fluorine as the result of remobilization of a portion of the fluorine bound in rocks undergoing metamorphism and the latter obtaining its fluorine through the concentration of volatiles during the differentiation and intrusion of igneous bodies. The contact skarns almost invariably occur at the contact between an intrusive igneous body and a highly calcareous country rock. If the country rock is non-calcareous, the resultant metasomatic rock is generally a hornfels. The fluorine content of the two contact rock types is different, being much lower for hornfels (1,630 ppm) than for skarns (9,780 ppm). The principal fluorine-bearing minerals in hornfels are hornblende and biotite, whereas a veritable host of fluoriferous minerals occur in skarns, including fluorite, apatite, hornblende, micas, topaz, sphene and humites. Contact metamorphic processes are characterized by a depletion of fluorine in the border zones of certain intrusive masses and by an increase in the rocks forming the metamorphic aureole, i.e. skarn, hornfels (Sahama, 1948; Seraphim, 1951); see also the section on Prospecting for Tin Deposits. The degree of depletion in the border zone and subsequent enrichment in the aureole are dependent on the prevailing physico-chemical conditions at the time of intrusion as well as on the mineralogical make-up of both the intrusive and country rocks.

During the intrusion of alkali magmas, such as carbonatites and alkali syenites, fenitization of the country rock may occur, especially where the host rock is quartzofeldspathic in composition. Data on the fluorine content of fenites are limited, and it is probable that the levels shown for fenites in Table 1.5 are too low, especially when the fluorine content of carbonatites (3,200 ppm) and alkali syenites (1,800 ppm) are taken into consideration. More data on these rocks are clearly required before even generalization can be made with assurance.

In certain granitic terrains where multiple intrusive phases appear, there are often marked manifestations of a gaseous phase generated by the late intrusive phases. The gases evolved invade both the granite and the country rock forming greisens, greisenized granites and kaolinized granites. The mineralogy and fluorine content of these deposits indicates that fluorine gases formed the largest component of the gaseous phases with boron and sulphur being of subsidiary importance. The principal gases which may have been present in the systems are HF, H_2SiF_6, SiF_4, BF_3 and SnF_6 or Na_2SnF_8. It is postulated by some economic geologists that the transport of tin into greisen deposits is accomplished by the highly volatile Sn-F compounds.

The principal fluorine-bearing minerals in greisens are fluorite topaz, tourmaline, lepidolite and muscovite (sericite); in kaolinized granites, fluorine generally substitutes in the kaolinite structure but in some places fluorite may accompany the kaolinite. The range of fluorine in greisens and greisenized granites is in the order of 1,600-20,400 ppm while in kaolinized granites the content is much less (1,100-7,400 ppm). Fluorine and lithium are the only common indicator elements for both these deposits.

During the deposition of hydrothermal deposits fluorine may be concentrated in the alteration zones of many types of vein, pipe and stratiform bodies. The types of wallrock alterations in which fluorine is most often found in these deposits are greisenization, topazization, tourmalization, sericitization, kaolinization, chloritization and argillitization. The principal fluoriferous minerals in these alteration zones are fluorite, topaz, tourmaline, zinnwaldite, lepidolite, sericite, chlorite, clay minerals and occasionally apatite.

1.2.6 Fluoriferous Deposits

High concentrations of fluorine occur in the following types of deposits:

1) Granitic and syenitic bodies: In these bodies fluorine occurs mainly in disseminations and patches of fluorite in the matrix of the rocks. Examples of deposits in granitic terrain are numerous, the fluorite granites of the Nueltin Lake area, N.W.T., Canada and the tin province of S.W. England being worthy of note. Although fluorite is not presently being mined from these occurrences, they do, however, offer a large reserve for the future. Examples of other high fluorine-bearing granitic bodies are the riebeckite and topaz granites; the former generally occur in alkaline igneous provinces and the latter in tin-bearing granitic provinces. Also of note are the villiaumite (NaF) syenites which occur in a number of alkaline igneous massifs (e.g. Lovozero Massif, USSR). Although not as yet exploited, these rocks are particularly appealing as a source of fluorine since NaF is very soluble and can be easily leached from the rock by water.

Fluorine is also enriched in the kaolin deposits developed as a result of the alteration of many types of granitic bodies. In these deposits fluorine occurs as a constituent of the clay minerals (F-OH substitution) or as fluorite.

2) Pegmatites: Fluorine occurs in a wide variety of minerals in these deposits, mainly as fluorite, apatite, cryolite, amblygonite-montebrasite, tourmaline, topaz, lepidolite, biotite, zinnwaldite and RE- fluocarbonates. In alkali pegmatites fluorine occurs predominately in fluorite, cryolite, RE-fluocarbonates and pyrochlore, whereas in acidic pegmatites the full spectrum of minerals mentioned above may occur. Complex pegmatites generally contain greater amounts of fluorine than simple pegmatites, mainly because of their more diverse mineralogy. With the exception of cryolite deposits (e.g. Ivigtut, Greenland and Miask, USSR) fluorine is generally not present in sufficient quantities to make pegmatite deposits economically important sources of fluorine. These deposits are, however, important sources for Li, Cs, Rb, Be, Y, La, REE, U, Th, Nb, Ta, Mo, W, Sn and a wide variety of industrial minerals.

3) Greisens: The main fluorine-bearing minerals in greisen zones and dykes are fluorite, topaz, tourmaline, lepidolite and zinnwaldite. These deposits are mined mainly for tin and in some places for molybdenum, tungsten and beryllium. The greisens are associated with granitic intrusions and may be developed both in the granites and their metamorphic aureoles.

4) Skarn deposits: These deposits are lenses, pods and irregular masses in which fluorine occurs primarily in fluorite, apatite and humites with lesser amounts in scapolite, phlogopite, amphibole, tourmaline, allanite and topaz. These deposits are mined mainly for Cu, Mo, W, Be, Sn and only in a few places for fluorite.

5) Hydrothermal deposits: These deposits comprise one of the main sources of fluorite, and consist of veins, flats, pipes, stockworks, stratiform bodies and fluorite-cemented sandstones. The principal fluorine-bearing mineral in these deposits is fluorite, although many of the high temperature hydrothermal deposits contain topaz, tourmaline and apatite (e.g. gold-quartz veins). These deposits have a widespread distribution

and occur in carbonate rocks, shales, sandstones and many types of acidic igneous rocks. They are less common in alkaline igneous rocks due probably to the high solubility and retention of fluorine in alkali melts which leads to the formation of disseminated deposits within the igneous masses (e.g. villiaumite syenites). Two types of deposits are recognized - those in which fluorite is the principal ore mineral and those in which fluorite is a gangue mineral of major or minor importance. In some metallogenic provinces fluorite is abundant, and in certain Pb-Zn-fluorite-barite provinces the distribution of the mineral is distinctly zonal, (e.g. Derbyshire field, UK, where the eastern part of the field is marked by a fluorite-calcite-lead-zinc mineralization which grades westward through a barite-minor fluorite-calcite-lead-zinc mineralization into a western zone marked mainly by a calcite-lead-zinc mineralization). In some metallogenic provinces marked by Pb-Zn-Cu mineralization in carbonate rocks fluorite is virtually absent (e.g. the base metal deposits of Ireland).

The principal elements associated with fluorite in hydrothermal deposits are Pb, Zn, Cu and Ba in carbonate rocks; Sn, W and Mo in acid igneous rocks; Hg in certain fault zones, and Au in quartz-fluorite veins (e.g. Cripple Creek, Colorado).

The stratiform fluorite deposits and the fluorite-cemented sandstone occurrences appear to have been formed by the replacement of carbonates by fluoriferous solutions. Associated minerals in the stratiform deposits are pyrite, marcasite, sphalerite, galena and barite. In the cemented sandstones only minor amounts of barite, calcite, sphalerite and galena accompany fluorite. Uranium is enriched in the fluorite-cemented sandstone occurrences at Wet Mountain, Colorado.

6) Carbonatites: Together with their fenitized zones carbonatites form circular masses, rings, dykes, sills and elongated complexes. They occur only in stable cratonic areas. Some carbonatites contain as much as 2% fluorine, the element being present mainly in fluorite, apatite, pyrochlore and to a lesser extent cryolite, weberite, bastnaesite and parisite. Niobium, tantalum, rare earths, copper, magnetite, apatite and portland cement have been commercially extracted from these deposits.

7) Kimberlites: The fluorine content of kimberlites varies from 500 to 2,500 ppm. Serpentinites and mica peridotites are the only other ultrabasics which may have fluorine within this range; all other ultrabasic rock types contain less than 200 ppm F. Although not of economic importance in kimberlites, fluorine is nevertheless a good indicator of their presence. Kimberlites are exploited solely for their diamonds, and like carbonatites are found only in stable cratonic areas. The principal fluorine-bearing minerals in kimberlites are phlogopite, serpentine, apatite and perovskite.

8) Phosphorites: These deposits of sedimentary apatite and francolite may contain more fluorine than is theoretically possible for the apatite structure to accommodate. The range for phosphorites is 2.47 to 4.20% fluorine and the maximum for fluorapatite is 3.8%. It is, therefore, probable that some of the fluorine may exist as coprecipitated fluorite. The fluorine in these deposits is extracted as a by-product of the phosphate industry. In the future phosphorites may also be an important source of uranium.

9) Residual deposits: Under certain weathering conditions fluorite and topaz may accumulate in the weathered residium overlying rocks in which these minerals are a major constituent. Most residual fluorite

deposits are derived from the weathering of fluorite-bearing limestones and shales (e.g. certain eluvial deposits in Kentucky and Illinois). They usually consist of weathered fluorite masses and lumps with associated barite, minor galena, iron and manganese oxides and residual clays. The residual topaz deposits are formed by the weathering of greisenized granites (e.g. Nigerian tin-bearing granites). Few of the residual fluorite or topaz deposits are of commercial importance.

1.2.7 The Role of Fluorine in the Formation of Ore Deposits

1.2.7.1 Introduction

Together with elements and compounds such as sulphur, oxygen, carbonate, phosphate and chlorine, fluorine is an important 'mineralizer' during the formation of numerous types of ore deposits. The element is perhaps unique in that it plays a major role in all types of mineralizing processes, ranging from magmatic-pegmatitic through pneumatolytic-hydrothermal to sedimentary processes. It should be noted that the presence of fluorine is not an essential element in these processes excepting perhaps the formation of complex pegmatites and productive carbonatites. On the other hand, numerous mineral occurrences, formed as the result of the above mentioned processes, can be cited where fluorine is the principal agent controlling the dispersion of various ore elements and compounds. It can further be stated that, when fluorine is present in a particular metallogenic province, higher grades of ore often occur.

The scope of this thesis precludes a rigorous approach in describing the role of fluorine in the formation of ore deposits; the author will, therefore, confine his description to those points which are of major consideration to the exploration geochemist, namely elemental associations, controls to mineralization (chiefly chemical)and alteration.

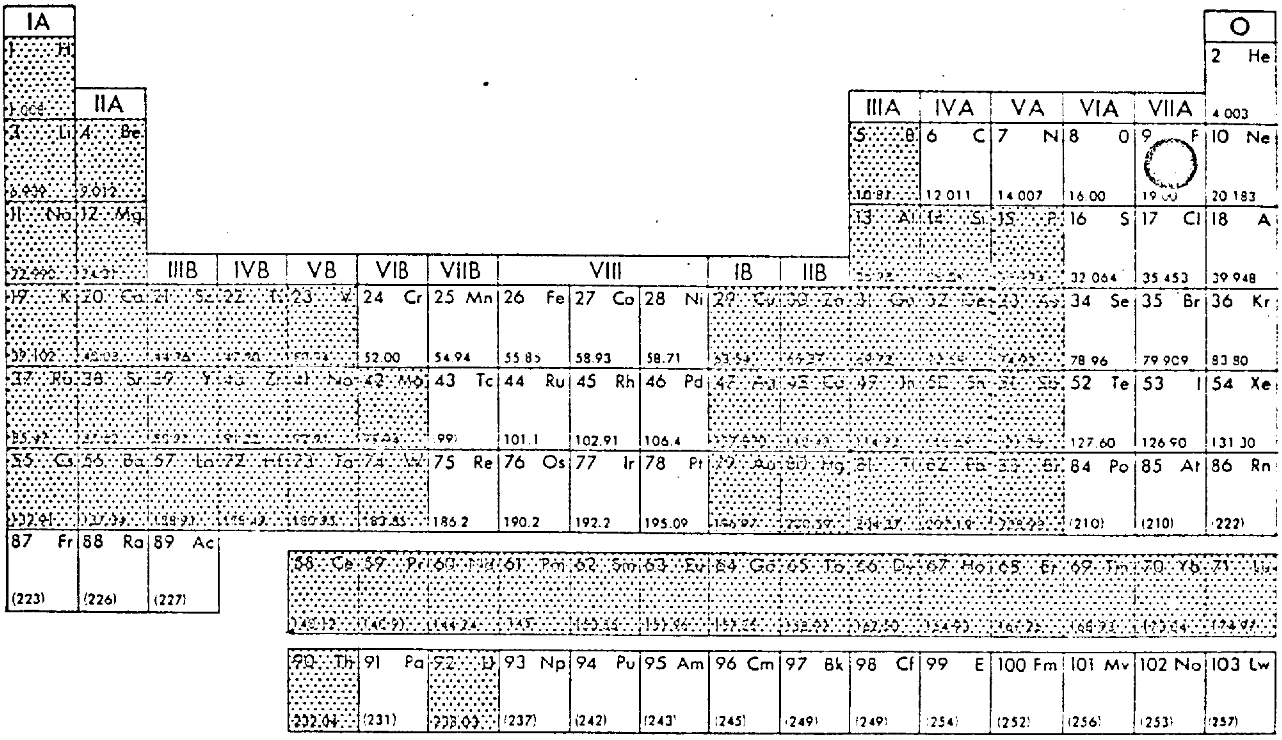


FIGURE 1.3

PRINCIPAL ELEMENTS ASSOCIATED WITH FLUORINE DURING MINERALIZING PROCESSES

TABLE 1.6

PRINCIPAL COMPLEXES OF FLUORINE IN HYDROTHERMAL SOLUTIONS AND MAGMATIC MELTS

COMPLEX*	REMARKS	PRINCIPLE COMPLEXING ELEMENTS
MF_n^{y-n}	Stable in anhydrous melts and acidic solutions; unstable in alkaline solutions	H, Be, Mg, Si, Y, La, REE, Th, Fe, B, Al, Ga, In, Tl, Si, Sn.
$M(O_xF_n)^{y-(x+n)}$	Stable in residual melts and acidic to neutral solutions; unstable in alkaline solutions	Be, Si, Y, La, REE, Ti, V, Zr, Hf, Nb, Ta, Mo, W, U, Ge, Sn, P, As, Sb, Bi.
$M(OH_xF_n)^{y-(x+n)}$	Stable in residual melts and alkaline solutions; unstable in acidic solutions	Be, Si, Y, La, REE, Fe, Al, Sn
$M((CO_3)_xF_n)^{y-(2x+n)}$	Stable in alkaline solutions and alkaline melts	Sc, Y, La, REE, Th, U.

* y = valence of M, and x and n are variable integers

NOTE: these complexes may also be bonded to an alkaline metal (Na, K, Li, Rb, Cs) to form complexes such as $Na_2Sn(OH_xF_n)^{(2+y)-(x+n)}$

1.2.7.2 Elemental Associations and Controls to Mineralization

The principal elements with which fluorine is associated during the formation of ore deposits are presented in Fig. 1.3; and the complex fluoride forms exhibited by these elements are given in Table 1.6 with their relative stabilities. The principal complexing element characterized by the four types of complexes shown are based to some extent upon their own stabilities as single cations, oxides, hydroxides, or carbonates in solutions and melts. Because of the ability of fluorine to isomorphously substitute for both the O^{2-} and OH^- ions, oxy- and hydroxy-fluoride complexes can exist in mineralizing fluids. The relative stabilities of these complexes compared to those of other mineralizers (e.g. Cl, S, SO_4^{2-}, CO_3^{2-}, etc), and the physico-chemical factors which affect their stabilities, are the chief controls to mineralization. Unfortunately, at the temperatures and pressures realized in the hypogene environment, very little is known about the chemistry and stability of complexes. Hence, we must extrapolate a great deal of low temperature - pressure data, taking notice of the obvious elemental associations that occur in nature, both in the primary and secondary environment. Fortunately for the purposes of geochemical exploration, the effect (i.e. the elemental associations) is more important than the cause, although one should never neglect the latter when formulating a total exploration philosophy. I will, therefore, stress the relationship between fluorine and the other elements commenting on their mode of transport when possible.

It is immediately apparent from the compilation of associated elements in Fig. 1.3 that fluorine, because of its high electro-negativity, exhibits no tendency to bond with those elements in its immediate vicinity in the periodic table (i.e. O, S, Se, Te, Cl, Br, I). As will be described later, the metalloid elements, P, As, Sb and Bi will bond with fluorine only as oxy-fluorine (e.g. BiOF-zavaritskite). Also apparent from the tabulation of associated elements is the complete lack of an association between fluorine and the central elements of the transition group (i.e. Cu, Mn, Fe, Co, Ni and the platinoids). Fluorine shows a weak association with Fe and Mn in the low temperature secondary environment (e.g. FeF_n^{y-n} complexing), but this association does not appear to continue to any great extent into the primary high temperature regime (an exception is the formation of triplite $(Mn, Fe)_2(F/PO_4)$). Fluorine may occur in gold deposits in the form of fluorite, as at Cripple Creek, Colorado, or in tourmaline associated with many of the high temperature hydrothermal gold deposits, but it is not clear whether it controls the dispersion and localization of gold in these deposits or whether it merely acts in a passive manner. Other elements not mentioned above, for which the association with fluorine is not clear are V, Mo and Hg. Vanadium occurs in a number of types of deposits in the supergene environment (e.g. uranium and copper sandstone deposits), but fluorine exhibits no particular affiliation with this element in these deposits. In the hypogene environment, however, V may be partly transported as the stable complex $VO_2F_n^{x-n}$, especially during metasomatic processes. The association between Mo and F is likewise tenuous. Fluorine is not enriched in most Mo-Cu porphyry deposits and, therefore, cannot be considered as a transporting agent. However, compounds of Mo-F are much more volatile than those of Cl, and this may account for the strong association between F and Mo in deposits formed under metasomatic and pneumatolytic conditions. In addition, the frequent occurrence of molybdenite in quartz-fluorite veins may be the result of transport of molybdenum as the $MoOF_n^{(x-n)}$ complex with subsequent dissociation to form the sulphide. In view of the higher volatility of Hg and Hg-chlorides, as opposed to Hg-fluorides, it is doubtful whether fluorine plays a dominant role in transporting Hg, although it is strongly associated (in the form of fluorite).with epithermal deposits containing this metal.

TABLE 1.7

CHARACTERISTICS AND ELEMENTAL RELATIONSHIPS OF FLUORINE IN ORE GENESIS

CHARACTERISTIC	ASSOCIATED ELEMENTS	TYPES OF MINERALIZING PROCESSES
Elements forming complexes with fluorine in primary and residual melts	Be, Sc, Y, La, REE, Th, U, Ti, Zr, Hf, Nb, Ta, B, Al, Ga, In, Tl, Si, Ge, Sn	Magmatic; pegmatitic
Elements forming complexes with fluorine in aqueous solutions	H, Be, Mg, Sc, Y, La, REE, Ti, Zr, Nb, Ta, W, Th, U, Fe, B, Al, In, Si, P, As, Sb Bi	Hydrothermal; sedimentary
Elements forming sparingly soluble compounds with fluorine in aqueous solutions and melts.	Ca, Mg	All types
Elements whose solubilities in aqueous solutions and melts are enhanced by the presence of fluorine	Li, Na, K, Rb, Cs, Sr, Ba, Cu, Pb, Zn, Ag, Cd	Pegmatitic; hydrothermal
Elements which form volatile compounds with fluorine	H, Mo, W, B, Si, Ge, Sn, Tl	Pneumatolytic; metasomatic; fumarolic

The remaining elements indicated in Fig. 1.3 and not mentioned above can be divided into five groups according to their physico-chemical relationship with fluorine. These groups and their common characteristics are presented in Table 1.7.

Those elements forming complexes with fluorine in primary and residual melts (Be, Sc, Y, La, REE, Th, U, Ti, Zr, Hf, Nb, Ta, B, Al, Ga, In, Tl, Si, Ge, Sn) are concentrated in magmatic (albitic granites, carbonatites, kimberlites) and pegmatic (mainly complex) deposits. With the exception of Si, Al, and perhaps Ti, the ore geneticist would be hard pressed to find anomalous concentrations of these elements occurring in the above mentioned deposits in the absence of high concentrations of fluorine. All of these elements form stable fluoride, oxy-fluoride, hydroxy-fluoride or fluorcarbonate complexes. With respect to Si, fluorine plays a dual role in that it acts as a depolymerizer in preventing the linkage of silica tetrahedra and, therefore, promoting the enrichment of the above mentioned elements in a residual melt. A number of workers have proposed the complexation and transport of the following elements as fluorides in magmatic and residual melts: Be-(Beus, 1957; Beus, 1962; Beus et al 1963 and Kosals, 1968); B- (Kosals, 1968); Sc-Y-La-REE- (Shcherbina, 1959; Kosterin, 1959; Bandurkin, 1961, and Mineyev, 1963); Ge-(Ganeyev, 1962 and Shcherba et al, 1966); Sn-(Barsukov, 1957 and others); Al- (as cryolite and many other alumino - fluorides mentioned by a large number of workers); Tl-(Voskenskaya, 1959); Th-U-Ti-Zr-Nb-Ta - (Beus, 1958 and Shcherbina, 1963).

Of the elements known to form complexes with fluorine in aqueous solutions, H, Be, Mg, Sc, Y, La, REE, Ti, Zr, Nb, Ta, W, Th, U, B, Al, In, Si, Ge, and Sn are probably the most important. Complexing of Fe appears to be confined to groundwaters and some acidic low temperature thermal waters. As mentioned previously, the metalloids (P, As, Sb, Bi) may combine with F in hydrothermal systems to form oxy-fluoride complexes with subsequent formation of apatite-fluorite, realgar-orpiment-fluorite, stibnite-fluorite, and bismuthinite-fluorite deposits. The relationship between fluorine and As, Sb, and Bi does not appear to extend beyond the formation of deposits where these elements are the principal ore-forming constituents. In many sulphide deposits, these metals show no association with fluorine whatsoever.

The order of first stepwise stability constants of cation-fluoride complexes for which data are available is given in Table 1.8. High stabilities of many of the elements mentioned above are evident, and although this data corresponds to low temperatures, it is reasonable to assume that this order is preserved (to a large degree) at higher temperatures. Thus, the elements above H^+ in this series, together with those elements known to form strong complexes with fluoride and for which no data are available, (Nb, Ta, Si, B, Ge, Tl, Mo and W), can be expected to travel in solution as fluoride complexes. All of these elements may be transported as fluoride complexes during hydrothermal, pneumatolytic, and metasomatic processes, and some will actually form fluoride minerals, Mg - (humites); Y - (yttrofluorite); La and REE - (rare earth fluorocarbonates and rare earth fluorides); Nb and Ta - (pyrochlore), and B - (tourmaline). Fluoride complexes undoubtedly play a marked role in transporting elements such as Be, W, U, B, Al, Si, Ge and Sn during hypothermal and pegmatitic processes. Hydrogen forms strong complexes with fluorine (HF, HF_2^-) in highly acidic solutions (less than pH 3.0) (See Fig. 1.4). The other elements form more stable complexes with fluorine when hydrolysis is minimized, but relatively stable hydroxy-fluoride complexes may also be present. The influence of fluorine on In occurs only in hydrothermal systems where the element is often concentrated in Pb-Zn-Fluorite-barite deposits. The elements Sc, Y, La, REE, Th, and U are often enriched in the fluorite of hydrothermal deposits. In the low-temperature sedimentary environment, there is strong evidence to suggest that fluorine forms fluoride and fluor-carbonate complexes with Y, La, REE, Th, and U, thus permitting their incorporation in apatite and francolite and eventual formation of phosphorite and phosphatic shale deposits in which these elements are enriched.

A number of elements form volatile compounds with fluorine (H, Mo, W, B, Si, Ge, Sn, Tl). Transport of these elements as volatile fluorides is characterized by their concentration in pneumatolytic-hydrothermal greisen and skarn deposits and in the case of H, B, and Si in fumarole gases. The relative importance of volatile transport in the formation of ore deposits is still a contentious matter. Many investigators have considered volatile migration to be a significant, if not predominant, mechanism of ore transport; examples are Sn-F (Daubree in Barsukov, 1957), Tl-F (Voskresenskaya, 1959), and H-, B-, Si-fluorides (known to be quite volatile). On the other hand a number of other authors, following thermodynamic considerations (Krauskopf, 1969), consider volatile transport of elements such as Mo, W, U, Th, Nb, Ta, Be, Al, Sc, Ti, Zr, Hg, As, and Sb improbable.

The final characteristic to be considered, as regards elemental associations and controls to mineralization, is the solubility of fluoride compounds in aqueous solutions and melts. This group can be divided into those elements forming sparingly soluble compounds with fluorine (Ca, Mg) and those elements which have their solubility enhanced by the presence of fluorine in aqueous solutions and melts. The latter group can be further divided into a pegmatitic suite, related to enhancement in residual melts (Li, Na, K, Rb, Cs) and a hydrothermal suite, related to enhancement in aqueous solutions (Sn, Ba, Cu, Pb, Zn, Ag, Cd). Considering the latter group first, all of these elements show little or no complexation with fluorine (See Table 1.7), and their solubilities as fluorides are extremely high. For the pegmatitic suite of elements, fluorine aids their enrichment in residual melts by depolymerizing the silica tetrahedra and thus preventing the formation of alkali-silicate minerals. In addition, these elements may combine with the fluorine complexes shown in Table 1.6 (e.g. $Na_2M(OH_xF_n)^{(2+y)-(x+n)}$ where y = the valence of M, and M may be Be, Sn, W, Nb, Ta, etc.), and therefore aid in the transport of metals commonly found in pegmatites, greisens and skarns. For the hydrothermal suite of elements (Sr, Ga, Cu, Pb, Zn, Ag, Cd) it is more than probable that the presence of large amounts of fluorine in hydrothermal solutions containing these elements will retard their complexation by other anions and increase the solubilities of the sulphides, sulphates, and carbonates of these metals. Any rapid loss of fluorine from the system, such as the formation of fluorite will result in lack of stability for these metals followed by deposition of their ore minerals. This brings us to the important group of elements typified by insolubility as fluorides, namely calcium and magnesium. Magnesium is of minor importance in this group, forming sellaite (MgF_2) only rarely. Calcium, on the other hand, is of primary importance, combining with fluorine to form the common mineral fluorite (CaF_2), which can be formed in a number of ways as follows:-

a) due to its insolubility in melts which results in the formation of disseminated fluorite deposits in igneous bodies.

b) as the result of metasomatic replacement of carbonate rocks by fluoride-rich solutions (skarns)

c) by hydrothermal replacement of stratiform carbonate rocks (stratiform deposits).

TABLE 1.8

ORDER OF FIRST STEPWISE STABILITY CONSTANTS OF CATION-FLUORIDE COMPLEXES IN AQUEOUS SOLUTION AT 25°C

CATION	STABILITY CONSTANT
$(Zr,Hf)^{4+}$	8.5
U^{4+}	7.2
$(TiO_2)^{2+}$	6.7
Al^{3+}, Sc^{3+}, Sn^{2+}	6.2
Th^{4+}	6.0
Pa^{5+}	5.4
Fe^{3+}	5.2
Ga^{3+}	5.0
Be^{2+}	4.9
$(UO_2)^{2+}$	4.5
In^{3+}	3.8
$(VO_2)^{2+}$	3.7
Y^{3+}	3.6
La^{3+}-Lu^{3+}	3.6-2.7
H^+	3.2
Pb^{2+}	1.7
Mg^{2+}	1.4
Hg^{2+}, Ag^+	1.0
Mn^{2+}, Zn^{2+}, Cu^{2+}	0.8
Ca, Cd, Sr, Ba Li, Na, K, Rb, Cs	0.5

*Data not available for Nb, Ta, Si, B, Ge, Tl, Mo and W

d) by leaching of calcium from wall rocks and subsequent formation of vein deposits in all types of rocks, but especially limestones and dolomites.

e) by precipitation in the supergene environment (residual deposits).

The availability of fluorine and calcium will determine whether or not fluorite is of major or minor importance in these deposits.

As a result of a variety of processes and associations, fluorine is an important constituent of almost all types of ore deposits. The only deposits which would seem to be precluded from this statement are the volcanogenic massive sulphide deposits, although recent work has shown that even some of these have considerable concentrations of fluorine in their wall rocks and stockworks (Cagatay, N. M., 1975 personal communication.).

1. 2. 7. 3 Alteration and Primary Halos

In mineral exploration, two of the most important features of mineral deposits which directly influence their detection are alteration and primary endogenic halos. The delineation, both visual and chemical, of alteration patterns associated with ore deposits has led to the discovery of many mineral occurrences, and the concept of primary halos, which both incorporate and extend beyond alteration patterns, is important in the discovery of blind ore deposits. The characteristics of fluorine halos and their detection are discussed at length in the introduction to Chapter III (Lithogeochemical Applications) as well as in the introduction to prospecting for the various types of deposits (also in Chapter III). The present section deals primarily

TABLE 1.9

TYPES OF ALTERATION CONTAINING ANOMALOUS AMOUNTS OF FLUORINE

TYPES OF ALTERATION	TYPES OF ASSOCIATED MINERAL DEPOSITS	PRINCIPAL FLUORINE BEARING MINERALS
Fenitization	Carbonatites (Nb-Ta, REE, Cu)	Fluorite, apatite sodic - amphiboles, humites, phlogopite
Carbonatization	Hydrothermal deposits in limestones (dolomitization) and basic rocks(ankeritization)	Fluorite
Skarnification	Skarns (W, Be, Mo, Sn, REE, Cu, fluorite)	Fluorite, tourmaline, micas, topaz, vesuvianite humites, amphiboles, scapolite
Greisenization	Sn, W, Be deposits in granites and associated host rocks.	Topaz, tourmaline fluorite, lepidolite, muscovite.
Tourmalinization	Hypothermal and pegmatitic deposits	Tourmaline
Topazization	Hypothermal and pegmatitic deposits	Topaz
Sericitization	Mesothermal-hypothermal and pegmatitic deposits	Sericite
Kaolinization	Kaolinized granites; some hydrothermal deposits; kaolinized stockworks and wallrocks of volcanogenic sulphide deposits.	Kaolinite, fluorite
Chloritization	Hydrothermal deposits	Chlorite
Argillitization	Hydrothermal deposits	Kaolinite, montmorillonite, dickite, illite, halloysite
Serpentinization	Ni, Cu, Co, Cr deposits in ultrabasic bodies; kimberlites; asbestos and talc deposits.	Serpentine

with a description of the types of alteration marked by the precence of above normal quantities of fluorine. The importance of these types of alteration in mineral exploration is stressed throughout the discussion.

The types of alteration marked by anomalous amounts of fluorine are summarized in Table 1.9. Before describing these types of alteration one point should be clarified. Many geologists, when describing alteration, have used the term fluoritization, when such minerals as fluorite, topaz, tourmaline and the mica minerals are the principal carriers of fluorine. This is an inappropriate term in some respects since, regarded in a more overall sense, fluoritization is merely a component of a much larger process involving various types of pervasive alteration such as greisenization, carbonatization, fenitization, and skarnification. Only rarely are fluorine-bearing minerals the only alteration products of mineralization. As a chemical term, however, fluoritization has some application but for those prospecting for mineral deposits, the more classical terms (e.g. fenitization, etc.) are more appropriate.

The term fenitization is synonymous with the emplacement of carbonatites and alkali syenites, although in more precise terms, it is a specialized case of carbonatization of alkali-metasomatism. Its distinct relationship to carbonatites warrants a separate description of which a more detailed version can be found in the introduction to prospecting for carbonatites (Chapter III). It is sufficient to state at this point that the principal fluorine-bearing minerals in fenitized zones are fluorite, apatite, sodic-amphiboles, humites, and occasionally phlogopite; and the extent to which fenetization may occur around a carbonatite complex depends largely on the composition and structure of the host rock and the size, composition, temperature, and emplacement characteristics of the alkali intrusive mass. Large amounts of fluorine, together with CO_2, H_2O, Ca, Na, K, and P may diffuse from the intrusive alkali centers to form relatively concentric fenitized zones, but more often this form of alteration is of a discontinuous nature, following the structures and more chemically reactive members of the host rocks. The importance of fenitization in mineral exploration lies mainly in the fact that its presence effectively increases the exploration target size for regional and reconnaissance surveys. In addition, blind alkali-rich bodies may only be characterized at surface by an overlying fenitized dome, and lithogeochemical identification of fenetization using fluorine and its associated elements would be the most viable method for finding these deposits.

Numerous hydrothermal deposits, especially those occurring in limestones and basic rock bodies are characterized by the presence of altered host rocks formed as the result of carbonatization (dolomitization in limestones and ankeritization in basic rocks). Fluorite is frequently one of the principal alteration minerals associated with these forms of alkali-metasomatism, and the types of mineral occurrences most often recognized are vein and stratiform Pb-Zn-Cu deposits. Dolomitization, unrelated to economic mineralization processes, occurs over large volumes of carbonate rocks, but this process is not normally associated with the development of large amounts of fluoriferous minerals. Fluorine, together with Ba, Pb, Zn, and Cu can, therefore, often be used to discriminate between productive carbonatized zones and those marked by barren dolomitization.

During the formation of skarn-type mineral deposits, a considerable amount of country rock may be altered by the processes of skarnification. Two types of skarn deposits have been recognized: one is the result of regional skarnification processes in metamorphic terrains; these often contain relatively high concentrations of fluorine but are not generally ore-bearing. The other is formed at or near the contacts of igneous intrusive bodies with country rocks and are generally called contact metasomatic skarns. The latter type of deposit is commonly ore-bearing and highly fluoriferous, the principal fluorine-bearing minerals being fluorite, tourmaline, mica, topaz, vesuvianite, humites, amphiboles, and scapolite. Compared to the size of the skarn ore body, the zone marked by skarnification is generally larger by orders of magnitude. Unlike many of the ore forming elements associated with skarn deposits, (Be, Sn, As, Cu, Mo, REE, Zn, Ti), fluorine generally migrates in relatively high concentrations during ore formation to the farthest extremities of the skarnified zone and may in places form economic fluorite deposits some distance from the main focus of skarnification. Effectively, this means that fluorine anomalously represents the entire skarnified zone, and the element is, therefore, an ideal pathfinder of most skarn-type deposits.

During the formation of hypothermal, pneumatolytic, and pegmatitic deposits, considerable amounts of fluorine may be introduced into the host wallrocks as the result of greisenization, tourmalinization, topazization, sericitization, or kaolinization processes. All of these alteration types are highly fluoriferous, with the principal fluorine-bearing minerals being topaz, fluorite, tourmaline, lepidolite, zinnwaldite, muscovite, and kaolinite. Greisenization, which encompasses the processes of tourmalinization, topazization, and sericitization, is most often associated with the formation of Sn-W-Be deposits in or near granitic bodies. Alteration consists of narrow zones dominated by tourmaline, topaz, sericite, or fluorite, the entire greisenized zone generally being no more than a few metres wide. In places a stockwork type of greisenization may occur at the Sn-bearing epicentres of granitic intrusions. Considering the relative immobility of Sn, W and Be in both the primary and secondary environment, fluorine is an important pathfinder for these deposits.

Tourmalinization, topazization, and sericitization may occur as separate processes related to the formation of pegmatites, high temperature hydrothermal deposits (gold-quartz-tourmaline-topaz deposits), and on a more regional scale, tourmalinized granites and topaz-granites. These last mentioned disseminated deposits are generally unrelated to economic mineralization and due account must be taken of these bodies during the interpretation stage of geochemical surveys when using fluorine as a pathfinder element in granitic terrains.

Kaolinization is a particularly common type of alteration accompanying hydrothermal activity. It is marked by the introduction of much water, together with such mineralizers as F, CO_2, S, and As. Fluorine is most strongly associated with this type of alteration during the kaolinization of granites. The kaolin deposits formed are highly fluoriferous and often contain disseminated fluorite. Anomalous concentrations of fluorine may also occur in the kaolinized wallrocks of hydrothermal vein and stockwork deposits. In acidic volcanic terrains, fluorine is often associated with the kaolinized stockwork portions of volcanogenic sulphide deposits in rhyo-dacitic host rocks. In andesitic and other intermediate rocks, where propylitization often gives rise to extensive kaolinization, fluorine does not appear to be a significant mineralizer and is, therefore, not a good indicator of sulphide deposits in this type of environment.

Fluorine is occasionally enriched in zones of chloritic and argillic alteration in the wallrocks of epigenetic deposits, the principal fluorine-bearing minerals being chlorite, kaolinite, montmorillonite, dickite, illite, and halloysite. Fluorine often occurs in very low concentrations in some of these alteration zones, and the presence of the element is, therefore, dependent on metallogenic vagaries and hence is not always an effective indicator of deposits marked by zones of chloritic and argillic alteration.

In ultrabasic complexes, serpentinization is commonly accompanied by the introduction of fluorine. This is most marked in serpentinized Ni, Cu, Co, and Cr deposits, kimberlites, and asbestos deposits, but taken over the entire spectrum of ultrabasic rocks, there is a significant increase in the fluorine content as serpentinization increases (See Table 3.5 Chapter III). Fluorine is, therefore, a useful indicator of the presence of serpentinized ultrabasic bodies. It should be noted, however, that many serpentinites are not of economic value, from which it follows that although fluorine may be used to outline these bodies supplementary pathfinders must be used to assess their ore potential

1.3 HYDROGEOCHEMISTRY

Fluorine occurs in detectable amounts in all natural waters (i.e. groundwaters, mineral and thermal waters, sea water, atmospheric precipitation, etc.). Unlike many other elements fluorine is highly mobile over the entire range of oxidation-reduction and acid-alkaline conditions occurring in the natural aqueous environment. Its concentration and mode of occurrence in natural waters depends on such factors as temperature, pH, total ionic strength, presence or absence of complexing or precipitating ions or colloids, solubility of fluorine-bearing minerals, the size and type of geological formations traversed by the water and the amount of time in which the water is in contact with a particular formation. For groundwaters and mineral and thermal waters, all of these factors are operative, but for surface waters and atmospheric precipitation a more restricted set of factors govern the concentration of fluorine.

The discovery that specific levels of fluorine (0.8-1.7 ppm) must be maintained in potable water supplies to prevent dental caries or dental

TABLE 1.10

FLUORINE CONTENT OF WATERS FROM IDENTIFIED ROCK TYPES

TYPE OF ROCK*	NO. OF SAMPLES	F CONTENT (ppm)		REFERENCE
		RANGE	AVERAGE	
Granitic (810)	78	n.d. - 9.0	1.4	1
	14	n.d. - 3.4	0.9	2
	14	0.06- 0.2	0.1	5
	31	0.03-0.25	0.11	4
Alkalic (1,800)	7	0.70-35.1	8.7	1
Basaltic (750)	44	n.d. - 0.5	0.1	1
	11	n.d. - 0.4	0.2	2
Ultrabasic(130)	11	0.02- 0.04	0.07	5
Andesitic (250)	4	n.d. - 0.1	0.1	2
Sandstones and quartzites (180)	69	n.d. - 2.7	0.1	1
	16	n.d. - 1.9	0.4	2
Shales and clays (790)	80	n.d. - 1.8	0.2	1
	16	n.d. - 2.8	0.6	2
	15	0.07- 0.2	0.1	5
Limestones (220	14	n.d. - 0.9	0.3	2
	116	n.d. - 1.8	0.3	3
	123	n.d. - 1.8	0.12	4
Dolomites (260)	21	n.d. - 0.3	0.02	1
	5	n.d. - 1.7	0.5	2
Marbles (--)	27	0.03- 0.2	0.1	4

NOTES:

n.d. - Not detected

* - Numbers in brackets refer to mean fluorine contents of the rock types as shown in Tables 1.2, 1.3, and 1.4

1. Bond, 1945; 2. White _et al_, 1959 _in_ Fleischer and Robinson, 1963;

3. Edmunds, 1971; 4. Lalonde, 1974; 5. Author's Data.

fluorosis has led to the publication of volumes of data on the fluorine content of groundwaters. Unfortunately, much of this data is of little value to the geochemist, since no indication of related rock types is generally given and valuable supplementary analyses are often lacking. Fleischer and Robinson (1963) have, however, presented a distribution map of the maximum fluorine content of ground-waters in each of the counties of the United States from such data. Their results indicate the presence of high detrimental fluorine concentrations in the groundwaters of much of the mid-western and south-western United States. Most of these high fluorine waters are related to saline conditions. On the other hand many counties have abnormally low levels of fluorine in their groundwaters (less than 0.4 ppm), and the potable waters in these areas have now been fluoridated to prevent dental caries.

The available data on the fluorine content of groundwaters associated with various rock types are given in Table 1.10. The overall range of fluorine contents for these waters varies from a trace to 35.1 ppm, and the range of average fluorine contents is 0.02 to 8.7 ppm. Of the igneous rocks, waters draining alkalic bodies contain the largest amounts of fluorine followed in order by those draining granitic, basaltic, andesitic, and ultrabasic rocks. The abundance of fluorine in these rocks types also follows this order. The large variations in the average fluorine content of groundwaters from granitic areas can be explained by the occasional alkalinity of these rocks and by the diversity of forms in which fluorine may occur (e.g. fluorite, apatite, micas, hornblende, etc.). For sedimentary rocks the variation in the average fluorine content of groundwaters from the various rock types is too great to make definite statements. In general, however, one would expect groundwaters traversing sandstones and quartzites to be quite low in fluorine, provided fluorite is not a major component of the cementing matrix. Shales and clays, because of their micaceous and phosphatic content, generally have associated groundwaters with higher fluorine concentrations.

Groundwaters draining limestones and dolomites have fluorine concentrations similar to those draining shale and clays despite the fact that limestones and dolomites have a much lower fluorine content. The reason for this lies in the greater solubility of carbonate rocks in contact with groundwater of low ionic strength and the subsequent release of fluorine through dissolution of fluorite. In shales and clays, fluorine is held in minerals (micas, apatite, etc.) which are more resistant to groundwater attack.

The most important fluoriferous minerals which have a direct bearing on the aqueous chemistry of fluorine are fluorite, apatite, the micas, amphibole, and villiaumite. By far the most important member of this group is fluorite. Apatite, the micas, and amphibole have extremely low solubilities and fluorine is leached from these minerals only under acidic conditions. Phosphate concentrations of more than 6 ppm in groundwaters decrease the concentration of fluoride due to the formation and precipitation of fluorapatite. This level of phosphate is attained only in groundwaters draining phosphatic deposits; the majority of groundwaters have phosphate concentrations less than 1 ppm (White et al, 1963). Apatite may, however, have a controlling effect on the concentration of fluorine in groundwaters through its formation and precipitation. The amount of fluorine released by the dissolution of fluorite in water of low ionic strength and neutral pH is of the order of 8 to 10 ppm. However, there are a number of other factors which may increase or decrease the solubility of this mineral in the natural environment, and these have, therefore, a direct bearing on the concentrations and mobility of fluorine in groundwaters. The most important of these factors are the Ca and Na concentration, the pH, and the concentrations of complexing ions, such as Al, Fe, etc.

An excess of Ca in groundwaters over that represented by the solubility of fluorite will suppress the dissolution of this mineral (common ion effect). Voroshilov (1966) has shown a distinct negative correlation between fluorine and Ca for groundwaters draining sedimentary strata in the Moscow region, and an examination of data obtained by Edmunds (1971) on the groundwaters draining the Derbyshire limestone region of England indicates that Ca is an important controlling factor in the concentration of fluorine in carbonate waters. Moreover, Voroshilov's work indicates that calcium in excess of that contributed by fluorite seriously affects the concentration of fluorine at levels of 0.5 to 3.0 ppm, well below the levels of fluorine (8-10 ppm) produced by the dissolution of fluorite in water of low ionic strength. It is not surprising, therefore, that the majority of groundwaters are greatly undersaturated with respect of CaF_2. For 'hard' groundwaters (low Na) the fluorine content is generally in the range 0.02 to 3.0 ppm.

Sodium enhances the concentration of fluorine in many types of groundwaters, especially those lacking a significant concentration of Ca. Over the temperature range 20° to 100°C, the solubility of fluorite is increased by a factor of 2 in the presence of 4,600 ppm Na and by a factor of 3 in the presence of 46,000 ppm Na (Struebel, 1965). With the exception of waters associated with alkali rocks (syenites, alkali granites, carbonatites, etc.) groundwaters possess Na concentrations of the order of 1 to 800 ppm. Consequently, with the above information in mind, we can assume that an enhancement factor of 0.1 to 1.5 is representative of most groundwaters. For waters draining alkalic rocks an increase in solubility by a factor of 2 or 3 is not unreasonable. Krainov et al (1969) have noted unusually high concentrations of fluorine (up to 15,000 ppm) in the subsurface waters of the Lovozero alkali massif (Kola Peninsula, USSR). The principal

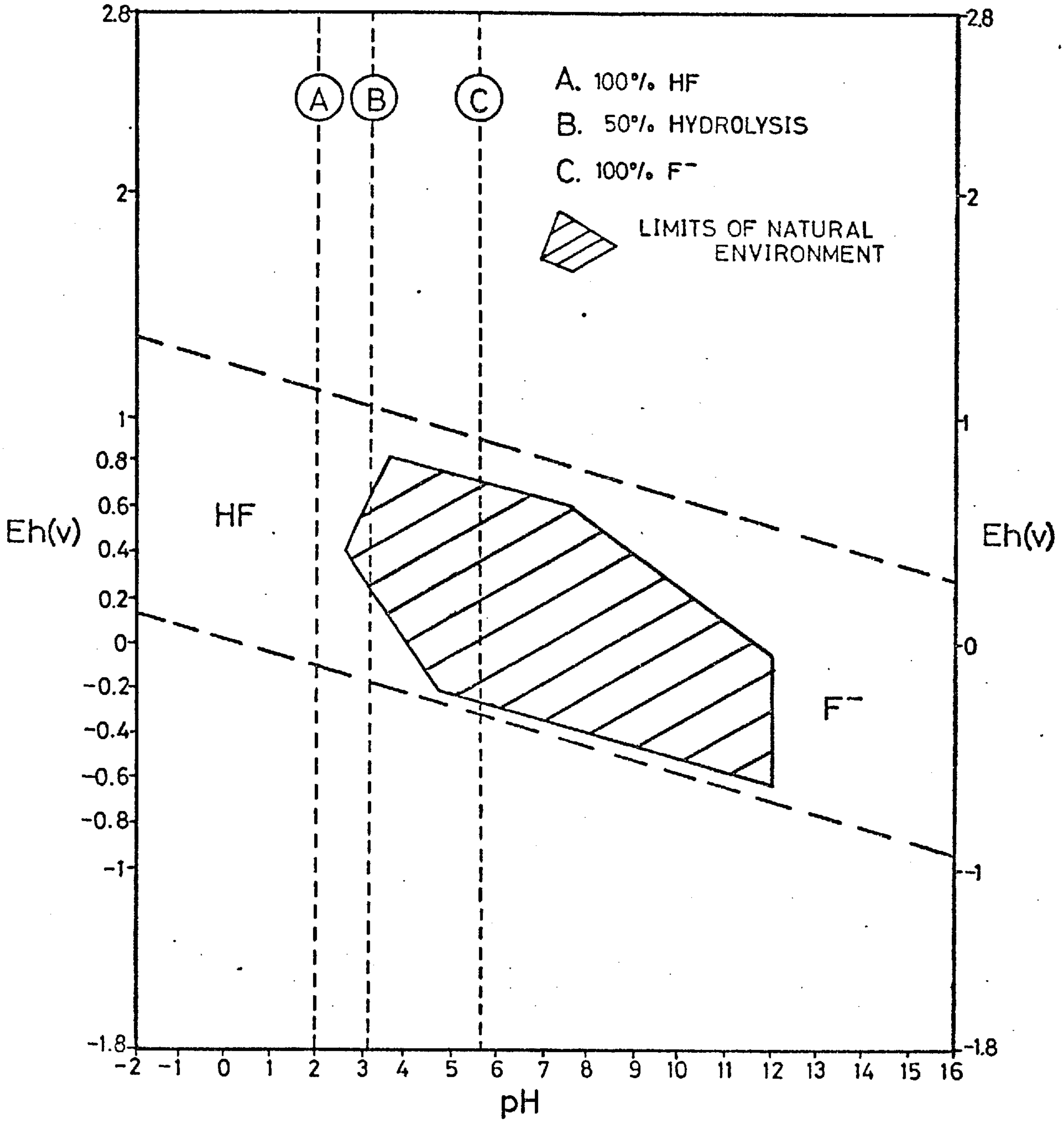


FIGURE 1.4

Eh-pH EQUILIBRIUM DIAGRAM FOR THE SYSTEM FLUORINE-WATER AT 25°C(for a total dissolved fluorine concentration less than 2000 ppm) fluorine-bearing mineral in this area is villiaumite (NaF) contained mainly in alkali syenites. This is an extremely soluble mineral (42 g/1), and taken together with the absence of Ca in these waters the result is very high concentrations of fluorine in the groundwaters. These same authors have found an excellent correlation between Na and F over the concentration ranges 0.1 to 10,000 ppm fluorine and 1.0 to 10,000 ppm Na for waters in this area. Although no investigations have been undertaken as yet, it is probable that K has the same effect on the solubility of fluorine (fluorides) as Na, since KF is also highly soluble (923 g/1). In short, calcium suppresses the fluorine concentration, while Na and K increase both the concentration and mobility of fluorine in groundwater systems.

Under certain conditions, fluorine forms complexes with cations in solution, notably H, Fe, Al, B, and Si. The relationship between F and H, for solutions containing less than 2,000 ppm fluorine, is shown in Fig. 1.4. At a pH of approximately 5.5 the hydrolysis of F^- begins and near the lower pH limit of the natural environment (3.0) approximately 50% of the free F^- is hydrolysed. At pH 2.0 fluorine occurs as HF only. For solutions containing more than 2,000 ppm F^-, an HF_2^- field begins to form at pH 3.0. Knowing the pH, it is, therefore, a relatively simple matter to predict how much of the total fluorine in acid waters is hydrolysed. The presence of complexing cations, such as Fe, Al, B etc. will disrupt this simple equilibrium since these cations compete with H to form stepwise complexes of the type $MF_n^{(x-n)}$ (x = valence of cation). Aluminium is probably the most important complexing element of this group and may combine to form supergene minerals such as gearksutite $Ca\ Al(F,OH)_5.H_2O$ creedite $Ca_3\ (Al(F,OH,H_2O)_6)_2/SO_4)$, prosapite $Ca\ Al(F,OH)_4\ {}_2$, and cryolite, Na_3AlF_6, or may occur in solution according to the following equilibrium:-

$$Al^{3+} + F^- \rightleftarrows AlF^{2+} + F^- \rightleftarrows AlF_2^+ + F^- \rightleftarrows AlF_3 + F^- \rightleftarrows AlF_4^- + F^- \rightleftarrows AlF_5^{2-} + F^- \rightleftarrows AlF_6^{3-}$$

The relative abundance of these complexes in any system will depend on the concentration of free F^- (Hem, 1968). For groundwaters leaching pneumatolytic-hydrothermal deposits in the USSR, Krainov et al, (1967) have demonstrated that a good correlation exists between the total fluorine content (free + complexed) and the aluminium content (Table 1.11). A similar type of equilibrium to that shown above for Al may also exist between Fe and fluorine. When present in sufficient amounts, B will also form complexes such as BF_4^-, $BF_3(OH)^-$ and BF_2OH (Krainov et al, 1967). For highly alkaline groundwaters such as those of the Lovozero Alkaline Massif, USSR (pH 12), Ti and Nb may be present as complexes of the type $M(F,OH)_n^{(x-n)}$, and the rare earth elements may be present as fluorcarbonate complexes (Krainov et al, 1969).

TABLE 1.11

CORRELATION BETWEEN THE TOTAL FLUORINE CONTENT (FREE + COMPLEXED) AND THE ALUMINIUM CONTENT OF GROUNDWATERS LEACHING PNEUMATALYTIC-HYDROTHERMAL MINERAL DEPOSITS IN THE USSR (after Krainov et al, 1967)

Number of Analyses	Mean Total Fluorine Content (ppm)	Mean Aluminium Content (ppm)
8	0.72	0.15
26	0.67	0.30
16	0.91	1.50
15	1.00	3.00
43	1.32	3.50

Savchenko and Tananaiev (1951) have shown experimentally that negative complexes of the type $MF_{n\ x}^{(x-n)}$ (x = valence of cation) are easily decomposed by calcium, and that their stability can be guaranteed only if large amounts of Na are present or if the concentration of Ca is well below the solubility limit for fluorite. Positive complexes of the type $MF_{n\ x}^{(x-n)}$ (x = valence of cation) are much more stable in the presence of Ca. In terms of pH, the stabilities of metal-fluoride complexes are probably relatively restricted; when the pH is much above 5.0 significant hydrolysis of the metal occurs, and when the pH is extremely low (less than 3.0), HF complexation is dominant. The optimum pH range for the formation of metal-fluoride complexes of the type $MF_n^{(x-n)}$ is probably 3.0 to 5.0. Because of its unique ability to substitute for the OH^- ion in chemical reactions, however, fluorine may combine with hydrated cations to form complexes of the type $M(OH_xF_n)^{y-(x+n)}$, where y = valence of M, and x and n are variable integers, and where M may be elements such as Be, Si, Y, Re, Ti, Zn, Nb, Ta, Fe, B, and Al. Those cations which form positively charged oxide complexes in solution, such as U and Ti may combine with fluorine to form complexes of the type $M\ O_xF_n^{\ y-(x+n)}$.

The presence in the groundwater regime of the above mentioned complexes depends largely upon the cation and fluoride ion concentrations (Hem, 1968; Mesmer and Baes, 1969). With the exception of Al, Fe, and B, many of the cations mentioned are generally present in low enough concentrations to preclude significant fluoride complexation.

At normal atmospheric pressures an increase in water temperature from 23°C to 100°C results in a two fold increase in the solubility of fluorite (8-10 ppm F to 16-20 ppm F). For thermal waters one would expect, therefore, only moderately higher fluorine concentrations than for groundwaters. This statement is founded not only on the basis of a small increase

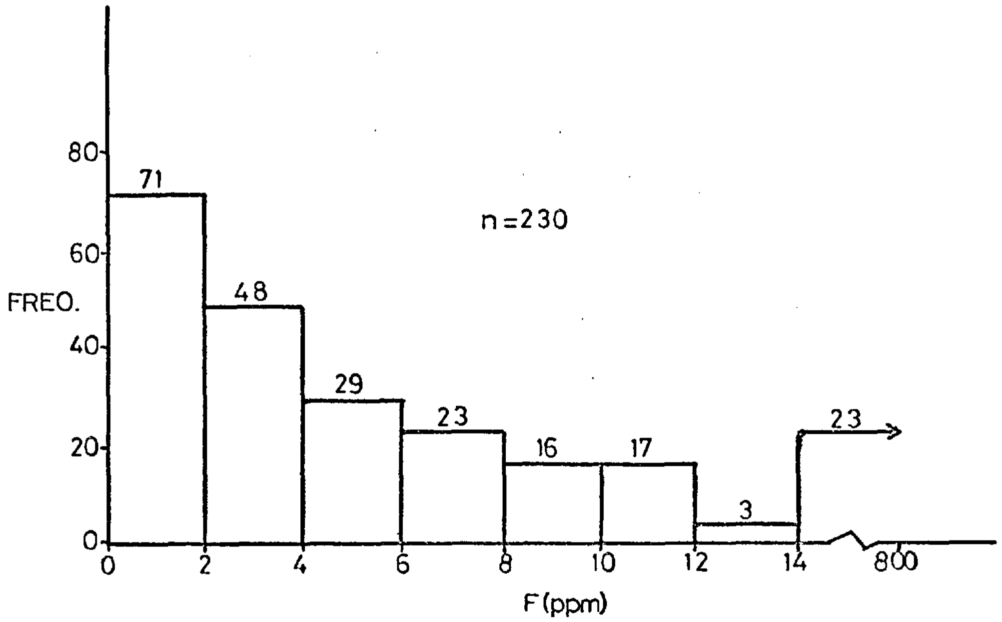


FIGURE 1.5

HISTOGRAM OF FLUORINE CONCENTRATIONS IN THERMAL WATERS

SOURCES: Mineral and Thermal Waters of the World, 23rd Inter. Geol. Congress, Czechoslovakia, 1968; White et al, U.S. Geol. Surv., 1963, Prof. Pap. 440-F; Mahon, W.A.J., 1964, N.Z. Jour. Sci, V. 7 no. 1. p. 3-28; Glover, R.B., 1967, N.Z. Jour. Sci, v. 10 no. 1, p. 70-96; Sigvaldason, G.E., 1964, Beitrage Z. Mineral u. Petrog., v.10, p. 263-274; Mahon, W.A.J. 1967, N.Z. Jour. Sci., v. 10, no. 1, p. 575-584; Ellis and Mahon, 1966, N.Z. Jour. Sci., v. 9, no. 2, p. 440-456; Kent, L.E., 1949, Trans. Geol. Sco. S. Afr., v. 52, p.232-264.

TABLE 1.12

FLUORINE IN THERMAL WATERS ASSOCIATED WITH EPITHERMAL DEPOSITS

(After White et al, 1963)

DEPOSIT	MINERALIZATION	F IN WATER (ppm)
Sulphur Bank mine, Lake County, Calif.	Hg, Sb	1.0
Abbott mine, Colusa County, Calif.	Hg	1.0
Valley mine, Napa County, Calif.	Hg	1.3
Amedee Springs, Lassen County, Calif.	Hg	4.5
Boiling Springs, Valley County, Idaho	Hg	11.0
Rose Creek Spring, Pershing County, Nev.	Mn, W	5.5
Abraham Springs, Juab County, Utah	Mn	4.5
Ouray Springs, Ouray County, Colo.	Mn, W	3.0
Warmwater Springs, Cape Province S. A.	Mn	0.2
Poncha Springs, Chaffee County, Colo.	Fluorite, (Mn, W)	11.0
Ojo Caliente Springs, Taos County, N. Mex.	Fluorite	16.0

in the solubility of fluorite due to increased temperature, but also on the fact that the amount of Ca available from sources other than fluorite will also increase and the common ion effect will be greater. A frequency distribution graph of the available fluorine data for thermal waters is given in Fig. 1.5. The largest proportion of the data population lies between 0.1 and 4.0 ppm, which is comparable to the general concentration range given above for non-alkaline groundwaters (0.1-3.0 ppm). In practically all of these waters, Ca occurs in concentrations well above that contributed by the dissolution of fluorite at 25°C (8-10 ppm Ca), and it would, therefore, appear that increased temperature cannot overcome the modifying effect that excess Ca has on the uptake of fluorine. In addition, the high concentrations of Ca prevents the formation of negatively charged complexes of the $MF_n^{(x-n)}$ stepwise series. For alkaline waters, in which many of the cations are hydrolysed the formation of cation hydroxy-fluoride complexes $M\ OH_xF_n^{y-(x+n}$ will not be affected, since these complexes would be quite stable in the presence of Ca. Thermal waters containing fluorine in amounts greater than 10 ppm generally have higher concentrations of the univalent cations (Na, K, Li, etc.), and those waters with extremely high fluorine contents such as the thermal waters of the alkaline province of Kenya (up to 180 ppm F) Walsh, (1968) are not only high in Na (up to 12,000 ppm) but also relatively low in Ca (less than 100 ppm).

The fluorine content of thermal waters issuing from epithermal mineral deposits is given in Table 1.12. Waters draining fluorite deposits are saturated with respect to CaF_2 while fluorine concentrations of thermal waters associated with other types of deposits (Hg-Sb and Mn-W) depend to a large extent on the amount of available fluorite. A considerable amount of information concerning the occurrence of epithermal mineral deposits can

TABLE 1.13

FLUORINE CONTENT OF STREAM WATERS DRAINING DIFFERENT ROCK FORMATIONS IN S.W. ENGLAND

ROCK TYPE*	FLUORINE RANGE (ppb)	FLUORINE MEAN (ppb)**
Killas (790) (matamorphosed slates and shales)	68-200	106 (14)
Granite (1,516)	60-194	96 (13)
Ultrabasics (130)	51-88	70 (11)

* Mean fluorine concentrations of rocks in brackets (from Tables 1.2 and 3.11)

** Total number of water samples for each rock type in brackets be gained from examinations of the fluorine content of thermal waters in areas of young igneous activity such as the Cordillera - Andes belt of North and South America.

The fluorine content of surface waters depends on the fluorine content of groundwaters feeding the drainage system and the amount of precipitation and run-off. The range of observed fluorine concentrations for surface waters (streams, rivers, lakes) varies from a trace to 14 ppm; the lowest values generally occur over ultrabasic complexes and the higher values ovdr alkalic igneous complexes or in saline lakes such as Great Salt Lake (14 ppm F); Connor and Mitchell, 1958, in Fleischer and Robinson, 1963). An average fluorine content for stream waters is essentially meaningless since large overall variations are usually observed. This point is emphasised by the calculations of Correns (1948) and Tageeva (1943) who obtained averages of 0.26 ppm fluorine and 0.11 ppm fluorine respectively. For rivers and lakes (with outlets), a mean fluorine concentration of 0.1 ppm (Carpenter, 1969) is probably reasonable due to the smaller variation for these bodies.

As previously mentioned, the fluorine content of groundwaters is closely related to rock types, and it seems reasonable to assume that stream waters should also reflect this relationship to some degree. The relationship between the fluorine content of stream waters and associated rock types is demonstrated in Table 1.13 which is based on data from Cornwall S.W. England. As would be expected waters draining ultrabasic rocks have a much lower mean fluorine content than those draining granitic and killas rocks. Despite the fact that the granites have a higher mean fluorine content than the killas, stream waters draining both these rock types have a remarkably similar range and mean fluorine content. This is primarily due to the fact that much of the fluorine in granites and their related soils occurs in tourmaline, topaz and other resistate minerals and is therefore not available to groundwaters. Over the killas, the fluorine is probably leached from clay minerals.

If the stream waters and groundwaters are in equilibrium one can expect correlation between the fluorine content of stream waters and the fluorine content of the associated rock formations. Departures from this correlation may occur during periods of heavy precipitation when the groundwaters become diluted and the fluorine content supressed; also during very dry periods, when surface waters have total ionic concentrations similar to groundwaters, the fluorine content being greatly increased in this case.

The average fluorine concentration of precipitation is of the order of 36 ± 9 pp.b (Bewers, 1972) which is roughly one third of the mean fluorine content for rivers and lakes. From this it follows that if one takes into account evaporation and subsequent increase in the ionic concentrations, then more than 50% of the fluorine in surface waters can be attributed to precipitation. The high fluorine content of precipitation is thought to be the result of evaporation or aerosol formation at the seawater surface (Carpenter, 1969; Bewers, 1972). The removal of fluorine from the oceans by sedimentation of clays and precipitation of $CaCO_3$ and phosphate accounts for only 10-20 per cent of the total fluorine introduced by rivers (Carpenter, 1969). It would appear, therefore, that on a global basis most of the fluorine in the hydrosphere is cyclic.

In order to obtain some idea of the amount of complexed fluorine which may be present in the surface drainage associated with different rock types, a number of stream waters in Cornwall (S.W. England) were analysed for their total and free (F^-) fluoride concentrations. In addition, Al, Fe, and Mn were also analysed to see if any systematic relationship exists between the percentage of complexed fluorine and the concentration of one or all of these elements. Collection was carried out by pumping the water through a millipore filter into a polypropylene collection flask, with eventual transfer of one litre of the water into a polythene bottle containing 1 ml of concentrated HCl and a further 200 ml into another polythene bottle containing no acid. The former was analysed for Al, Fe and Mn and the latter for total and free (F^-) fluoride using the Orion Fluoride Electrode system described in Chapter II. The use of the millipore filter in the field eliminates the majority of particulate matter before acidifying or analysing for fluorine. Although filtering does not remove all the colloidal material, it was felt that the amount remaining would not seriously affect the metal concentrations or the determination of the amount of complexed fluorine. The Al, Fe, and Mn determinations were done by atomic absorption on an acid-leached 500 ml residue. To prevent changes in the ionic equilibrium of the waters, the fluorine analysis was done on the same day of collection. The samples were collected in the winter after a period of relatively little rainfall. The pH of these waters varies from 6.5 to 7.0. Buffering of the samples for fluorine analysis is not required since the H^+ and the OH^- ions do not interfere. This is fortunate since the measurement of the free (F^-) concentration requires little disturbance of the ionic equilibrium if the determined percentage of complexed fluorine is to be meaningful. In order to ensure a constant ionic strength for the measurement of the free (F^-) concentration 1 ml of 0.01M KNO_3 was added to 50 ml of sample. To determine whether the addition of KNO_3 displaced the equilibrium between complexed and free fluoride, the change in millivolt potential of the specific

TABLE 1.14

THE COMPLEXATION OF FLUORINE IN SURFACE WATERS DRAINING DIFFERENT ROCK TYPES

(SAMPLES FROM CORNWALL, S.W. ENGLAND)

Type of Rock	Free Fluoride (ppb)	Total Fluoride (ppb)	% Fluoride Complexed	Al(ppb)	Fe(ppb)	Mn(ppb)
Metamorphosed shales & slates	100	110	9.1	685	49	2
	104	114	8.8	760	38	1
	90	98	8.2	950	95	2
	88	94	6.4	710	71	3
	98	88	0.0	620	124	3
	116	112*	0.0	620	62	1
Granite	52	60	13.3	95	41	2
	118	134	11.9	182	45	5
	61	69	11.6	235	84	3
	98	108	9.3	335	114	17
	68	74	8.1	143	68	4
	82	88	6.8	320	36	2
	70	75	6.7	500	41	28
	75	79	5.1	225	55	3
	80	83	3.6	143	50	2
	68	69	1.5	91	67	3
	164	166	1.2	700	42	20
	194	194	0.0	320	55	3
Ultrabasics	62	66	6.1	440	35	1
	58	59	1.7	305	30	2
	82	80*	0.0	860	136	3
	53	53	0.0	320	77	2
	51	50*	0.0	350	90	2
	68	66*	0.0	290	80	1
	84	84	0.0	375	92	1
	85	88	0.0	155	91	3
	75	73*	0.0	250	52	1
	78	76*	0.0	530	165	2

* for these samples the total fluoride concentration measured was less than the free fluoride concentration

ion electrode (due to change in ionic strengths) was compared for three representative samples with the millivolt change obtained by adding the same amount of KNO_3 to a deionized sample of water. The difference in the observed millivolt readings was well within the analytical error of the instrument (± 1% at the 100 ppb level). The total fluorine content was measured according to the method described under Water Analysis in Chapter II but, instead of using a dilution factor of 1:1, 1 ml of the citrate-acetate buffer was added to 50 ml of sample. Using a large sample to buffer ratio ensures greater precision over a much higher range of fluoride concentrations (50-100 ppb). The buffering ability of these waters is not a problem even at a ratio of 50:1.

The results of this investigation are tabulated in Table 1.14. Considering the analytical errors involved in the two methods for fluorine, only percentages of complexation greater than 5.0 should be taken as significant. The slightly higher total fluoride concentrations for some of the samples as compared to their free fluoride content indicates that the method for total analysis is no more biased towards higher concentrations than is the method for free fluoride.

A number of conclusions can be drawn from this data:

a) The amount of complexed fluoride in these waters varies between 0 and 13%, indicating that the majority of fluoride exists in the uncombined state as F^-. Whether this statement can be extended to all surface waters having near neutral pH values requires further investigations. It seems unlikely on the evidence that complexed forms of fluoride would be dominant in surface waters.

b) Waters draining terrains of ultrabasic rocks show very little if any complexation of fluoride, whereas those draining shales, slates, and granites possess a more noticeable amount of complexation. The reason for this cannot be accounted for by the Al, Fe, and Mn contents since these are all comparable for the three classes of water draining these rocks. The answer would, therefore, have to come from investigations of a more detailed nature.

c) There appears to be no systematic relationship between the amount of complexation and the individual or combined Al, Fe, and Mn contents of these waters. This is not to say that complexation of fluoride by one or more of these cations does not occur, but rather that over the concentration ranges observed for these metals, which are unfortunately small, a significant correlation could not be discerned.

d) There is no significant correlation between the concentrations of Al, Fe, and Mn in the waters and the total fluoride content. The range of Al concentrations observed for the waters is not great (95-860 ppb); for similar levels of Al, Krainov et al (1967) have also found a poor correlation with fluorine (See Table 1.11). Over a much larger Al range (150 to 3, 500 ppb), however, these same authors have found a good correlation between fluorine and Al, indicating that fluoride may be dispersed as Al-F complexes when the Al content is high.

Although the above data indicate that fluorine is dispersed chiefly as the free fluoride (F^-) ion in freely drained environments, this may not be the case in poorly drained areas where the waters have a high concentration of organic colloids. Thus Shipulin et al (1971) have shown that for waters in

TABLE 1.15

ADSORPTION CAPACITIES OF CLAY MINERALS AT DIFFERENT INITIAL FLUORIDE CONCENTRATIONS AND VARIOUS pH LEVELS (AFTER PLUGER AND FRIEDRICH, 1972)

pH	Initial Fluoride Concentration (ppb)	Adsorption Capacity (ug F^-/g)		
		Kaolinite	Illite	Montmorillonite
4.0	200	3.0	4.2	4.0
	600	10.5	14.0	13.8
	1000	18.6	23.7	23.4
5.0	200	2.7	4.2	2.8
	600	9.3	13.1	11.6
	1000	16.9	21.5	20.8
6.0	200	0.8	3.0	-
	600	7.5	9.6	7.3
	1000	13.5	17.6	15.0
7.0	200	-	0.9	-
	600	5.0	6.4	-
	1000	11.9	12.3	3.8

TABLE 1.16

FLUORINE CONTENT OF STREAM, SPRING AND OCEAN PRECIPITATES

DESCRIPTION	FLUORINE CONTENT (ppm)
Fe precipitate, Bath thermal spring, England	260
Mn precipitate, Annapolis Royal, N.B. Canada	133*
Mn precipitate, Georgeville Brook, N.S., Canada	200*
Mn nodule in stream, N.B., Canada	400*
Mn nodule, Indian Ocean	180**
Mn nodule, Atlantic Ocean	2**

* Data from Boyle, R.W. (Pers. comm) (by fluoride ion electrode)

** Data from Cronan, D.S. (Pers. comm.) (by mass spectrometry) tundra regions, fluorine migrates predominantly as a constituent of organic colloids and its mobility can be greatly reduced when these colloids precipitate. A direct relationship was found between the fluorine content and the content of organic matter in the waters studied by these authors.

Once dispersed in a mobile free form into groundwaters and surface drainage, fluorine may take part in adsorption-precipitation processes at the water-sediment interface. Anion exchange reactions will occur chiefly with the clay minerals, with fluorine substituting for the OH^- ion under favourable conditions. For kaolinite, illite, and montmorillonite the adsorption capacity of fluorine increases with decreasing pH, from 7.0 to 4.0 (Table 1.15). At pH values below 6.0 there appears to be very little difference between the adsorption capacities of these clays, but in neutral solutions the adsorption capacity of montmorillonite is greatly decreased. That other minerals such as quartz, corundum, and feldspar will adsorb fluorine has been demonstrated by Warren and Kitchener (1972), who found that feldspar and corundum adsorbed greater amounts of fluorine than quartz in dilute fluoride solutions and that the principal mechanisms of adsorption were Al-F and Si-F bonding. Adsorption was also found to increase with decreasing pH.

Cold extractable analysis by the author, of various stream sediments from different geological environments, indicates that as much as 30% of the total fluorine in drainage sediments is in a readily extractable form. This fluorine is most probably adsorbed by the clay and colloidal constituents of the stream sediments.

The role of fluorine during the precipitation of colloids (Fe, Mn, etc.) has not been investigated. The available data on this subject are given in Table 1.16, and although limited, they show that significant amounts of fluorine may co-precipitate with or be adsorbed by Fe and Mn hydroxides. The adsorption mechanism may be either one of (Fe, Mn)-F complexation, or F-OH substitution, or both. It is interesting to note the large difference between the fluorine contents of Mn nodules from the Indian and Atlantic oceans (180 ppm and 2 ppm respectively), nodules from the former being of more economic importance than those of the latter.

1.4 PEDOGEOCHEMISTRY

Fluorine occurs in detectable amounts in all soil types. It occurs predominantly in the finer fractions of soils principally in the colloids and clays, and may also be present as fluorapatite or in many of the resistate minerals in which it is a constituent (e.g. topaz, tourmaline, etc.). The element reaches its highest concentration in phosphate-rich soils and its lowest concentration in sandy soils. The range and mean contents in soils from different countries is shown in Table 1.17.

The compilation of data by Fleischer and Robinson (1963) indicates that the overall range for fluorine in soils is approximately 10-7,000 ppm, and the average is in the order of 385 ppm.

The relationship between the fluorine content of residual soils and the underlying rock is shown in Table 1.18. It is evident that the range of values in the soils reflects to a considerable degree the type of underlying rock present. For igneous rocks, soils over granites contain higher levels of fluorine than those developed on ultrabasics. The medians of the ranges for soils developed over these rocks (870 and 150 ppm fluorine, respectively), compare favourably with their mean content (810 and 130 ppm respectively).

TABLE 1.17

THE FLUORINE CONTENT OF SOILS FROM VARIOUS COUNTRIES

LOCATION	NO. OF SAMPLES	FLUORINE (ppm)		REFERENCE
		RANGE	AVERAGE	
USA	16	10-1,500	250	1
	137	10,7,070	290	2
	339*	130-5,600	980	3
	9**	104- 284	190	3
Sweden, sandy	11	43- 198	90	4
clayey	20	248- 657	450	4
Germany	19	80-1,100	530	5
	24	120-1,100	390	6
USSR	46	30- 320	200	7
Japan	6	260- 520	370	8
New Zealand	23	68- 540	200	9
England, Cornwall	84	280- 800	490	10
Africa and Australia Tropical soils	12	68- 895	173	11
Canada, Nwfd. A_O		-	180	12
B	10,000	-	220	12
C		-	250	12

* Includes samples with high phosphate contents

** Samples containing less than 0.55% P_2O_5

1. to 9. in Fleischer and Robinson, 1963 (1. Steinkoenig, 1919; 2. Robinson and Edgington, 1946; 3. MacIntire et al, 1958; 4. Nommik, 1953; 5. Michael and Blume 1952; 6. Jahn-Deesback, 1958; 7. Vinogradov, 1957; 8. Kokubu, 1956; 9. Gemmell, 1946); 10 Author's data; 11. Hall and Cain, 1972; 12. Tilsey, 1971 (Pers. Comm.)

TABLE 1.18

RELATIONSHIP BETWEEN FLUORINE CONTENT OF RESIDUAL SOILS AND UNDERLYING ROCKS

UNDERLYING ROCKS	NO. OF SAMPLES	FLUORINE RANGE (ppm)	REFERENCE*
Ultrabasics, Cornwall	3	96- 216	1
Serpentinite, Switz.	1	49	4
Granite, Cornwall	33	620- 1,120	1
Granite, Harz, Ger.	1	50	2
Schist, Rhodesia	25	90- 220	1
Schist, USA	6	200- 1,500	3
Gneiss, Switz.	1	71	4
Amphibolite, Canada	6	360- 900	1
Shales and slates, Cornwall	150	300- 900	1
Limestone, Ireland	42	80- 1,120	1
Limestone, Germany	7	630- 3,680	5
Dolomite, Switz.	1	334	4
Sandstone, Zambia	30	64- 136	1
Sandstone, Ireland	6	480- 750	1
Sandstone, Germany	11	90- 880	5
Phosphate Rock, USA	6	290- 7,070	6
Carbonatite, Zambia	52	7,000-18,800	1

* 1. Author's data; 2-6 in Gmelin 1959 (2. Koritnig, 1951; 3. Steinkoenig, 1919; 4. v. Fellenberg, 1948; 5. Correns, 1956; 6. Robinson and Edginton, 1946).

Similarly, for sedimentary rocks, low levels of fluorine characterize soils developed over sandstones whereas much higher levels are generally found in soils over limestone and shales. Soils developed over rocks rich in apatite or fluorite (rockphosphates and carbonatites) exhibit extremely high fluorine contents. It is further apparent from the data in Table 1.18. that considerable regional variations exist for soils developed on the same rock types. Thus, soils developed on schists, limestones and sandstones from different localities possess fluorine ranges which barely overlap.

During the weathering of rocks and the subsequent formation of soils fluorine is partitioned between the mobile and immobile chemical phases. The degree of partitioning depends on the form or forms in which fluorine exists in the parent rock. Thus, soils developed on rocks in which fluorine is held chiefly in resistate minerals such as topaz, tourmaline or apatite will possess high fluorine contents since fluorine in these minerals will not in general be readily leached. For rocks in which fluorine occurs either as fluorite or in the micaceous minerals more fluorine will enter the mobile aqueous phase during soil formation. Where the soil has a high colloid and clay component much of this fluorine may be taken up by these constituents. On the other hand where the soil has a low colloid and clay mineral content the fluorine will move directly into the mobile aqueous phase and be extensively leached.

Few data are available on the distribution of fluorine in the various solid phases of soils. The author's analyses indicate that most of the fluorine is held in the clay-size fractions. Robinson and Edgington (1946) found that as much as 50% of the fluorine content of well developed soils may be held in the colloid fraction. Many workers (Hall and Cain, 1972; Lalonde, 1974; the author; and others) have found that less than 10% of the total fluorine is water soluble. For podzols, Lalonde (1974) found that the organic-rich horizons contained more water-soluble fluorine than other horizons. He attributed this to the fact that fluorine is excreted at the tips and edges of plant leaves and may be washed down into the soil by rain and become loosely bound when the leaves undergo decomposition. This process gives rise to higher exchangeable fluorine levels in the organic horizons.

A number of factors control the fixation of fluorine in soils. For soils developed over carbonate-rich rocks (limestones, shales, etc.), Gisinger (1968) has found that $CaCO_3$ inhibits the mobility of fluorine, probably because the Ca content in the soil solutions exceeds the solubility limit for apatite, $Ca_5(PO_4)_3(F\ OH)$ and fluorite (CaF_2) and the fluorine is, therefore, precipitated as fluorapatite or fluorite. High fluorine can also be expected in soils in arid and semi-arid climates where there is an accumulation of lime in the lower horizons. On the other hand, fluorine is relatively mobile in soils which have solutions rich in the alkaline elements (K, Na) such as those over alkaline igneous rocks. This is due both to the high solubility of K and Na fluorides and the fact that K and Na increase the solubility of fluorite and apatite.

The relationship between fluorine and the phosphate, colloidal and clay constituents of soils has been extensively studied, largely as a result of attempts to understand the parameters controlling the fertility of many types of soils. Johnson and Olsen (1972) have found that the highly acidic root tips of plants are capable of releasing Ca from the apatite matrix thus increasing the amount of mobile or exchangeable fluorine in soils. In addition the ability of soils to take up large quantities of exchangeable phosphate is seriously hindered if fluorine is present in appreciable amounts in the soil solution (Samson, 1952). The phosphate merely precipitates as insoluble apatite. A study of the ability of humic acids to attack and dissolve various minerals has shown that fluorite is significantly more soluble (12-fold) in dilute humic acid solutions than in ordinary water (Baker, 1973). MacIntire et al (1955) have indicated that fluorine in soils form insoluble aluminium silicofluorides ($Al_2(SiF_6)_3$) but that Ca is the dominant precipitating ion for fluorine.

Various adsorption studies (Samson, 1952; Larsen and Widdowson, 1971) have shown that aluminium hydroxides are much more efficient adsorbers of fluorine than clay minerals. Of the clay minerals, kaolinite possesses a greater adsorption capacity than montmorillonite. The adsorption of fluorine on clays and aluminium hydroxides was found to be rapid; equilibrium being reached in less than 16 hours (Larsen and Widdowsen, 1971; Bower and Hatcher, 1967). By using the isotope F^{18} as a tracer, Romney et al (1969) showed that for solution concentrations up to 16 ppm fluorine, kaolinite and illite adsorbed about 98% of the available fluorine, wheras montmorillonite and clinoptilolite accommodated less than 4%.

Pluger and Friedrich (1972) found that the adsorption capacity of clay minerals depends to a large extent on the pH of the soil solution. Thus, for the solution concentration range 200 to 1,000 ppb fluorine, kaolinite and illite possessed adsorption capacities similar to those of montmorillonite over the pH range 4.0 to 6.0. At pH 7.0, however, the adsorption capacity of montmorillonite was much less than that for kaolinite and illite. For all of these clay minerals the investigators found a decrease in the adsorption capacity with increasing pH.

The relationship between fluorine and soil depth is to some degree unique. A distinct increase in fluorine with depth has been noted by several workers (Robinson and Edgington, 1946; Vinogradov, 1959; Michael and Blume, 1952; Tilsley, J.E. pers. comm. and the author). This feature is pronounced even in well-developed soils where one would expect a high clay content in the B horizon and hence a much higher fluorine content. The reason for this phenomenon has to some extent been explored by Butler (1953) who, as a result of investigations of the weathering of basic igneous rocks, found that on an 'Al constant basis' there was a distinct decrease in the fluorine content when passing from rock to clay. More specifically, he found that only a portion of the fluorine content of fresh biotite is retained in the weathered product (clays). Micaceous minerals in the upper horizons of soils are almost entirely converted to clays during soil formation, whereas, those in the lower horizons are only partly decomposed. As a large percentage of the fluorine content of most rocks is held in the micaceous minerals (Koritnig, 1951) we should, therefore, expect fluorine to increase with depth. Koritnig (1951) has conducted a study similar to Butler's for soils developed over granite. He found that the most stable fluorine-bearing mineral during weathering was apatite; the micas being considerably leached and the fluorite completely dissolved. Rimsaite (1967, 1970) and Hubner (1969) have investigated the weathering of the micaceous minerals and the resultant influence on the occupancy of the F/OH structural position in great detail. The latter author has noted that the total ionic strength and the pH of the soil solutions have a marked influence on the ability of fluorine to be adsorbed by clay minerals. These features were also born out by the investigation of Larsen and Widdowson (1971) who found that greater amounts of fluorine were leached from soils at both low (4-5) and high (7-8) pH values, with the minimum amount of leaching occurring at pH 6.0.

The precise mechanism controlling the exchange-adsorption reactions between fluorine and clay minerals is not yet clearly understood. Many scientists have speculated that the process is a simple F-OH substitution, but this theory is open to serious doubt as a result of more recent work in the field. Thus, Hubner (1969) has found that the exchange-adsorption process is closely associated with the chemical decomposition of the layered silicates, and that chemical decomposition and exchange-adsorption will act in opposite directions in aqueous environments, fluorine being adsorbed under acidic conditions and desorbed under alkaline conditions.

Conflicting data exist on the fluorine content of organic-rich soil horizons. Vinogradov (1959) has observed an increased fluorine content in the A horizon of certain soils in the USSR and has attributed this to the enrichment of difficultly soluble fluorine-bearing minerals (mica, etc.) in this horizon. Robinson and Edgington (1946) in their study of 30 soil profiles from different regions of the USA found that the fluorine content increased with depth in 17 profiles; remained constant in 8 profiles, and exhibited an enrichment in the A horizon over other horizons in only one profile. Similarly, Tilsley (pers. comm.) and Boyle (pers. comm.) have also found a marked decrease in the fluorine content of the A horizon with respect to the inorganic horizons in Newfoundland and New Brunswick respectively. The author has found that, although this is commonly the case, exceptions do exist. Thus, in the Bancroft area of Canada the A horizon of soils developed over pegmatites show a marked enrichment in fluorine compared with the B horizon. Similarly for soils in the vicinity of the fluorite deposits of the Madoc area in Canada, Lalonde (1974) has also found significant enrichments in the A horizon. In both these areas fluorine is available as a result of the chemical weathering of fluorite, and the soils are well-developed podzols. It would appear, therefore, that in areas where soils are developed over rocks in which fluorite is the primary fluorine-bearing mineral, the A horizon may show a significant enrichment in this element.

For soils in which fluorine is more tightly bound in the micaceous or resistate minerals there is less uptake by plants and, therefore, no significant concentration in the organic-rich horizons.

Until recently the occurrence of organo-fluorine compounds in soils has not been considered. A detailed examination of fluorine in tropical soils by Hall and Cain (1972) has indicated, however, that organo-fluorine compounds do exist in soils and that much of the fluorine in this form is present as fluoroacetate. It seems improbable, however, that organo-fluorides contribute significantly to the overall fluorine content of soils, much of the fluorine in organic debris being largely present as fluorapatite.

Each year large quantities of phosphatic fertilizers containing fluorine are added to agricultural soils. Less than 10% of the fluorine added through fertilization is normally removed by groundwater leaching and harvesting (Oelschlager and Hohenheim, 1971). We can, therefore, expect a large build-up of fluorine in those soils that are heavily fertilized, but the effect of this increase on agricultural productivity has not yet been determined. Robinson and Edgington (1946) have shown, that for soils which have been fertilized for 40 to 50 years, the fluorine content as compared with nearby non-fertilized soils increased by more than 50% in the topsoils but no significant increase was found in the subsoils. This suggests that fluorine is rapidly fixed in the upper or productive layers of agricultural soils after it has been released by the decomposition of phosphate.

1.5 BIOGEOCHEMISTRY

Fluorine is found in detectable amounts in almost all species of vegetation. As with many other elements its uptake is governed by a number of factors related to soil and biochemical processes. It has been classed as an important accumulator in biological material surpassed only by P, S, Cl, Ca, K, Mg, Na, Sr, B, Zn, As and Mo (Perelman, 1967). According to Underwood (1962) the highest accumulations of fluorine are found in the leaves and roots of plants.

Plant roots absorb fluorine directly from soil solutions or as a result of the decomposition of fluorine-bearing minerals near the root-soil interface. The latter method has been shown to be operative for apatite (Johnston and Olsen, 1972), and it seems probable that the acidic root tips of plants are also capable of stripping fluorine from micaceous minerals and soil colloids. The ability of roots to attack the more resistant fluorine-bearing minerals (e.g. topaz, tourmaline etc.) has not been investigated. Plants may also take up fluorine from the air. Those plants which take in elements chiefly by absorption from the atmosphere are called epiphytes; the Spanish Moss (Tillandasia usneoides L.) is the principle fluorine-bearing member of this group. It may contain up to 624 ppm fluorine (Fleischer and Robinson, 1963).

The concentration of fluorine in plants on a dry weight basis may vary from only a trace to as much as 8,200 ppm. This large concentration range indicates the specificity which some plants have for fluorine. The highest concentrations are found in the tea plant (Theacea sp.), the elderberry (Sambucus sp.) and the camellia (Ebandler eleganus). Fluorine in these plants may vary from 100 ppm up to maxima of 8,200, 1,400 and 6,400 ppm fluorine (dry weight) respectively (Matuura <u>et al</u>, 1954; Fleischer and Robinson, 1963).

Matuura et al (1954) measured the fluorine content of more than 300 species of plants and were able to divide them into three main groups according to their content. The largest group comprised plants with less than 50 ppm fluorine (dry weight), of which the largest number of these were in the range 8-20 ppm. Next, an intermediate group having 50 and 500 ppm fluorine (dry weight) was recognized; less than 10 percent of the total population fell within this group. The last group comprised a fluorine-rich group of which the plants mentioned above are the dominant members. These are few in number.

From the data of Matuura et al (1954) it can be concluded that the average fluorine content of terrestrial plants is of the order of 10 ppm on a dry weight basis. Marine plants have much lower values of fluorine (4.5 ppm F) than land plants (Young and Langille, 1958).

The specific mechanism by which plants take up fluorine from soils is as yet unknown. There are, however, a number of factors which affect uptake. A high Ca content (probably held as $CaCO_3$) in soils inhibits the uptake of fluorine due to CaF_2 precipitation (MacIntire et al, 1955). A greater uptake will occur in acidic and alkaline (low Ca) soils mainly because a greater percentage of the total fluorine is water soluble and, therefore, available for absorption by plants (Larsen and Widdowson, 1971).

In addition to pH and the aqueous solubility of fluorine species, the presence of elements such as Al, Fe, and B may also have a controlling effect on uptake. Collett (1969) has shown for instance that a greater uptake may occur in soils having a high B content, a feature which they have attributed to the synergistic effect of unbound boron on fluorine. The formation of fluorine complexes of Al and Fe may also result in a more favourable uptake, although detailed information on this is unavailable.

Studies of the fluorine uptake by plants arising from the use of fertilizers have produced inconsistent results. Hart et al (1934), MacIntire (1942) and Oelschlager and Hohenheim (1971) could not detect any appreciable uptake from soils which had been generously fertilized, whereas Okamura and Matsushisa (1967) and Gordon (1970) have found a significant increase in uptake for fertilized soils. According to Marier (1971) the discrepancy in these results may be due to different soil types; acidic soils present more available fluorine for uptake, whereas high Ca soils inhibit the uptake of the element, a conclusion that should be confirmed by more detailed studies.

Until recently, fluorine was thought to occur in plant tissues solely as fluorapatite. However, the discovery in Australia, Africa and Brazil of certain plants capable of synthesizing fluoracetate, and fluor-oleic and fluoro-palmitic acids (Hall and Cain, 1972) has led to the general acceptance that organo-fluorides exist in plant tissues. This is particularly important as plants high in these organo-fluorides are extremely toxic to mammals. When ingested, the fluoracetate is converted to fluorcitrate with resulting aconitase inhibition in the Krebs Cycle pathway. The fluorine in these toxic plants, however, only rarely exceeds 150 ppm, and it is not known whether the element is essential in their metabolism. In fact no evidence exists to suggest that fluorine performs any essential function in plant nutrition whether it is in an organic or inorganic form.

The relationship between the fluorine content of plants and their associated soils is naturally tenuous since many factors other than the fluorine concentration in the soil must be considered. It would appear from recent studies (Matuura et al, 1954; Marier and Rose, 1971) that plants have a remarkably high tolerance towards high concentrations of fluorine in soils. This is not, however, the case for airborne fluoride which may be extremely toxic to plants (Marier and Rose, 1971). No plants (i.e. geobotanical indicators) are known which specifically seek areas of high fluorine in their substrate.

In animals, fluorine is concentrated mainly in the skeletal tissues as fluorapatite. Soft tissues rarely contain more than 5 ppm fluorine on a dry weight basis. Animals which ingest vegetation or water having a high concentration of fluorine may suffer from a disease known as fluorosis. This results from the greater amount of fluorine available for conversion of hydroxyapatite to fluorapatite causing the skeletal tissues to become brittle and calcification of tendons to occur. The teeth are also greatly affected, dental disintegration eventually prevents the animal from eating. On the other hand, if fluorine is present in very low concentrations an adequate bone structure will not develop, and dental caries or softening of the teeth will occur. No mention has been made of the levels which will cause fluorosis or dental caries. This is mainly because long term trials have not been conducted to determine the maximum or minimum levels which will eventually give rise to these diseases. Concentration levels which produce visible effects in the short term have, however, been established. For waters the 'available limits' set by the US Public Health Service are 0.8 and 1.7 ppm and the 'maximum permissible limits' are 0.4 and 2.4 ppm (Marier and Rose, 1971). For vegetation no limits have been set. For subclinical effects it is possible that the so-called 'safe range' of 0.8 - 1.7 ppm is much too wide. For this reason a fluoridation level of 1.0 ppm is used in most public water supplies.

1.6 ATMOGEOCHEMISTRY

The concentration of fluorine in the air in non-industrial areas may be as high as 0.9 ug/m^3 but is generally less than 0.05 ug/m^3 (Marier and Rose, 1971). In industrial areas substantially higher concentrations will occur.

The atmosphere receives fluorine from many sources. Large quantities of HF are introduced into the atmosphere by volcanic activity (White and Waring, 1963). This gas may comprise as much as 1 or 2% of the total gases expelled during vulcanism, and of the active gases (total minus H_2O) it may comprise as much as 32%. Recent investigations on the global circulation of fluorine suggest that large quantities of the element are introduced into the atmosphere at the seawater surface (Carpenter, 1969; Bewers, 1972), but it is not known whether this is an evaporative process or the result of aerosol formation. Other natural processes which may introduce fluorine into the atmosphere are the hydrolysis of solids and the formation of organic exudates from vegetation. The latter process, although confirmed for many of the metals, has not been authenticated for fluorine. It is known, however, that many types of plants excrete fluorine onto their leaf surfaces (Bovay, 1969 and Romney et al, 1969 in Marier and Rose, 1971), and although most is thought to be washed into the soil by rain some may enter the atmosphere, especially in areas having little rainfall. The hydrolysis of fluorine-bearing solids and the subsequent formations of volatile HF has been confirmed by the author. A detailed description of these experiments is given in the section on Vapour Geochemistry. They show that significant amounts of fluorine may be evolved from both dry and wet fluorspar and may, therefore, be concentrated in soil gases. In wet environments the amount of hydrolysis depends on pH, a greater evolution of fluorine occurring in acid environments. More detailed experiments are required to ascertain the contribution of fluorine to the atmosphere as a result of hydrolysis of other fluorine-bearing minerals.

Each year large quantities of volatile fluorides are added to the atmosphere as a result of industrial activity. The sources of this fluorine are numerous and have been of such great concern that this element has been classed along with sulphur dioxide and ozone as one of the most serious air pollutants. Because of its unique ability to form volatile compounds with silicon (SiF_4), hydrogen (HF), boron (BF_3) and many other elements, it is evolved during many of the processes involving combustion or smelting. The most common sources of industrial fluorine pollution are coal-burning plants, superphosphate factories, aluminium and iron smelters and brickmaking factories. The active fluorine gases emitted from these sources may have severe toxic effects on the surrounding animal population. The levels of airborne fluorine in the vicinity of some of the mentioned sources may be as high as 1,130 ug/m^3 (Marier and Rose, 1971).

No information is available on the actual forms in which fluorine is present in the atmosphere. It seems probable that most of the gaseous fluorine is in the form of HF. The remainder is probably in the form of silicofluorides (SiF_4, H_2SiF_6). A specific fraction of the total is normally tied up in aerosols, either as an absorbed or adsorbed constituent.

Most of the fluorine in the atmosphere is removed by rainwater. For non-industrial areas, the fluorine content of precipitation is in the range 23-52 ug/kg (Bewers, 1972). For industrial areas the contents are much higher probably by an order of magnitude. Smaller amounts of fluorine are removed by adsorption on terrestrial materials and absorption by certain epiphytic plants (i.e. Spanish moss).

CHAPTER II

ANALYTICAL RESEARCH AND DEVELOPMENT

2.1 INTRODUCTION

Our basic knowledge of the geochemistry of fluorine can largely be attributed to two major analytical developments; the distillation method of Willard and Winter (1933) and the invention of the specific fluoride ion electrode by Frant and Ross (1966).

Prior to 1933 the analysis of geochemical material for fluorine was not only time consuming but highly unreliable. . The analytical data obtained were of such dubious quality that for their monograph on elemental abundance Clarke and Washington (1924) calculated the fluorine content of rocks on the basis of their phosphorous content, assuming that apatite was the principal host mineral. This method was later shown by Shepperd (1935) to be in serious error. For example, in many rock types significant amounts of fluorine occur in the micaceous and amphibole minerals as well as a number of other minerals. It was not until Willard and Winter (1933) had developed a distillation and volumetric method of fluorine analysis that reliable data were obtained. This technique involved a suitable method of digesting the sample, usually by alkaline fusion, followed by steam distillation of the fluorine as H_2SiF_6 by boiling the digested sample in concentrated acid containing silica powder. The fluorine was then determined volumetrically. Modifications of this method were developed after 1933, and a system of fusion - distillation - colorimetric determination was subsequently adopted.

Although this method is both accurate and precise, it requires considerable expertise, and the number of samples that can be analysed is very low (10-20 samples/day). The fusion-distillation-colorimetric method or modifications thereof have been used extensively until recently and are still the preferred methods in some analytical circles, although the colorimetric step has generally been superceded by the fluoride ion electrode. For the purposes of exploration geochemistry, this method is unsatisfactory since it does not meet the balanced requirements of speed, precision, and low cost.

Recent adaptations of the Willard and Winter (1933) method for the analysis of rocks have been described by Grimaldi et al (1955), Hollingworth (1957), Hall and Walsh (1962) and Shapiro (1967).

The development by Frant and Ross (1966) of a selective electrode which was capable of measuring very low levels of fluorine (down to 20 ppb) in solution was a major breakthrough for the analytical geochemist interested in fluorine analysis. As a result of this invention, fluorine has become a valuable element in the exploration geochemist's repertoire of pathfinder elements. Analytical investigations have shown that this electrode is truly specific in determining fluoride provided it is used in the proper pH range (5.0 - 7.5) and fluoride complexes are absent. It has been necessary, therefore, that the geochemist devise methods of presenting fluoride in an uncomplexed form to the electrode instrumentation.

Van Loon (1968) published a preliminary paper on the analysis of rocks and minerals using the fluoride electrode, and since then a number of methods have been described (Edmond, 1969; Ficklin, 1970; Peters and Ladd, 1971; Pluger and Friedrich, 1972; and Farrell, 1974). The literature is also replete with methods of analysing waters for fluorine. These methods have demonstrated the relative ease with which waters can be analysed provided the samples are properly buffered and fluoride complexing is negated.

The analysis of organic material is presently done by more classical colorimetric or chromatographic techniques because the biochemist is often interested in both the inorganic and organic bound fluoride present in biological material; the latter form of fluoride cannot be analysed by means of the specific ion electrode. For the purpose of exploration geochemistry the author has successfully determined fluorine in organic-rich soils using the methods developed for inorganic materials.

Recent reviews on the analytical chemistry of fluorine are lacking. Elving (1954) has presented an extensive review of the methods in use prior to the introduction of the specific ion electrode.

The following sections describe the development and detailed investigations of analytical methods for fluorine used in the present research on the application of fluorine geochemistry to mineral exploration. Descriptions of the analytical methods used for other elements discussed in this thesis are given in Appendix V.

2.2 INSTRUMENTATION AND ELECTRODE PROPERTIES

The electrode used for this research was the Orion 94-09 Eu-doped LaF_3 membrane electrode developed by Frant and Ross (1966). The electrode may be coupled to most millivolt meters with high impedence, and if direct reading is required the Orion Ionalyzer can be used. Where rapid analyses are required, such as in exploration geochemistry, the latter instrument is preferred. The only other requirement is a suitable

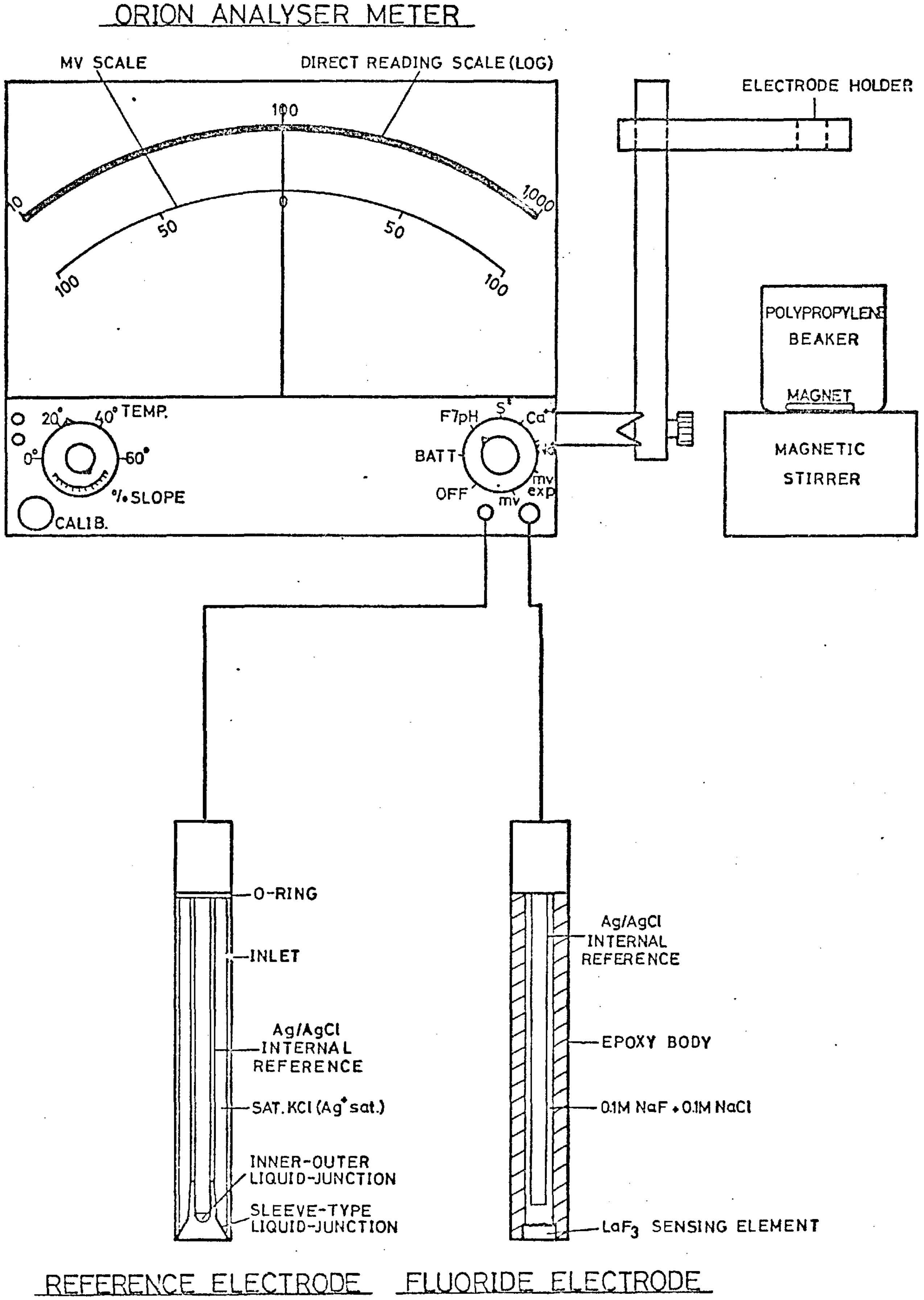


FIGURE 2.1

INSTRUMENTATION FOR FLUORINE ANALYSIS

reference electrode. Orion have developed a compatible reference electrode (Model 90-01) to accompany the LaF_3 electrode. Fig. 2.1 shows the schematic instrumentation set-up used for the research described in this thesis.

The Orion Ionalyzer is not only capable of direct readout but also possesses an adjustable millivolt scale and a millivolt exponent scale. The latter can be used to check whether or not the electrode is exhibiting Nernstien response (see below for definition) for any particular solution matrix. The direct reading scale is a two cycle logarithmic scale. Fluoride concentrations from 0.01 to 10,000 ppm can, therefore, be covered using the three calibrated scales (0.01 to 1.0; 1.0 to 100 and 100 to 10,000). The meter operates on four 4.5 volt batteries, and a battery check is provided to ensure good meter performance. The meter also incorporates a temperature and Nernstien slope calibration to be used when working with solutions at a temperature other than 25°C. In terms of field portability the meter is ideal, being both robust and light. The entire meter and electrode system is supplied with a carrying case and can be easily carried in the field.

If an Orion Ionanalyzer is not available a high impedence millivolt meter having a suitable scale expansion can be used. It is necessary, however, to construct a calibration curve (mV vs. concentration) for the particular solution matrix being used. In addition a temperature correction factor may have to be applied if the solution temperature is not at 25°C.

The reference electrode used in the system is the Orion 90-01 single junction reference electrode (Fig. 2.1). It is a sleeve-type Ag/AgCl electrode designed to be compatible with the fluoride electrode. Two types of filling solution can be used depending on the total ionic strength of the sample solution. For solutions having a total ionic strength less than 2×10^{-1}M an equitransferent solution containing Na^+, K^+, NO_3^- and Cl^- ions and saturated with Ag^+ ions is used. For concentrated solutions a saturated KCl (saturated with Ag^+ ions) is recommended. In most cases the latter filling solution is adequate. This electrode matches the potential characteristics of the saturated calomel electrode. Like the ion electrode it is made of rugged unbreakable plastic to prevent loss of fluoride by chemi-sorption. Orion now market a combined fluoride-reference electrode, but in the opinion of the author this is impractical as the reference electrode if properly cared for will last much longer than the specific ion electrode which may lose efficiency much sooner, especially if used in strong citrate, bicarbonate or acetate solutions. As these de-complexing agents are required for geochemical analysis an uncombined fluoride-reference electrode system is advised.

The Orion 94-09 fluoride electrode consists of a Eu-doped LaF_3 membrane crystal of approximately 11mm diameter embedded in the end of a tubular epoxy body. Within this tubular body a stable inner reference system is housed. The entire electrode can be represented by the following cell specification.

$$\text{Ag; } AgCl_{(s)} \;\Big|\; \text{NaF (0.1M), NaCl (0.1M)} \;\Big|\; LaF_{3(c)}$$

The electrode assembly is strong and durable and may be operated over the temperature range 0-80°C. The performance of the electrode depends essentially on the ionic conductivity of the LaF_3 crystal over a certain temperature range. In this system only fluorine is involved in the conduction process, and the conduction proceeds by a lattice defect mechanism.

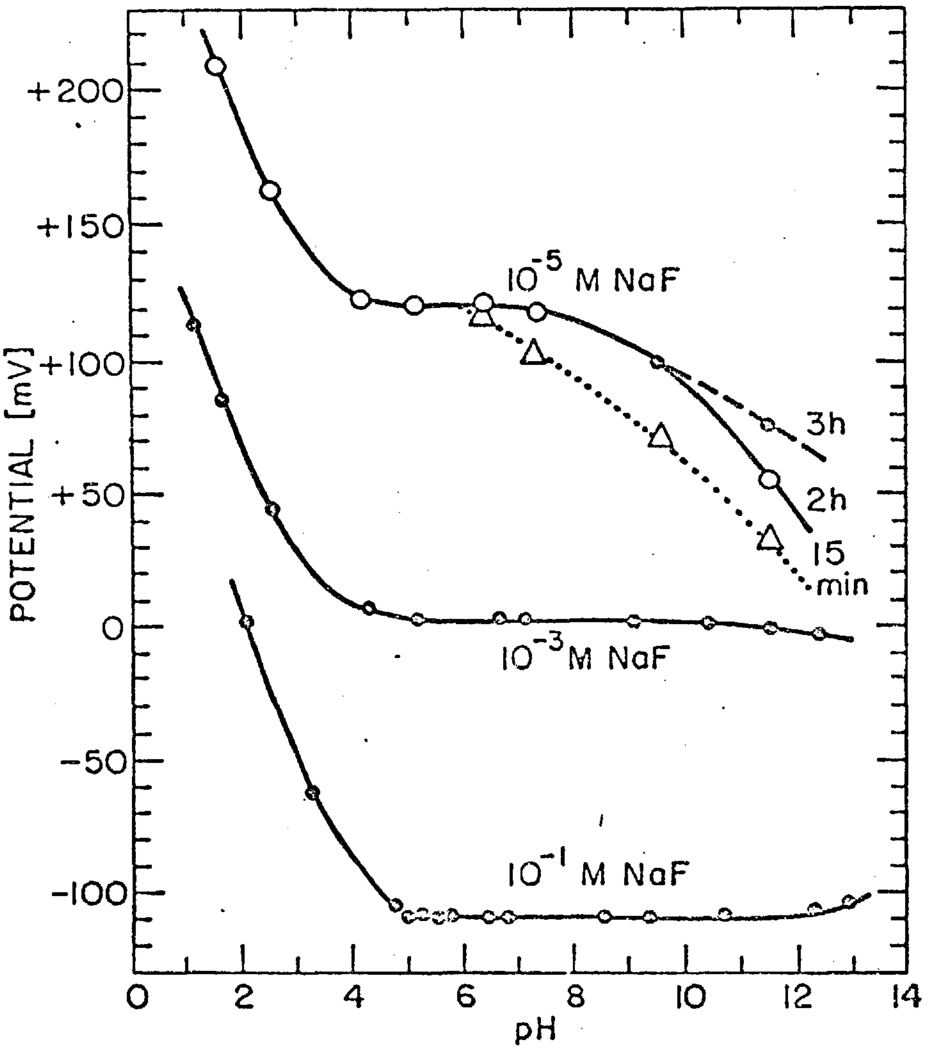


FIGURE 2.2

RELATIONSHIP BETWEEN pH and POTENTIAL (mV) READINGS OF THE ORION FLUORIDE ELECTRODE FOR 10^{-1}M, 10^{-3}M, AND 10^{-5}M NaF SOLUTIONS (After Durst, 1969)

It follows from this theory, therefore, that the only ion capable of interferring in the conduction process is OH^-. This is due to the similar ionic radii and charges of OH^- and F^-. Investigations have shown that when the level of hydroxide is less than one tenth of the level of fluoride present no significant interference will occur. Furthermore, OH^- interference can normally be controlled by adjusting the pH to within the 5.0-7.5 range. Below a pH of 5.0 the formation of HF will seriously affect electrode readings. The effect

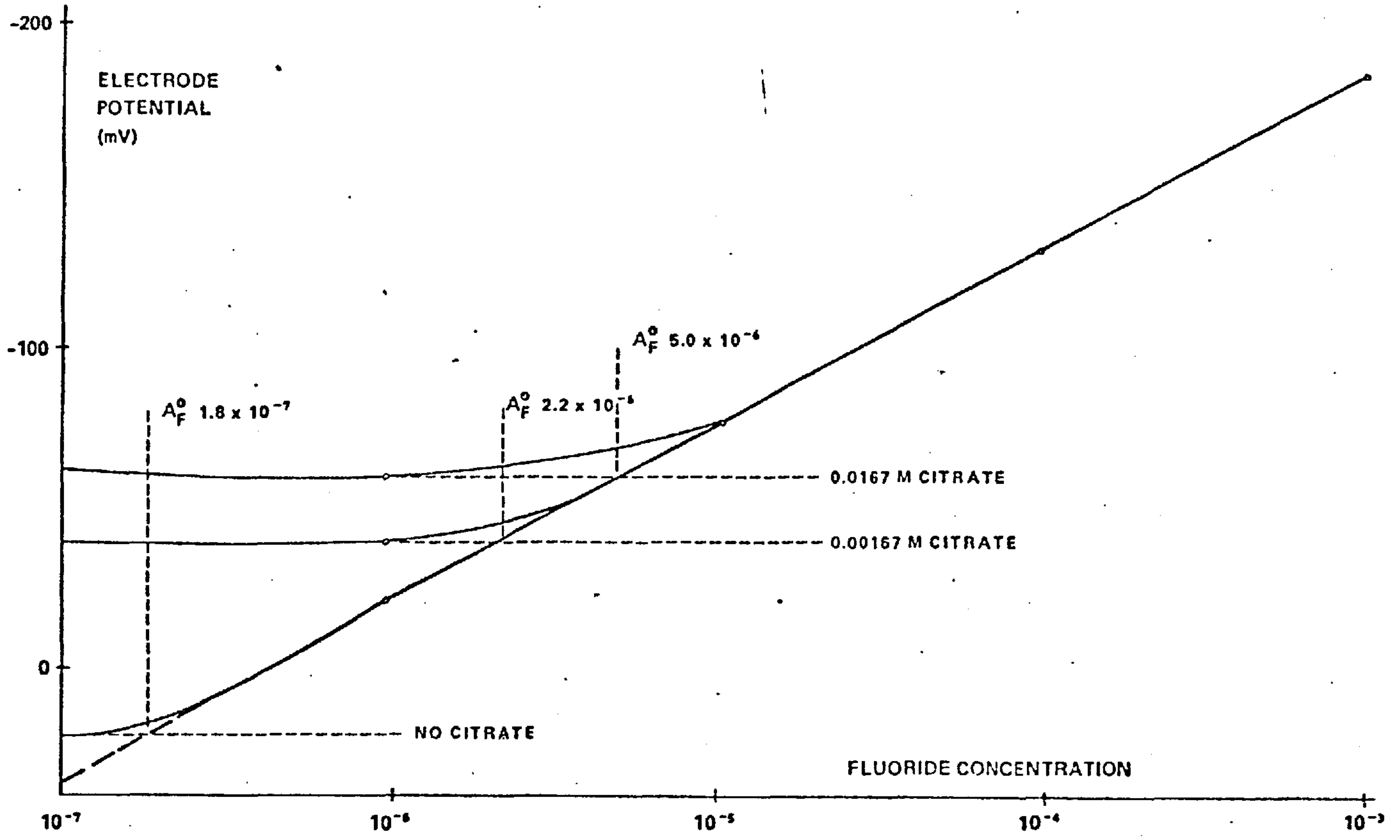


FIGURE 2.3

THE EFFECT OF CITRATE ON ELECTRODE POTENTIAL (mV) FOR THE ORION FLUORIDE ELECTRODE (After Durst, 1969)

of pH on the LaF_3 membrane electrode can be seen in Fig. 2.2. Interference from other anions such as Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^- or PO_4^{3-} does not occur, even at very high concentrations. It is for this reason that the fluorine ion electrode is considered to be truly specific. Anions such as citrate, bicarbonate and acetate may produce elevated fluoride levels by binding the La of the crystal and releasing fluorine. These anions are, however, only a problem when working with very low levels of fluorine (20-200 ppb). This is fortunate as these anions are required to prevent cation complexation (Al, Fe, etc.) of fluorine during the analysis of geochemical materials. The effect

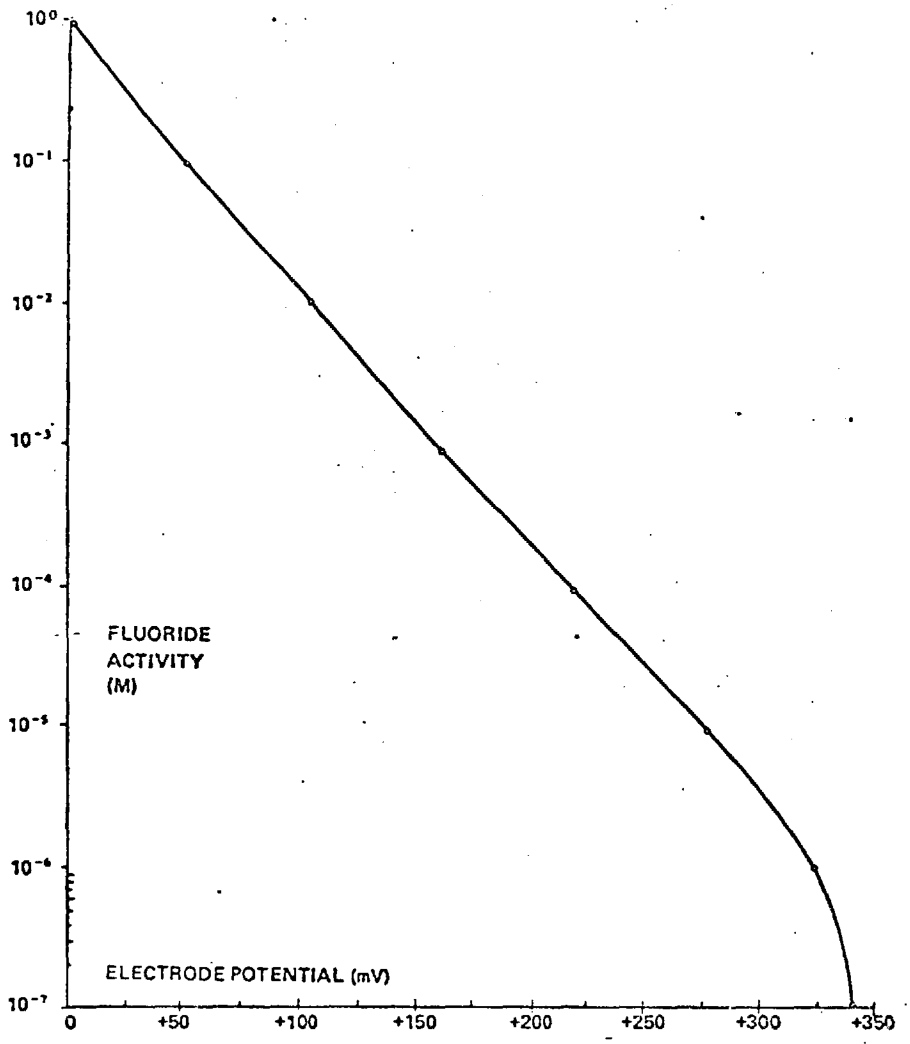


FIGURE 2.4

TYPICAL CALIBRATION CURVE FOR ORION FLUORIDE ELECTRODE (FROM ORION HANDBOOK)

of citrate on the fluoride electrode is shown in Fig. 2.3. These data do not, however, take into account the fact that for geochemical samples much of the citrate is tied up in complexing the major cations (Fe, Al, etc.) present in solution.

The fluoride ion electrode, when coupled with a suitable reference electrode, exhibits Nernstian response according to the equation $E = E_a - 2.303\frac{RT}{\mathcal{F}} \log a_{F}^{-}$ where E_a is equal to the portion of the total potential due to choice of internal and external reference electrodes and internal solutions, $2.303\frac{RT}{\mathcal{F}}$ is the Nernstian factor (equal to 59.16 mV at 25°C), and a_{F}^{-} is the fluoride ion activity. E_a is a constant determined by calibration in a solution of known fluoride ion activity. It can be seen from this equation that the measured potential is dependent only on the temperature of the solution and the activity of fluoride ion. Values for $2.303\frac{RT}{\mathcal{F}}$ can be calculated for a given temperature and the percentage change in the slope of the Nernstian equation can be accounted for by adjustment of the slope calibration on the Ionalyser. The ionic activity a_{F}^{-} is equal to the ionic concentration C_{F}^{-} multiplied by the ions activity coefficient (v). The ion activity coefficient will decrease with increasing total ionic strength. Provided both standard and unknown solution have approximately equal total ionic strengths direct concentrations can be read from the Ionalyser. Fig. 2.4 represents a typical Nerstian calibration curve for the fluoride activity range 10^{0}M to 10^{-7}M. (approximately 19,000 ug/ml to 1.9 ug/l.) The theoretical detection limit for the electrode system is 10^{-6}MF^{-} or approximately 20 ug/lF^{-}, based on the solubility of LaF$_3$.

Durst and Taylor (1967) have studied the stability of the fluoride electrode over a one week period using standard solutions. They found the potential drift to be random and obtained 95 percent confidence limits of ±5 mV on the mean of 21 measurements. Despite this low drift it is advisable to calibrate the instrument daily since temperature conditions may not always be the same. Stirring of the sample solution will both reduce response time and minimize drift, especially at the low fluoride levels (Srinivasan and Rechnitz, 1968). Teflon-coated magnets combined with a magnetic stirrer are, therefore, used to increase speed of analysis and minimize analytical variance (Fig. 2.1). The response of the electrode is almost instantaneous at high concentrations, and at very low concentrations (20 ug/lF^{-}) complete equilibrium can be attained in about three mintues.

For solutions of high total ionic strength (greater than 1M) the time for complete equilibration at the 20 ug/lF^- level may be considerably longer (20-30 minutes).

The precision of the determination is limited by such factors as temperature, instrument drift and electronic noise. For sample solutions an overall precision of ±10 percent over the concentration range 0.1 to 10.0 ug/mlF^- is normal if frequent calibration is carried out. This precision is obtained only for repetitive analyses of the same sample solution, and best approximates that found for water analysis. For other methods employing rocks, soils etc. the precision will be affected by such factors as sample attack and sample matrix. The reader is referred to the relevant sections describing these methods and their respective precisions.

Normally, solution volumes as low as 1 ml can be easily analysed. Solution volumes as low as 30 ml can be analysed by inverting the fluoride electrode and placing the sample solution between the LaF_3 membrane surface and the end of the reference electrode (see the section on vapour geochemistry).

The following cell configuration represents the entire system:

METER

Ag;$AgCl_{(s)}$	0.1MCl^- 0.1MF^-	$LaF_{3(c)}$	TEST SOLUTION	4MKCL(Ag^+ sat)	Ag;$AgCL_{(s)}$

——Fluoride Electrode—— —— Reference Electorde——

A good review of the characteristics of the fluoride selective electrode and its application in many types of investigation is given in Durst (1969) and Evans et al (1971).

It is important to note at this stage that since ionic fluoride in solution can be easily bound by glass, no glassware should be used when carrying out the analyses. Sample solutions should, therefore, be made up in polyporpylene beakers and standards should be stored in polypropylene bottles.

2.3 WATER ANALYSIS

The analysis of waters can be performed with relative ease using the specific ion electrode. As the majority of fluorine in natural waters is in the free ionic state (see Table 1.14) it is only necessary to add a buffer solution containing a small quantify of de-complexing agent to prevent metal-fluoride complexation. CDTA (diaminocyclohexanetetra-acetic acid) has been advocated by some (Orion Research, 1971) for this purpose. This is an expensive chemical, and tests by the author comparing this de-complexing agent with a citrate-acetate buffer indicated that there was little justification for its use. Fluoride analysis of standard mixtures of F, Al and Fe using CDTA and citrate buffers indicated that the differences seem random (Table 2.1). For the purposes of geochemical exploration the citrate-acetate method is, therefore, more practical.

TABLE 2.1

COMPARISON OF CDTA AND CITRATE-ACETATE BUFFERS FOR THE DETERMINATION OF FLUORIDE IN WATER SAMPLES (100 ppm Fe and Al added)

Complexing Ion	F Added (ppm)	F Measured (ppm)	
		CDTA Buffer	Citrate-acetate buffer
Fe	0.10	0.10	0.098
Al	0.10	0.10	0.10
Fe	0.50	0.48	0.50
Al	0.50	0.51	0.49
Fe	1.00	0.98	1.00
Al	1.00	1.00	1.05
Fe	1.50	1.50	1.51
Al	1.50	1.48	1.50

The effects of citrate on the detection limit and Nernstian response of the electrode has been discussed earlier (see Fig. 2.3). In view of these effects it is essential to have a low concentration of citrate in the buffer (0.1 M). Any polyvalent ions capable of complexing fluorine (Fe, Al, etc.) will be bound by citrate and acetate. A description of the method of analysis for waters is given below:-

Reagents: (all chemicals are Analor grade)

a) TISAB buffer. Add 57 ml of glacial acetic acid, 58 gm of NaCl and 0.30 gm of sodium citrate to 500 ml of deionised water. Slowly add 5MNaOH until the pH is approximately 5.5. Make up to one litre with deionised water.

b) Calibration standards. Dissolve 2.2108 gm NaF which has been dryed at 110°C for 24 hrs. in one litre of deionised water to make a stock solution of 1,000 ug/ml F^-. Make up a working solution of 100 ug/ml F^- by diluting 100 ml of stock solution to one litre in deionised water. Make up calibration standards of 10, 1 and 0.1 ug/ml F^- by diluting 100 ml, 10 ml and 1 ml of working solution respectively to one litre using a 1:1 solution of TISAB and deionised water. All standards and stock solutions should be made up and stored in polythene bottles and not glassware.

Apparatus:

a) 100 ml polypropylene beaker

b) 50 ml clear plastic cylinder.

c) magnetic stirrer and magnets

d) fluoride specific ion electrode, reference electrode and Ionanalyser (Orion) of millivolt meter (Fig. 2.1).

Procedure:

Calibrate fluoride electrode system using the 1 and 0.1 ug/ml F^- standards. Adjust for variation in temperature if necessary. The 10 ug/ml F^- standard should be used for those samples having fluoride concentrations outside of the

> calibration range. In a 100 ml polypropylene beaker add 50 ml of the water sample to 50 ml of TISAB solution. Add a magnet and analyse stirred sample. The reading should be taken when the meter indicates steady equilibrium for the electrode system.
>
> The fluorine concentration in ug/ml is equal to twice the instrumental reading.

In natural waters the concentration of fluorine is generally of the order of 100-1,000 ppb. A 1:1 dilution with the buffer can generally be used without sacrificing precision or falling below the detection limit. If the fluorine levels are less than 100 ppb then a smaller dilution should be used. Full equilibration of the system, using a 1:1 dilution, is achieved in 2-3 minutes.

Precision (at 95% confidence level) over the normal concentration range (0.1 to 1.0 ppm F^-) varies from ±10% at the 1.0 ppm F level to ±20% at the 100 ppb F level. If required, the precision can be best increased by using titration methods as described in the Orion Handbook. For geochemical purposes the precisions shown above are more than adequate. Although no international water standards exist we can assume that the method is also accurate provided suitable decomplexing agents are used.

One of the unique features of the fluoride electrode is its ability to measure either ionic or total (ionic + complexed) fluorine in aqueous solutions. The author has used this characteristic to show that most of the fluorine in surface and groundwaters is in the free ionic state (See Table 1.14 Chapter I).

2.4 COLD-EXTRACTABLE FLUORINE (CxF$^-$) METHODS

Since the specific ion electrode is capable of measuring fluoride concentrations directly in solution without preconcentration, cold-extractable methods of fluorine analysis can be usefully employed by the exploration geochemist. Unlike most other methods of cold-extractable analysis the sample solution can be presented directly to the electrode instrumentation without carrying out tedious procedures of centrifuging and filtering. Suspended matter does not affect the performance of the electrode. In addition, the analyses are not prone to the bias and variation in analytical skill from which most colorimetric methods suffer.

Numerous extractant solutions can be used for CxF analysis, thus restricting the analyst only to such practical considerations as

a) the ability to adjust the pH and total ionic strength of the extractant solution

b) the most effective sample weight to solution ratio to obtain an adequate detection limit, and

c) the time required to reach a steady level of extraction.

Fortunately, since the specific ion electrode is capable of measuring very low levels of fluorine (down to 20 ug/1), point (b) is generally of little consideration and an adequate ratio can easily be adopted.

The most acceptable cold extractable method must give the highest possible contrast between background and anomalous results. The author had investigated three of the most practical extractants in an attempt to establish an optimum method that may be used in prospecting for a broad spectrum of ore deposits in which fluorine may occur. The extractants investigated were 0.01M NaOH; 0.01M HCl and TISAB (total ionic strength adjustment buffer). The TISAB contains IM NaCl, 0.25M acetic acid, 0.75M sodium acetate, and 0.001M sodium citrate and has a pH between 5-6.

TABLE 2.2

COMPARISON OF THE ANOMALY CONTRASTS OBTAINED BY VARIOUS METHODS OF FLUORINE ANALYSIS (-80 mesh)

Sample Description	Cold Extractable Fluorine (ppm)			Acid Diffusible Fluorine (ppm)	Total Fluorine (ppm)
	Tisab Buffer	0.01M NaOH	0.01M HCl		
Wheal Jane Tin Lode:					
Background Soil	26	32	34	260	560
Background Soil	32 (0.4)	67 (0.3)	84 (0.3)	500 (3.6)	780 (3.6)
Anomalous Soil	11	16	17	1150	2360
Anomalous Soil	11	17	22	1550	2400
Bepe Pegmatite:					
Background Soil	7	7	7	17	128
Background Soil	24 (1.4)	31 (1.7)	31 (2.1)	18 (15.3)	112 (13.7)
Anomalous Soil	39	61	68	370	2240
Anomalous Soil	5	6	13	175	1040
Richardson Pegmatite:					
Background Soil	6	11	44	300	780
Background Soil	12 (6.6)	14 (10.8)	145 (18.5)	380 (20.2)	640 (19.3)
Anomalous Soil	48	125	1000	2750	6200
Anomalous Soil	70	145	2500	11000	21200
Kaluwe Carbonatite:					
Background Soil	5	6	12	100	300
Background Soil	4 (15.6)	4 (18.2)	8 (97.0)	2650 (71.0)	260 (51.0)
Anomalous Soil	15	17	1600	8700	9760
Anomalous Soil	125	165	340	60	18800
Background Stream Sediment	3	3	45	95	155
Background Stream Sediment	11	11	96	170	350
Background Stream Sediment	3 (3.0)	3 (3.7)	4 (29.5)	125 (28.1)	185 (25.6)
Anomalous Stream Sediment	17	20	1900	3100	5000
Anomalous Stream Sediment	17	22	950	4200	6750

Numbers in brackets represent contrast factors calculated from $\frac{\text{Av. Anomalous F}}{\text{Av. Background F}}$

It is also used to neutralize the 0.01M NaOH and 0.01M HCl extractant solutions after leaching of the samples. The 0.01M HCl and 0.01M NaOH extractants, especially the former were eventually adopted by the author for the present research. Details of the analytical method are given at the end of this section.

Other cold extractants which can be employed are H_2O (deionized) and $FeCl_3$. The former has been used on granodiorite rock powders in an attempt to relate water-extractable fluoride to porphyry copper mineralization (Kesler et al 1973). This project, however, met with limited success. The use of H_2O as an extractant for soils and stream sediments is impractical as it lacks the ability to strip fluorine from clay minerals and colloidal precipitates. Schwartz and Friedrich (1973) have recently described the application of a 0.037M $FeCl_3$ solution for cold-extractable fluorine determination. For fluorite mineralization, this method gave an anomaly contrast which was greater than that obtained with the TISAB method and the total (NaOH fusion) method. In this study, no direct comparison was made with the HCl method, but work done in the same area by Pluger and Friedrich (1972) using 0.01M HCl as an extractant resulted in a contrast which is slightly greater than that obtained using $FeCl_3$.

A comparison of the various methods of fluorine analysis is given in Table 2.2 (for detailed descriptions of the acid diffusible and total methods of fluorine analysis see the relevant sections following this one). The calculation of the contrast factors may be considered somewhat tenuous on the basis of the amount of data available, but they do permit a rough comparison of the various methods. It should be noted that a contrast factor of less than one signifies a negative anomaly. Thus for the Wheal Jane tin lode none of the cold extractable methods are satisfactory. A large portion of the fluorine in these soils is probably in tourmaline (up to 0.4% F) and would not be extractable. Over the Bepe Pegmatite, where the fluorine in the soils is most probably present in micaceous minerals and apatite, the cold extractable methods give a slight contrast. Of the methods tried the HCl extractant appears to be the most effective, but even it gives a contrast which is far below that for the acid diffusible and total methods. For the Richardson pegmatite deposit a good contrast is achieved by all of the cold extractable methods, but again the HCl method is more effective. The B soil horizon over this deposit gives no anomalous expression, but the analyses given in Table 2. 2 for the Ao horizon soils show that considerable amounts of fluorine can be extracted from organic rich soil horizons. The contrast shown by the HCl method compares favourably with those for the acid diffusible and total methods. Pluger and Friedrich (1972) obtained similar results in a survey carried out in the Osor fluorspar area of Spain.

For the Kaluwe carbonatite area the HCl method shows the highest contrast. This is the only area where this method shows higher contrast than the acid diffusible and total methods. Fluorine is present in the soils and stream sediments primarily as fluorite, apatite and pyrochlore. Both fluorite and apatite are much more easily attacked by 0. 01M HCl than by 0. 01M NaOH (Table 2. 3).

TABLE 2. 3

COMPARISON OF NaOH AND HCl COLD-EXTRACTABLE METHODS FOR FLUORITE AND APATITE

Mineral (-200 mesh)	CxF$^-$ (ppm) (0. 01M NaOH)	CxF$^-$ (ppm) (0. 01M HCl)
Fluorite	5,100	11,000
Apatite	410	5,800

TABLE 2.4

COMPARISON OF TWO COLD EXTRACTABLE FLUORINE METHODS FOR VARIOUS CLAY MINERALS (-200 Mesh, all values in ppm)

Clay Mineral	CxF$^-$ (0.01M NaOH)	CxF$^-$ (0.01M HCL)	Total F
Kaolinite	260	260	22,400
Kaolinite	14	17	960
Kaolinite	5	12	204
Illite	130	310	2,240
Illite	14	110	900
Illite	9	23	1,420
Montmorillonite	11	26	780
Montmorillonite	16	27	1,940
Montmorillonite	22	37	1,560
Dickite	10	16	2,450
Dickite	38	48	4,192
Hectorite	110	120	16,800
Sepiolite	360	1,100	13,200
Halloysite	360	380	2,880
Halloysite	14	27	1,080
Attapulgite	280	580	4,060
Pyrophyllite	6	58	520
Metabentonite	6	15	740
Clinoptilolite	13	25	584

Furthermore the carbonate-rich soils over the carbonatite will be attached more vigorously by the HCl solution thus releasing more fluorine. If the soils contain high concentrations of carbonate (greater than 2%) this may have the adverse effect of neutralizing the HCl. For the Kaluwe soils the neutralizing effect of carbonate is noticeable when the individual values are compared with those obtained by other methods. The overall contrast obtained is, however, certainly high enough to compensate for this interference. In areas where low contrast may occur in carbonate-rich soils (e.g. fluorite deposits in limestone environments) a higher concentration or larger volume of HCl may be required for extraction. Initially, representative soil samples from the area to be surveyed should be used to determine the optimum concentration and volume of HCl solution required.

It is clear from the data of Table 2.2 that 0.1M HCl is a much more effective leaching agent than 0.01M NaOH or TISAB buffer. From this it follows that it is advisable to use HCl as an extractant in the majority of cases. However, if investigations are being carried out in areas having carbonate-rich soils and suspected low anomaly contrasts, it may be advisable to use the NaOH method because the larger volume or concentration required, as well as the resultant increase in the volume of TISAB solution for neutralization of the HCl, may result in a detection limit that is unacceptable. Comparisons of these two methods are given in the next chapter on prospecting applications.

A comparison of the leaching power of the NaOH and HCl extractants for various clay minerals is given in Table 2.4. For a number of clay minerals (kaolinite, dickite, hectorite and halloysite) both leaching agents exhibit an equal ability to extract fluorine;

TABLE 2.5

ANALYTICAL PRECISION FOR COLD-EXTRACTABLE (0.01M NaOH) FLUORINE METHOD

(10 analyses from 10 separate runs, all values in ppm, all samples -80 mesh)

Sample Description	Range	Mean	Stnd. Dev.	Precision (%)
Stream Sediment Draining Sandstone	1.2- 1.4	1.3	0.07	10.9
Stream Sediment Draining Granite	4.7- 5.1	4.9	0.15	6.2
Stream Sediment Draining Carbonatite	7.5- 8.5	8.0	0.25	6.2
Organic Soil	13.8-15.2	14.6	0.20	2.7

$$\text{Precision}_{(95\%\ \text{confidence limit})} = 200 \times \frac{\text{Stnd. Dev.}}{\text{Mean}}$$

TABLE 2.6

ANALYTICAL PRECISION FOR COLD-EXTRACTABLE (0.01M HCl) FLUORINE METHOD

(10 analyses from 10 separate runs, all values in ppm, all samples -80 mesh)

Sample Description	Range	Mean	Stnd. Dev.	Precision (%)
Stream Sediment Draining Sandstone	5.0- 6.5	5.5	0.58	21.1
Soil over Limestone	12.0-15.0	13.4	1.20	17.9
Soil over Sandstone	390-410	400	6.40	3.2
Stream Sediment Draining Carbonatite	450-500	471	16.49	7.0
Organic Soil	700-760	728	21.84	6.0

$$\text{Precision}_{(95\%\ \text{confidence limit})} = 200 \times \frac{\text{Stnd. Dev.}}{\text{Mean}}$$

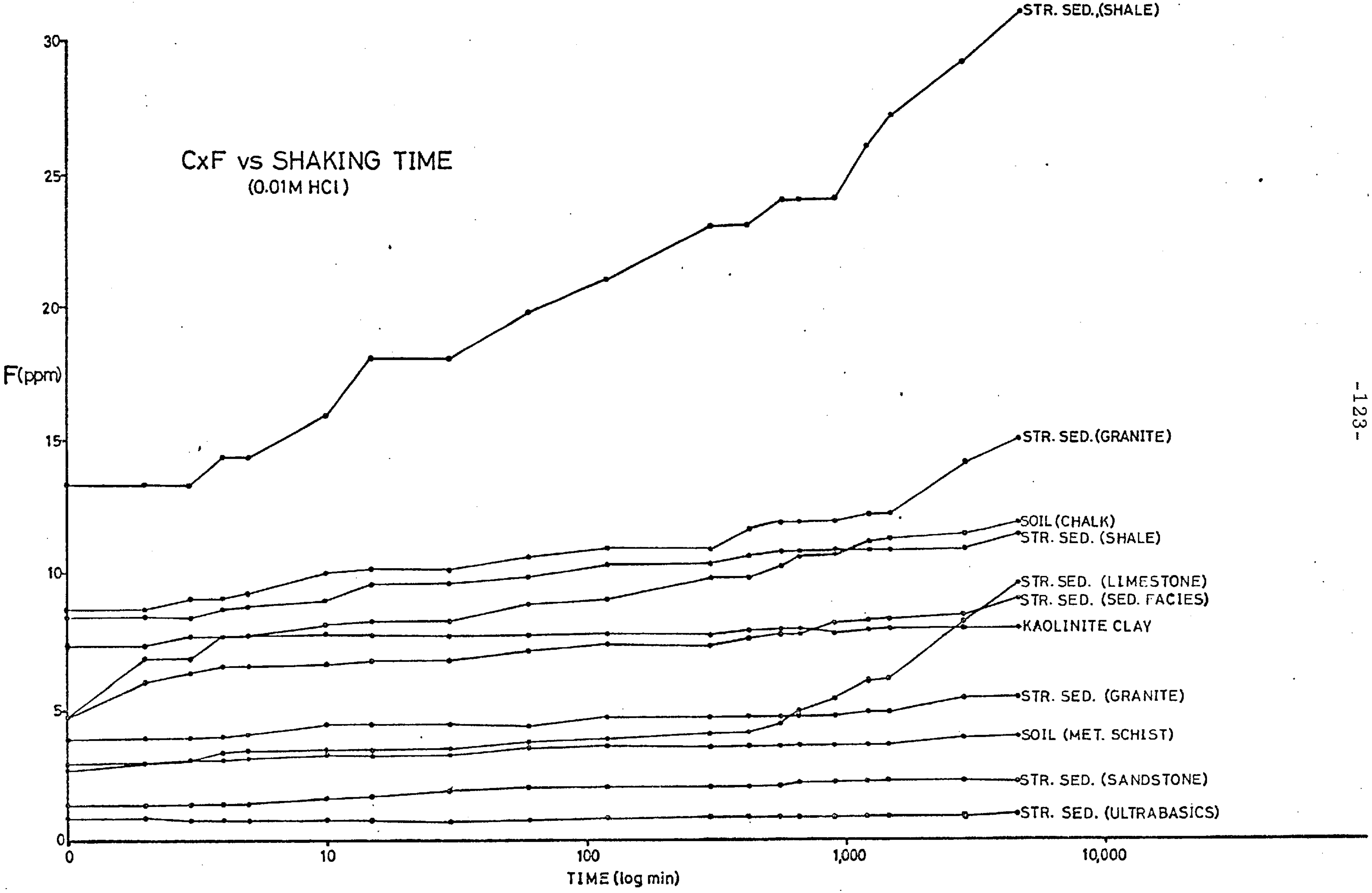


FIGURE 2.5 RELATIONSHIP BETWEEN EXTRACTABLE FLUORINE AND SHAKING TIME FOR 0.01M HCl CxF

for the clay minerals as a whole, however the HCl solution is a much more efficient extractant. The variation in leaching power between NaOH and HCl for the various clay minerals can be attributed to differences in the ability of the OH^- ion to isomorphously substitute for the F^- ion and for the H^+ ion to remove and bind F^- from its lattice positions. For example the fluorine in montmorillonite is more susceptible to H-F binding than to OH-F substitution, whereas, for kaolinite the two processes seem to be equally effective. In no case, however, does the leaching power of NaOH exceed that of HCl.

An assessment of the precision of these two extractant methods over the normal concentration range and for various sample types is given in Tables 2.5 and 2.6. For both methods there is a distinct increase in precision with increasing concentration. For the HCl method the precision varies from 21 percent at the 5 ppm level to 6 percent at the 700 ppm level. For the NaOH method the precision varies from 11 percent at the 1 ppm level to 3 percent at the 15 ppm level. The NaOH method is clearly the more precise method, but the precision for the HCl method is quite acceptable for the purposes of exploration. It is important, however, that the precision levels of these two methods are considered when planning an exploration program, especially if one expects to encounter low contrast anomalies.

The relationship between extractable fluorine and shaking time for the HCl method is given in Fig. 2.5. For most types of samples equilibrium is reached relatively quickly but a number of sample types may not reach equilibrium even after three days shaking. From this it follows that a constant shaking time be used. Large batches of samples can be shaken overnight (15 hours) and analyzed next day without any risk of significant leaching while the samples are awaiting analysis. Racks capable of holding eighty cylindrical 25 mm x 75 mm polyethylene containers can be accommodated overnight on a horizontal shaker.

The procedure for cold-extractable analysis using either 0.01M NaOH or 0.01M HCl as a leaching agent is as follows:

<u>Reagents</u>: (All chemicals are Analar grade)

a) 0.01M HCl or 0.01M NaOH

b) TISAB buffer. Dissolve 58g sodium chloride, 61.5g sodium acetate and 0.30g sodium citrate in 500 ml of deionised water. Add 57 ml glacial acetic acid. Slowly add 5M NaOH until the pH is approximately 5.5 and make up to one litre with deionised water.

c) Calibration standards. Dissolve 2.108g NaF which has been dryed at 110°C for 24 hours in one litre of deionised water to make a stock solution of 1,000 ug/ml F^-. Make up a working solution of 100 ug/ml F^- by diluting 100 ml of stock solution to one litre in deionised water. Make up calibration standards of 10 ug/ml F^-, 1 ug/ml F^- and 0.1 ug/ml F^- by diluting 100 ml, 10 ml and 1 ml of working solution respectively to one litre using a 1:1 solution of TISAB buffer and extractants (0.01M HCl or 0.01M NaOH). All standards and stock solutions should be made up and stored in polythene bottles and <u>not</u> glassware.

<u>Apparatus</u>:

a) 25mm x 75mm snap top polyethylene container.

b) racks capable of holding 80-100 containers

c) horizontal shaker

d) automatic dispenser capable of dispensing 15 ml of solution.

e) 100 ml polypropylene beakers

f) magnetic stirrer and magnets

g) fluoride specific ion electrode, reference electrode and Ionalyser (Orion) or millivolt meter (Fig. 2.1).

Procedure:

Weigh 0.25 gm of the sample into a cylindrical 25 mm x 75 mm polyethylene container with a hinged snap top lid and add 15 ml of extractant solution (0.01M HCl or 0.01M NaOH) by automatic dispenser. Put the racks containing the polyethylene containers on a horizontal shaker and shake for 15 hours (overnight). Using an automatic dispenser add 15 ml of TISAB buffer to give a 1:1 dilution. The resultant solution should be in the pH range 5-6. Calibrate the electrode system using 0.1, 1.0 and 10 ug/ml F^- standards, adjusting for temperature variation if necessary. Pour the contents of the polyethylene containers into corresponding polypropylene beakers (100 ml) and add a small magnetic stirrer to each. Solution concentration can be read directly from the Orion Analyser. Care should be taken not to allow the electrode to come into contact with the stirrer as the LaF_3 crystal may become scratched and will no longer exhibit true Nernstian response. Stirring the sample diminishes the response time of the electrode. From two to three hundred samples can be analysed per man-day. The following formula gives the fluorine concentration of the sample.

$$\text{Concentration (ug/gm)} = \frac{\text{ug/ml x 30 ml}}{\text{0.25 gm}}$$

The theoretical detection limit in 2.4 ug/gm (based on the solubility product of the LaF_3 membrane).

The highly portable nature of the electrode instrumentation makes cold extractable fluorine analysis particularly attractive as an in-field method of analysis. The instrumentation can be set up easily in a tent or mobile laboratory, and the method of extraction employed can be mechanized along the lines of those described above.

2.5 ACID DIFFUSIBLE FLUORINE ANALYSIS

In geochemical exploration it is often desirable to use a method of analysis which, in addition to being fast, efficient and reasonably precise, will determine a major proportion of the element present and produce a significantly high anomaly contrast. The method need not be a total method

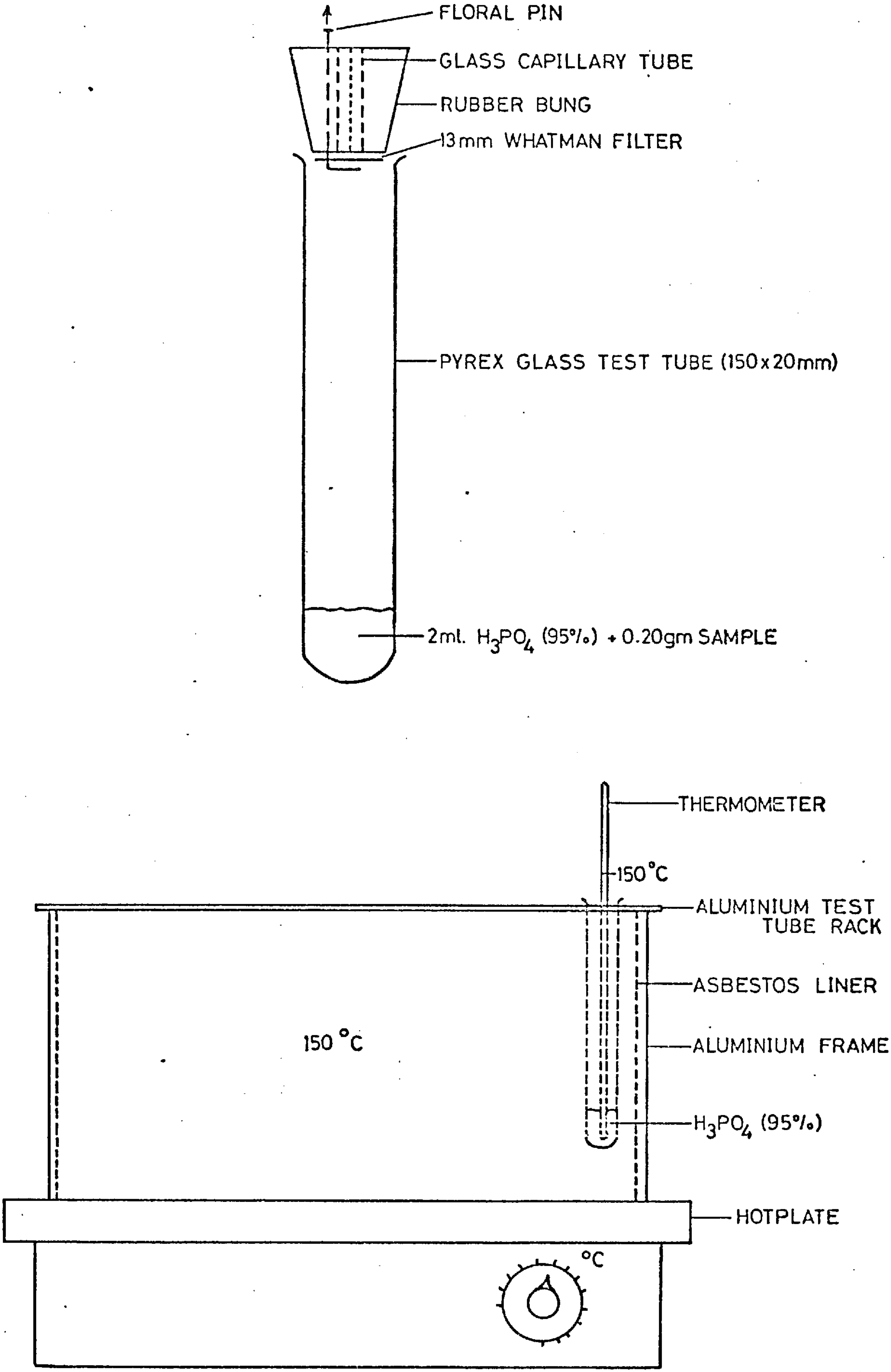


FIGURE 2.6

SCHEMATIC DIAGRAM OF DIFFUSION CELL AND HEATING FRAME FOR THE DETERMINATION OF ACID DIFFUSIBLE FLUORINE (not to scale) but should give reproducible results. The chemical attack stage of most of these methods requires the use of either a hot acid or weak alkaline flux. The efficiency of attack of weak alkali fluxes is often difficult to control and may result in poor precision. For the present research it was decided, therefore, to develop a method of partial extraction for fluorine using hot acid as the attacking agent.

The desire for an efficient partial extractant analytical method for fluorine is further emphasized when one considers that the cold-extractable methods fail to give adequate contrast for a large number of mineral deposits (see Table 2. 2). For this reason the author has utilized the ability of fluorine to volatilize as HF from acid solution in the development of an acid diffusion method of analysis.

Acid diffusion methods have long been used in biological analysis. Hall (1960), Frere (1961) and more recently Stuart (1970) have described micro-diffusion methods for the determination of fluorine in biological materials. These methods unfortunately require the use of perchloric acid for attacking the ashed sample. Ashing of organic-rich geochemical samples to prevent explosive reactions with the perchloric acid is time consuming and, therefore, unacceptable. In addition any attempt to speed up diffusion by increasing the temperature would result in partial volatization of the perchloric acid and hence eventual attack of the trapping medium. This latter point is true for all strong acids with the exception of phosphoric acid. On this account it was decided to develop a method using orthophosphoric acid (95%) as the attacking agent.

A description of the method eventually adopted is given below.

Reagents: (All chemicals are Analar grade)

a) Analar orthophosphoric acid (95%).

b) 5M NaOH. Dissolve 200g NaOH in one litre of deionised water and store in a polythene bottle.

c) TISAB buffer. Dissolve 58 gm sodium chloride, 61.5 gm sodium acetate and 0.30 gm sodium citrate in 500 ml of deionised water. Add 57 ml glacial acetic acid. Slowly add 5M NaOH until the pH is approximately 5.5 and make up to one litre with deionised water.

d) Calibration standards. Dissolve 2.108 gm NaF which has been dryed at 110°C for 24 hours in one litre of deionised water to make a stock solution of 1,000 ug/ml F^-. Make up a working solution of 100 ug/ml F^- by diluting 100 ml of stock solution to one litre in deionised water. Make up calibration standards of 10 ug/ml F^-, 1 ug/ml F^- and 0.1 ug/ml F^- by diluting 100 ml 10 ml and 1 ml of working solution respectively to one litre using TISAB buffer. Add 1.5 ml of 5M NaOH to each standard (before making up to one litre) to give a solution matrix similar to that for the sample solution. All standards and stock solutions should be made up and stored in polythene bottles and not glassware.

Apparatus: (see Fig. 2.6)

a) heating frame consisting of a hot plate, aluminium frame, asbestos lining and aluminium test tube rack capable of holding 100 test tubes (Fig. 2.6).

b) fume cupboard for heating frame

c) one hundred 150 x 20 mm pyrex test tubes

d) 100 filter traps consisting of a rubber bung (No.15), glass capillary tube, floral pin and 13 mm Whatmann filter papers. Put floral pin and glass capillary tube in bung as shown in Fig. 2.6. Bend the end of the floral pin. Pierce the filter paper with the end of the pin and draw the pin out to hold the paper tight against the capillary tube.

e) 30 microlitre Eppendorf pipette and an automatic dispenser capable of dispensing 20 ml of solution.

f) one hundred 100 ml polypropylene beakers.

g) magnetic stirrer and magnets.

h) fluoride specific ion electrode, reference electrode and Ionanalyser (Orion) or millivolt meter (Fig. 2.1).

Procedure:

Set the heating frame (Fig. 2.6) up in a fume cupboard. Cover the aluminium test tube rock leaving one hole for a test tube containing a few mls of orthophosphoric acid and a thermometer. Adjust the temperature until the acid is at 150°C.

Weigh 0.20g of sample into a test tube. Add 2 ml of orthophosphoric acid (95%). Add 30 µl of 5M NaOH to the filter paper on the end of the bung and securely fasten the bung in the end of the test tube. Carry out the above procedure for 100 samples (including 10 replicates and 2 blanks).

Put the test tubes in the test tube rack of the heating frame and allow diffusion to proceed for 20 hrs. (overnight) at 150°C. Remove the test tubes from the heating frame and allow to cool. Using an automatic dispensor add 20 mls of TISAB buffer to each of 100 polypropylene beakers. Remove the bungs from the test tubes and immerse the filter ends in the TISAB buffer for 10 minutes. Remove the bungs from the beakers giving them a stir in the buffer beforehand.

Calibrate the electrode system using 10, 1 and 0.1 ug/ml F^- standards and correct for temperature variation if necessary. Add a magnet to each sample solution and measure the F^- concentration, checking standards when necessary. The following formula gives the fluorine concentration of the sample.

$$\text{Concentration (ug/gm)} = \frac{\text{ug/ml x 20 ml}}{\text{0.20 gm}}$$

The theoretical detection limit is 2 ug/gm (based on the solubility product of the LaF_3 membrane).

A standard pyrex glass test tube is used both to aid diffusion and permit the use of a high diffusion temperature (150°C). Any HF which may react with the glass before reaching the filter trap will produce H_2SiF_6 which is also volatile. The capillary tube in the rubber bung allows pressure equilization and at the same time ensures that any fluorine vapour is trapped on the filter and does not escape. The diffusion should take place in a

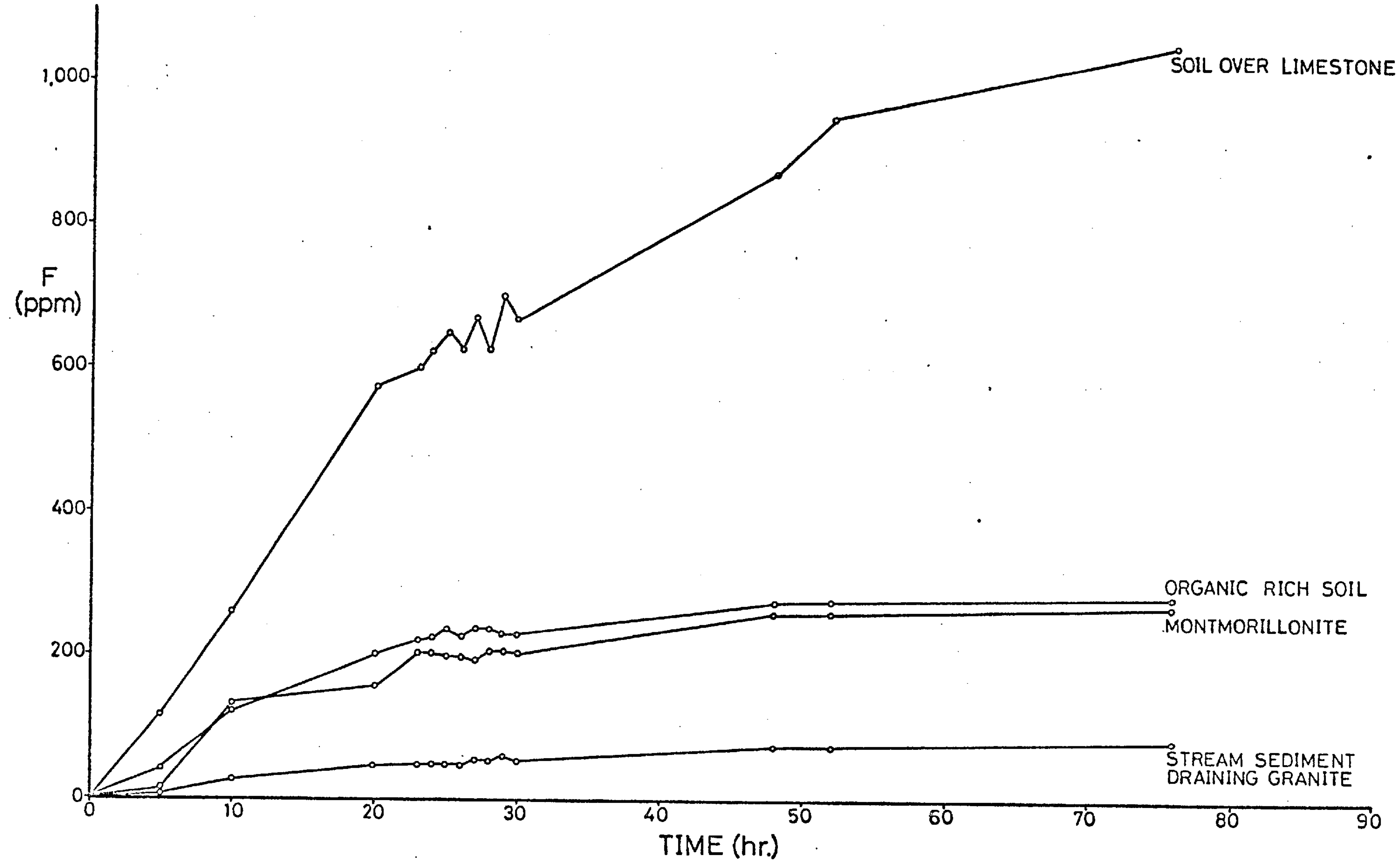


FIGURE 2.7

RELATIONSHIP BETWEEN DIFFUSIBLE FLUORINE AND DIFFUSION TIME FOR VARIOUS SAMPLE MATRICES (-80 mesh) fume cupboard, but the draught should not be turned on as this causes a temperature gradient across the heating frame.

One of the critical factors which must be considered with diffusion analysis is time. In order to test the efficiency of the diffusion method, standard F^- concentrations were allowed to diffuse overnight (Table 2.7). It can be seen from these data that complete diffusion for readily available F^- occurs within 20 hours.

TABLE 2.7

EFFICIENCY OF ACID DIFFUSION METHOD FOR STANDARD FLUORIDE SOLUTIONS (20 hour diffusion)

F^- added (ug)	F^- measured (ug)
Blank	0.0
0.5	0.5
1.0	1.0
5.0	4.9
10.0	10.0
50.0	49.0
100.0	98.0
1000.0	1000.0

A plot of the measured fluorine concentration against diffusion time for various sample types is given in Fig. 2.7. With the exception of carbonate-rich samples most of the fluorine which can be diffused from the sample is trapped on the filter within 24 hours. Furthermore, the variation in fluorine content obtained after 20 hours compared with that after 30 hours is small. For carbonate-rich samples the evolution of CO_2 may cause some retardation of the HF diffusion. Tests using standard fluorine concentrations added to $CaCO_3$ indicated, however, that this was not as serious a problem as originally anticipated (Table 2. 8).

TABLE 2. 8

EFFECT OF CARBONATE ON THE DIFFUSION OF FLUORINE (Standard F concentrations added to 0. 1 gm of $CaCO_3$; 20 hour diffusion)

F^- added (ug)	F^- measured (ug)
1	0. 0
5	4. 0
10	9. 2
50	45. 0
100	95. 0
1000	900. 0

A sample would have to contain more than 50 percent $CaCO_3$ before any serious interference would occur. If carbonate-rich samples are suspected longer diffusion times and a higher temperature should be employed. In this respect representative samples should be used to determine optimum time and temperature. During routine analysis carbonate-rich samples can be easily detected by noticeable (but not vigorous) bubbling of the acid. These samples can then be allowed to diffuse for a slightly longer period of time (30 hours). In the case of the Kaluwe carbonatite the presence of carbonates has had little effect on the anomalies obtained by the diffusion method (Table 2. 2).

TABLE 2.9

EFFECTS OF COMPLEXING IONS ON HF DIFFUSION (500 mg of complexing ion added)

Complexing ion	F^- added (ug/ml)	F^- measured after diffusion (ug/ml)
Fe	0.50	0.50
Fe	1.00	0.99
Fe	10.00	10.00
Al	0.50	0.50
Al	1.00	0.98
Al	10.00	9.90
B	0.50	0.52
B	1.00	1.00
B	10.00	10.05

As shown in Table 2.9 there is no noticeable effect on analyses of fluorine from ions which are capable of complexing fluorine in aqueous solution. In acid solution HF is the dominant complex.

The analytical precision of the diffusible method for various sample matrices is given in Table 2.10. There is a trend towards better precision with higher concentration and the effect on precision of the different sample matrices is clearly evident. Although not often described this is a common feature of all methods of analysis in geochemistry based on strong partial attack of the sample. The data in Table 2.10 certainly suggest that over the concentration range of 56 to 2,870 ppm the precision

TABLE 2. 10

ANALYTICAL PRECISION FOR ACID DIFFUSIBLE FLUORINE ANALYSIS (15 analyses from 15 separate runs, all values in ppm, all samples -80 mesh except clays which are -200 mesh)

Sample Description	Range	Mean	Stnd. Dev.	Precision (%)
Stream Sediment Draining Ultrabasics	40- 65	56	6. 3	22. 6
Stream Sediment Draining Sandstone	70- 90	79	6. 8	17. 2
Stream Sediment Draining Granite	75- 95	86	8. 0	18. 6
Stream Sediment Draining Granite	100-130	110	9. 7	17. 7
Stream Sediment Draining Shale	125-160	137	12. 4	18. 0
Stream Sediment Draining Marl	125-170	156	12. 3	15. 8
Soil over Sandstone	240-270	252	10. 3	8. 2
Montmorillonite	300-360	328	16. 9	10. 3
Organic Soil	310-350	330	15. 1	9. 1
Kaolinite	320-360	333	16. 9	10. 2
Soil over Tin Mineralization	365-390	379	7. 7	4. 1
Stream Sediment Draining Shale	360-500	467	55. 7	23. 8
Soil over limestone	459-490	473	14. 8	6. 3
Stream Sediment Draining Granite	450-510	485	15. 8	6. 5
Soil over Carbonatite	2600-3100	2870	143. 8	10. 0

$$\text{Precision}_{(95\%\text{ confidence limit})} = 200 \times \frac{\text{Stnd. Dev.}}{\text{Mean}}$$

TABLE 2.11

COMPARISON OF TOTAL AND ACID DIFFUSIBLE FLUORINE ANALYSIS FOR VARIOUS MINERALS

Mineral	-80 + 200 mesh			-200 mesh			Total fluorine -80+200/-200 (%)
	Total F	Acid Diffusible F	% of Total	Total F	Acid Diffusible F	% of Total	
Apatite	40,000	36,000	90	40,000	38,000	95	100
Topaz	97,500	50	0.05	100,000	225	0.25	98
Tourmaline	4,900	120	2	5,000	125	2.5	98
Pyrochlore	-	-	-	42,500	28,500	66	-
Zircon*	150	25	17	440	40	9	34
Beryl*+	65	0.0	0.0	65	5	8	-
Rutile	-	-	-	60	5	8	-
Perovskite	-	-	-	7,600	4,600	60	-
Augite	60	0.0	0.0	60	5	8	100
Hornblende	700	260	37	750	400	53	93
Nepheline	70	10	14	80	30	38	88
Kyanite	410	30	7	450	30	7	91
Goethite	100	30	30	100	30	30	100
Bauxite	175	40	23	175	85	49	100
Tantalite+	160	90	56	325	150	46	49
Gadolinite	1,010	460	46	1,175	750	64	86
Amblygonite	72,500	20,000	28	72,500	31,000	43	100
Monazite	150	90	60	210	125	60	72
Samarskite	900	750	83	1,025	750	73	88
Triphylite	305	160	53	330	225	64	93
Cerite	23,000	14,500	63	29,500	17,000	58	78
Xenotime	1,450	900	62	2,100	1,750	83	69
Thorite*	675	800	119	800	900	113	84
Columbite	65	15	23	65	35	54	100
Axinite	120	20	17	160	25	16	75
Allanite	190	35	19	190	135	71	100
Talc	90	5	6	90	5	6	100
Serpentine	90	0.0	0.0	95	5	5	95
Biotite	39,000	13,000	33	39,000	13,500	35	100
Phlogopite	15,500	325	2	15,250	335	2	98
Muscovite	1,400	550	39	1,425	700	49	98
Lepidolite	6,000	2,850	48	7,500	3,750	50	80
Vermicullite	11,000	3,900	35	11,000	4,100	37	100
Chlorite	100	50	50	100	60	60	100

\+ Mineral not completely attacked by NaOH fusion

* Total fluorine content of these minerals is low due to interference by Zr, Be and Th complexation.

of this method is better than ±25% at the 95% confidence level. It should be born in mind, however, that it is useful to have some idea of the actual precision for the different sample matrices when making a final interpretation of the geochemical data. This is especially so if one expects to encounter low contrast anomalies.

As with any analytical method which involves a partial attack of the sample, it is useful to have some understanding of the ability of the attacking agent to decompose various minerals. This is particularly important if one wishes to apply the method to mineral exploration. Table 2.11 illustrates the ability of orthophosphoric acid to attack various fluorine-bearing minerals. Two size fractions have been used to determine the effect of grain size on the efficiency of attack by the acid. Fluorspar is not included in this table as its fluorine content (45%) is much greater than can normally be handled by the trapping filter. It is known, however, that hot orthophosphoric acid readily dissolves fluorspar. For a number of minerals a decrease in size fraction results in a more efficient attack by the orthophosphoric acid (see last column of Table 2.11). The differences are, however, not marked enough to warrant the use of a finer size fraction such as -200 mesh. Furthermore, many of these minerals would not be present in the -200 mesh in nature. Apatite, hornblende, the rare earth pegmatite minerals and the micaceous minerals are appreciably attacked by hot orthophosphoric acid. Apatite is almost completely dissolved and its fluorine content readily released for diffusion. Phlogopite is the only micaceous minerals which shows a significant resistance to acid attack. Allanite, axinite, columbite, nepheline and zircon are moderately attacked, whereas kyanite, tourmaline and talc are only slightly attacked. Augite, serpentine and the important fluorine bearing mineral, topaz, are extremely resistant to attack.

TABLE 2.12

COMPARISON OF TOTAL AND ACID DIFFUSIBLE FLUORINE ANALYSIS FOR VARIOUS CLAY MINERALS (-200 Mesh, all values in ppm)

Clay Minerals	Acid Diffusible F	Total F	% of Total
Kaolinite	11,750	22,400	52
Kaolinite	350	960	36
Kaolinite	50	204	25
Illite	725	2,240	32
Illite	450	1,420	32
Illite	325	900	36
Montmorillonite	350	1,560	23
Montmorillonite	550	1,940	28
Montmorillonite	190	780	24
Dickite	2,550	4,192	61
Dickite	1,200	2,450	49
Hectorite	7,250	16,800	43
Sepiolite	3,250	13,200	25
Halloysite	1,500	2,880	52
Halloysite	650	1,080	60
Attapulgite	1,150	4,060	28
Pyrophyllite	150	520	29
Metabentonite	300	740	41
Clinoptilolite	125	584	21

In view of the large variation in the ability of orthophosphoric acid to attack various fluorine-bearing minerals it is important to have some understanding of the form in which fluorine exists in the mineral deposits prior to carrying out geochemical surveys employing fluorine as an indicator. The anomaly contrasts obtained for the various deposits studied by the author (Table 2.2, see CxF section) would suggest that the acid diffusion method is as good as, if not better than, the total method. In terms of speed of analysis it is also comparable to the total method.

The ability of orthophosphoric acid to attack various clay minerals is shown in Table 2.12. The amount of fluorine obtained by diffusion varies from 20 to 60 percent. Of the more important clay minerals, kaolinite and illite are more easily attacked than montmorillonite.

There is a very poor correlation between the percentage of total fluorine which can be diffused from the various clay minerals and the percentage of total fluorine which can be extracted by 0.01M HCl (Fig. 2.8). It would appear therefore that the amount of fluorine extracted from clays by hot orthophosphoric acid will vary with the ability of the acid to attack the

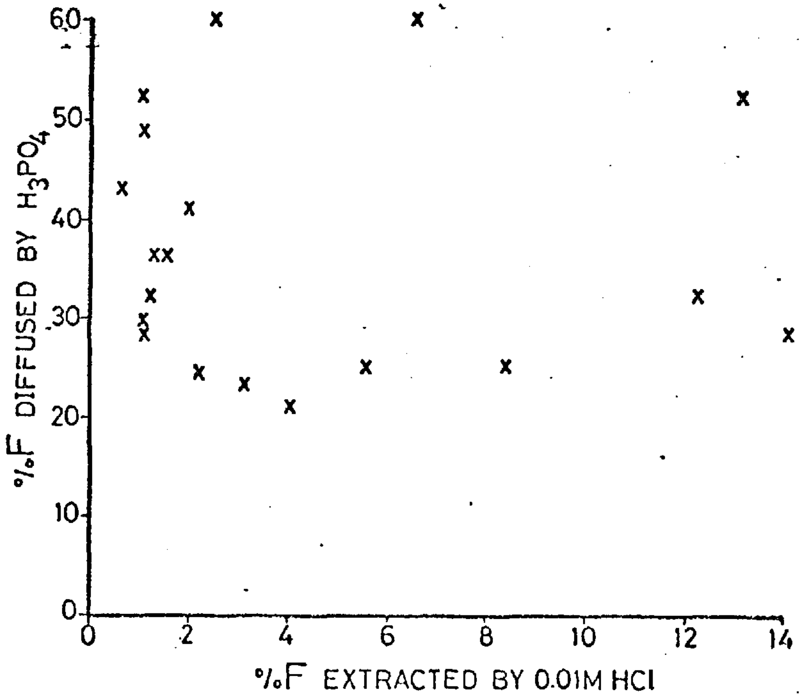


FIGURE 2.8

RELATIONSHIP BETWEEN THE PERCENT OF TOTAL FLUORINE EXTRACTED FROM VARIOUS CLAY MINERALS BY THE CxF(0.01M HCl) AND ACID DIFFUSIBLE METHODS structure of a particular clay mineral and release lattice bound fluorine.

2.6 TOTAL FLUORINE ANALYSIS

Prior to the development of the specific ion electrode the analysis of geochemical materials for total fluorine could be accomplished only by the steam distillation method of Willard and Winter (1933) or some adaptation of it. For silicates this method necessitated a preliminary fusion attack on the sample before distillation. The steam distillation was then carried out using sulphuric, perchloric or phosphoric acid and measurement of the fluorine concentration was done either volumetrically or colorimetrically. Although accurate, the method is slow, and the number of samples that can be analysed per day is low. A considerable amount of proficiency is also required in carrying out the distillation technique. For the purposes of geochemical exploration this method is, therefore, unacceptable. It is however, commonly used in more precise geochemical work, although the final measurements are generally performed with the aid of the specific fluoride ion electrode. Recent methods utilizing distillation techniques are described by Grimaldi et al 1955; Hollingworth, 1957 and Ingram and May 1971.

Since the introduction of the specific ion electrode by Frant and Ross (1966), a number of methods which obviate the use of steam distillation have been described. With the exception of a specific method for the analysis of phosphates (Edmonds, 1969) all of these methods involve fusion of the sample, leaching of the fusion product, and measurement of the fluorine in a suitably buffered solution.

Considering the great variety of minerals in which fluorine may occur the use of a proper flux is important in the development of a total method. Ficklin (1970) described a method which requires sintering of the sample with Na_2CO_3-KNO_3, but the ability of this flux to completely decompose many of the fluorine-bearing resistate minerals is doubtful. The significantly lower results which he obtained from samples which had been previously analysed by the distillation method would seem to bear this out. Farrell (1974) modified this method slightly by fusing the sample matter rather than sintering it. Higher and more consistent results were obtained, but the above comment on the ability of the flux to completely break down the more resistate minerals still applies. Peters and Ladd (1971) investigated the use of $Na_2O_2 + Na_2CO_3$ as a flux. They found that the majority of samples analysed were readily attacked, but those samples which were high in CaO were found to be resistant to the $Na_2O_2 + Na_2CO_3$ fusion. The use of $Na_2CO_3 + KNO_3$ or $Na_2O_2 + Na_2CO_3$ as fluxes for total analyses is only justified for fluorine-bearing minerals that are not highly resistant to attack by these fluxes.

A more universal total method for fluorine requires a stronger alkaline flux than the ones described above. For this reason, NaOH has been investigated both by the author and other workers (Van Loon, 1968 and Pluger and Friedrich, 1972). Although NaOH is one of the most powerful alkaline flux at our disposal, problems arise in its use for fluorine analysis since the resultant fusions are difficult to buffer because of high alkalinity.

The methods described by Van Loon (1968) and Pluger and Friedrich (1972) have a number of serious drawbacks as regards their application in geochemical exploration. To allow for the eventual pH adjustments the former method requires the counting out of a specific number of NaOH pellets for the fusions while the latter method requires the use of a specific weight of NaOH. Both these methods of controlling the amount of flux are not only time consuming but difficult to perform, because NaOH is an extremely hygroscopic compound and a difficult chemical to handle in the dry state. These methods also suffer from the fact that a number of steps are required to buffer the final solution. The author has alleviated these problems by using the high solubility of NaOH in deionised water to make up a concentrated 'wet flux' and by matching a specific aliquot of this flux (2.8 ml) to 100 ml of a concentrated buffer (pH 5.0) to give a final solution pH of 7.0 - 7.5. In the analytical procedure the flux can, therefore, be added to the sample much more easily and buffering of the fused sample requires only one step.

A detailed description of this method follows:

Reagents: (All chemicals are Analar grade)

a) Concentrated NaOH solution. In a large thick walled 2 litre polythene bottle containing 1l of deionized water add 1kg of NaOH in 100 gm portions, waiting for each portion to dissolve before adding the next. Shake the solution until all the NaOH has dissolved. NOTE: this is an exothermic reaction.

b) Citrate-acetate buffer. To a 20 litre container add 2.5kg sodium citrate and 500 gm sodium chloride. Make up to 20 litre mark with deionised water adding 550 ml of glacial acetic acid before mark is reached. Shake until all chemicals have dissolved. Check effectiveness of buffer by adding 3.0 ml of the concentrated NaOH solution to 100 ml of the buffer. The pH should be in the range 7.0-7.5. If the pH is too alkaline then slowly add more acetic acid continually checking until the right pH range is achieved. Similarly if the pH is too acidic add 5M NaOH. This is enough buffer for 200 determinations.

c) Calibration standards. These should be made up in the citrate-acetate buffer solution to which has been added enough concentrated NaOH (approximately 30 ml/l of buffer) to give a pH of 7.0-7.5. For a stock solution of 1,000 ug/ml F^- dissolve 2.108 gm NaF (which has been dryed at 110°C for 24 hrs) in one litre of the above solution. For a working solution of 100 ug/ml F^- dilute 100 ml of stock solution to one litre using the adjusted buffer solution. Make up calibration standards of 10, 1 and 0.1 ug/ml F^- by diluting 100 ml, 10 ml and 1 ml of working solution respectively to one litre with the adjusted buffer solution. Standards will have the same solution matrix as the sample solution.

d) Isopropyl alcohol

Apparatus: (for 100 determinations)

a) muffle furnace

b) one hundred 20 ml nickel crucibles and lids

c) six crucible racks made from 1/16" sheet steel with three rows of six holes and the corners turned down for legs. Racks can be labelled using metal stamps.

d) metal tongs and asbestos sheets to put hot racks on

e) drying over capable of 200°C

f) one hundred 100 ml polypropylene beakers

g) magnetic stirrer and magnets,

h) pipette calibrated to deliver 3.0 ml and fitted with a suction bulb.

i) pH paper covering neutral range

j) fluoride specific ion electrode, reference electrode and Ionanalyser (Orion) or millivolt meter (Fig. 2.1).

Procedure: (for 100 determinations)

Weigh 0.25 gm of sample into a nickel crucible. Do this for 100 samples (including replicates and blanks). Add to each crucible 3.0 ml of concentrated NaOH solution. Add 1 to 2 ml of isopropyl alcohol to facilitate the mixing of the sample and flux.

Place the racks of samples in a drying oven at 200°C for 1 to $1\frac{1}{2}$ hours or until all of the water has been evaporated from the flux. Remove each rack in turn from the drying oven and place nickel lids on the crucibles. Place each rack in turn in a muffle furnace at 420°C for 20 minutes, after which remove the rack and let the samples cool. Racks of samples should be left in the heating oven until it is time for them to be fused. This prevents the flux from taking on water which may result in a violent reaction in the muffle furnace.

After the samples have cooled put the crucibles and lids in polypropylene beakers containing 100 ml of citrate-acetate buffer. Let the fused samples soak in the buffer solution for 10 to 15 minutes with the crucibles on their sides. Stir the samples using a plastic stirring rod until the fusion is completely disintegrated. Remove the crucibles and lids and add a magnetic stirrer to each beaker. Test the final pH with pH paper to ensure a pH of 7.0 to 7.5. If the pH is out of this range add dropwise 1M NaOH or 1M HCl, whichever is required, until the right pH is attained. Allow sample solutions to cool to room temperature before analysis.

Calibrate fluoride electrode system using 10, 1 and 0.1 ug/ml F^- standards and adjust for temperature variation if necessary.

Sample concentrations can be measured using the following formula

$$\text{Concentration (ug/gm)} = \frac{\text{ug/ml x 100 ml}}{\text{0.25 gm}}$$

The theoretical detection limit is 8 ug/gm (based on the solubility product of the LaF_3 membrane).

Although the use of a muffle furnace greatly increases production, fusions can be done over a bunsen burner, and the method can easily be adapted for use in a mobile laboratory.

TABLE 2.13

ANALYTICAL PRECISION FOR TOTAL FLUORINE ANALYSIS (15 analyses from 15 separate runs, all values in ppm, all samples -80 mesh except rocks which are -200 mesh)

Sample Description	Range	Mean	Stnd. Dev.	Precision (%)
Picrite	24- 36	31	4.7	30.4
Stream Sediment Draining Ultrabasics	140-152	144	4.0	5.6
Stream Sediment Draining Sandstone	148-156	149	3.3	4.4
Stream Sediment Draining Granite	152-180	164	5.7	6.9
Stream Sediment Draining Granite	200-220	209	6.5	6.2
Stream Sediment Draining Marl	372-396	379	7.5	4.0
Black shale	540-580	557	14.9	5.3
Stream Sediment Draining Shale	580-640	604	24.1	8.0
Organic Soil	580-672	621	30.1	9.7
Stream Sediment Draining Shale	1120-1280	1213	42.5	7.0
Stream Sediment Draining Limestone	1280-1440	1372	43.3	6.3
Soil over Limestone	1320-1480	1383	45.8	6.6
Quartz Porphyry	1960-2090	2012	33.8	3.4

$$\text{Precision}_{\text{(95\% confidence limit)}} = 200 \times \frac{\text{Stnd. Dev.}}{\text{Mean}}$$

TABLE 2.14

COMPARISON OF ANALYTICAL DATA FOR FLUORINE CONTENT (ppm) IN UNITED STATES GEOLOGICAL SURVEY STANDARD ROCK SAMPLES

Standard	Reference*	Reported Range	Reported Mean**	Range, This Study	Mean, This Study**
G-2 (Granite)	1,3,4,5,7	1190-1320	1230(13)	1240-1280	1267(3)
GSP-1 (Granodiorite)	1,3,5,6,7	3300-3900	3720(12)	3720-3800	3773(3)
BCR-1 (Basalt)	2,4,5,7	400- 500	465(12)	448- 460	456(3)
AGV-1 (Andesite)	1,4,5,7	320- 440	377(12)	396- 400	397(3)
PCC-1 (Peridotite)	2,4,7	11- 30	18(8)	14- 15	14.2(3)
DTS-1 (Dunite)	2,4,7	10- 24	18(8)	15- 16	15.7(3)

* 1. Abbey (1968) in Flanagan (1969); 2. Cattermole and Fuge (1969); 3. Fuge and Power (1969); 4. Huang and Johns (1967); 5. Sen Gupta (1968); 6. Hall and Walsh (1962); 7. Terashima (1974).

** numbers in brackets represent number of analyses

Table 2.13 gives the analytical precision for a variety of sample types over the concentration range 31-2,012 ppm. For concentrations greater than 100 ppm, the precision is better than ±10 percent at the 95 percent confidence limit. It is interesting to note that the precision for concentrations greater than 100 ppm does not decrease numerically with increasing concentration as would normally be expected for samples of constant matrix. The precision, therefore, depends on the sample matrix. The variation in precision with sample composition follows no recognized pattern, and no generalizations can be made with the exception that samples rich in organic matter may give slightly poorer precision. For geochemical exploration the differences in the precision levels are not great enough to seriously affect interpretation, and the overall precision of ±10 percent for concentrations greater than 100 ppm is quite acceptable. For concentrations between 8 (detection limit) and 100 ppm the precision is much less than at the higher concentrations (±30% at the 30 ppm level). The precision at these levels must, therefore be taken into consideration when interpreting data sets within this concentration range. With the exception of ultrabasic rocks most solid geochemical materials contain more than 100 ppm F, and good precision can, therefore, be expected.

The accuracy of the method described is demonstrated in Table 2.14. The range and mean fluorine contents for the various rock standards compare very well with the reported ranges and means in the literature.

A number of factors which may affect the accuracy and precision of the method described have been studied.

The effect of fusing time on the determination of total fluorine is shown in Table 2.15. No appreciable increase in the fluorine content occurs after fusing for 10 minutes. It would appear that the majority of the sample

TABLE 2.15

EFFECT OF FUSING TIME ON THE DETERMINATION OF TOTAL FLUORINE (samples fused at 420°C after H_2O had been driven from flux at 200°C for 45 minutes)

SAMPLE TYPE	FUSING TIME (min.)	FLUORINE (ppm)
Organic soil (-80 mesh)	10	700
	20	700
	30	700
	40	688
	50	700
	60	712
Inorganic soil (-80 mesh)	10	1,760
	20	1,800
	30	1,840
	40	1,800
	50	1,890
	60	1,800
Rock (quartz porphyry)	10	2,400
	20	2,480
	30	2,600
	40	2,400
	50	2,560
	60	2,440

TABLE 2. 16

VARIATION IN TOTAL FLUORINE CONCENTRATION WITH STANDING TIME FOR VARIOUS SAMPLE TYPES

Sample Description	Fluorine (ppm)			% Increase (24 hrs.)	% Increase (48 hrs.)
	After Leaching	24 Hours	48 Hours		
Basalt (BCR-1)	488	500	500	2. 50	2. 50
Granite (G-2)	1300	1340	1360	3. 10	4. 60
Granodiorite (GSP-1)	3800	3800	3800	0. 00	0. 00
Kaolinite	22000	22400	22400	1. 64	1. 64
Kaolinite	940	960	960	2. 15	2. 15
Illite	16400	16800	16800	2. 45	2. 45
Montmorillonite	1480	1520	1560	2. 70	5. 40
Montmorillonite	584	584	584	0. 00	0. 00
Soil over slate	724	768	780	5. 50	7. 70
Soil over limestone	1280	1340	1340	4. 35	4. 35
Soil over sandstone	488	500	500	2. 45	2. 45
Organic soil	800	800	800	0. 00	0. 00
Stream sediment (Sandstone)	154	154	154	0. 00	0. 00
Stream sediment (Shale)	644	644	644	0. 00	0. 00
Stream Sediment (Granite)	204	208	208	1. 95	1. 95
Stream Sediment (Ultra-basics)	152	156	156	2. 60	2. 60
Stream Sediment (Limestone)	1520	1540	1560	1. 30	2. 60

TABLE 2.17

THE EFFECT OF POSSIBLE INTERFERING ELEMENTS ON FLUORINE DETERMINATION (elements weighed as specpure oxides or chlorides to give a 1,000 ug/ml concentration equivalent to 40% for a 0.25 gm sample, 100 ug of F added to compound to give a 1ug/ml F final concentration. Compounds were fused and analysed according to the method described in the text).

Element	F(ug/ml) Blank	F(ug/ml) Measured	F(ug/ml) After Correction	%F Complexed
Sc	0.06	0.14	0.08	92
Zr	0.0	0.15	0.15	85
Th	0.03	0.27	0.24	76
Be	0.03	0.37	0.34	66
Ce	0.03	1.00	0.97	3
Ti	0.04	1.00	0.96	4
U	0.031	1.00	0.97	3
Al	0.62	1.65	1.03	0
Nb	0.06	0.98	0.92	8
Cr	0.0	1.00	1.00	0
Mn	0.10	1.10	1.00	0
V	0.0	1.00	1.00	0
Si	0.0	1.00	1.00	0
Fe	0.06	1.05	0.99	1
B	0.0	1.00	1.00	0
Sn	0.05	1.05	1.00	0
Ta	0.10	1.10	1.00	0
Hg	0.06	1.06	1.00	0
Mo	0.00	1.00	1.00	0
Ti	0.0	1.00	1.00	0
In	0.0	1.00	1.00	0

TABLE 2.18

EFFECT OF COMPLEXING ELEMENTS (Be, Zr, Th, Y, Sc) ON FLUORINE DETERMINATION

(50 ug/ml of element equivalent to 2000 ppm for a 0.25 gm sample)

Element	ug/ml Element added	ug/ml F added	ug/ml F measured	% F complexed
Be	100	1.0	0.50	50
Be	50	1.0	0.85	15
Be	100	0.1	0.088	12
Be	50	0.1	0.10	0
Zr	100	1.0	0.78	23
Zr	50	1.0	0.83	17
Zr	100	0.1	0.092	8
Zr	50	0.1	0.10	0
Th	100	1.0	0.73	27
Th	50	1.0	0.95	5
Th	100	0.1	0.10	0
Th	50	0.1	0.10	0
Y	100	1.0	0.85	15
Y	50	1.0	0.92	8
Y	100	0.1	0.090	10
Y	50	0.1	0.10	0
Sc	100	1.0	0.62	38
Sc	50	1.0	0.96	4
Sc	100	0.1	0.080	20
Sc	50	0.1	0.095	5

is attacked by the NaOH while it is in the drying oven at 200°C to drive off the H_2O in the flux. Fusing at 420°C insures that the entire sample has been attacked. A fusing time of 20-25 minutes is, therefore, adequate for most analyses.

The relationship between measured concentration and standing time of the sample solutions for various sample types is given in Table 2.16. Sample solutions which are allowed to stand overnight (24 hours) show a variable increase from 0 to 5.5 percent fluorine. A further increase over 48 hours was observed only for granite, montmorillonite, and slate; all other samples reached equilibrium within 24 hours. The increase in fluorine observed for most of these samples is probably due to the inability of the citrate-acetate buffer to completely free fluorine from its complexes immediately after leaching. There is, however, no systematic relationship between the degree of increase and the composition of the samples. For exploration purposes these increases are not significant enough to warrant long standing times. If more accurate analysis is required the sample solutions should be allowed to stand overnight.

A number of elements are known to form complexes with fluoride in aqueous solution (Al, Fe, Th, Be, Zr etc.). It is, therefore, essential to assess the capability of the buffer system to prevent complexation by these elements. The results shown in Table 2.17 indicate that for samples containing fluorine in the order of 400 ppm and the presence of interfering elements in the order of 40 percent, the buffer is capable of preventing complexation for all elements with the exception of Zr, Be, Th, Y and Sc. A more detailed study indicates that over the range 40-400 ppm fluorine these elements (Table 2.18) must be well below the 2,000 ppm level before the buffer can be considered effective in inhibiting complexation. With

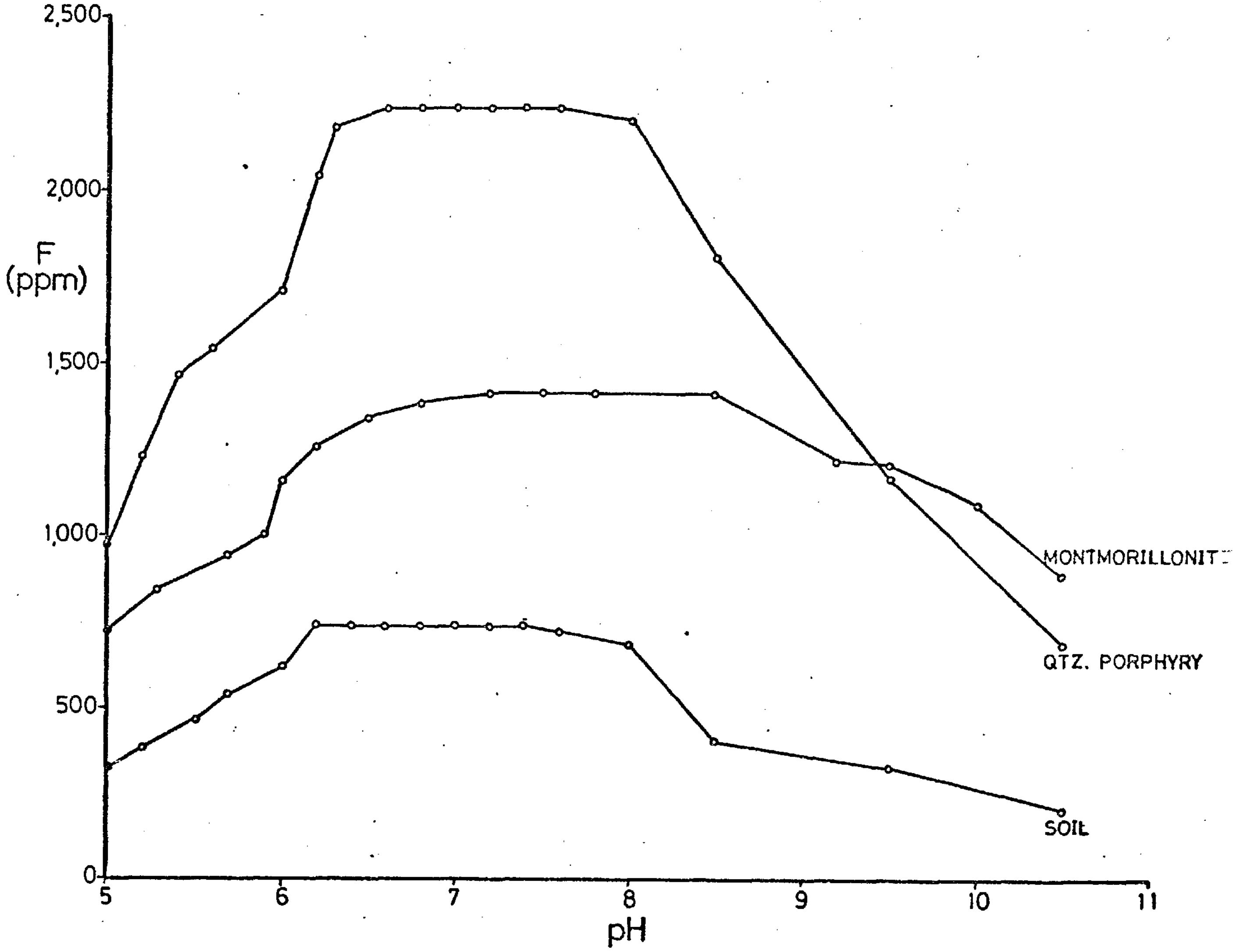


FIGURE 2.9

RELATIONSHIP BETWEEN pH OF FINAL SAMPLE SOLUTION AND MEASURED FLUORINE CONCENTRATION FOR TOTAL FLUORINE METHOD

the exception of some minerals and rocks (e.g. pegmatite) these elements are generally below the 100 ppm level for most geochemical materials and will, therefore, have little or no complexing power in the buffered sample solution. Their ability to complex fluorine must certainly be taken into account when analysing minerals or rocks in which they are a major constituent.

A number of minerals are not completely attacked by the NaOH flux when their partical size is greater than -200 mesh (see the last column of Table 2.11). Beryl, tantalite, xenotime, monazite, cerite and lepidolite are the principal members of this group. For rocks and minerals it is, therefore, essential that as fine a fraction (-200 mesh) as possible be used for analysis.

The final factor which must be considered in the method described is pH. Fig. 2.9 gives the relationship between the pH of the final sample solution and the measured fluorine concentrations for montmorillonite, quartz porphyry and soil samples. A distinct plateau is present over the pH range 6.5 to 7.5. On either side of this range the concentration decreases rapidly. Above pH 5.0 there is no HF complexation (see Fig. 1.4, Chapter I) and OH is only a serious interference.above pH 10.0. The low concentrations observed over the range 5.0 to 6.5 and 7.5 to 10.0 can possibly be attributed to the formation of fluoride complexes which resist decomplexing by citrate ions. Citrate is an effective masking agent for Fe and Al but not for silicate ions; the low fluorine concentrations which occur over the above pH ranges may, therefore, be due to the formation of H-F-SiO_2 complexes. In view of the above observations it is essential that the final solution pH be in the range 6.5 to 7.5 and preferably in the range 7.0 to 7.5. By matching a specific aliquot (3.0 ml) of the concentrated 'wet NaOH flux' to 100 ml of the buffer this can easily be done. This technique has the advantage that the final pH of the leach does not have to be adjusted and complete dissociation of the H-F-SiO_2 is, therefore, insured.

The procedure described for total analysis can easily be adjusted to suit most sample types. For samples containing less than 100 ppm fluorine, better precision can be obtained by using a larger sample weight (0.40 gm) with only slight adjustments having to be made to the flux-buffer system in order to retain a final solution volume of 100 ml. Organic samples can be readily attacked by the NaOH flux without having to ash or pre-treat the sample. The fluorine content of dry plant material is of the order of 1 to 100 ppm and hence a weight of 0.40 gm should generally be used to obtain good precision. The use of a wet NaOH flux is particularly advantageous in this respect as it ensures that the larger volume of organic material required to make up 0.40 gm is completely mixed with the flux before fusion.

The anomaly contrasts obtained for various types of deposits using the total fluorine method (Table 2.2) compare well with those obtained by the acid diffusible method. In terms of production and ease of analysis both these methods are equivalent. The total fluorine method, however, is required to make sound interpretation with regard to the type of fluorine dispersion encountered (hydromorphic, resistate minerals etc.). The acid diffusible method will not be as effective as the total method when fluorine is dispersed solely in the form of resistate minerals such as tourmaline and topaz.

CHAPTER III

APPLICATION OF FLUORINE GEOCHEMISTRY TO MINERAL EXPLORATION

3.1 REVIEW OF PREVIOUS APPLICATIONS

3.1.1 Introduction

Fluorine has only recently been recognized as a valuable pathfinder and indicator element for mineral exploration. This has been largely due to an increase in our basic knowledge of the geochemistry of fluorine, particularly with respect to its presence in many types of mineral deposits. In addition, recent advances in the analytical geochemistry of fluorine, as a result of the development of the specific ion electrode, have led to the evolution of analytical techniques which are rapid, inexpensive, and of sufficient precision to be used effectively in geochemical exploration.

The first description of the application of fluorine in mineral exploration is that by Nackowski (1952) concerning exploration in the Illinois-Kentucky fluorspar district. Although significant fluorine anomalies were detected over these deposits, he concluded that fluorine was 'technically unsuited as an indicator element'. At that time analyses for fluorine were carried out by a tedious distillation method. Whereas the above statement still applies for many potentially useful pathfinder elements (e. g. Se, Te, rare earths, etc.), fluorine no longer belongs to this 'unsuited' group of elements and should become a useful pathfinder and indicator element for many types of deposits.

In recent years more than fifty investigations relating to the application of fluorine in mineral exploration have been published, but no comprehensive review of these investigations has, however, appeared. To remedy this, an extensive review of the work to date is given, followed by a detailed account of the author's research on the geochemical application of fluorine in mineral exploration. An overall assessment of the efficacy of fluorine as an indicator and pathfinder element is given in Chapter IV (Summary and conclusions).

For ease of description, the methodology of fluorine geochemistry in mineral exploration can be described under the headings: Litho-, Pedo-, Hydro-, Bio-, and Atmogeochemical applications.

3.1.2 Lithogeochemical Applications

Research on the use of fluorine as a primary indicator of mineralization has followed two main themes - that of differentiating between barren and mineralized host rocks (generally igneous intrusions) and that of detecting primary halos associated with mineralization.

It has long been known that tin-bearing granites contain high concentrations of F, B, and Li, as well as a number of other characteristic elements. It is not possible, however, to differentiate tin-bearing from non tin-bearing granites solely by their fluorine concentrations, since many other types of granites often contain much higher fluorine contents than the tin-bearing varieties. For differentiation purposes, employment of a suite of elements such as F, B, and Li would probably be more effective. Fluorine analyses of granites located in known tin provinces may be particularly useful in determining directional vectors which may lead the prospector to areas of greisenization. Thus, Kesler et al (1973a) have shown that the fluorine content of the Mountain Pine Ridge granite (British Honduras) increases in the direction of tin mineralization.

To date, attempts at differentiating barren and mineralized Cu-Mo porphyry intrusives using fluorine have met with little success. Whole rock analyses of barren and porphyry copper-bearing intrusives in the Caribbean and Central America by Kesler et al (1975a) gave two fluorine populations with considerable overlap; their average fluorine contents (130 and 142 ppm respectively) were so similar that discrimination by the use of large sample populations is doubtful. A similar study of the Chilean porphyry copper province by Haynes and Clarke (1972) showed that the fluorine content of intrusive rocks in this province does not vary systematically with modal composition, depth of emplacement, age of intrusive, or degree of copper mineralization.

Considerable sampling error can often by incurred when utilizing whole rocks for the purposes described above. Kesler et al (1975a) found that K-rich rocks generally exhibited higher fluorine contents, but the variation was not systematic and therefore could not be used as an interpretive aid.

Often the best way to alleviate the errors caused by the inability to classify whole rocks is to analyse a specific mineral phase which is common to all the rock types. For mineral exploration, biotite has been widely used. Investigations of the relationship of the fluorine content of biotite to porphyry copper mineralization in intrusive rocks have given negative results. Three separate extensive studies by Kesler et al (1975b) Parry and Jacobs, (1975), and Haynes and Clarke (1972) on North and South American porphyry copper deposits have shown that little, if any, difference exists between the fluorine populations for biotites for barren and mineralized intrusives. Kesler et al (1975b) obtained a slightly higher fluorine average for biotites from mineralized intrusives, but the ranges in all the above studies for barren and mineralized intrusives indicate considerable overlap.

In using biotite as an indicator mineral, one must make the assumption that it is either formed contemporaneously with the ore, or its composition has been altered by ore-forming processes. With respect to porphyry copper mineralization, this assumption is questionable. Most porphyry copper deposits occur in intrusive complexes which are marked by a polyphase intrusive lithology, the units of which may be greatly separated from one another in time. Consequently biotite samples may have no relationship whatsoever to the formation of ore. Provided the intrusive phases related to the ore can be identified the biotite method may, however, have merit.

For contact metasomatic W-Mo-Cu deposits in the Western USA, Darling (1971) found that biotite associated with an ore-bearing intrusive phase contained higher amounts of fluorine (and Zn, Cu, and Li) than those from barren phases. In addition, the fluorine content of the biotite was found to decrease as the ore was approached. According to Seraphim (1951) and others this feature is apparently common at the contact zones of many types of intrusives, both barren and ore-bearing, and hence may not be useful for detecting ore.

By far the most useful lithogeochemical application of fluorine is in the detection and delineation of primary halos associated with many types of ore deposits, especially pegmatites, carbonatites, skarns, greisens, and fluorite deposits. The extent of a fluorine halo depends to a large degree on the activity of fluoride in the ore-forming solutions, the physio-chemical conditions under which the deposit was formed, the porosity and composition of the host rock, and depth of emplacement. All of these factors must be considered when using fluorine as an indicator of primary halos. Concealed orebodies may often contain large primary 'dome halos' which may be outlined with the aid of fluorine.

For a number of the iron, rare metal, borate, fluorite, and polymetallic deposits in the USSR, Komarov and Naktinas, (1965) found that fluorine formed the widest and most stable dispersion halos, and outlined both exposed and concealed deposits. For beryllium deposits in apogranites, Be, Li, and F formed noticeable concentrations in the country rocks above the mineralized granites (Beus and Subbotin, 1964). In the Chatkal-Kurama area, Salish (1969a) found a positive correlation between fluorine and its associated elements (W, Pb, Zn, Bi) in primary dispersion halos over rare metal skarn deposits. A similar study (Salish, 1969b) over the Aurakhmet and Paltau fluorite deposits revealed the presence of significant fluorine halos. Filimonova (1970) has described the successful application of fluorine in outlining primary halos associated with phlogopite-bearing skarns, and more recently Rabinovich (1973) has noted the presence of fluorine aureoles over epigenetic nickel deposits. The latter author further states that the fluorine content of the aureole and the size of the aureole vary directly with the Ni content and the thickness of the ore body. According to Komarov and Glaglev (1969) a study of primary elemental dispersion around carbonatites in the Siberian Shield of the USSR indicated the presence of large fluorine aureoles around these bodies. These aureoles are most probably the result of extensive fenitization of the country rock.

A recent review of fluorometric prospecting in the USSR has been given by Shipulin et al (1973). Although the use of fluorine for detecting and outlining primary halos shows excellent promise in the USSR, other countries have been slow to exploit the potential of the element.

3.1.3 Hydrogeochemical Surveys

By far the greatest use of fluorine in mineral exploration has been in hydrogeochemical surveys, involving both stream sediment and water sampling. The latter is the most important method to date. Apart from the research reported in this thesis, only five cases have been recorded in the literature where fluorine has been used in stream sediment surveys.

In the French Pyrenees, Cachau-Herreillat and Proulet (1971) carried out a large drainage survey over areas of granitic intrusions with the objective of outlining tungsten and other types of skarn deposits. They obtained stream sediment anomalies which were consistent with mineralization around the granitic intrusions and which increased in size in the order arsenic-phosphorus-fluorine. It would appear, therefore, that fluorine is an ideal element for low sample density programs in this type of environment.

A successful mining exploration venture using fluorine in stream sediments has been outlined by Ney et al (1972) for the Sam Goosly Cu-Mo deposit in British Columbia, Canada. In this area a fluorine anomaly was found to coincide with a low priority Cu-Zn anomaly. On the basis of these results, follow-up work was carried out, which resulted in the discovery of a Cu-Mo sulphide deposit associated with volcanics in contact with an igneous complex. The fluorine anomaly is most probably related to tourmalinization and sericitization of the deposit.

The remaining stream sediment surveys have been concerned with the detection of fluorite vein deposits in various environments. In the Osor fluorite district of Spain, Schwartz and Friedrich (1973) sampled dry stream beds and using a cold-extractable method of analysis obtained dispersion trains of approximately 300 metres and an anomaly contrast of eight fold. They also found a good correlation between streams sediment and spring water anomalies.

TABLE 3.1

HYDROGEOCHEMICAL FLUORINE SURVEYS

Region and type of deposit	Type of water sampled	Landscape	Fluorine Content* of waters (ppb)	Anomaly contrast	Extent of aureole or dispersion train from source (km)	Reference
Fluorite deposits Nfld., Canada	Stream waters and springs	Glacial terrain	500-2000	4	-	1
Fluorite deposits Madoc, Ont. Canada	Groundwaters	Temperate forest	200-800	4	1-4	2
Fluorite deposits Osor, Gerona, Spain	Stream waters	Mountainous	400-800	2	3-4	3
Fluorite deposits, Black Forest, W. Germany.	Stream waters	Temperate forest	200-1200	6	0.1-0.5	4
Fluorite deposits, Bohemian Massif, Czech.	Stream waters and springs	Temperate forest	200-800	4	-	9
Fluorite deposits, Central Asia, USSR	Groundwaters	Alpine	up to 3.5	10	-	5
Fluorite deposits, Voznesensk, USSR	Groundwaters	Forest Steppe	200-2300	10	2.0	5
Pegmatite field, Nauka, USSR	Groundwaters	Mountainous dry steppe	300-500	2	0.1-0.3	5
Pegmatite field, Altyn-Tau, USSR	Groundwaters	Desert	2000-4000	2	-	5
Pegmatite field, Durulguevsk, USSR	Groundwaters	Forest Steppe	400-600	1.5	0.5	5
Phlogopite deposits Aldan Shield USSR	Groundwaters	Taigaperma-frost	150-450	3	0.01-0.02	6
Skarn field, Chorukh-Dayron, USSR	Groundwaters	Dry steppe	300-800	2	-	5
Skarn field Koy-Tash, USSR	Groundwaters	Mountainous steppe	200-1200	6	-	5
Skarn field Tetyukhe, USSR	Groundwaters	Mountainous-taiga	500-1800	4	0.5	5
Tungsten deposits Belukhinsk, USSR	Groundwaters	Mountainous-taiga	600-3500	7	1-3	5
Mo-Bi deposits, Mulalin Massif, USSR	Groundwaters	Forest steppe	2000-10000	5	-	8
Zn-Pb massive sulphide deposit, New Norzone, Que. Canada	Groundwaters	Glacial terrain	150-200	1	1-1.5	7
Zn-Cu massive sulphide deposit Mobrun, Que. Canada.	Groundwaters	Glacial terrain	150-200	1	0.1	7
Cu-Zn massive sulphide deposit, Savard Lake, Que. Canada	Groundwaters	Glacial terrain	100-200	2	0.1	7
Zn-Cu massive sulphide deposit Barvallee, Que. Canada	Snow	Glacial terrain	5-16	3	0.1-0.2	7
Au deposit Duquesne, Que. Canada	Groundwaters	Glacial terrain	100-300	3	0.1	7
Au deposit Halliwell, Que. Canada	Groundwaters	Glacial terrain	100-300	3	0.1	7
Au deposits Wasamack, Que. Canada.	Groundwaters	Glacial terrain	100-200	2	0.1	7

*Lower and upper limits of fluorine content given represent threshold and peak anomaly values respectively.

Reference: 1. Tilsley, 1975; 2. Lalonde, 1974; 3. Schwartz and Friedrich, 1973; 4. Friedrich and Pluger, 1971; 5. Krainov et al 1967; 6. Shipulin et al, 1973; 7. Lalonde, 1975; 8 Durnev et al, 1970; 9. Pokorny, 1971.

In the fluorspar district of southwest Texas, Carlson et al (1974) found fluorine in stream sediments to be an effective indicator of fluorite mineralisation; adequate dispersion trains were developed and the element exhibited a good decay of concentration from source.

For the Madoc fluorspar district of Ontario, Canada, Lalonde (1974) observed a good correlation between stream sediment anomalies, groundwater anomalies, and mineralisation. The fluorine anomalies generated in the stream sediments did not exceed the regional mean by more than 27%; from this it follows that groundwaters would appear to be a more effective medium in this area.

It is clear from the above descriptions that, although having considerable potential, the application of fluorine in drainage surveys has not been adequately assessed. The author has attempted to rectify this problem somewhat by investigating the dispersion of fluorine in the drainage systems associated with various types of mineralisation. The results of these investigations are described in the sections following this review.

A considerable number of water surveys using fluorine as the indicator or pathfinder element have been conducted over various types of mineralisation. The author has summarized these studies in Table 3.1 giving the type of deposit, the landscape, fluorine content of waters (threshold to peak anomaly), the anomaly contrast and the extent of aureole. Before describing some of the individual case histories and problems involved with water surveys, it may be beneficial to comment on this compilation of studies as a whole. The following points are evident from the data:

a) Landscape would appear to have a modifying effect on the fluorine content of ground and surface waters. This can best be seen in the studies carried out over pegmatite fields. In desert environments where conditions are highly saline and the ionic strength of the groundwaters are high, fluorine is concentrated in large amounts (2, 000-4, 000 ppb). This can be contrasted with the forest and mountainous steppe areas which have intermediate fluorine concentrations (400-600 ppb and 300-500 ppb respectively) and the taiga-permafrost areas which are characterized by low fluorine concentration in the groundwaters (150-450 ppb) due to the restricted weathering and dispersion conditions. The fluorine content in the waters from the other landscapes can be similarly compared.

b) With few exceptions, the threshold value for fluorine in waters is in the region of 200±100 ppb and the anomaly contrasts obtained are, therefore, strongly dependent upon the amount of available fluorine in the different types of deposits.

c) The highest anomaly contrasts are associated with those deposits rich in fluorite, this mineral being more soluble than other common ore minerals which have high fluorine contents (micas, tourmaline, topaz, hornblende, humites, etc.). Fluorite deposits show the highest anomaly contrasts (4-10 fold) followed by skarn deposits (4-7 fold), which generally contain significant amounts of fluorite, and pegmatite and gold deposits (1.5-3 fold). The fluorine in waters draining pegmatite and gold deposits is probably derived from micaceous minerals. The anomaly contrasts (1-2 fold) obtained by Lalonde (1975) for the polymetallic massive sulphide deposits in Quebec, Canada, would appear to be much too low for fluorine to be an effective indicator of this type of mineralisation.

d) The extent of the aureole developed will depend largely on the size of the mineral field, the geologic structure, and the type of mineralisation sought. In some cases, the aureole can be quite extensive (up to 4 km from source) but more generally an aureole of less than 0.5 km can be expected. For taiga-permafrost areas the aureoles developed around phlogopite deposits are small (100-200m).

A number of controlling factors affecting anomaly contrast and dispersion must be considered when using fluorine in water surveys. Calcium has the ability to suppress the concentration of fluorine in waters when in amounts greater than that contributed by the solubility of fluorite (8 ppm Ca at 23°C). This effect is most critical at relatively high, or what could be termed anomalous, concentrations of fluorine. For this reason, anomaly contrasts may be significantly lowered in water regimes of high calcium content. Alternatively, if sodium is present in large amounts it will enhance the concentration of fluorine, even in the presence of calcium, and may give rise to anomalous fluorine levels unrelated to mineralisation. It is, therefore, important that the approximate concentration of these two elements be determined to correctly assess the fluorine data. Rigorous corrections cannot be made because the precise effect that these elements have on the concentration and dispersion of fluorine cannot be quantified.

In her study of geochemical methods of prospecting for phlogopite deposits in permafrost terrain, Filimonova (1970) (also Shipulin et al 1973) found that fluorine enters the aqueous system mainly through the decay of organic matter and is dispersed as a constituent of organomineralic gels. This process of organic sequestration is thought to be related to the absence of an oxidation barrier in the permafrost stratum of the soils. By ratioing the fluorine content and the permanganate oxidizability (mg/1 O_2, equal in fresh water to the organic content) it was possible to separate a background population of data from an anomalous group related to the presence of phlogopite deposits. The halos formed in the water regime were considerably larger than the metasomatic alteration zones around the deposits, which previously were the only prospecting indicators in this type of terrain.

The effectiveness of water surveys in mineral exploration is often hampered by seasonal changes in the elemental content of the waters, making the collation of data collected over a long period of time a non-viable approach to interpretation. In the case of fluorine, a number of investigations into seasonal effects have been carried out. In the Madoc fluorspar area of Ontario, Canada, Graham et al (1975) collected groundwater samples in October and February and found that only 30% of the samples fell outside the 95% confidence interval of the correlation (line of least squares) between the two sample sets. They gave no indication whether the samples which fall outside the confidence level are significant to the interpretation, and they interpret these results as 'indicating that seasonal variation is less than analytical variation in most cases and that long-term fluoride surveys are feasible'. Over this same area a joint study by Lalonde (see Lalonde, 1974) and the author in 1972 on seasonal variation yielded results which are incompatible with the conclusions of Graham et al (1975). Samples collected over mineralisation and background areas by Lalonde (1974) in May were resampled by the author in August after a reasonably wet summer. The samples were analysed by the same method, using the same equipment and standards. The results together with the percent change in concentration are presented in Table 3.2. In all cases, an increase in fluorine concentration was observed over this time period. The percentage increase varied from 34 to 93 per cent, and although the anomalies related to mineralisation are still indicated in the August samples, the merging of data sets taken at these two periods cannot be justified. Clearly the large amount of precipitation over the summer gave rise to an increased influx of fluorine into the groundwater system. Where well waters are readily available for sampling, such as in the Madoc area, a large water survey during the winter months may be feasible since precipitation (snow) during this period will have the least effect on the groundwater system. Similar results to the above were obtained by Lebedeva (1969) for groundwaters associated with tin mineralisation in the USSR. For an area having an annual precipitation of 700 mm with the maximum in July, she found a positive increase in the fluorine concentration of the groundwaters with increased precipitation. The survey was, therefore, completed at the end of a dry season in May when background values were stabilised at 210 ppb. Any values above background after stabilisation were considered anomalous. Although no data are given, Schwartz and Friedrich (1973) found the seasonal variation for waters of small streams and springs in the Osor fluorspar district of Spain to be negligible for the period August/ September, 1970 and April/May, 1971. This, however, is an area of restricted rainfall and seasonal variations are probably of minor importance. For moist temperature areas where stream water and spring samples can be collected, Tilsley (1975) has suggested a possible method of correcting for seasonal variations based on the contribution rate of fluorine to the groundwater system and the discharge of the surface drainage. The contribution rate (mg F^-/m^2 of exposed CaF_2/hr) is relatively constant in moist climates, and the concentration of fluoride ion in the surface drainage varies inversely with discharge. By sampling a number of control stations in a large survey area and measuring the fluoride concentration and discharge one can normalise data taken over a long period of time.

A unique approach to hydrogeochemical prospecting has been described by Lalonde (1975). He studied the dispersion of fluorine in snow above the concealed Zn-Cu Barvallee deposit in northern Quebec, Canada. The anomalies obtained coincided perfectly with the area of suboutcropping mineralisation, and the anomaly contrast was in the order of 3-fold. Lalonde (op. cit.) attributes the concentration of fluorine in snow to the

TABLE 3.2

SEASONAL VARIATION OF FLUORINE CONTENT OF WELL WATERS, MADOC FLUORSPAR DISTRICT, ONTARIO, CANADA

	Fluorine Analysis (ppb)		% Increase in concentration
	Lalonde May, 1972	Boyle Aug., 1972	
Background wells	57	770	93
	106	530	80
	145	440	67
	154	420	63
Mineralised wells	237	1240	81
	318	480	34
	397	700	43
	398	700	43
	398	820	52
	616	1200	49

exhalation of fluorine vapour (HF) from the underlying soils, to the dispersion of fluoride ions into the snow from the organic A soil horizon, or to a combination of both. He has also indicated that the occurrence of an ice crust in the snow profile may be essential for the development of a favourable geochemical contrast. Snow sampling programmes can be of great benefit in temperate climates because exploration can be carried out year round.

Apart from the work in the Madoc area on seasonal variations (Table 3.2) and in the Cornwall area on the mode of occurrence of fluorine in surface waters (Table 1.16) the author has not included water surveys in his research program since it was felt that this subject has been adequately covered and assessed by previous workers.

3.1.4 Pedogeochemical Surveys

During the weathering of fluorine-bearing ore deposits or their associated halos, fluorine is partitioned between a relatively immobile mineral phase and a mobile aqueous phase. In this respect, the element can be classed as a moderately mobile element in the secondary environment. The degree of partitioning between the above two phases depends largely on the form in which fluorine is present in the mineral deposit; the more resistate minerals (topaz, tourmaline, apatite, etc.) pass into the pedosphere and undergo mechanical transport, whereas minerals such as fluorite, the micas, and the amphiboles being less resistant to chemical attack, release a significant proportion of their fluorine into the aqueous phase. Part of the fluorine in soil solutions may in turn be taken up by the clay, colloid, and organic components, while the rest moves out of the area of primary fluorine enrichment into the groundwater system, possibly to be concentrated in some other phase (e.g. stream sediments). The analysis of soils and transported overburned for fluorine is, therefore, under most conditions an ideal method of detecting and delineating ore deposits with which this element is associated.

Pedological media are generally used in detailed follow-up surveys and in this respect, it is useful to have some prior knowledge of the type of medium to use, the degree of contrast that can be expected, and the size and type of dispersion pattern that will be produced. Unfortunately, the vast majority of pedogeochemical applications described to date are concerned with fluorspar exploration only. The author has attempted to rectify this situation by carrying out orientation studies over a more diversified group of ore deposits as described in the next section.

The first pedogeochemical application of fluorine reported in the literature was carried out by Nackowski (1952) in the Illinois-Kentucky fluorospar district. Three areas of mineralisation were studied, two of which were characterised by bedding replacement deposits and the third by vein deposits. In all of these areas the soil covering the bedrock is in turn covered by 20-30 feet of loess necessitating auger drilling to obtain representative soil samples at depth. All three areas exhibited fluorine anomalies having contrasts of less than one fold, and although these contrasts compared very well with those obtained for the heavy metals, it was concluded that fluorine was an unsuitable indicator on technical grounds. However, later work in this district by Van Alstine (1965) and Carlson et al (1974) revealed areas having fluorine anomalies with 2 to 3 fold contrasts.

Soil surveys carried out by Van Alstine (1965) in the Browns Canyon fluorspar district of Colorado produced fluorine anomalies with contrasts between 6 and 20 fold.

Studies of fluorine dispersion over fluorspar deposits in Texas by Carlson et al (1974) indicated anomaly contrasts of as much as 100 times background. For this same area they found that heavy metals were ineffective in outlining these deposits, a fact which is probably the rule rather than the exception for fluorspar deposits.

In the Derbyshire lead-zinc-fluorspar district of England, fluorine in soils has been shown to be effective in outlining fluorspar mineralisation (Michael et al 1973; Farrell, 1974), but considerable contamination in this district due to old mining activity severely hampers interpretation of any results. Anomaly contrasts obtained by these writers varied from 5 to 30 fold. The Derbyshire district is strongly zoned with respect to mineralisation and each of the elements, fluorine, lead and zinc, show different degrees of effectiveness as indicators depending on the mineral zone being explored. It is probably best, therefore, to use these elements as an 'indicator group', the relative intensities of the anomalies produced by each possibly indicating the type of mineralisation. A regional soil survey of the southern part of Derbyshire Dome (Farrell, 1974) successfully outlined a known fluorspar zone, but again contamination in the area greatly affected overall interpretation.

For the sulphide-bearing fluorspar deposits of Osor, Spain, Schwartz and Friedrich (1973) demonstrated that fluorine, besides producing anomalies with contrasts of 7 to 20 fold, also exhibits dispersion patterns which are better developed than the corresponding lead and zinc dispersion patterns. Earlier work in this area (Pluger and Friedrich, 1972) indicated that selection of analytical technique was also very important. Of the cold extractable methods tried by these authors, only 10^{-2}M HCl (Pluger and Friedrich, 1972) and 0.037M $FeCl_3$ (Schwartz and Friedrich, 1973) were capable of producing acceptable anomaly contrasts.

In the Madoc fluorspar district of Ontario, Canada, Lalonde (1974) found that the organic A horizon produced fluorine anomalies of higher contrast and better correspondence with mineralisation than the B or C horizons. This is in agreement with the author's own findings for the fluorite-uraninite pegmatite deposits in the nearby Bancroft area. Other workers (Boyle and Dass, 1967) have shown that the A horizon may be a better horizon to sample in areas characterized by podzolic or well differentiated soils. The investigations in the Madoc area also emphasize the importance of obtaining adequate background information for interpretative purposes. In this area, soils taken over marble may contain more fluorine than those taken in the vicinity of fluorspar veins and, therefore, it is important to have either a knowledge of the underlying geology or a method of differentiating bedrock anomalies from those associated with mineralisation. The width of the anomalies in the Madoc area (50-200 feet) and in the other areas described above, suggest that careful attention should be paid to the sampling interval used. A sampling interval of not more than 50 feet and in some cases not more than 20 feet is needed to obtain well developed anomalies.

A detailed investigation of the secondary dispersion of various elements in the vicinity of the Aurakhmet and Patau fluorspar deposits of the USSR (Salish, 1968b) indicated that fluorine gave the most contrasting and widest dispersion halos compared to copper, tin, titanium, and manganese. In addition, the size of the fluorine halo was found to decrease with increased sampling depth.

For fluorspar deposits not located in limestone environments, the problem of filtering legitimate anomalies associated with mineralisation from those associated with disseminated fluorite and other fluorine-bearing deposits is always present. Federenko (1964) has used the F/P ratio with fair success to overcome this problem for the quartz-fluorite deposits in the granitic and granite-gneiss terrain of the Zhipkosh and Bliskii areas of Eastern Transbaikaliya USSR. Apatite, which is not present in the quartz-fluorite veins is often associated with the disseminated fluorite occurrences, and the ratio F/P can, therefore, be used to filter out false anomalies.

Only two investigations concerning the use of fluorine for fluorspar exploration in areas of transported overburden have been described. In the Harz Mountain fluorspar district of Germany, Lutzens and Zimmermann (1974) have shown that overburden profiling (using fluorine as a pathfinder), together with vein-float-mapping, geophysics, classification of overburden material, and morphological studies is an efficient method of detecting and delineating fluorspar veins. In the St. Lawrence fluorspar district of Newfoundland, Tilsley (1975) has successfully used deep overburden drilling techniques, developed for prospecting in areas of glaciated terrain, to detect fluorspar mineralisation beneath 5 to 15 metres of glacial overburden. In this same area he describes the occurrence of an iron oxide placon in the soils (1-30 mm thick) which acts as a chemical barrier to the transport of fluoride ions. Over fluorspar mineralisation no anomalous expressions were obtained for samples taken above the placon, and it was, therefore, essential to sample below this barrier.

In-field methods of fluorspar exploration utilizing neutron activation analysis of soils for fluorine have been described by Bartosek et al (1971), Lutze (1974), and Gorbatschen et al (1974). Portable instrumentation capable of measuring fluorine down to 500 ppm has been developed, but as yet, the method appears to lack adequate sensitivity and the detection limit is much too high for many types of environments.

The use of fluorine as an indicator in pedological media for mineral deposits other than fluorspar has not been well documented. Over rare metal (Bi-W-fluorspar) skarn deposits in the Chatkal-Kurama area of the USSR, Salish (1968a) found a positive correlation between fluorine and accompanying elements (W, Pb, Zn, Bi) in both the primary and secondary (eluvial-deluvial) dispersion halos. Similarly, Cachau-Herreillat and Prouhet (1971) have found that the tungsten skarn deposits in the French Pyrenees are characterized by fluorine soil anomalies that are located over the outer, less productive zones of the contact metasomatic deposits, whereas the W, Cu, Zn, Pb and As anomalies occur over the more productive zones. In this respect fluorine may be a good indicator of blind skarn deposits, since it appears to migrate much farther into the country rocks than other indicator elements.

Over sub-outcropping tin deposits in the Tekka Hill district of Perak, Malaya, Teh et al (1975) have found fluorine to be a better and more reliable pathfinder for tin than arsenic. Based on the author's own work (see section on tin deposits) this statement would appear to be well founded.

Provided careful consideration is given to the mode of occurrence and dispersion characteristics of fluorine in the pedologic environment, and proper sampling and analytical methods are chosen to ensure adequate anomaly contrast, fluorine is a valuable pedogeochemical pathfinder and indicator element in mineral exploration.

3.1.5 Biogeochemical Prospecting

The use of fluorine as a biogeochemical indicator of mineralisation has been investigated in only the most cursory manner. In fact, the author knows of only one case history (Lalonde, 1975) in which fluorine in vegetation has been used as a possible guide to mineralisation. In this study Lalonde (op. cit.) measured the fluorine contents of alder leaves over the Barvallee Zn-Cu sulphide deposit in Quebec, Canada. This deposit lies under fifty feet of glacial lacustrine clay and basal till. The fluorine anomalies generated in the vegetation were laterally displaced from the zone of mineralisation but corresponded reasonably well with the zinc and copper anomalies outlined in the basal till by deep overburden sampling. The anomaly contrast, however, was only in the order of 2- to 3-fold.

It would appear from recent studies (Matuura et al, 1954; Marier and Rose, 1971; Shipulin et al, 1973) that plants have a remarkable tolerance to high concentrations of fluorine in soils and rocks. Shipulin et al (1973) have found that the fluorine concentration of plants (0.5-0.1% in the ash) remains practically constant when the fluorine content in the bedrock alters in the range from 0.003% to 2%. Matuura et al (op. cit.) have, however, demonstrated an anomalous situation for the species Diosypyros kaki in Japan. The fluorine content of this species over background areas is 14 ppm (dry weight) and over the Zinmu fluorite mine the fluorine content was 80 ppm (dry weight). Clearly more comprehensive investigations are required before an adequate assessment of the biogeochemical use of fluorine in mineral exploration can be made.

No indicator plants are known which specifically favour areas of high fluorine concentration in their substrates, and for this reason geobotanical prospecting in mineral exploration is not a viable venture as far as fluorine is concerned.

Due to lack of vegetation or homogeneity of species in the areas studied, biogeochemical investigations were not included in the author's research programme.

3.1.6 Atmogeochemical Prospecting

This subject is treated in detail in a later section on vapour geochemistry in mineral exploration and the reader is, therefore, referred to this section.

3.2 PROSPECTING FOR MINERAL DEPOSITS OF MAGMATIC ORIGIN

3.2.1 Introduction

Fluorine has many useful applications as a pathfinder and indicator element when prospecting for a variety of mineral deposits of magmatic origin. This is due to its strong affiliation, as a lithophilic element, with magmatic processes. It is commonly enriched in the late and generally more mineralized phases of magmatic intrusions and also possesses the ability to concentrate in both the acidic (granites) and alkalic (alkali-syenites, carbonatites, kimberlites) end-members of parental magmas. In addition it plays a major role in the processes of fenetization, serpentization and skarnification associated with deposits of these types. The principal deposits of magmatic origin with which fluorine is associated are as follows:

a) Carbonatites
b) Kimberlites
c) Pegmatites
d) Deposits (Ta-Nb, Sn, W, Be, Fluorspar, kaolin) in coarse-grained albitic granites, alkali syenites and rhyo-dacitic volcanics.
e) Sulphide deposits in serpentinized basic intrusions.

Only carbonatites, kimberlites and pegmatites have been studied in detail by the author; the other deposits will only be discussed briefly for purposes of completeness in assessing the prospecting potential of fluorine.

3.2.2 Prospecting for Carbonatites and Kimberlites

3.2.2.1 Introduction

Although carbonatites and kimberlites show many similarities as well as differences in their chemistry and geology, one marked feature warrants their joint description in terms of prospecting; they are confined almost exclusively to the interiors or margins of stable cratonic shield areas. Thus, when prospecting in these areas it is often advantageous to select methods that are applicable to both types of deposits. The principal broad areas of interest for prospecting for carbonatites and kimberlites are the African, Brazilian, Indian, Siberian, Canadian and Scandinavian shields. Conclusions are drawn at the end of this section on integrated methods of prospecting forboth types of deposits in shield environments.

3.2.2.2 Geology and Mineralization of Carbonatites and Kimberlites

3.2.2.2.1 Introduction

On a regional basis, carbonatites and kimberlites exhibit a close spatial relationship in shields, occurring in major horst areas or in strongly upwarped areas. In places they are found in grabens such as the Lucapa graben of Angola. More locally, kimberlites and carbonatites are commonly associated with areas characterized by much larger intrusive bodies of silica-poor rocks such as syenites, alkali-syenites, nephelinites and melilitites together with their related dike rocks (alnoites, monchiquites, ouachitites, etc.).

Both types of intrusive bodies are found in the basement and overlying sedimentary and volcanic sequences of shield areas; kimberlites, are however, more numerous in areas characterized by sedimentary and volcanic cover (e.g. African and Siberian Shields). Although carbonatite and kimberlite provinces tend to predominate within shield areas, it should be noted that their occurrence throughout the entire lithologic column in shield environments prevents large areas from being entirely eliminated for exploration purposes.

3.2.2.2.2. Carbonatites

With the exception of a few sill-like bodies, carbonatites per se generally form a small part of a much larger alkali complex in which they occur as stocks, pipes or plugs, ring-dikes, conesheets, radial dikes, tangential dikes and brecciated bodies. The alkaline igneous complex may be formed as the result of extensive fenetization processes (alkali-metasomatism) or as the result of multiphase igneous alkalic intrusion of which carbonatite forms one phase, the other phases generally being urtites, ijolites, melteigites (nepheline-pyroxene rocks), and alkalic syenites. Ultramafic rocks such as pyroxenites, peridotites, and kimberlites commonly occur in or are associated with carbonatite complexes. In size, the area of the complex may vary from 1 to 20 sq. miles, with 3 sq. miles generally being the average (Heinrich, 1966). Carbonatite complexes often occur within or satellitic to igneous alkalic provinces in stable shield environments.

Carbonate-rich rocks occurring in alkalic complexes can be classified as carbonatites (sovite-a calcic species or rauhaugite-a dolomitic species), silicocarbonatites (calcite > silicate), and carbonatitic ijolites (silicate < calcite).

Many types of dyke rocks such as lamprophyres, ultramafic dykes (kimberlite, pyroxenite, etc.), micromelteigites, microijolites, trachytes, and phonolites occur within or neighbouring these complexes.

Most carbonatite complexes are surrounded by a metasomatically altered zone commonly called fenite. The size of this altered zone depends on the size of the complex, the nature of the host rock, and the physico-chemical conditions during emplacement.

Carbonatite complexes can contain economic or potentially economic deposits of niobium (chiefly as pyrochlore), rare earths of the cerium subgroup, thorium, iron (magnetite, hematite), titanium (rutile, brookite, ilmenite), manganese, copper, apatite, barite, fluorite, vermiculite, nepheline and limestone (for portland cement). In some deposits these elements or minerals may be concentrated in economic amounts in the overlying residuum. Economic concentrations of niobium, rare earths, thorium, iron, titanium, manganese, copper, apatite, and of limestone suitable for cement are generally associated with the carbonatite phase of the complexes. Barite and fluorite may also be found in carbonatites but are generally present as late-stage vein deposits. Vermiculite is formed from the alteration of ultramafic rocks (peridotites, pyroxenites, etc.) within the complex, and nepheline (as a source of Al) occurs in the silicocarbonatite and ijolite rocks.

Descriptions of the geology of carbonatites are presented in works by Heinrich (1966) and Tuttle and Gittens (1967).

3.2.2.2.3 Kimberlites

Kimberlites may be defined as 'serpentinized and carbonated mica-peridotites of porphyritic texture, containing nodules of ultrabasic rock-types characterised by such high-pressure minerals as pyrope and jadeitic diopside' (Dawson, 1967). They occur principally as small diatremes and dykes, less commonly as sills. The diatremes are generally round to ovoid in shape, and their surface outcrop rarely exceeds 0.5 sq. miles. They taper gradually downward giving them a characteristic 'carrot shape' and are often located on kimberlitic dykes. The dykes which commonly occur in swarms are generally relatively narrow (less than 10 metres) and may be many kilometers long. In places lenticular enlargements known as 'blows' occur along the dykes.

Kimberlite provinces such as those in the Kimberley, Lesotho, and Lucapa graben (Angola-Zaire) areas are common in shield areas, but many kimberlites occur in isolation seemingly outside of well defined provinces.

Internally, kimberlites consist of a decomposed and oxidized zone ('yellow-ground') grading into a zone of slight decomposition ('blue-ground') which is succeeded at depth by unweathered kimberlite ('hardebank'). The distribution of the weathered types of kimberlites is controlled mainly by climatic and groundwater conditions. The diatremes may be characterised by more than one phase of kimberlite intrusion; the dykes generally consist of a single phase. Three varieties of kimberlite are generally recognized:-

a) Massive kimberlite: Essentially a porphyritic rock containing few or no inclusions of country rock and generally of two types - a 'basaltic' variety (olivine or serpentinized olivine being the dominant mineral and phologopite $< 5\%$) and a 'micaceous' variety (phlogopite $> 5\%$).

b) Intrusive kimberlite breccias: These consist of massive kimberlite containing 30 to 60% of fragments of either massive kimberlite of a previous generation (autolithic) or country rocks (heterolithic).

c) Kimberlite tuffs and tuff breccias: These rocks consist of 60 to 90% of fragments of kimberlite and country rocks cemented by hydrothermal-type minerals. Two types of xenoliths may occur in the diatreme kimberlites (a) foreign xenoliths consisting of angular blocks of country rocks and basement rocks and (b) cognate xenoliths consisting of rounded masses of eclogites, peridotites, lherzolites, saxonites and griquaites derived from considerable depths. With the exception of brecciation (see Figs. 3.1 and 3.2) the wallrocks in kimberlite diatremes show little alteration, suggesting that these bodies have been intruded as relatively cold, gas-charged magmas.

Economically, kimberlites are the only primary source of diamonds; other sources are alluvial deposits and synthetic manufacturing. Diatreme and dyke deposits are presently the most important of these sources.

Detailed descriptions of the geology and occurrence of kimberlites are given in books by Williams (1932) Wagner (1914), Wyllie (1967) and Nixon (1975).

3.2.2.3 Geochemistry of Carbonatites and Kimberlites

3.2.2.3.1 Introduction

Both kimberlites and carbonatites exhibit a number of marked differences in their chemistry when compared with other types of rocks. A comparison of the chemistry of kimberlites, carbonatites, other igneous rocks, and clays and shales is presented in Table 3.3. Also presented in the table is a comparison of the author's analyses for 26 kimberlite deposits and the reported analyses collated from the literature. With few exceptions, the author's data compare well with the reported data. The

TABLE 3.3

A COMPARISON OF THE CHEMISTRY OF KIMBERLITES, CARBONATITES, OTHER IGNEOUS INTRUSIVE ROCKS AND CLAYS AND SHALES

(all values in ppm except oxides which are in Wt. %)

	Kimberlites		Kimberlites(3)	Carbonatites	Ultrabasics	Basalts	Intermediate	Granites		Syenites	Clays and Shales
	(1)	(2)	(this study)					Low Ca	High Ca		
SiO_2	34.85	27.81	37.69	10.29	40.60	51.30	55.60	74.36	67.29	62.20	51.00
TiO_2	2.34	1.63	2.20	0.73	0.05	1.50	1.30	0.20	0.57	0.58	0.75
Al_2O_3	4.22	3.40	4.79	3.29	0.85	16.50	16.70	13.60	15.49	16.60	19.74
Fe_2O_3	6.50	5.40	4.33	3.46	-	-	-	-	-	-	-
FeO	4.05	2.82	5.11	3.60	12.12	11.12	7.50	1.83	3.80	4.70	4.28
MgO	26.19	25.53	27.18	5.79	42.90	7.40	3.60	0.27	1.57	0.96	2.23
CaO	8.48	12.21	7.23	36.10	1.00	9.40	6.50	0.71	3.54	2.50	3.54
K_2O	1.03	0.66	1.97	1.36	0.04	0.99	2.80	5.06	3.04	5.40	2.75
Na_2O	0.30	0.33	0.85	0.42	0.77	2.60	4.10	3.48	3.83	5.40	0.89
P_2O_5	0.77	0.50	0.76	2.09	0.04	0.32	0.36	0.14	0.21	1.80	0.18
CO_2	3.88	-	3.05	28.52	0.04	0.04	0.07	-	-	-	-
H_2O^+	7.43	-	5.95	1.44	-	-	-	-	-	-	-
H_2O^-	2.43	-		-	-	-	-	-	-	-	-
Li	20 (31)		23	-	0.5	16	20	24	40	28	60
Rb	160 (157)		110	-	2	40	100	110	170	110	210
Cs	20 (100)		6	-	0.x	1.1	-	2	4	0.6	0.01
Be	3 (18)		1	0.x(?)	0.x	1	1.8	2	3	1	2
Sr	305 (568)		470	3890 (117)	5	450	810	440	100	200	450
Ba	1799 (81)		790	3600 (134)	1	300	650	420	840	1600	810
Sc	16.5 (109)		10.9	10 (16)	10	25	2.5	14	7	3	11
Y	19 (78)		-	96 (31)	5	25	-	44	41	14	31
La	207 (116)		-	284 (31)	O.x	20	-	84	55	20	41
Ce	199 (98)		-	1925 (16)	O.x	45	-	10.0	57	30	51
Pr	5.36(24)		-	48 (2)	1.8	8.5	-	17	7.2	5.2	5.1
Nd	110 (92)		-	183 (2)	6.2	32	-	55	33	19	23
Sm	9.80(101)		-	32 (2)	1.1	6.9	-	8.5	7.1	2.7	6.5
En	2.43(104)		-	11 (2)	0.32	2.7	-	1.7	1.1	0.88	1.1
Gd	4.54(36)		-	29 (2)	1.2	5.9	-	6.7	7.1	2.7	6.5
Tb	1.10(92)		-	6.8(2)	0.31	1.1	-	1.0	1.3	0.48	0.91
Dy	0.72(24)		-	-	1.3	9.0	-	8.0	5.0	2.0	4.5
Ho	0.18(9)		-	3.6(2)	0.18	1.1	-	2.2	1.2	0.46	1.1
Er	0.28(10)		-	9.5(2)	0.53	3.3	-	3.8	4.4	1.8	2.5
Tm	-		-	2.5(2)	0.068	0.44	-	0.6	0.68	0.27	0.25
Yb	1.10(97)		-	5.3(2)	0.50	2.7	-	4.0	4.0	1.5	3.1
Lu	0.16(78)		-	2.4(1)	0.072	0.5	-	1.1	1.2	0.27	0.71
Th	21.7 (95)		-	-	0.005	4	7	8.9	20	13	11
U	4.2 (78)		--	--	0.002	0.x	1.8	2.3	4.7	3.0	3.2
Zr	208 (543)		193	83 (25)	40	120	260	140	175	500	210
Hf	15.6 (12)		-	-	0.5	6	1	2.3	5.5	11	6.1
V	169 (477)		172	-	40	230	100	88	44	30	130
Nb	79 (537)		-	1600 (42)	10	20	20	20	21	35	21
Ta	8 (76)		-	-	0.x	0.x	0.7	3.6	4.2	2.1	3.5
Cr	1004 (732)		1020	48 (1)	1800	180	50	22	4.1	2	110
Mo	3 (18)		1	42 (5)	0.3	1.5	0.9	1.0	1.3	0.6	2.1
W	-		-	4.5(7)	0.8	0.7	1.0	1.3	2.2	1.33	2.1
Mn	1046 (696)		1240	5268 (140)	1040	1500	1200	540	390	850	670
Co	51 (78)		80	17 (20)	180	45	10	7	1	1	21
Ni	1090 (676)		1125	8 (20)	2000	150	55	15	45	4	95
Pt	-		-	-	0.2	-	-	-	-	-	-
Cu	62 (473)		52	2.5(16)	15	90	35	30	10	5	57
Ag	1		1	-	0.06	0.11	0.07	0.051	0.037	0.0x	0.11
Au	-		-	-	0.005	0.002	-	0.002	0.002	0.002	0.001
Zn	57 (66)		59	-	50	105	72	60	39	130	81
Cd	-		1	-	0.05	0.22	-	0.13	0.13	0.13	0.31
Hg	0.11(1)		-	-	0.01	0.01	-	0.02	0.04	0.0x	0.41
B	190 (226)		-	0.x(200)	3	5	15	9	10	9	110
Ga	9 (14)		6.8	1 (16)	1.5	17	20	17	17	30	31
In	-		-	-	0.01	0.22	-	0.x	0.26	0.x	0.05
Tl	-		-	-	0.04	0.21	0.5	0.72	2.3	1.4	1.1
Ge	1 (2)		-	-	1	1.3	1.5	1.3	1.3	1	2.1
Sn	-		12	4 (5)	0.5	1.5	-	1.5	3	x	11
Pb	13 (18)		30	-	1	6	15	15	19	12	21
N	-		-	-	6	20	22	20	20	30	610
As	-		-	-	0.8	2	2.4	1.9	1.5	1.4	6.6
Sb	-		-	-	0.1	0.12	0.20	0.2	0.2	2.2	2.1
Bi	-		-	-	0.001	-	0.01	-	-	-	0.011
S	1760 (25)		800	5600 (105)	300	300	200	300	300	300	3100
Se	-		-	-	0.05	0.05	0.05	0.05	0.05	0.05	0.61
Te	-		-	-	0.001	-	0.001	-	-	-	0.011
F	2110 (19)		1470	8100 (96)	130	375	500	520	850	1360	510
Cl	19 (32)		-	280 (5)	100	160	100	200	200	430	160
Br	-		-	-	0.8	3.6	4.5	4.5	1.3	2.7	6.1
I	-		-	-	0.01	0.5	0.3	0.5	0.5	0.5	1.1

1. Kimberlites from Africa, India, Greenland and North America
2. Kimberlites from the Siberian Platform, USSR.
3. Based on analyses of 25 kimberlite deposits from Africa and 1 kimberlite deposit from North America. See Appendix III for list of references.

TABLE 3.4

PRINCIPAL MINERALS IN CARBONATITES AND KIMBERLITES

CARBONATITES	KIMBERLITES
Carbonates:	Primary Minerals:
Calcite	Olivine
Siderite	Pyrope
Ankerite	Chrome-pyrope
Dolomite	Diopside
Strontianite	Chrome-diopside
Silicates:	Enstatite
Olivine	Bronzite
Diopside	Ilmenite
Augite*	Phlogopite(0.51)*
Aegirine-Augite*	Chrome-spinel
Aegirine*	Apatite*
Riebeckite*	Magnetite
Chrysotile	Perovskite*
Antigorite	Zircon
Phlogopite*	Chromite
Vermiculite*	Graphite
Chlorite	Diamond
Nepheline	Secondary Minerals:
Orthoclase	Auto-metamorphic
Microcline	Serpentine*
Zircon	Serpophite
Sphene	Magnetite
Wollastonite	Chlorite
Vesuvianite*	Hydrothermal
Sulphides and sulphates:	Calcite
Barite	Dolomite
Pyrite	Serpophite
Galena	Magnetite
Sphalerite	Pyrite
Chalcopyrite	Barite
Pyrrohotite	Strontianite
Oxides and hydroxides:	Quartz
Magnetite	Chalcedony
Hematite	Zeolites
Pyrochlore*	Supergene
Ilmenite	Hydroxides of Iron
Rutile	Vermiculite*
Perovskite*	Montmorillonite*
Pandaite	Kaolinite*
Betatite	Illite*
Columbite	Chlorite*
Fersmite	Nontronite
Halides:	
Fluorite*	
Phosphates:	
Apatite*	
Monazite	

*Indicates fluorine-bearing minerals.

principal minerals in kimberlites and carbonatites are given in Table 3.4. Both types of deposits contain a large selection of minerals, many of which are, however, of only minor importance.

Kimberlites have a major elemental composition (including Ni, Cr and Co) which is similar to ultrabasic rocks, but show a marked increase in the amounts of K, Li, Ba, Sr, Rb, Y, La, Zr, Th, U, Ti, P, Nb, and the light rare earths, due mainly to the increased abundance of phlogopite, ilmenite, calcite and apatite.

Carbonatites are composed almost entirely of calcium and magnesium carbonates with smaller amounts of phosphates and minerals containing silica, alumina and iron oxides. They have a distinctly different major element composition when compared to other igneous rocks.

Kimberlites can be distinguished from other rock types by their abnormally high contents of F, B, Nb, Ta, Cr, Co, Ni, and the rare earth elements. No single element in this group can, however, be used to discriminate between kimberlites and all other rock types. For example, Cr, Co, and Ni present similar concentrations in both kimberlites and ultrabasic rocks. Certain of the remaining elements mentioned above can, however, often be used to differentiate between these two rock types.

Carbonatites are characterised by high concentrations of Ba, Sr, Nb, Ta, Nb, F and the rare earth elements. As described above, many of these elements also show considerable enrichment in kimberlites. Carbonatites may, however, be easily distinguished from kimberlites by their low Cr, Co and Ni content.

Consideration should be given to the above-mentioned chemical characteristics when planning a geochemical exploration programme utilizing stream sediments and soils. Proper selection of a suite of elements capable of detecting both kimberlites and carbonatites and differentiating between them would be required for efficient prospecting. This aspect is discussed in the conclusions of this section.

3.2.2.3.2 Fluorine in Carbonatites

The range and mean fluorine content of carbonatites is 200-24,000 ppm and 8,100 ppm respectively. Compared with the fluorine content of alkali-syenites (1,800 ppm Table 1.2, Chapter I), with which carbonatites are closely associated, there is an enrichment of fluorine in the carbonatitic phase of alkali igneous complexes. The principal fluorine-bearing minerals in carbonatites are apatite, fluorite, pyrochlore, vermiculite, phlogopite, augite, aegirine, riebeckite and vesuvianite (Table 3.4). The first three minerals are the most important of this group. The large range for fluorine observed in carbonatites is a reflection of the various types of carbonatites that may be present in alkali igneous complexes. The silicocarbonatites generally contain much lower concentrations of fluorine than the calcic (sovite) or dolomitic (rauhaugite) carbonatites.

The rocks most closely associated with carbonatites are ijolite-melteigites and fenites, the latter being formed as the result of alkali metasomatism of country rock. Both these rock types may contain variable amounts of fluorine depending on the activity of fluorine in the carbonatitic magma and the compositional nature of the country rocks. Analyses available for fenites givea range of 200-1,100 ppm F and a mean of 560 ppm F.

On the whole, alkali syenite complexes, whether they contain carbonatites or not, are characterised by high concentrations of fluorine. Once these complexes are found, however, it is often possible to differentiate the various phases within them on the basis of their fluorine contents.

3.2.2.3.3 Fluorine in kimberlites

The analyses for 45 kimberlite deposits (Table 3.6) give an overall range and mean fluorine content of 210-7,490 ppm and 1,740 ppm respectively. The large variation in fluorine content is due mainly to the large variation in modal content of the minerals capable of concentrating fluorine. The principal fluorine-bearing minerals in kimberlites are phlogopite, apatite, serpentine, and perovskite (Table 3.4). In the supergene zone of kimberlite deposits various clay minerals such as vermiculite, montmorillonite and kaolinite also concentrate fluorine.

The fluorine content of 27 kimberlite deposits studied by the author are presented in Table 3.5. The samples have been divided into hardebank, blue ground, and yellow ground material. For hardebank and blue ground material those deposits for which there are more than one analysis often exhibit considerable variation in fluorine content. This is undoubtedly a reflection of the great variation in mineralogic composition observed for these deposits; many kimberlites also consist of a number of kimberlitic phases. Comparing the fluorine content of the types of kimberlite material there appears to be little difference between the fluorine content of hardebank and blueground. The fluorine content of yellow ground is similar to that for blue ground (e.g. Pike Co, Montrose, and Du Toit's Pan kimberlites), but since there is a considerable difference in the compositions of blue and yellow ground in kimberlites (increase in silica and alumina

TABLE 3.5

FLUORINE IN KIMBERLITES

Location and name	Type	Fluorine (ppm)		
		Hardebank	Blue ground	Yellow ground
SOUTH AFRICA				
Premier mine	B	640;800	520;1,280	-
De Beers mine	B	1200;2400	-	-
Kimberley mine	B	-	2400	-
Klipfontein mine	B	1000;1680	-	-
Du Toit's Pan mine	B	-	1040	960
Montrose mine	B	-	288	860
Wesselton mine	B	1680	-	-
Benfontein sill*	B	1680	-	-
Frank Smith mine	M	2480	-	-
Lion Hill mine	M	1480	-	-
Voorspeed mine	M	-	800	-
Lace Din mine	M	-	-	800
Boshof District	M	1120	-	-
LESOTHO				
Blow 300*	?	1280	-	-
Ngopetsoeu*	B	1520	-	-
Lipilaneng*	?	2240	-	-
Letseng-La-Terrae	?	680	-	-
Kao Quarry	B	710;860	-	-
Kao Satellite	B	1255	-	-
Matsoku*	?	1440	-	-
Marakebei MR-1*	M	-	1920	-
Marakebei MR-2*	M	2400	-	-
Monastery mine	B	1645	-	-
Pipe 200	B	1830;2440	-	-
SIERRA LEONE				
Koidu pipe 1	B	1000;1160 1680;1800	-	-
Koidu pipe 3	B	1240;1240	-	-
USA				
Pike Co. Arkansas	M	-	2520;2000 1600;1640	2000, 2700

1. Deposits marked with an asterisk are not diamond bearing

2. B - basaltic kimberlite
M - micaceous kimberlite
? - type unknown

TABLE 3.6

FLUORINE IN ULTRABASIC AND ULTRAMAFIC ROCKS

Rock Type	Range	Mean*	Reference
Ultramafic Inclusions in Basalt			
Dunite	-	8(1)	48
Pyroxenite	-	8(1)	48
Peridotite	8-86	25(10)	48
Alpine Ultramafic Intrusions			
0-5% Serpentine			
Dunite	8-58	27(7)	48
Peridotite	8-20	8(4)	48
10-75% Serpentine			
Dunite	8	8(3)	48
Peridotite	8-8	8(2)	48
Serpentinite	8	8(4)	48
95-100% Serpentine			
Serpentinite	8-540	97(11)	11,48
Ultramafic Rocks from Layered Intrusions			
Pyroxenite	138-143	140(2)	48
Peridotite	-	8(2)	48
Picrite	-	81(1)	48
Serpentinite	-	88(1)	48
Ultramafic Rocks from Metamorphic Provinces			
Eclogite**	80-192	136(2)	66
Micaceous Ultramafic Rocks			
Mica Pyroxenite	500-1,600	940(6)	40
Mica Peridotite	1920-2000	1960(2)	26
Alkaline Ultramafic Rocks			
Melteigites	Tr. -2000	1200(9)	6,12
Vibetoites	3000-3500	3200(3)	6,12
Jacupirangites	600-4400	2600(8)	6,12
Kamperite	-	700(1)	6
Shonkinite	-	900(1)	6
Barkevikite	-	1100(1)	6
Lamprophyre Dyke Rocks			
Spessartites-Vogesites	700-1600	1200(17)	34
Minettes-Kersantites	1200-2400	1700(17)	34
Monchiquites-Camptonites	-	8700(?)	7
Damkjernites	1000-1500	1200(4)	6
Grorudites	-	450(?)	7
Sannaite	-	800(1)	6
Alvikites	Tr. -3700	1900(15)	12
Alnoites	Tr. -3000	1400(6)	12
Ultramafic Inclusions in Kimberlites			
Dunite	-	530(1)	46
Pyroxenite	520-600	560(2)	46
Peridotite	190-660	346(6)	46,48
Eclogite	96-410	253(1)	46,48
Kimberlites**	210-7490	1740(45)	46,62,63, 64,65,66
Carbonatites	200-24000	8100(96)	6,12,13,20 38,41,53

NOTES:

See Appendix II for list of references

*number of analyses in brackets

**includes author's data

content respectively), a recalculation of the composition of the yellow ground material normalised against the blue ground material (on an Al constant basis) indicates a slight enrichment of fluorine in the yellow ground, probably in the clay minerals. Those kimberlites which can definitely be classed as micaceous (See Table 3.5) do not have consistently higher fluorine contents than the basaltic varieties. The fluorine content can not, therefore, be correlated with the phlogopite content, although those deposits which exhibit a low fluorine content (below 1,000 ppm) are all basaltic. The apatite content, and more probably the degree of serpentinisation with subsequent introduction of fluorine into the serpentine lattice by $F^- - OH^-$ substitution, also have some effect on the fluorine content of these deposits. From this it follows that it is impossible to estimate the fluorine content of kimberlites on the basis of their mineral composition.

There is no correlation between the fluorine content of kimberlites and their diamond content. The range of fluorine contents of deposits which are not diamond-bearing (indicated in Table 3.5) falls within the upper part of the range observed for all kimberlites.

A detailed analysis of two drill cores taken from Pipes 1 and 3 of the Koidu kimberlite deposits of Sierre Leone is presented in Fig. 3.1 and 3.2. These pipes are intruded into basement granites; wallrock brecciation is a common feature. For both pipes the anomalous patterns observed for Cr, Ni, Co, Ti and Fe indicate their ultrabasic composition. The anomalous pattern observed for fluorine coupled with the above mentioned patterns for the basic elements indicates the kimberlitic nature of these deposits. It is possible, therefore, to differentiate between kimberlites and most other rock types of basic composition, although this may not

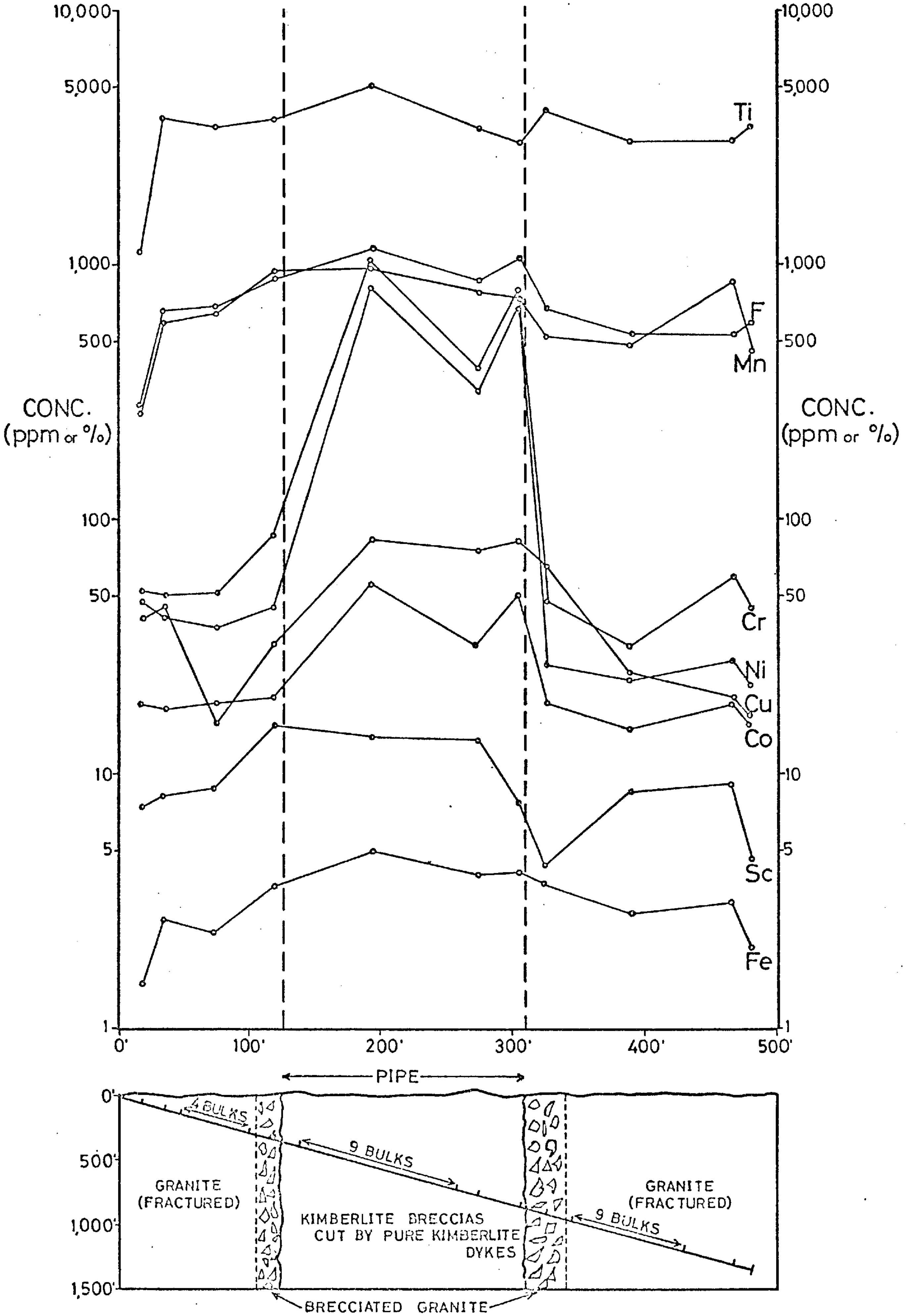


FIGURE 3.1 DISTRIBUTION OF TOTAL FLUORINE AND OTHER ELEMENTS IN A DRILL CORE THROUGH THE KOIDU No. 1 KIMBERLITE PIPE, SIERRE LEONE (All element concentrations in ppm except Fe which is in Wt. %)

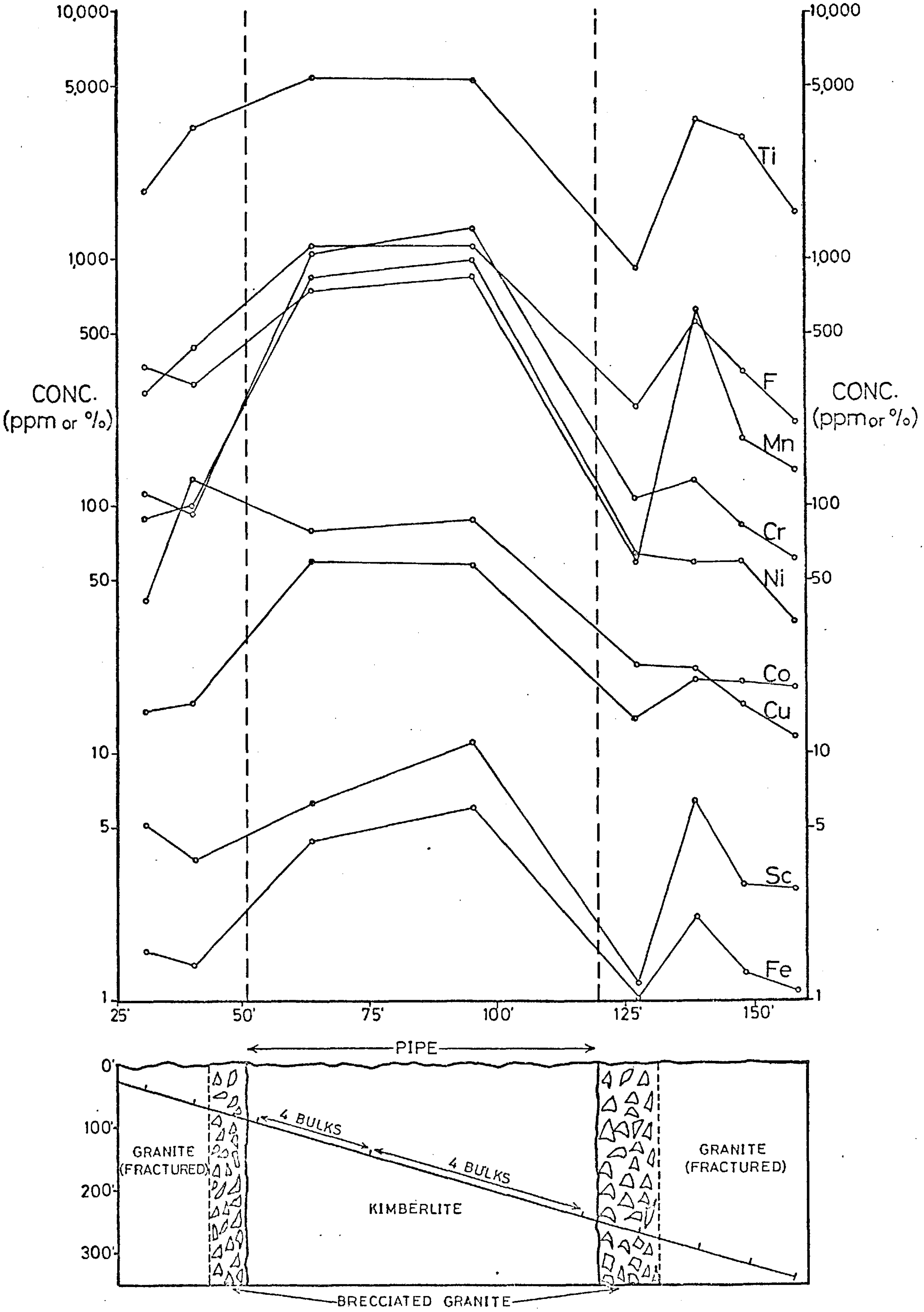


FIGURE 3.2 DISTRIBUTION OF TOTAL FLUORINE AND OTHER ELEMENTS IN A DRILL CORE THROUGH THE KOIDU No. 3 KIMBERLITE PIPE, SIERRE LEONE (All element concentrations in ppm except Fe which is in Wt. %)

always be possible solely on the basis of the fluorine and basic element contents since many micaceous and alkali-ultramafic rocks and lamprophyre dykes also contain high concentrations of fluorine. A comparison of the fluorine content of kimberlites and other ultrabasic and ultramafic rocks is given in Table 3.6. Dunites, pyroxenites and peridotites generally have fluorine contents of less than 100 ppm. As serpentinization increases in these rocks the fluorine content may reach as much as 500 ppm, which falls within the lower part of the concentration range for kimberlites. Differentiation of these rocks from kimberlites is generally possible on the basis of fluorine content of the rocks or overlying soils. For the micaceous and alkaline (mainly potassic) members of the ultrabasic rocks (e.g. mica pyroxenites and peridotites, alkaline ultramafics, and lamprophyres) the fluorine content is commonly well within the range for kimberlites and occasionally greater. These rock types generally contain high concentrations of Ni, Cr and Co and are often found in kimberlite and carbonatite provinces. Other elements characteristic of kimberlites such as Nb, Ta and the REE would also have to be employed to distinguish these rocks from kimberlites.

3.2.2.4 Methods of Prospecting for Carbonatites

3.2.2.4.1 Introduction

Both geochemical and geophysical methods of exploration have been applied successfully in the search for carbonatite complexes. Magnetic and radiometric surveys (both ground and airborne) are the principal geophysical techniques used when carbonatites of high magnetic and/or high U and Th content are suspected. Radiometric methods are often attenuated by deep overburden or when the carbonatite has little sub-outcropping exposure. Geochemical reconnaissance surveys are more effective in areas where little or no response can be achieved by geophysical methods.

Carbonatites exhibit relatively high concentrations of Nb, Ta, Y, La, REE, P, Mn, Fe, Ba, Sr, Zr, Be, U, Th and F. In some complexes Cu, Pb, Zn and Mo may also be enriched. Alkaline ultramafic rocks (mica peridotites and pyroxenites, melteigites, etc.) and lamprophyre dyke rocks (alvikites, alnoites, etc.) may often occur within carbonatite complexes and these rocks will be enriched in Ni, Cr, Co, V, Ti, P and F. To date, fluorine is the only element of the above-mentioned indicators which has not been examined as a prospecting pathfinder for carbonatites. Stream sediment surveys utilizing such elements as Nb, Zn, La, Mo, P and Be are effective in outlining carbonatite complexes of a sub-outcropping nature (Watts, 1960; Watts et al, 1970; Bloomfield et al, 1971; and Reedman, 1974). In addition, all of the elements mentioned above, with the exception of fluorine have been used in detailed soil surveys to map the various alkaline phases found in carbonatite complexes (Van Wambecke, 1960; Watts, 1960; Bloomfield et al, 1971; and Reedman, 1974). The use of these elements for mapping the lithology of alkaline igneous complexes is particularly applicable in residual environments.

An example of the efficacy of fluorine in geochemical prospecting for carbonatites is given in the following descriptions of the Kaluwe carbonatite area of Zambia.

3.2.2.4.2 Kaluwe Carbonatite Area, Zambia

3.2.2.4.2.1 Introduction

The Kaluwe carbonatite, located in south-central Zambia (Fig. 3.3), is a tilted synclinal mass having a thickness of approximately 800 feet and outcrops as a low curving scarp, 8 miles long and 0.75 to 1.5 miles wide.

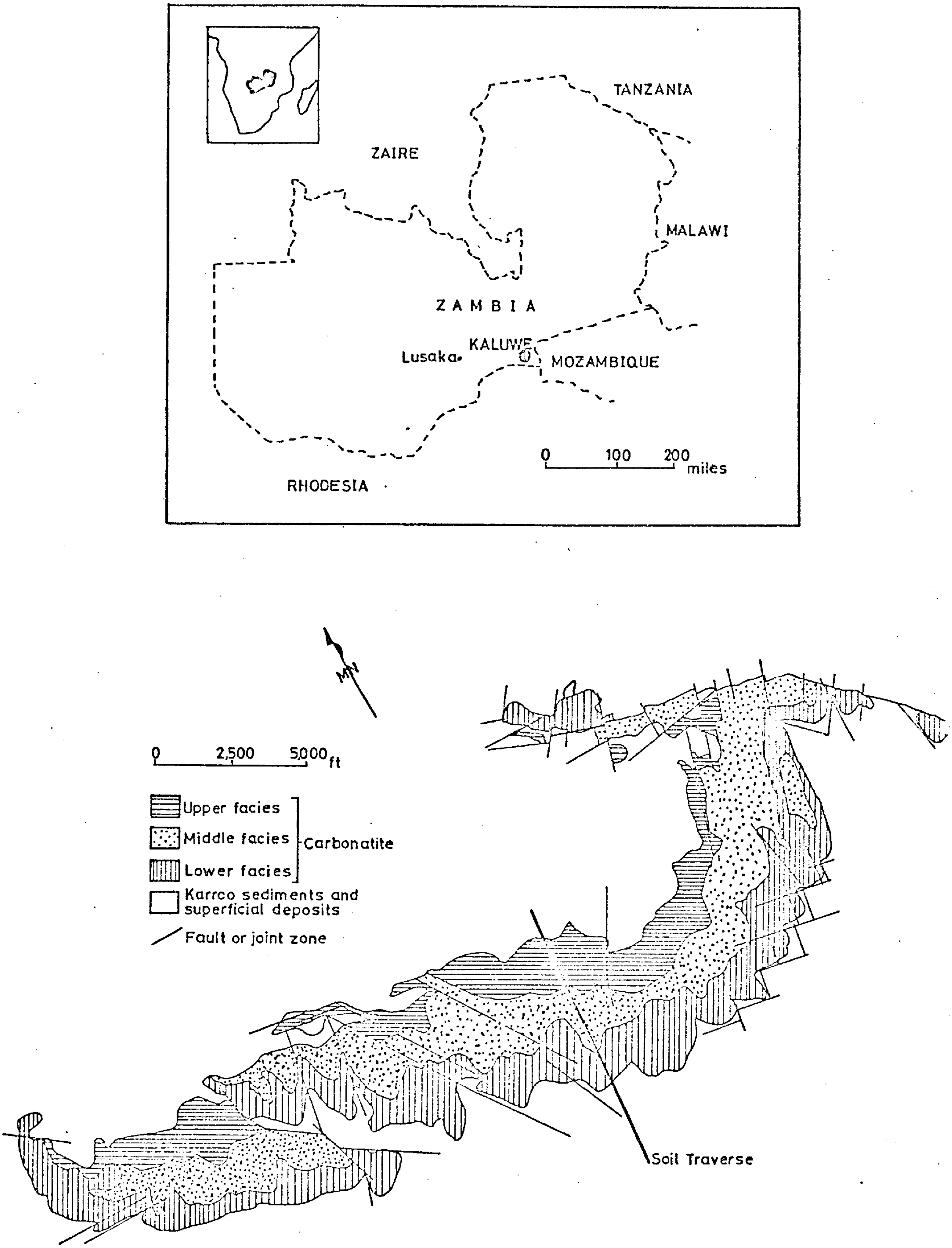


FIGURE 3.3 GEOLOGY AND LOCATION OF THE KALUWE CARBONATITE, ZAMBIA (Geology after Bailey in Tuttle and Gittins, 1967).

It is one of a number of carbonatites which lie within the Zambesi-Luangwa rift valley. The geology of both the deposit and the surrounding lithology have been described by Bailey (in Tuttle and Gittins, 1967). The carbonatite is intruded into Karroo sandstones and conglomerates. Unlike most carbonatites the body has neither a fenetized zone nor associated ijolite-melteigite and other ultramafic rocks. North of the deposit is a large area of basement schists and gneisses. The carbonatite itself consists of three facies; a middle facies of coarse agglomerate layers composed of fragments of a wide variety of medium to coarse grained sovites, with an abundant concentration of the accessory minerals martite, apatite, vermiculite and pyrochlore; a lower facies, essentially similar to the middle facies but consisting of finer grained agglomerates and a large amount of debris from the Karoo sandstones and conglomerates; and an upper facies similar to the lower facies but more coarsely agglomeratic. The middle facies is distinctly richer in Nb and P than the lower facies, and slightly richer than the upper facies.

The area is featured by hilly terrain and extensive alluvial flats along major rivers and many of the larger tributaries. The drainage pattern is typically dendritic. The residual soils are thin and juvenile.

As yet the deposit is not an economic source of Nb.

A detailed investigation of the dispersion in stream sediments and soils of Nb and a number of other associated elements has been carried out by Watts (1960; see also Watts et al, 1962). It is from this survey that samples were obtained for studies on the dispersion of fluorine.

3.2.2.4.2.2 Dispersion of Fluorine in Stream Sediments

Stream sediments (-80 mesh, 200 u) from the Kaluwe carbonatite area were analysed for total, acid-diffusible, and cold-extractable (0.01 M HCl and 0.01 M NaOH) fluorine. The results are plotted in Figs. 3.4, 3.5, 3.6, and 3.7 and the range and mean fluorine contents of stream sediments associated with the various rock types in the area is given in Table 3.7. All of the methods investigated adequately outline the carbonatite, but the 0.01M NaOH cold-extractable (CxF) method, although producing a definite anomaly and large dispersion trains associated with the carbonatite, also produces a number of erratic anomalies unrelated to the presence of carbonatite over both the basement and Karoo rocks. The anomaly contrast (3-fold) is much lower than that obtained by the 0.01M HCl method (15-fold), and the latter method is, therefore, a preferable method for CxF. For reconnaissance surveys the 0.01M HCl CxF method would appear to be adequate, but the acid diffusible and total methods may be preferred since these methods produce much higher anomaly contrasts. There is little difference between the anomaly contrasts for acid diffusible and total fluorine but the latter exhibits a much more clearly defined and longer dispersion train.

The difference between the mean 0.01M HCl cold-extractable, acid-diffusible and total fluorine contents of stream sediments draining the carbonatite (620, 3,024 and 5,770 ppm respectively) is largely a reflection of the ability of these methods to release fluorine from the various mineral forms in which it occurs. In carbonatites the principal fluorine-bearing minerals are pyrochlore (up to 4.6% F), apatite (up to 4% F) and fluorite (48% F), with lesser amounts occurring in vermiculite, amphiboles and rare earth fluoro-carbonates. None of these minerals are resistant to

TABLE 3.7

FLUORINE IN THE STREAM SEDIMENTS OF THE KALUWE AREA, ZAMBIA

Analytical Method	Rock Type	Number of Samples	F (ppm)	
			Range	Mean
CxF(0.01MNaOH)	Carbonatites	16	3.0-10.0	6.0
	Basement schists and gneisses	28	2.0-8.0	3.2
	Karroo	21	1.5-7.5	2.8
	Volcanics	3	2.0-3.5	2.5
CxF(0.01MHCl)	Carbonatites	16	140-800	620
	Basement schists and gneisses	28	14-60	40
	Karroo	21	8-120	27
	Volcanics	3	9-17	13
Acid Diffusible Fluorine	Carbonatites	16	440-5250	3024
	Basement schists and gneisses	28	20-270	86
	Karroo	21	23-225	94
	Volcanics	3	38-75	54
Total Fluorine	Carbonatites	16	875-8750	5770
	Basement schists	28	90-400	224
	Karroo	21	70-490	220
	Volcanics	3	75-215	145

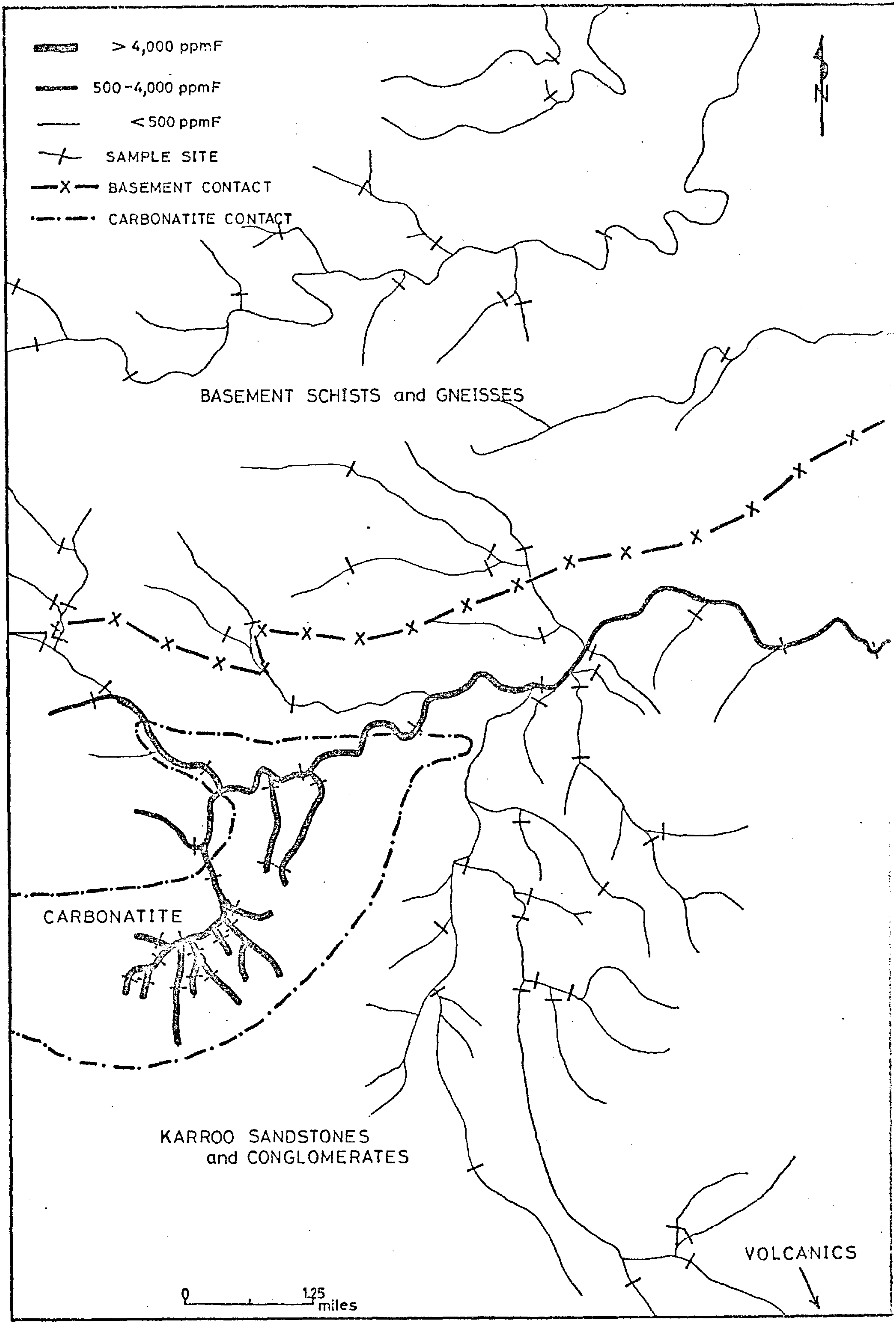


FIGURE 3.4 DISPERSION OF TOTAL FLUORINE IN STREAM SEDIMENTS, KALUWE CARBONATITE AREA, ZAMBIA (Geology and samples after Watts, 1960), -80 mesh, 200u)

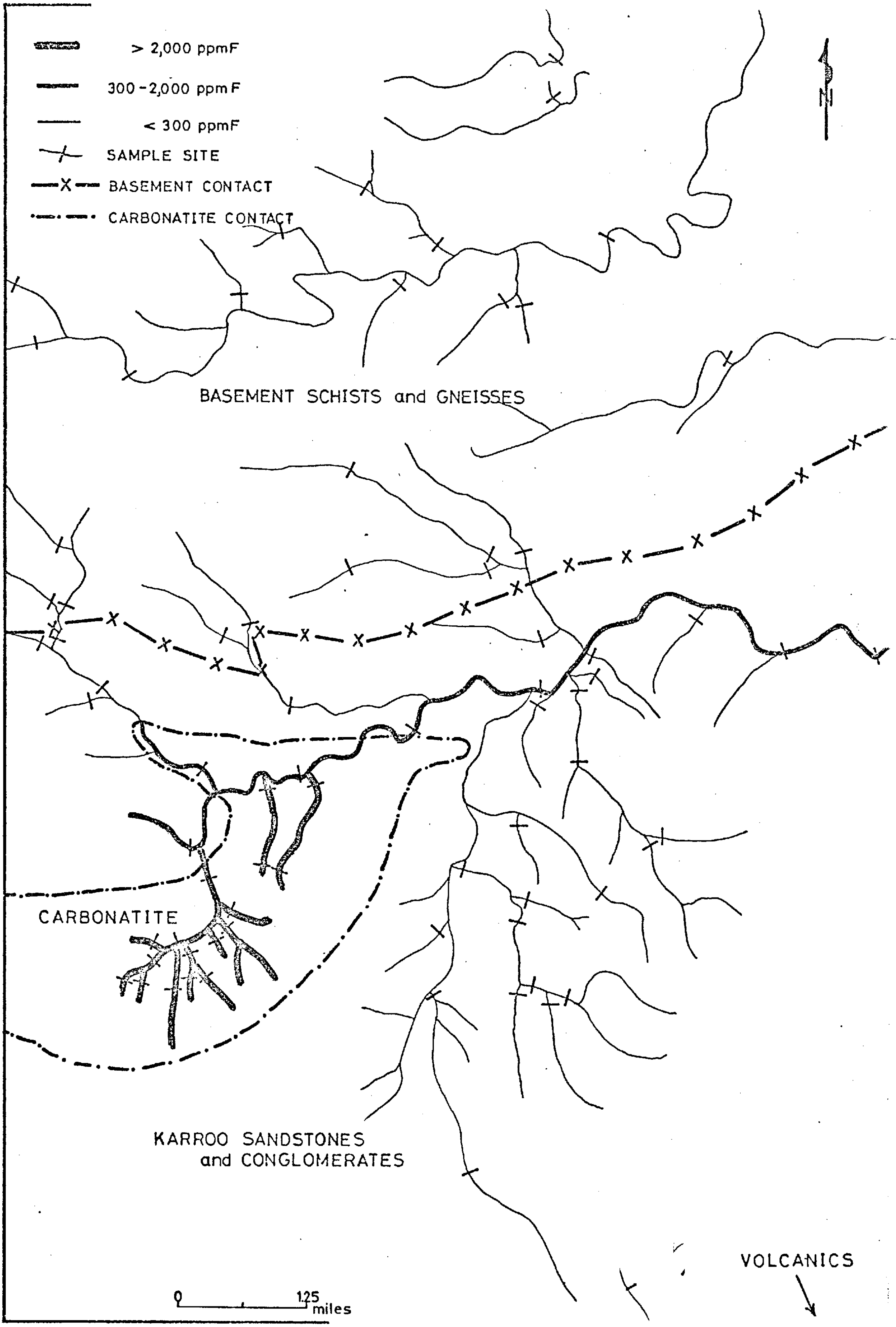


FIGURE 3.5 DISPERSION OF ACID DIFFUSIBLE FLUORINE IN STREAM SEDIMENTS, KALUWE CARBONATITE AREA, ZAMBIA (Geology and samples after Watts, 1960); -80 mesh, 200u)

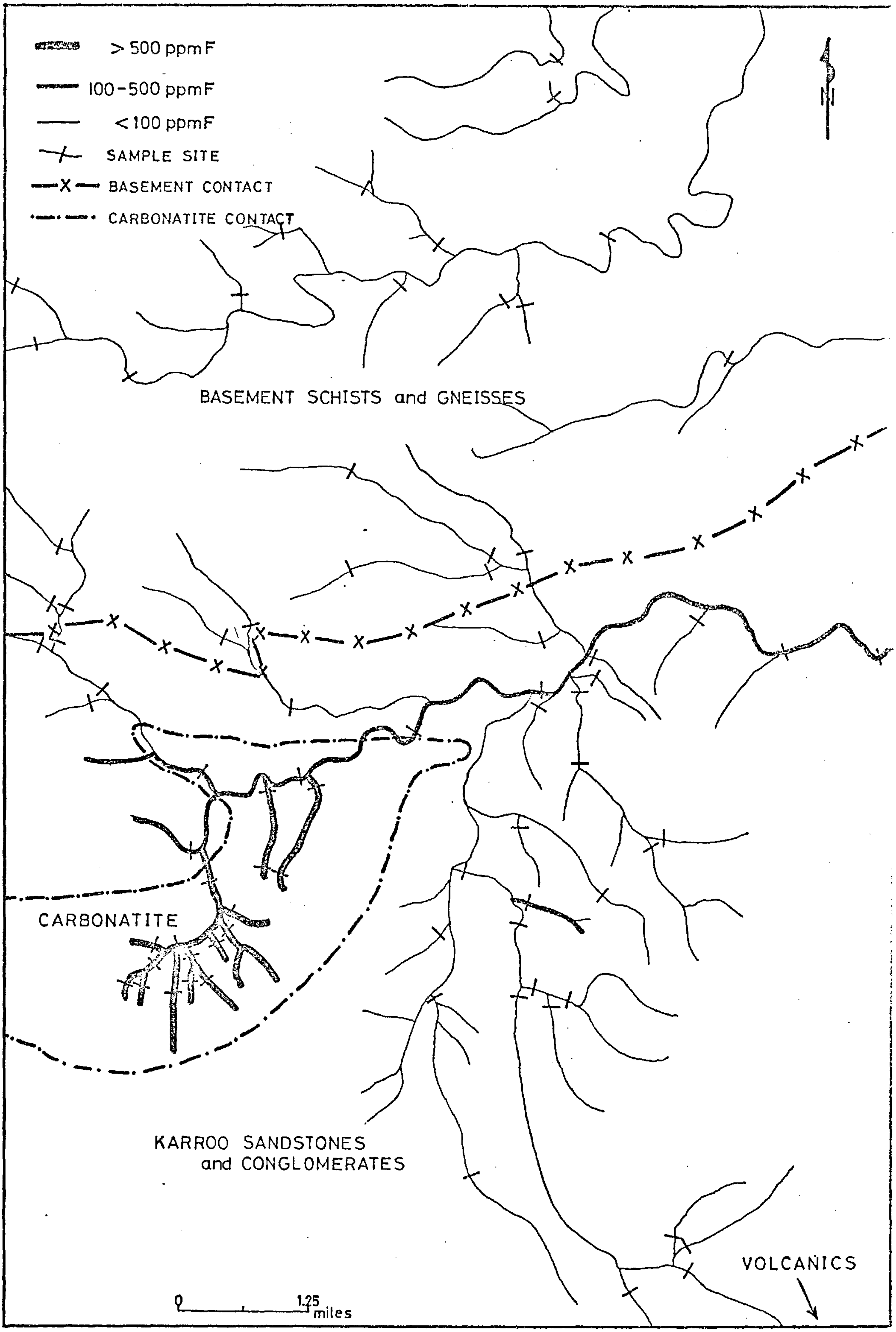


FIGURE 3.6 DISPERSION OF CxF (0.01M HCl) IN STREAM SEDIMENTS, KALUWE CARBONATITE AREA, ZAMBIA (Geology and samples after Watts, 1960); -80 mesh, 200u)

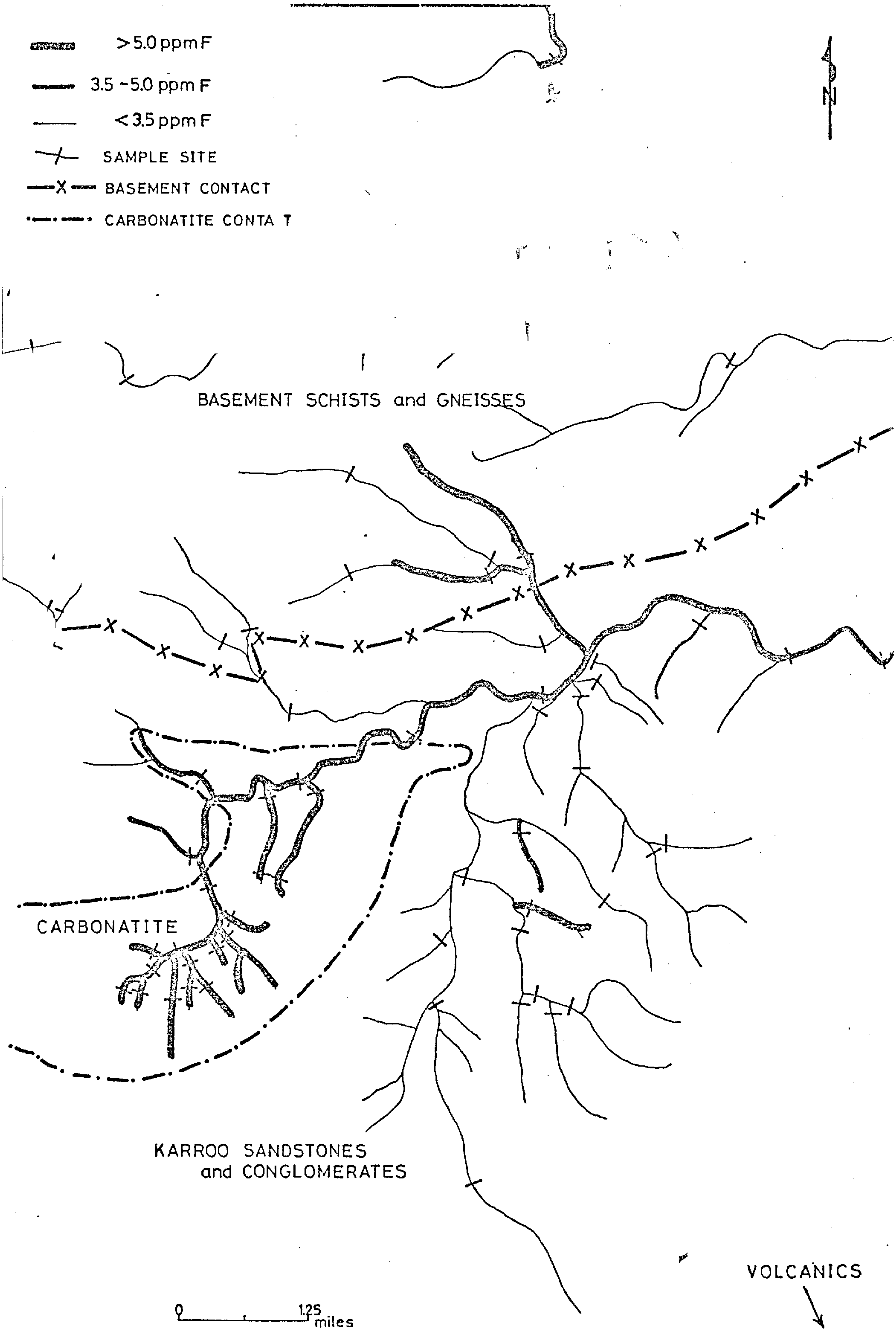


FIGURE 3.7 DISPERSION OF CxF (0.01 M NaOH) IN STREAM SEDIMENTS, KALUWE CARBONATITE AREA, ZAMBIA (Geology and samples after Watts, 1960; -80 mesh, 200u)

the NaOH fusion attack of the total method. The acid diffusible method readily attacks apatite and fluorite but not pyrochlore, and the 0I.01M HCl method attacks apatite and fluorite only slightly but extracts considerable amounts of the fluorine adsorbed on clays (Table 2.4, Chapter II). Assuming that the means for the various methods are representative of the stream sediments draining the carbonatite, these results indicate that more than 40% of the total fluorine is in a mineral form or forms which cannot be digested by the orthophosphoric acid of the acid diffusible method. Pyrochlore is undoubtedly the chief mineral of this group; its presence in large amounts in these streams has been confirmed by Watts (1960), who found that more than 80% of the Nb present was in the non-magnetic fractions. Pyrochlore, being both non-magnetic and the principal concentrator of Nb, undoubtedly makes up the major part of this fraction. Of the remaining amount of fluorine not accounted for by pyrochlore approximately 90% of the element (50% of total F) is in a form or forms not attacked by 0.01M HCl. Apatite, fluorite, and some of the micaceous and rare earth fluorocarbonate minerals must, therefore, account for 50% of the total fluorine while less than 10% of the total fluorine (extracted by 0.01M HCl) can be attributed to fluorine dispersed in the ionic state. It should be noted that these percentages are only approximations since the 0.01M HCl method will attack apatite and fluorite to some degree, and pyrochlore is not entirely resistant to the orthophosphoric acid attack.

Based on the evidence just presented it appears that a large percentage of the fluorine (80-90%) is dispersed in a mechanical form as discrete minerals (pyrochlore, apatite, fluorite, etc.). It is essential, therefore, when prospecting for carbonatites in areas where mechanical transport is not thought to be operative (i.e. carbonatites not exposed at surface) that careful orientation studies be carried out to determine whether the 0.01M HCl cxF method would be more useful in reconnaissance surveys than the acid diffusible or total methods.

3.2.2.4.2.3 Dispersion of Fluorine in Soils

The soils in the Kaluwe area are freely drained, thinly developed (2 to 3 feet) juvenile soils. Over the basement schists and gneisses the soils are grey micaceous sandy soils with good accumulation of iron oxides in the B horizons. The fluorine content of soils over basement rocks, as shown in Fig. 3.8, increases almost constantly with depth from approximately 200 ppm in the topsoil to 400 ppm in weathered bedrock. Over the Karoo rocks the soils are reddish brown, sandy or pebbly soils commonly exhibiting an accumulation of calcium carbonate. The distribution of fluorine in the soil profile over these rocks (Fig. 3.9) is one of increasing concentration with depth similar to that for soils over basement rocks. The fluorine content increases from about 50 ppm in the topsoil to about 450 ppm in the weathered bedrock. This pattern of increasing concentration with depth observed for the Karoo and basement rocks is consistent with the process of weathering and leaching of bedrock with subsequent release of fluorine from fluorine-bearing minerals that are not resistant to weathering, followed by removal of the fluorine from the soil profile into the groundwater system. The soils over the carbonatite are ferruginous calcareous soils that have a reasonably well developed B horizon and are generally less than six feet deep. The distribution of fluorine in these soils (Fig. 3.10) is antipathetic to that for the Karoo and basement soils in that there is a general decrease with depth as bedrock is approached. The decomposed bedrock contains approximately 10,000 ppm F. Although a general decrease in concentration with depth is evident for the soil regolith there is also a slight

DEPTH	DESCRIPTION
0-1"	Fine dark brown sandy soil with litter
1-3"	Fine dark brown sandy soil; less friable
3-30"	Very hard reddish-brown slightly sandy soil
	Bedrock. (Hard gneiss).

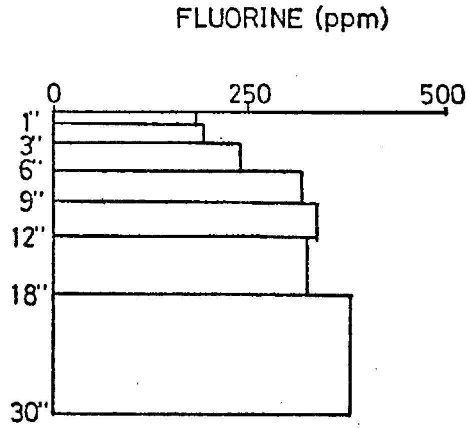


FIGURE 3.8

DISTRIBUTION OF TOTAL FLUORINE IN A SOIL PROFILE OVER THE BASEMENT SCHISTS AND GNEISSES, KALUWE CARBONATITE AREA ZAMBIA (Samples and profile description after Watts, 1960; -80 mesh, 200u)

DEPTH	DESCRIPTION
0-$\frac{1}{4}$"	Fine loose red sand
$\frac{1}{4}$-2"	Red-grey fine sandy soil with rootlets
2-12"	Quartzite pebble layer with reddish sand
12-24"	Fine red sand, becoming harder with depth
24-28"	Fine red slightly calcareous sand, becoming harder with depth
28-48"	Rather hard fine calcareous sandstone
48-84"	Hard fine reddish-buff sandstone
84-108"	Hard fine reddish-buff sandstone with calcareous nodules

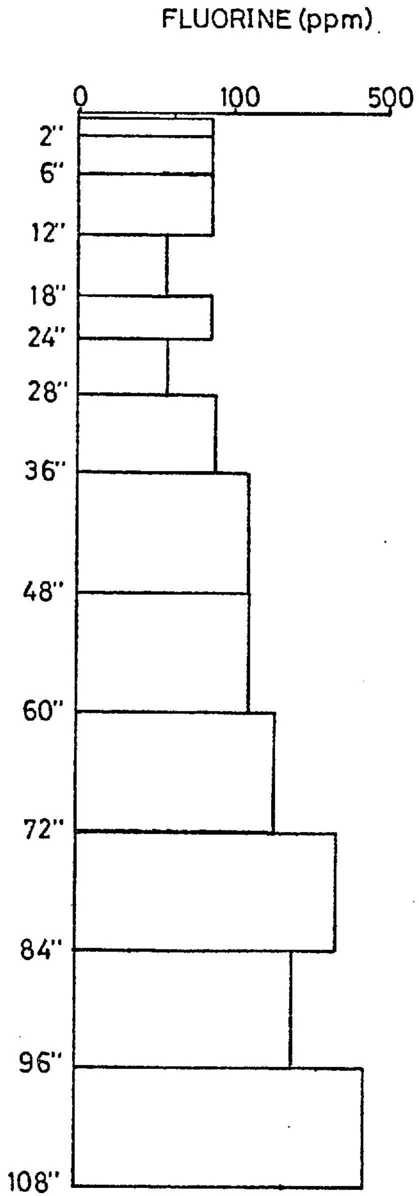


FIGURE 3.9 DISTRIBUTION OF TOTAL FLUORINE IN A SOIL PROFILE OVER THE KAROO SANDSTONES AND CONGLOMERATES, KALUWE CARBONATITE AREA, ZAMBIA (Samples and profile description after Watts, 1960; - 80 mesh, 200u)

DEPTH	DESCRIPTION
0-3"	Dk.brn.org.soil w. carbonatite fragments
3-6"	Dark brown fine soil
6-12"	Dk.brn.fine soil w. carbonatite fragments
12-24"	Medium brown fine soil with small carbonatite fragments
24-48"	Greyish-brown hard fine soil
48-60"	Very hard grey-brown calcareous soil
60-72"	Very hard decomposed carbonatite

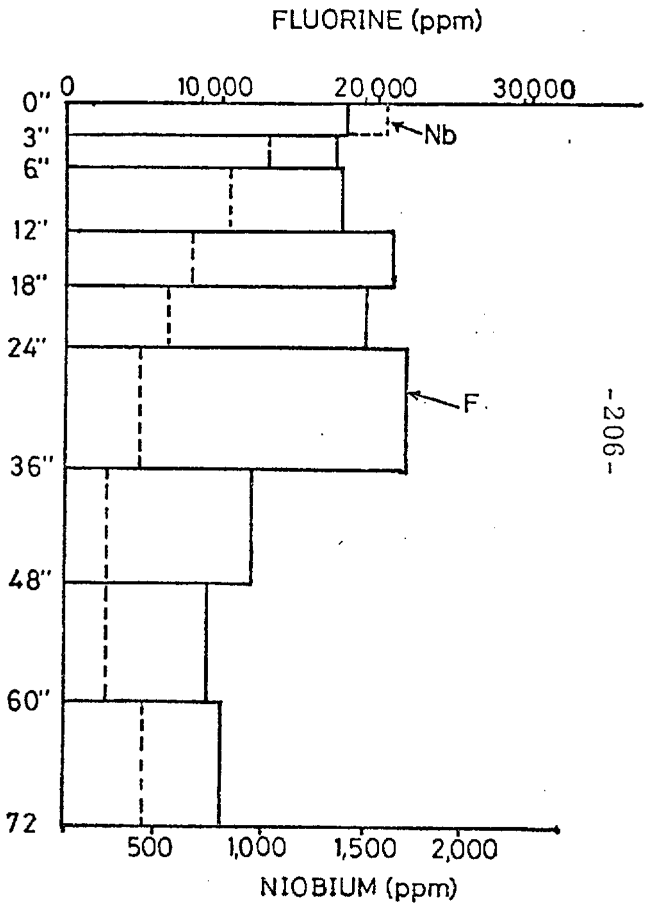


FIGURE 3.10 DISTRIBUTION OF TOTAL FLUORINE AND NIOBIUM IN A SOIL PROFILE OVER THE KALUWE CARBONATITE, ZAMBIA

(Samples, Nb analyses and profile description after Watts, 1960; - 80 mesh, 200 u)

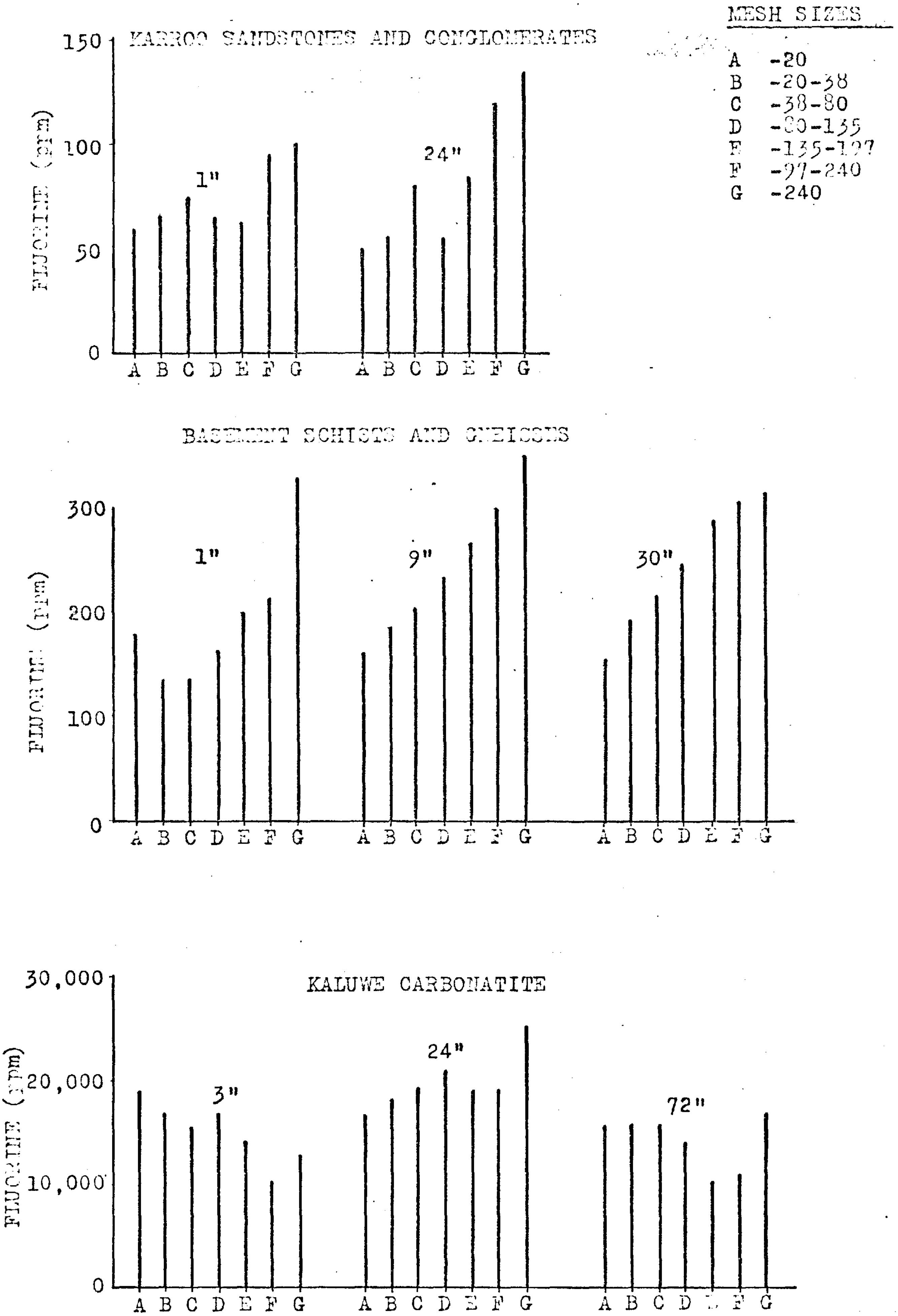


FIGURE 3.11 DISTRIBUTION OF TOTAL FLUORINE IN VARIOUS SIZE FRACTIONS (B. S. S.) OF SOILS OVER DIFFERENT ROCK TYPES IN THE KALUWE CARBONATITE AREA, ZAMBIA (Samples after Watts, 1960)

accumulation of fluorine in the B horizon with values reaching 22,000 ppm F. In the topsoil the fluorine concentration is approximately 18,000 ppm. This pattern of decreasing fluorine content with depth has also been noted for Nb (Fig. 3.10) in the Kaluwe soils (Watts, 1960). This author attributes the enrichment of Nb in the upper horizons of the soil to progressive leaching of the calcareous matrix of the carbonatite and the accumulation of chemically resistant pyrochlore and magnetite which are the principal Nb-bearing minerals. The Nb content decreases constantly with depth. For fluorine the increased concentration in the upper horizons can be attributed to the accumulation of pyrochlore, but the increased accumulation of fluorine in the B horizon relative to the A horizon indicates that some chemical remobilization occurs, probably as the result of partial dissolution of fluorite and apatite. The excess fluorine in the B horizon is most probably contained in the iron oxide and hydroxide phases (F-OH substitution).

Comparing the fluorine contents of soils over the various rock types, there is almost a 200-fold increase in the fluorine content of the carbonati soils compared to the Karoo soils and a 100-fold increase compared to the basement soils.

The variation in fluorine with particle size for various soil depths is shown in Fig. 3.11. For the Karoo and basement soils there is a gradual increase in the fluorine content with decreasing particle size from -20 to -240 mesh. There is little difference between the fluorine distribution patterns of the size-fractions of soils taken at different depths over these two rock types. Over the carbonatite there is a general tendency for the coarser size-fractions to contain the same or occasionally slightly more fluorine than the finer fractions. The higher fluorine contents observed for the coarser size-fractions may be related to the accumulation in these fractions of discrete fluorine-bearing minerals such as pyrochlore, apatite and fluorite. This is most marked in the upper horizons of the soil profile where leaching of the calcareous bedrock material is greatly pronounced.

The dispersion of total, acid diffusible and cold-extractable (0.01M HCl) fluorine in soils over the Kaluwe carbonatite is presented in Fig. 3.12, 3.13, and 3.14 (traverse located on Fig. 3.3). For purposes of correlation the Nb and P dispersions, related chiefly to the presence of pyrochlore and apatite respectively, are given in Fig. 3.15. For fluorine, the patterns observed for total, acid diffusible, and (0.01M HCl) cold extractable fluorine are similar although the difference in the chemistry of the carbonatite facies are much more clearly defined by (0.01M HCl) cxF. For total fluorine (Fig. 3.12) there is little difference between the fluorine content of soils taken at 0"-3" and 12"-15"; the latter generally have a slightly lower fluorine content except for soils over the upper facies where the 0"-3" soils contain less fluorine than the 12"-15" soils. The pattern over the upper facies can be related to the accumulation of fluorine in the B horizon of these soils as discussed earlier for Fig. 3.10. The highest concentration of fluorine over the carbonatite for all analytical methods occurs over the upper facies. The anomalous concentration of fluorine over this facies relative to the other facies is most probably due to an increased concentration of fluorite in the upper facies. The following evidence suggests this.

a) As indicated by the Nb dispersion (Fig. 3.15, after Watts, 1960) the upper facies contains much less pyrochlore than the middle facies. This is also in keeping with Bailey's observations (<u>in</u> Tuttle and Gittins, 1967) on the distribution of pyrochlore in this deposit.

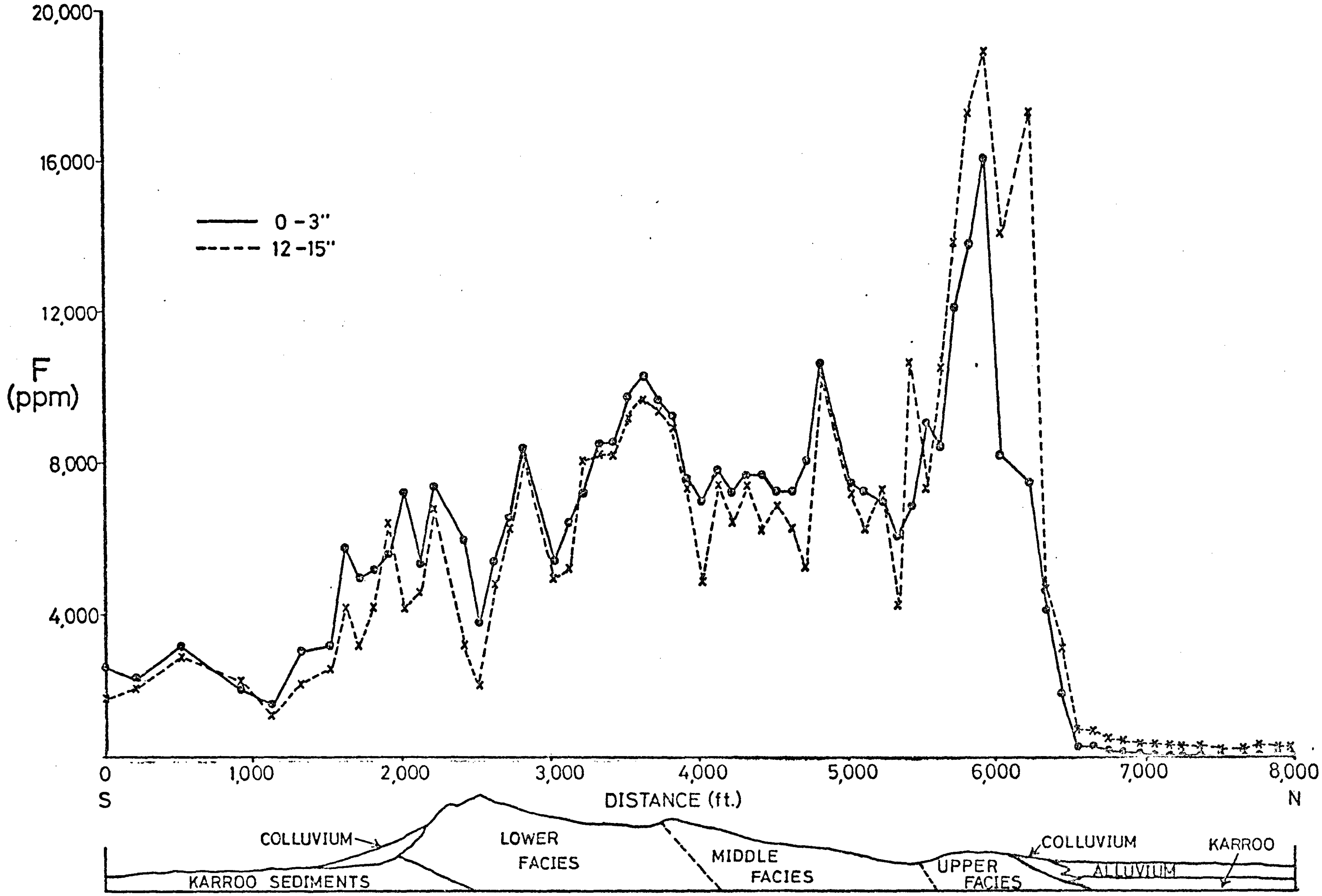


FIGURE 3.12 DISTRIBUTION OF TOTAL FLUORINE IN SOILS (-80 mesh, -200u.), KALUWE CARBONATITE, ZAMBIA (Samples after Watts, 1960, geology after Bailey in Tuttle and Gittins, 1967)

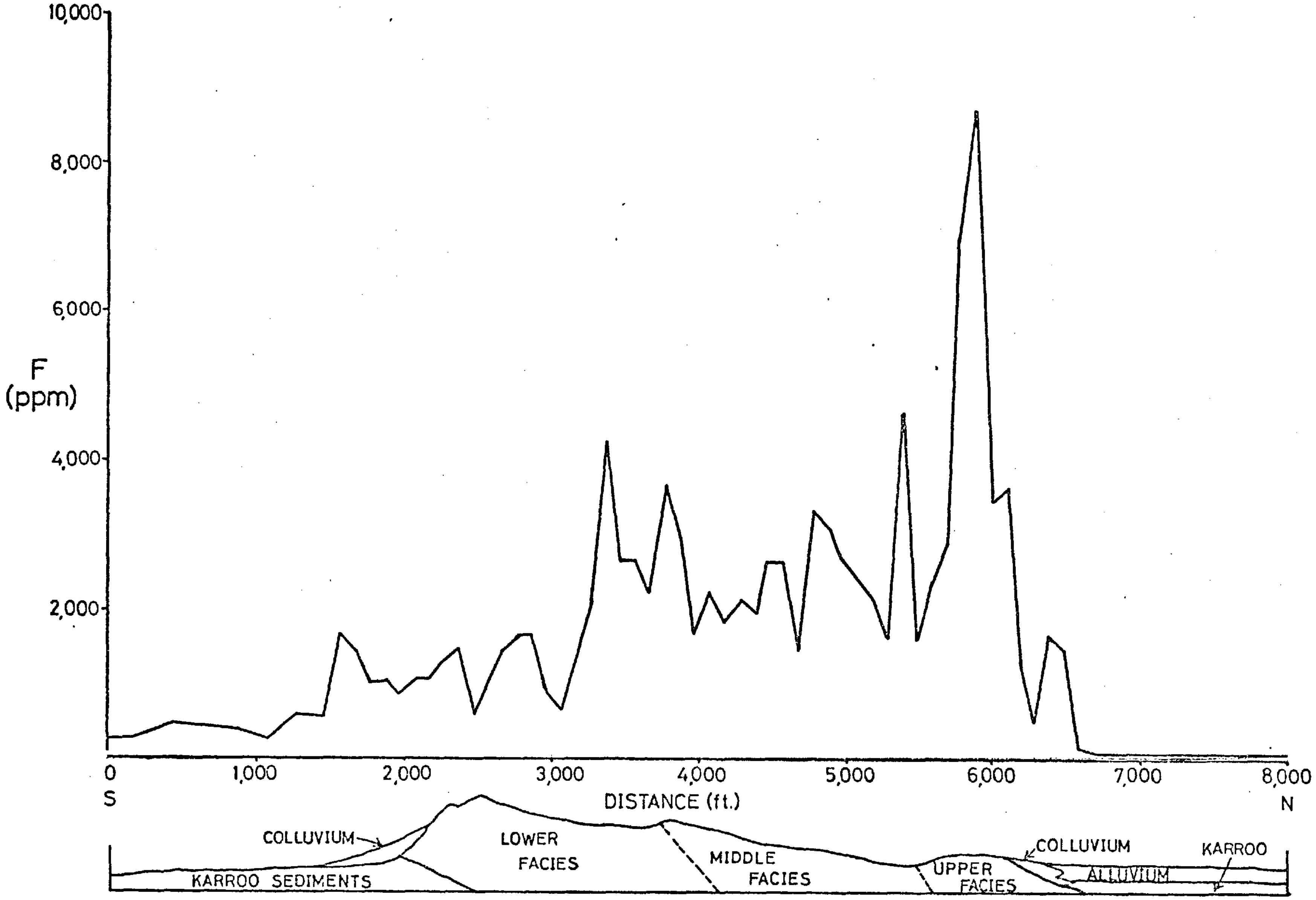


FIGURE 3, 13 DISTRIBUTION OF ACID DIFFUSIBLE FLUORINE IN SOILS (12-15", -80 mesh, <200μ) KALUWE CARBONATITE, ZAMBIA (Samples after Watts, 1960; geology after Bailey in Tuttle and Gittins, 1967)

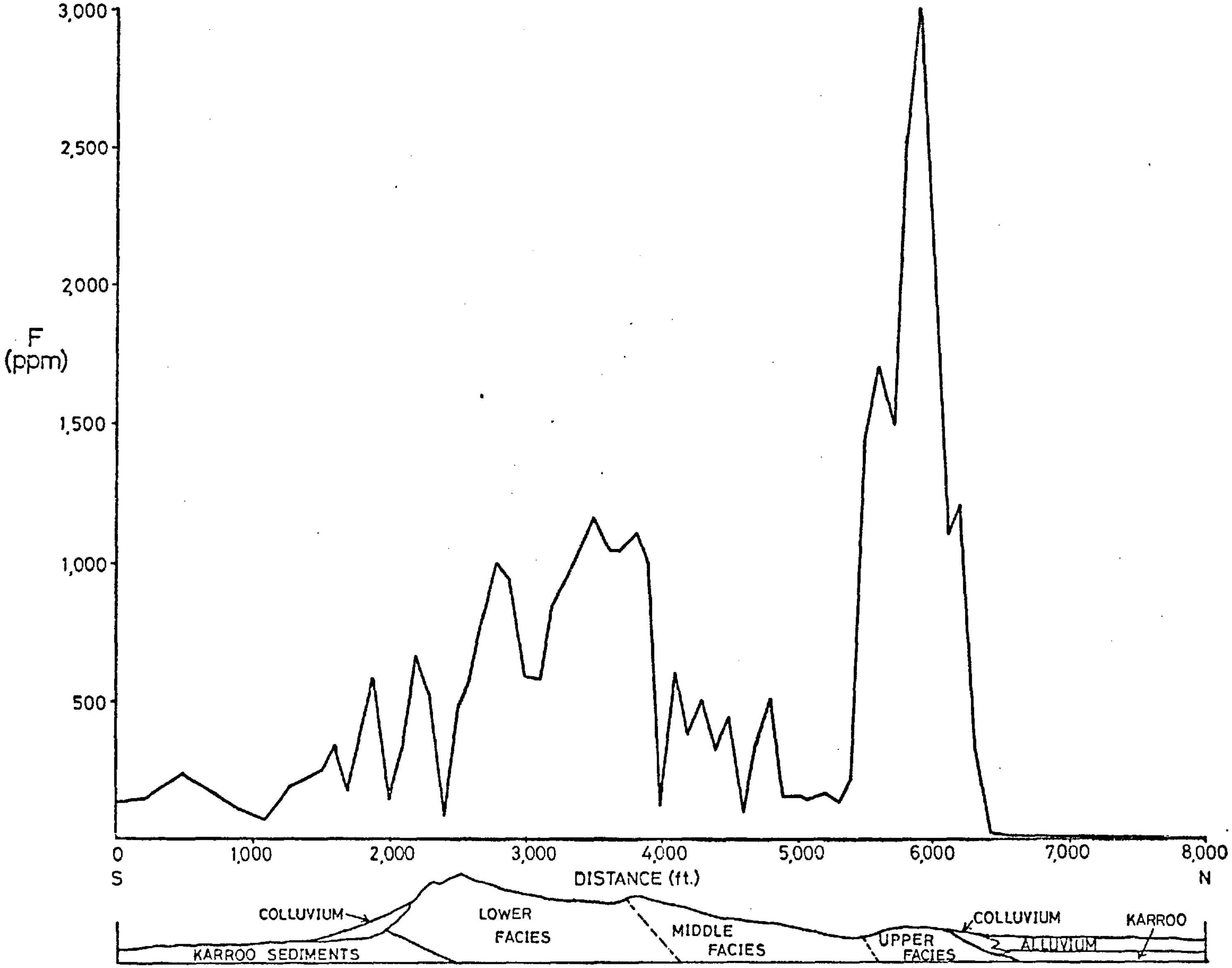


FIGURE 3.14 DISTRIBUTION OF CxF (0.01 M HCl) IN SOILS (12-15", -80 mesh, 200µ), KALUWE CARBONATITE, ZAMBIA (Samples after Watts, 1960; geology after Bailey *in* Tuttle and Gittins, 1967)

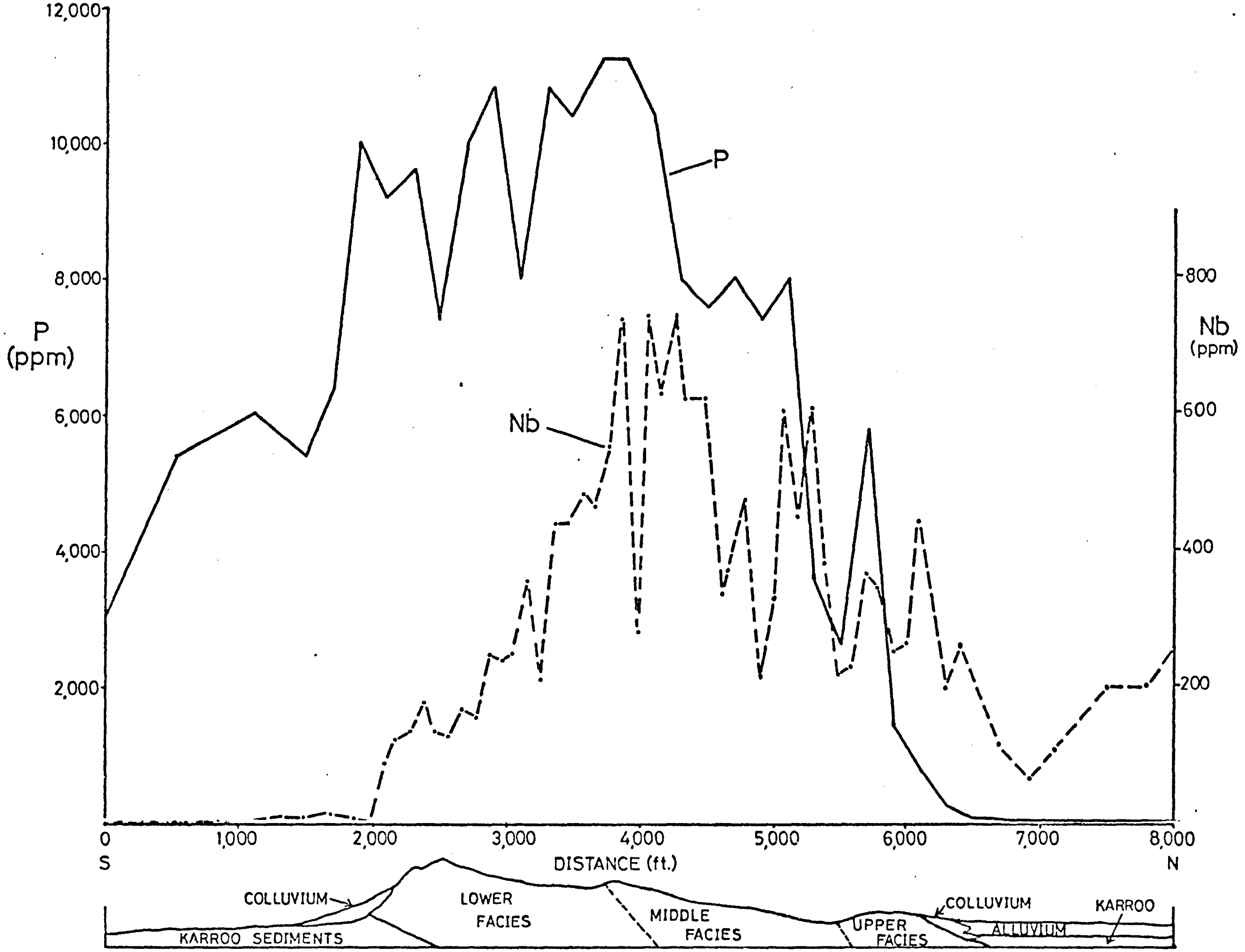


FIGURE 3, 15 DISTRIBUTION OF PHOSPHORUS AND NIOBIUM (12-15", -80 mesh, 200u), KALUWE CARBONATITE, ZAMBIA (samples and Nb analyses after Watts, 1960; geology after Bailey in Tuttle and Gittins, 1967).

b) The lowest concentrations of P over the carbonatite occur over the upper facies, and this facies must, therefore, be depleted in apatite relative to the other facies.

c) The relatively large amounts of fluorine in the soils over the upper facies that can be extracted by 0.01M HCl and the greater concentration of fluorine in the B horizon soils as opposed to the surface horizon (0"-3") suggests that most of the fluorine in these soils occurs in a mineral form which is more easily destroyed by chemical weathering (i.e. fluorite).

d) Both fluorite and apatite are completely dissolved by the orthophosphoric acid of the acid diffusion method. Pyrochlore is only slightly attacked. The evidence of (b) together with the fact that more than 60% of the total fluorine in these soils is released by this method compared with percentages of 30% to 40% for the middle and lower facies strongly suggests the presence of large concentrations of fluorite.

Over the middle facies which is richer than the upper and lower facies in pyrochlore (Bailey, in Tuttle and Gittens, 1967) the average cxF, acid diffusible and total fluorine contents of the soil are 300, 2,000 and 7,000 ppm respectively. This facies is also richer in apatite than the upper facies but does not contain as much apatite as the lower facies (see the dispersion of P in Fig. 3.15). The cxF content of these soils is less than 5% of the total fluorine and hence very little fluorite and exchangeable fluorine is present. The acid diffusible fluorine is about 30% of the total fluorine and much of this is probably derived from apatite. About 70% of the fluorine in these soils must, therefore, be contributed by pyrochlore.

Over the lower facies, soils covering the inner contact zone with the middle facies have high concentrations of fluorine and phosphorus. The niobium content is not significantly high over this area and the pronounced fluorine anomaly in these soils is most probably due to the enrichment of apatite in the bedrock. Despite the fact that phosphorus is high over the scarp zone of the lower facies, both fluorine and niobium exhibit their lowest concentrations over this part of the carbonatite. The low fluorine content is probably related both to the absence of large amounts of pyrochlore (as shown by the Nb content) and the increased amount of Karoo sandstone and conglomerate debris (Bailey, in Tuttle and Gittins, 1967).

North of the carbonatite the soils covering the alluvial material have very low fluorine and phosphorus contents while the niobium remains relatively high. The fluorine results do not support the existence of pyrochlore in the alluvial material and the high Nb content is more probably related to the enrichment of magnetite. For stream sediments draining the carbonatite Watts (1960) found Nb to be concentrated in large amounts (700-1,100 ppm) in the magnetic heavy mineral fraction. Fluorine may, therefore, be used to separate Nb anomalies related to the enrichment of magnetite from those related to the presence of pyrochlore.

South of the carbonatite the fluorine and phosphorus contents of the Karoo soils are relatively high (about 4,000 and 2,000 ppm respectively) whereas the niobium content is very low. The fluorine content of soil taken over the Karoo, well away from the carbonatite, is approximately 100 ppm (Fig. 3.9) and the elevated concentrations of this element over the Karoo soils near the carbonatite are probably related to the mechanical dispersion of apatite from the lower facies.

The results presented for the Kaluwe carbonatite indicate that fluorine is not only a valuable aid in mapping the lithology but is also useful for investigating the type of anomaly produced by the economic indicator element, in this case niobium.

3.2.2.5 Methods of Prospecting for Kimberlites

3.2.2.5.1 Introduction

Numerous methods of prospecting for kimberlites utilizing aerial photography, geophysics (airborne and ground), heavy mineral surveys, and geochemical prospecting have been investigated. Only the last two methods have demonstrated a reasonable degree of effectiveness. The general lack of surface expression and characteristic floral associations render aerial photography of limited application when prospecting for most kimberlite bodies. Similarly, because of the relatively small target size of kimberlites, airborne geophysical methods (radiometrics and magnetics) have had little success in detecting these bodies of rocks. Although, gravity methods have been applied successfully in outlining kimberlites once they have been found, other ground geophysical methods (mainly magnetics) have proved to be of only limited application in reconnaissance surveys due mainly to the low anomaly contrasts observed and the presence in the country rocks of bodies which give much greater anomaly contrasts (Wheildon, J. pers. communication).

To date, the most reliable indication of the presence of kimberlite deposits is the occurrence in drainage channels of diamonds accompanied by the more resistant kimberlite minerals such as pyrope garnet, chrome diopside and picro-ilmenite. Thus, heavy mineral surveys have been used extensively by the mining industry as a method of prospecting for kimberlites. Used on their own, however, these surveys pose a number of problems in terms of application. Many diamondiferous kimberlites contain very low concentrations of the indicator minerals, and detectable mineral trains are not formed in many places (e. g. Arkansas kimberlite province, USA; Gregory, 1969). In addition well marked mineral trains are not developed in areas of impeded or very little drainage such as in dambo and peneplaned areas. In these environments, which are often characteristic of the shield areas in which kimberlites are found, the prospector is limited to more detailed methods of exploration in areas selected as favourable on a geological basis. Taking into consideration the time-consuming and expensive nature of heavy mineral reconnaissance surveys, together with the above-mentioned problems, it is not surprising that methods of geochemical prospecting for kimberlites have been extensively investigated.

Although a number of workers (Holman, 1956; Alcard, 1959; Jedwab, 1958, 1959; Gregory, 1969; Gregory and Tooms, 1969; Correria, 1965; Litinskiy, 1961, 1963; Krivonov and Romanov, 1971; and Parra, 1974) have shown that Ni, Cr and Co produce strong geochemical anomalies in the residuum overlying kimberlites, these elements on their own are not conclusive pathfinders for kimberlites since similar anomalies may be obtained for other types of ultrabasic and basic rock bodies. Thus, in Sierre Leone kimberlite province Webb (1956) found that kimberlites could not be differentiated from basic schists on the basis of the Ni, Cr and Co contents of the soils, and in the Arkansas kimberlite province of the USA, Gregory (1969) found that due to the variable chemistry of the underlying lithology, Ni, Cr, Co and exchangeable Mg could not be used to detect kimberlites without the aid of a more specific pathfinder, in this case niobium.

Other investigators have also noted that elements characteristic of basic rocks (Ni, Cr, Co, Mg, Ti) cannot be used entirely on their own as indicators of kimberlites (Krivonov and Romanov, 1971; Litinskiy, 1961, 1963). Elements which have been proposed as qualifiers of the presence of kimberlites are Nb, Y, La, REE (Litinskiy 1961, 1963); Gregory 1969; and Krivonov and Romanove, 1971), and F (author's research). By incorporating one or a number of these elements in reconnaissance and detailed surveys and using them to investigate the Ni, Cr, Co, Mg, or Ti anomalies found during these surveys it is generally possible to differentiate between anomalies related to kimberlites and those that are not.

The high concentration of fluorine in kimberlites compared to most other ultrabasic and basic rocks, the ease with which geochemical materials can be analysed for this element and the need for qualifying pathfinders' as discussed above make fluorine an ideal choise as a pathfinder element of the presence of kimberlites. An example of the application of fluorine in prospecting for kimberlites is given below for the Arkansas kimberlite province of the USA. A summary on prospecting for kimberlites is given in the section entitled Conclusions on Prospecting for Kimberlites and Carbonatites.

3.2.2.5.2 Arkansas Kimberlite Area, USA

3.2.2.5.2.1 Introduction

The Prairie Creek kimberlite, the largest of the pipes, and the American Mine kimberlite, both representative of a number of other deposits in the Arkansas kimberlite area, are located near Murfreesboro in southwest Arkansas (Fig. 3.16). The geology of the area and a description of the Prairie

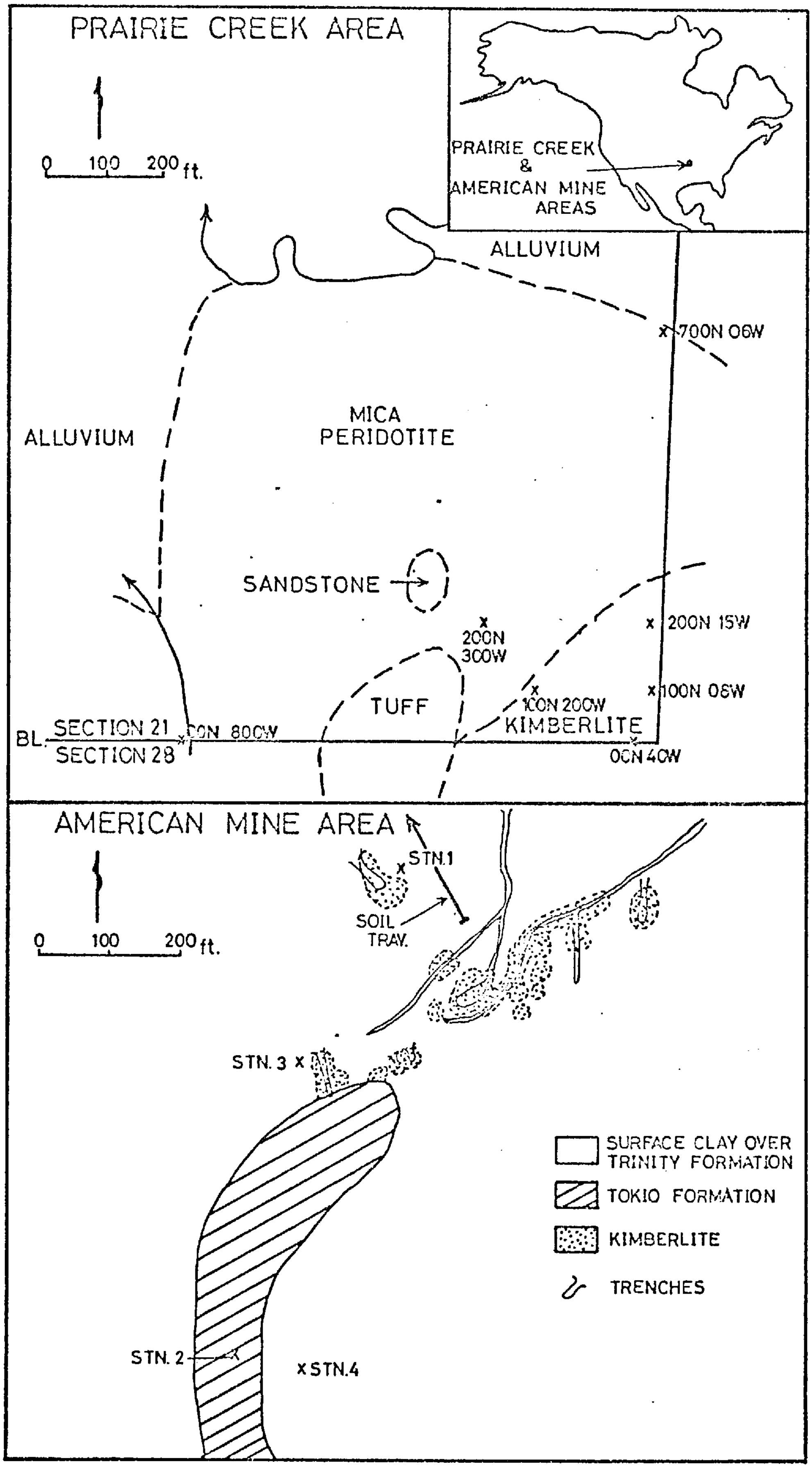


FIGURE 3.16 GEOLOGY AND LOCATION OF THE PRAIRIE CREEK AND AMERICAN MINE KIMBERLITE AREAS OF SOUTH WEST ARKANSAS, USA. LOCATION OF SOIL TRAVERSE AND SOIL PROFILES ALSO GIVEN. (Geology and samples after Gregory, 1969)

Creek kimberlite are given by Miser and Purdue (1929) and Miser and Ross (1923) respectively. A detailed study of the dispersion of Ni, Cr, Co, Mg, and Nb in stream sediments and soils over the Prairie Creek and American mine areas was carried out by Gregory (1969; Gregory and Tooms, 1969).

The Prairie Creek and American Mine kimberlites are intruded into Cretaceous conglomerates, clays, siltstones, limestones and marls of the Trinity, Woodbine and Tokio formations. Miser and Ross (1923) have described the Prairie Creek body (of which only the undisturbed portion is outlined in Fig. 3.16) as consisting of a mica peridotite (essentially non-diamondiferous) phase which encloses volcanic breccia (diamondiferous kimberlite) and fine-grained breccia (tuff) phases. Although differing slightly in their diamond content and mineralogy, there is little difference between the chemical compositions of the mica peridotite kimberlites (Table 3.8). Thus, Gregory (1969; Gregory and Tooms, 1969) was unable to differentiate geochemically between kimberlites and mica peridotites, associated with kimberlites. For exploration purposes it would seem advantageous to consider bodies such as the Prairie Creek intrusive as a kimberlitic intrusion of which only a single or a few phases are diamondiferous. This is quite a common feature of some of the African kimberlites (e. g. Tetseng-la-Terrae of Lesotho).

The American Mine area consists of small kimberlite bodies intruded into the Trinity Clay Formation. Only limited trenching and pitting have been done in this area, the deposits being uncommercial.

In the Prairie Creek complex the mica peridotite consists of a phlogopite-rich ground mass (56%) containing accessory perovskite and olivine, the

TABLE 3. 8

CHEMICAL COMPOSITION OF KIMBERLITE, MICA PERIDOTITE AND VOLCANIC TUFF, PRAIRIE CREEK KIMBERLITE AREA, USA (Samples after Gregory, 1969)

Element	Kimberlite (7)*		Mica Peridotite	Volcanic Tuff**
	Range	Mean		
Fe	5.5-9.3	7.3	9.7	1.1
Mn	927-1312	1084	1213	500
Cu	34-115	90	110	39
Pb	27-54	36	43	-
Zn	63-130	104	177	-
Cd	2-3	3	3	-
Ag	-	n. d.	n. d.	-
Mo	-	n. d.	n. d.	-
V	61-276	152	75	60
Co	50-96	81	105	43
Ni	1484-2035	1656	1996	210
Cr	1461-2000	1724	2130	120
Ti	12720-19000	15800	18978	7000
Mg	9.1-12.3	11.7	12.7	-
Ca	1.1-3.7	2.0	2.6	-
Sr	234-440	346	427	1200
Ba	290-2000	720	1017	7000
K	2.4-8.0	4.8	3.3	-
Na	200-12000	4600	2600	-
Li	9-35	24	10	-
Al	1.5-9.2	5.0	7.1	-
Ga	4.0-13.3	8.0	10.4	-
Be	-	n. d.	n. d.	-
Sc	4.1-14.2	10.1	10.4	-
F	1600-2500	1890	1920	600

* number of analyses in brackets

** analyses for Tuff after Gregory (1969) except F

All values in ppm except Fe, Mg, Ca, K and Al which are in Wt. %

latter almost completely serpentinized. The kimberlite or volcanic breccia is a brecciated serpentinized mica peridotite, which in addition to very fine-grained ilmenite, contains only a little pyrope garnet and chrome diopside. The tuff is composed of chlorite, phlogopite, serpentinite and carbonates, and has a chemistry distinctly different from that of the volcanic breccia and mica peridotite (Table 3.8).

3.2.2.5.2.2 Fluorine in Stream Sediments

The almost complete absence of indicator minerals such as pyrope garnet, chrome diopside and ilmenite in the kimberlites of the Arkansas kimberlite area dictates the use of geochemical drainage surveys for their detection. The work of Gregory and Tooms (1969) has shown that Ni and exchangeable Mg produce the largest anomaly contrast and longest dispersion trains in the drainage systems in the kimberlite area. A considerable number of false Ni and Mg anomalies were also found in the siltstone and limestone areas and hence the 'qualifying pathfinder' niobium was used to indicate conclusively the presence of kimberlites. In view of the difficulty of analysing for niobium and the ease of analysis for fluorine the latter element would seem to be more useful to the prospector.

The dispersion of fluorine in the drainage system associated with the American Mine kimberlites is shown in Fig. 3.17. Both the anomaly contrast and the length of dispersion train are similar to that obtained by Gregory (1969) for Ni and exchangeable Mg. Fluorine together with Ni and exchangeable Mg can, therefore, be used both in reconnaissance surveys and detailed studies specifically aimed at the differentiation of false and legitimate anomalies. Fluorine cannot be used on its own in reconnaissance surveys since a number of other types of fluoriferous deposits (alkali

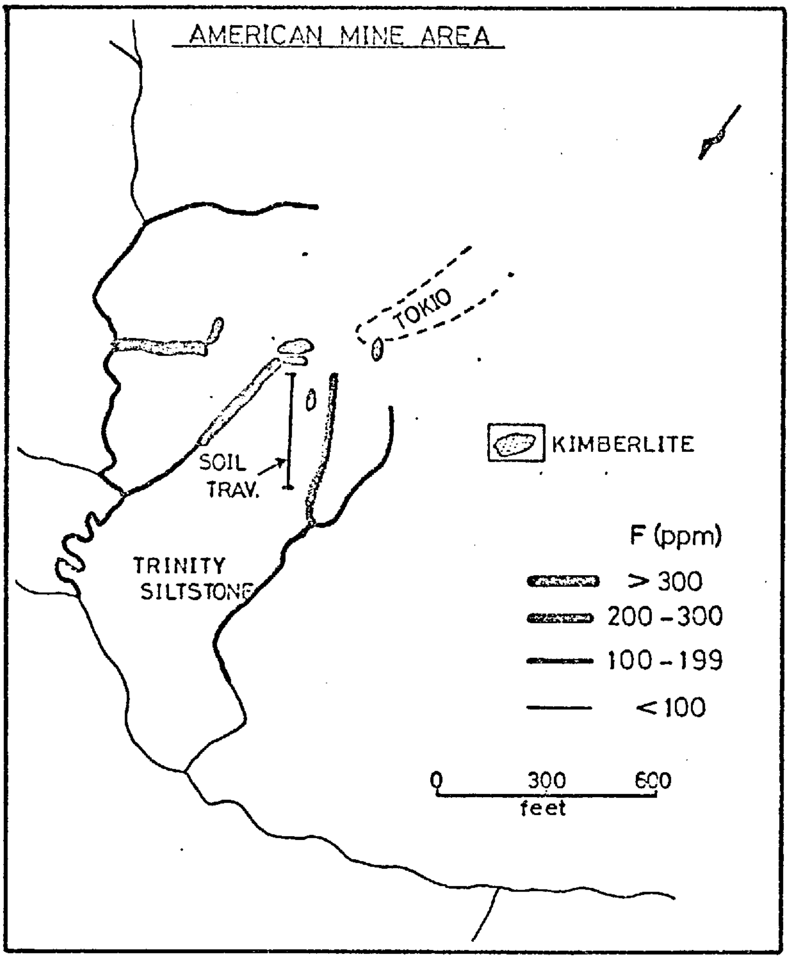


FIGURE 3.17 DISPERSION OF TOTAL FLUORINE IN STREAM SEDIMENTS OF THE AMERICAN MINE AREA, ARKANSAS, USA (-80 mesh, 200u, samples after Gregory, 1969)

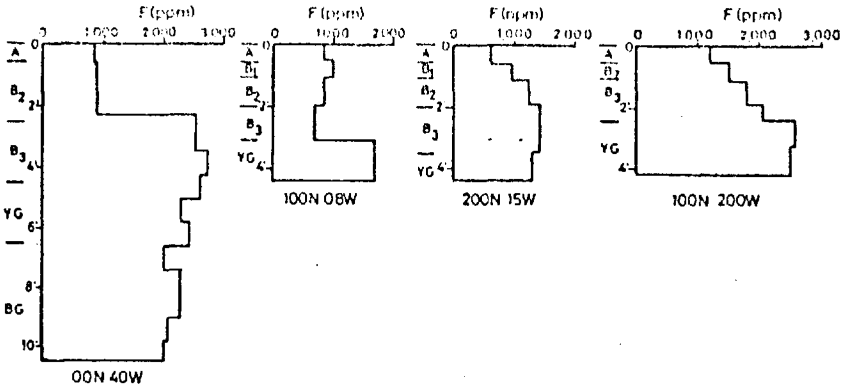
ultramafics, lamprophyres, carbonatites, alkali granites and syenites, pegmatites, and hydrothermal deposits) may also be present in kimberlite provinces. Properly used in conjunction with other elements characteristic of kimberlites, fluorine can, however, be a valuable aid in detecting these bodies of rock.

3.2.2.5.2.3 Dispersion of Fluorine in Soils

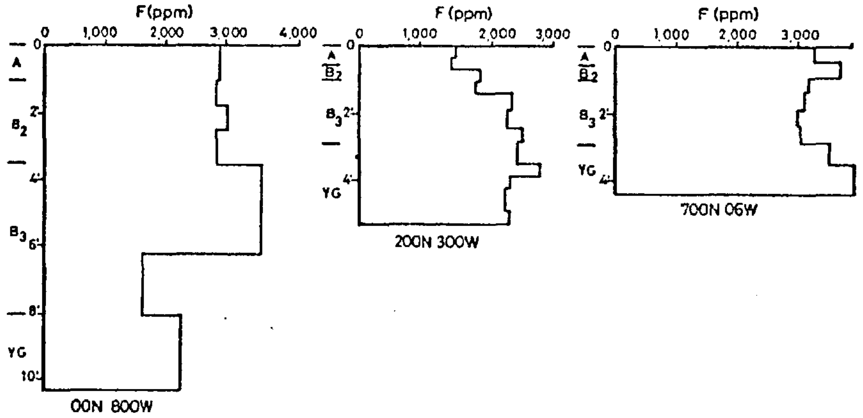
Soil profiles in the Arkansas kimberlite area, although somewhat variable from one rock type to another, are generally well developed and exhibit characteristic A, B, and C horizons over most rock types. Soils developed over the intrusive rocks are predominantly montmorillonitic whereas those on other rock types are mainly kaolinitic. In some areas such as the Prairie Creek area an alluvial cover may also be present.

A study by Gregory (1969) of the distribution of various elements in the soil profiles over the rock types of this area indicated that Ni, Fe, Mn, Co, U and P were enriched in the B and/or the base of the A horizons; Mg increased in concentration with depth. A study of the distribution of fluorine in the same soil profiles (Fig. 3.18) does not permit a simplified conclusion as to its behaviour.

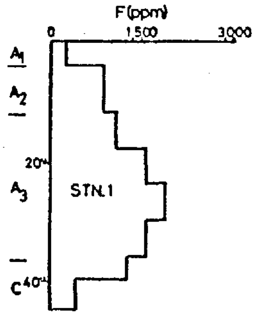
Soils developed over the intrusive rocks can be easily identified by their greater concentration of fluorine (1,000-3,000 ppm) compared to the concentration of the element in soils over the Trinity and Tokio formations (100-400 ppm). The concentration of fluorine increases consistently with depth in soils over the Trinity clays and siltstones but shows little variation with depth for soils over the Tokio conglomerates. Apart from lower fluorine concentrations in the A horizon compared with the B horizon, the



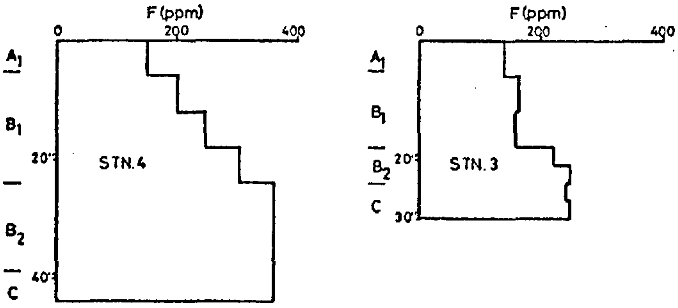
KIMBERLITE, PRAIRIE CREEK



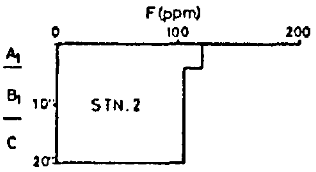
MICA PERIDOTITE, PRAIRIE CREEK



AMERICAN MINE KIMBERLITE



TRINITY FORMATION



TOKIO FORMATION

FIGURE 3.18 DISTRIBUTION OF TOTAL FLUORINE IN VARIOUS SOIL PROFILES OVER KIMBERLITE, MICA PERIDOTITE, THE TRINITY CLAY FORMATION, AND THE TOKIO CONGLOMERATES OF THE PRAIRIE CREEK AND AMERICAN MINE AREAS OF SOUTH WEST ARKANSAS, USA (See Fig. 3.16 for profile locations; samples after Gregory, 1969) fluorine content of soil profiles developed over the Prairie Creek kimberlite exhibit no consistent pattern with depth. This is also true for the soils over the mica peridotite where distribution of fluorine is even more erratic. This failure to form a consistent pattern with either depth or profile development is probably related to the formation and distribution of clays since fluorine is not an element which is strongly concentrated in the sesquioxide phase of the B horizon. During the weathering of phlogopite, the principal fluorine-bearing mineral in kimberlites, much of the primary fluorine is accommodated in the secondary clay minerals (montmorillonite). The weathering of other fluorine-bearing minerals such as apatite and serpentine releases fluorine which may be taken up by clays or sesquioxides. Gregory (1969) noted a general increase in the silt-clay fraction towards the surface for these soils, but the effect of illuviation also produces a lower clay content in the A horizon than in the B horizon. Coupled with the fact that weathered phlogopite of clay size is the primary source of fluorine, mechanical distribution of both primary and secondary micas is doubtless a strong factor in producing the erratic patterns of fluorine concentration in these soils.

Over the American Mine kimberlite (single profile Fig. 3.18) the fluorine distribution probably reflects the increase in clay content towards the base of the A horizon. The B horizon is not developed in this soil profile, and no generalizations can, therefore, be made without a study of more profiles. However, the general depletion of fluorine in the A horizon relative to the B horizon which was noted for the Prairie Creek area also holds true for this area.

The lateral dispersion of fluorine from the Arkansas kimberlites is not great (Fig. 3.19) and only a slight advantage in increasing the size of the anomaly can be gained by sampling the A horizon rather than the B horizon.

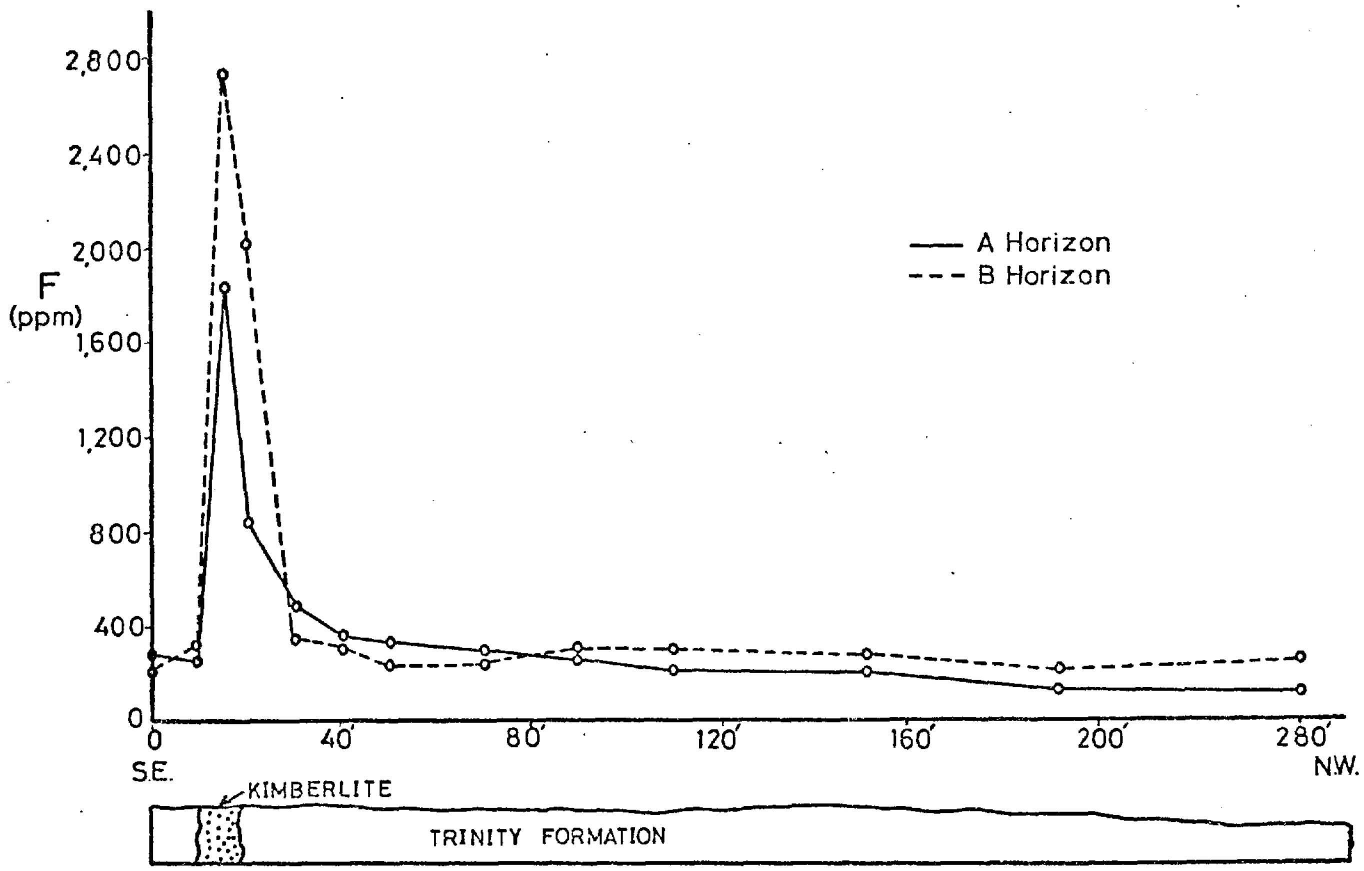


FIGURE 3.19

DISTRIBUTION OF TOTAL FLUORINE IN SOILS OVER THE AMERICAN MINE KIMBERLITE, ARKANSAS, USA (-80 mesh, 200u ., samples after Gregory, 1969)

Only limited lateral dispersion for other elements (Ni, Cr, Co) has also been noted (Alcard, 1959; Jedwab, 1959; Parra, 1974). For the American Mine kimberlite the lateral dispersion of Ni and Nb is slightly greater than that for fluorine (Gregory, 1969). It would appear, therefore, that in areas where kimberlites are suspected, soil sampling on a very closely spaced grid should be carried out in order to outline the bodies adequately. A sample spacing of 10 to 15 feet is recommended in order to cover both small (less than 10 feet in diameter) and large kimberlite intrusions. Fluorine and/or niobium can be used to differentiate between Ni, Cr, Co and Mg anomalies related to kimberlites and those related to ultrabasic and basic rocks. It does not appear possible on the basis of the work to date to separate, geochemically, diamondiferous from non-diamondiferous phases within a kimberlite complex such as the Prairie Creek intrusive. This can only be done by analysing the diamond content of bulk soil samples taken on a grid pattern over the intrusion.

3.2.2.6 Conclusions on Prospecting for Carbonatites and Kimberlites

Carbonatites and kimberlites are closely associated in that they occur principally in alkaline igneous provinces or graben zones within carbonatite complexes and vice versa. For this reason it is advisable when prospecting in these areas to choose a group of pathfinding elements which will account for and differentiate between these two types of deposits. For reconnaissance surveys a satisfactory group is Ni, Cr, Co, Nb and F. All of the first three basic elements need not necessarily be used, but as a group they give a better indication of the presence of ultrabasic and basic bodies. Kimberlites are generally characterized by anomalous concentrations of all these elements in stream sediments, whereas for carbonatites only F and Nb are commonly present in anomalous concentrations, with Ni, Cr, and

Co in background concentrations. It should be noted, however, that anomalies characterized by high concentrations of all of these elements may also be related to the presence of micaceous ultrabasic (peridotites, pyroxenites), alkaline ultramafic and/or lamprophyric rocks since these rocks are also generally enriched in this suite of elements (Table 3.6 for F). This feature is not detrimental to exploration since all of these rocks are usually found in close proximity, commonly within carbonatite complexes and kimberlite provinces. More detailed surveys of the soil overburden using a wider range of indicator and pathfinder elements can generally differentiate these bodies from their carbonatite and kimberlite neighbours. Basalt and diabase dykes may also present some interference in exploration, especially for Ni, Cr and Co, but these rock types generally have low niobium and fluorine contents (average 375 ppm Nb and 420 ppm F respectively).

Once an anomaly suspected of being related to a carbonatite or kimberlite is outlined by reconnaissance and more detailed drainage surveys, the overburden in the area should be examined using indicator elements such as F, Nb, Ni, Cr, Co, Cu, Zn, REE, P, Ba, Sr, Ti, Fe, U and Th for both detection of the bodies and as lithological mapping aids. Carbonatites contain a wide variety of economic elements and minerals (Nb, Cu, Fe, REE, apatite, fluorite, barite, etc.) a feature which dictates that all of the above indicator elements including fluorine should be analysed for in the bodies and their secondary halos.

For kimberlites, there are as yet no elemental associations which can be linked to diamond content, and although many of the elements mentioned above can be used to detect and outline these bodies, bulk sampling of kimberlites or the overburden covering them must be carried out to determine their economic potential.

3.2.3 Prospecting for Disseminated Deposits in Granite, Syenitic and Rhyo-Dacitic Intrusions

There are a number of types of disseminated mineral deposits for which fluorine is an excellent pathfinder. Although many of these deposits are not presently of economic value they do, however, constitute a large reserve for the future.

Granitic bodies, especially coarse-grained albitic and alkali granites, often contain large reserves of fluorite (e.g. Neultin Lake area, N.W.T. Canada), Sn as cassiterite (tin provinces), Nb as pyrochlore and Nb-Ta as columbite-tantalite (Nigerian granites), Li in micas (tin provinces) and Y, La, REE, U, and Th minerals (monazite, xenotime, bastnaesite, etc.). All of these disseminated bodies are highly fluoriferous and may, therefore, be detected by employing fluorine in reconnaissance geochemical survey programs (stream sediments, rocks, etc.). It is interesting to note that fluorine, in anomalous amounts, is not associated with Cu-Mo porphyry mineralization in granitic intrusions (Haynes and Clarke, 1972; Kesler _et al_ 1975a) and the element is, therefore, not a good indicator of these deposits.

Intrusions of syenite often contain enriched amounts of U and Th and more rarely the NaF mineral villiamite (e.g. Lovozero massif, USSR). Deposits of this nature may contain as much as 2.5% F, a feature that readily permits their detection using this element as an indicator.

Disseminated deposits of Sn, W, Mo and Bi in hypabyssal rhyodacitic intrusions (e.g. Mount Pleasant deposit, New Brunswick, Canada) contain large amounts of fluorite and topaz in their matrix. Fluorine is, therefore, a good indicator of these deposits.

When prospecting for fluoriferous disseminated deposits such as those mentioned above fluorine can best be employed in low density reconnaissanc surveys since these bodies offer relatively large target areas for exploration.

3.2.4 Prospecting for Sulphide Deposits in Serpentenized Basic Intrusions

Although adequate research still remains to be done, fluorine would seem to have considerable potential as a pathfinder of sulphide deposits in serpentenized basic intrusions. This is due mainly to the association of fluorine with both autometamorphic and hydrothermal processes of serpentinization and its subsequent incorporation in the serpentine lattice. Kimberlites, as noted above, are one of the best examples of this relationship, but many Ni-Cu sulphide deposits in serpentinized basic rock may also exhibit high fluorine concentrations. Recently M. Hale (pers. comm.) found large fluorine anomalies (in excess of 2,000 ppm F) in soils overlying Cu mineralization in basic rocks in Zambia. In the Pechaga district of the USSR, Rabinovich (1973) found fluorine to be a good lithogeochemical indicator of Ni sulphide mineralization in ultrabasic rocks. He further concludes from his work that the fluorine content and the size of the aureole vary directly with the Ni content and thickness of the ore body.

Serpentinization is a relatively common process which accompanies the emplacement of Ni-Cu sulphide mineralization in basic and ultrabasic bodies. It is not, however, a process which is exclusive to mineralized basic bodies, from which it follows that it is unlikely that fluorine can be used solely on its own to differentiate between barren and mineralized intrusives. In environments where the weathering is so intense that Ni and Cu concentrations are equally high over barren and mineralized basic bodies, fluorine can be usefully employed to detect those bodies which have been serpentinized. Before using the element in this manner it should first be established that serpentinization is a major feature associated with Ni-Cu mineralization in a given metallogenic province.

Considerable research is still required before the full potential of fluorine as an indicator of serpentinized deposits can be assessed. The main aim of this research should be directed towards determining whether serpentinized Ni-Cu deposits in basic bodies are more fluoriferous than their serpentinized barren counterparts. The role of fluorine in both hydrothermal and autometamorphic processes of serpentinization should also be established.

3.2.5 Prospecting for Pegmatites

3.2.5.1 Introduction

The word pegmatite is a morphological term which is not based on chemical composition. Pegmatites are exceptionally coarse-grained igneous rocks that occur in the form of irregular dikes, lenses or veins. They occur characteristically within or near the borders of igneous intrusive bodies but may also be present in regionally metamorphosed terranes. Pegmatites are generally considered to be late residual fractions of magmatic differentiation, and as such are commonly greatly enriched in fluorine with respect to their parent magmas.

A voluminous literature on the geology, mineralogy and occurrence of pegmatites is available. Jahns (1955) has presented a review of the study of pegmatites, and Vlasov et al (1966) have given an excellent description of alkaline pegmatites.

TABLE 3.9

PRINCIPAL MINERALS ASSOCIATED WITH THE THREE MAIN TYPES OF PEGMATITES

TYPE OF PEGMATITE		
Acid	Gabbroic	Alkalic
Quartz	Hornblende (n. d.)	Orthoclase
Feldspar	Apatite (n. d.)	Albite
Muscovite(0. 03-2. 18)	Augite	Aegirine (up to 0. 3)
Lepidolite (0. 64-9. 19)	Labradorite	Nepheline
Biotite (0. 23-5. 00)	Andesine	Eudialyte
Phlogopite (2. 70-3. 70)	Perthite	Lamprophyllite(1. 65-1. 90)
Zinnwaldite(3. 82-7. 67)	Quartz	Fluorite(47. 81-48. 80)
Apatite(2. 37-3. 36)	Albite	Cryolite(53. 48-54. 37)
Amblygonite(1. 40-11. 80)	Epidote	Pyrochlore (up to 3. 7)
Fluorite (47. 81-48. 80)	Sphene (n. d.)	Perovskite (up to 0. 08)
Tourmaline (Tr-2. 10)		Natrolite
Topaz (15. 7-20. 5)		Analcite
Sphene (0. 11-1. 15)		Hackmanite
Idocrase (0. 91-3. 07)		Ramsayite
Garnet		Ussingite
Spodumene		Nb-Ta minerals*
Beryl		Rare earth minerals*
Zircon		
Scheelite		
Pollucite		
Cassiterite		
Sulphide minerals		
Graphite		
Nb-Ta minerals*		
Rare earth minerals*		

*Many of the minerals in these groups are fluoriferous, the values in brackets after the minerals are the fluorine content in %, taken from Table 1. 1

n. d. = no data

Pegmatites can be classified as acidic (or granitic), basic (or gabbroic), and alkalic. Acidic pegmatites are the most common and are generally found within and bordering acidic igneous intrusives. Basic pegmatites are relatively rare and are confined to basic and ultrabasic igneous bodies. Alkaline pegmatites are invariably associated with alkaline igneous massifs. Pegmatites can be further classified in terms of structure and mineralogy into simple and complex bodies. The former are characterized by a simple mineralogy and generally lack well developed zoning, and the latter are easily recognized by the presence of a complex assemblage of common and rare minerals arranged in characteristic zones.

Most pegmatites are simple and are composed mainly of quartz, feldspars and occasionally large amounts of mica. Their economic importance depends on a suitable concentration of one or more of these industrial minerals. In addition to quartz, feldspars and micas, complex pegmatites often contain economic concentrations of many rare elements, particularly Li, Rb, Cs, Be, Y, rare earths, Zr, Ta and Nb. In addition, U, Th, W, Mo, Sn and gems may also be extracted profitably from certain complex pegmatites.

The mineralogy of the three compositional types of pegmatites is summarized in Table 3.9. Most of the fluoriferous minerals occur in the acidic and alkaline pegmatites. In the gabbroic pegmatites the principal fluorine-bearing mineral is hornblende. The gabbroic pegmatites are rare, generally not of economic value, and are not discussed further. The principal fluorine-bearing minerals are marked with an asterisk in Table 3.9 and where possible their range of fluorine contents is given. Practically all of the economic minerals in the complex acidic and alkaline pegmatites contain large concentrations of fluorine making the element an ideal indicator for these deposits.

Much has been written concerning the types of wall-rock alterations associated with pegmatites. The types of alteration depend predominantly on the composition of the host rock and the composition of the pegmatitic fluid, and include sericitization, silicification, tourmalinization and feldspathization (microclinization). Alteration haloes rarely exceed a few meters in width and are primarily the result of metasomatic processes. Zagorskii (1972) has shown that the metasomatic alteration intensity of wall-rocks, as well as the magnitude of the elemental haloes (F, Li, Rb, etc.), are greater for magmatic pegmatites than for those of metamorphic origin. There are no descriptions of the wall-rock alteration and element haloes associated with alkaline pegmatites.

Because of their intimate spatial association with igneous complexes, prospecting for pegmatite deposits has been carried out mainly by geological methods, mainly mapping. These have been most effective for outcropping deposits, but for concealed deposits alternative methods are required. Gamma-ray spectrometry, as well as the more conventional scintillation methods, have greatly aided exploration for uranium-bearing pegmatites, and for the detailed examination of beryllium-bearing pegmatites the berylometer has proven useful (Brownell, 1959; and Debnam, 1961). Although these instrumental methods are appealing in terms of exploration they rely heavily on the presence of a relatively high concentration of uranium and beryllium respectively to be effective. Their ability to penetrate overburden is also severely restricted. Different types of economic pegmatites (mica, rare metals, uranium, etc.) are often associated with particular igneous massifs or metamorphic provinces, and it is, therefore, desirable to have an exploration method capable of detecting the presence of pegmatitic bodies in general. Subsequent evaluation of the anomalies can then be done using more direct methods.

Pegmatites are characterized by increased amounts of such elements as Li, Rb, Cs, Be, Sr, Y, rare earths, Nb, Ta, U, Th, B, P and F. All of these elements have been examined as potential indicators of pegmatitic bodies. The ease with which F can be analysed compared with most of these indicator elements makes it an attractive lithogeochemical pathfinder.

Lithogeochemical methods of prospecting for pegmatites have been described by Stavrov and Bykova (1961), Kochemasov (1968), Skvortsov and Pritkazchitkov (1970), Kluev and Komarkov (1971), Mogarovskii (1971) and Yusupov (1973). These studies have shown that Li, Rb and F yield the most extensive primary haloes around pegmatites, and that these elements are effective pathfinders for blind pegmatites. Yusupov (1973) has noted the occurrence of negative fluorine anomalies in the wall-rocks surrounding productive chamber pegmatites, whereas around unproductive pegmatites such anomalies are absent. Negative haloes of fluorine around pegmatites are generally rare, and where they occur it is probable that the element has been expelled from the immediate vicinity of the crystallizing pegmatite where the wallrock was highly heated. This is suggested by the high concentration of fluorine in a restricted zone some 20 to 30 meters from the pegmatites described by Yusupov (1973). A study of New England pegmatites by Seraphim (1951) has shown that fluorine forms positive haloes around these deposits. The author has observed that this is also the case for the beryl pegmatites in Rhodesia (See the following sections). As is the case with wall-rock alteration, the size, composition and temperature of emplacement of a pegmatite, as well as the composition and permeability of the host rock, determines the magnitude and characteristics of primary haloes.

Okikadze (1971) has used F to differentiate between barren and rare-metal pegmatites in the Greater Caucasus of the USSR. For a variety of barren pegmatites (5 areas) he obtained an overall range of 100 to 900 ppm F and an overall range of means of 300 to 700 ppm F For the rare-metal pegmatites (3 areas) the overall range was 800 to 2, 500 ppm F and the overall range of means was 1, 200 to 1, 800 ppm F.

There appear to be few if any published studies on the secondary dispersion of F from pegmatite bodies. For other elements, significant dispersion patterns for Li, Rb, Cs, Nb, B, Sn and Be have been observed with Li giving the most extensive dispersion haloes (Debnam, 1961; Iskiv and Savadskii, 1968; Bugaets et al, 1971; Glebov et al, 1972). Since F is often concentrated in Li-bearing minerals (muscovite, lepidolite, etc.), as well as in many other pegmatitic minerals (See Table 3. 8), it is reasonable to assume that it too would give rise to marked secondary dispersion haloes. In this respect the mobility of F in the secondary environment is similar to that for the monovalent alkali metals (Li, Na, K, Rb, Cs).

Biogeochemical methods of exploration for pegmatites have been investigated by Zagorskii et al (1971). They found that the alkalies Li, Rb and Cs give pronounced anomalies over mica-pegmatites but yield no anomalous expressions over non-mica pegmatites. In view of our present knowledge of the biological demand of F by certain plants and the ability of many other types of plants to tolerate high contents of fluorine, it is reasonable to assume that fluorine should be a good indicator in biogeochemical surveys.

3. 2. 5. 2 Bepe 2 Beryl Pegmatite, Rhodesia

3. 2. 5. 2. 1 Introduction

The Bepe 2 pegmatite is situated near the eastern border of Rhodesia (Fig. 3. 20). It is one of a number of pegmatite deposits in this area.

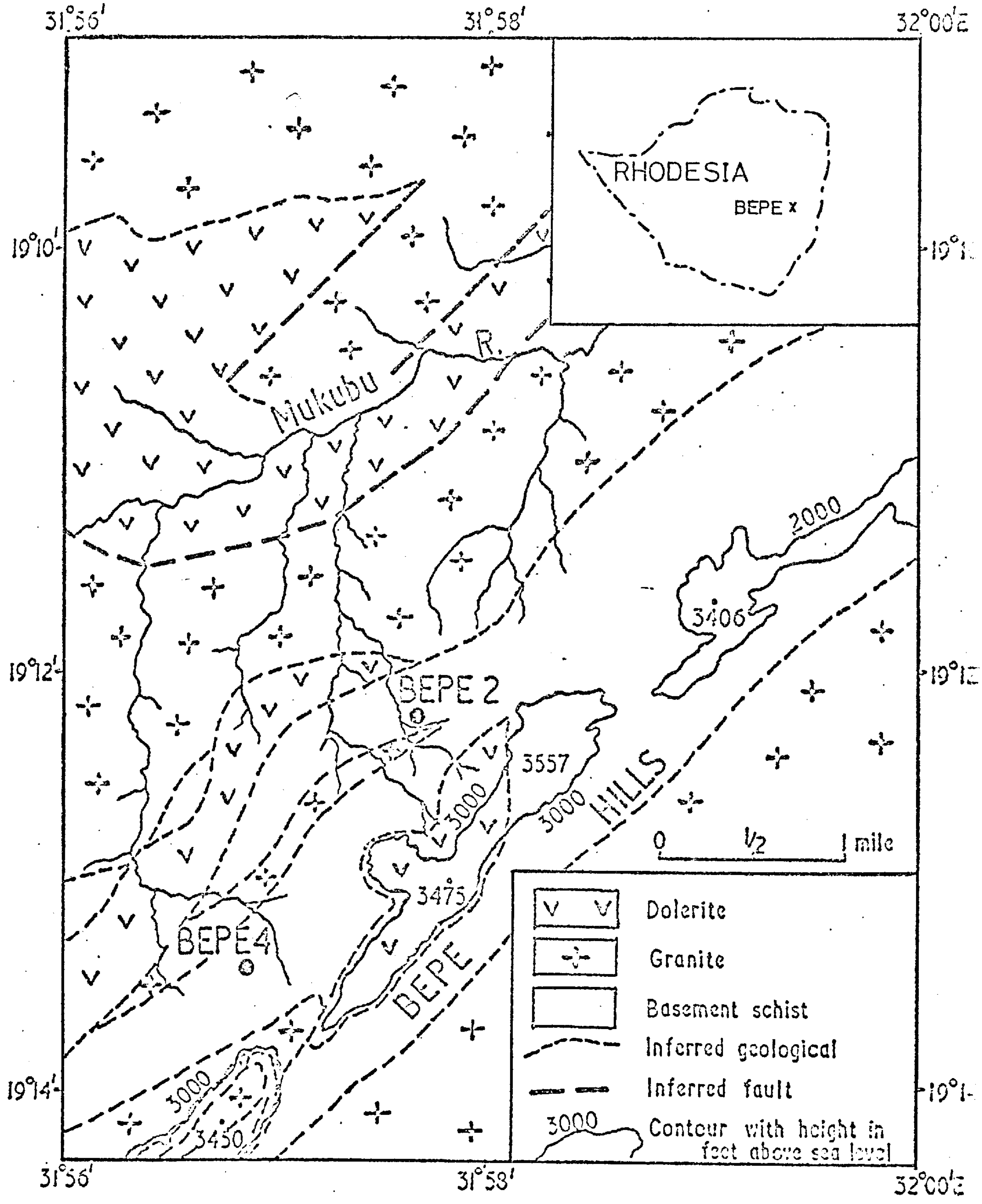


FIGURE 3.20 GEOLOGY AND LOCATION OF BEPE 2 PEGMATITE AREA, RHODESIA (Geology after Swift, 1956 in Debnam, 1961)

The climate of the area is sub-tropical and the vegetation consists mainly of open deciduous forest. The pegmatite forms a minor topographic feature in an otherwise gently rolling terrain.

Soils within the area are typically residual, but differentiation into distinct horizons is not a common feature. There is no well-developed drainage associated with the deposit itself, and the present study is confined to an examination of primary and secondary dispersion characteristics in wall-rocks and soils respectively.

The geology of the deposit has been described by Debnam (1961). This same author has also carried out detailed investigations of the dispersion of Be in the vicinity of the deposit.

The pegmatite, which is intruded into basement schists (Fig. 3.20), is roughly eliptical in outline having a width of about 300 feet and a length of about 500 feet. It is a zoned pegmatite consisting of an outer zone of medium-grained quartz-feldspar-mica (30-50 feet wide) and an inner zone of giant crystal-blocks of potassium feldspar (microcline-perthite) with scattered quartz blocks. Running through almost the entire length of the deposit is a weakly developed beryl-quartz core. Economic quantities of beryl have been extracted from this zone in the western extremity of the pegmatite. The central and eastern sections of the pegmatite are undisturbed.

Based on Debnam's (1961) description of the mineralogy of this deposit the principal fluorine-bearing minerals are apatite, biotite, muscovite and tourmaline, although it should be remembered that almost all of the minerals in pegmatites are enriched in fluorine relative to their intrusive counterparts.

3.2.5.2.2 Dispersion of Fluorine in Wallrocks.

The contact zone between pegmatite and schist is characterized by a 6-18 inch aplitic selvage which is hard, fine-grained and composed mainly of albite, spodumene, quartz and kaolin. Here and there a thin band of biotite-tourmaline schist is present at the contact.

The distribution of F and Be in the north and south wallrock zones is presented in Table 3.10. For both F and Be there is a large difference between the concentration levels in these two zones. The reason for this may lie in the fact that, in the contact areas where the samples were taken, the beryl-bearing quartz zone is in much closer proximity to the southern contact. Greater chemical activity probably occurred in this region of the pegmatite which resulted in the introduction of large quantities of F and Be in the wallrocks. At the southern contact the F concentration decreases graduall from 6,800 ppm at the contact to 440 ppm 12 feet from the deposit. This pattern is also observed for Be. At the northern contact, the fluorine concentration is much lower at the contact (520 ppm) and decreases erratically to levels of about 100 ppm 16 feet from the deposit. Again the same pattern is observed for Be.

Although closely spaced sampling would be required, the data shown in Table 3.10 suggests that F may be usefully employed in the detection of primary haloes associated with pegmatites of this type. The element shows excellent potential as a lithogeochemical indicator of concealed pegmatite deposits the only signature of which may be a 'dome halo'.

TABLE 3.10

DISPERSION OF FLUORINE AND BERYLLIUM IN WALLROCKS OF THE BEPE 2, PEGMATITE, RHODESIA (Samples and Be analyses after Debnam, 1961)

Sample No.	Location	F (ppm)	Be (ppm)
	SOUTH CONTACT		
203758	at contact	6800	15.0
203760	1' from contact	3800	13.0
203762	3' from contact	2480	7.0
203763	4' from contact	2400	7.0
203764	5' from contact	1920	6.5
203765	6' from contact	1680	6.0
203766	8' from contact	960	4.0
203768	10' from contact	680	2.0
203769	12' from contact	440	1.5
	NORTH CONTACT		
203395	at contact	520	2.5
203396	1' from contact	344	2.0
203397	1.5' from contact	244	1.0
203398	2' from contact	180	1.0
203399	2.5' from contact	172	1.0
203400	3.5' from contact	144	1.0
203546	4.5' from contact	116	1.0
203547	6' from contact	88	0.5
203548	8' from contact	100	1.0
203549	10' from contact	144	1.0
203550	12' from contact	180	1.5
203551	14' from contact	116	0.5
203552	16' from contact	88	0.5

3. 2. 5. 2. 3 Dispersion of Fluorine in Soils

The distribution of fluorine in soil profiles taken over pegmatite, schist near the pegmatite, background schist, and granite north of the pegmatite is shown in Fig. 3. 21.

Over the pegmatite the fluorine content of the soils increases gradually with depth. This is a trend which is generally found for siliceous soils which do not have a marked organic-rich horizon and pronounced differentiation (See Pedogeochemical Section in Chapter I). The highest concentration of fluorine in these profiles occurs over the southern schist contact zone where the levels increase from about 2, 000 ppm in the topsoil to about 6, 000 ppm at a depth of 3 feet. This agrees well with the results for the dispersion of fluorine in the wallrocks (Table 3. 10). Over the other pegmatite zones the fluorine content varies from 500 to 1, 000 ppm.

In contrast to the observations for the pegmatite soils, the fluorine content of soils over schist near the pegmatite decreases markedly with depth from values in the order of 500 ppm at surface to about 100 ppm at a depth of 10-20 inches. Soils over background schists contain about 100 ppm F and exhibit very little variation in concentration with depth. The high fluorine content in the top few inches of soils over schists near the pegmatite can be attributed to lateral mechanical dispersion of fluorine-bearing pegmatite minerals probably by down-slope creep. A certain amount of saline dispersion cannot, however, be ruled out.

Soils over granites have fluorine concentrations in the order of 100-200 ppm, and the pattern is one of increasing concentration with depth.

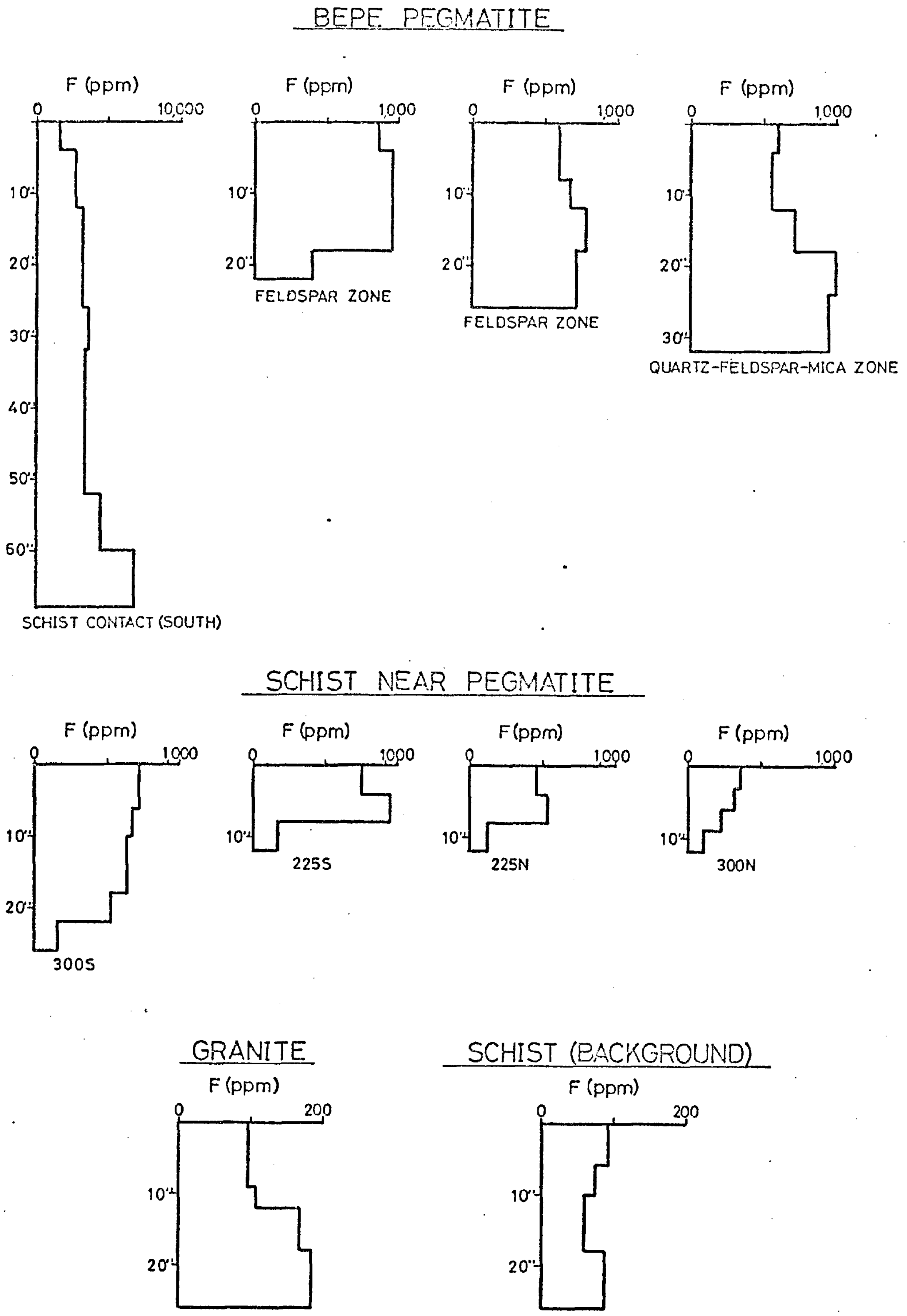


FIGURE 3.21 DISTRIBUTION OF TOTAL FLUORINE IN SOILS OVER VARIOUS ROCK TYPES IN THE BEPE 2 PEGMATITE AREA, RHODESIA (samples taken by Debnam, 1961)

TABLE 3.11

THE FLUORINE CONTENT OF VARIOUS SIZE FRACTIONS OF SOILS OVER PEGMATITE, SCHIST, AND GRANITE, BEPE PEGMATITE AREA, RHODESIA (Samples taken by Debnam, 1961; size fractions are B. S. S.)

Sample No.	Location	Depth	SIZE FRACTION AND FLUORINE CONTENT							
			-10+20	-20+36	-36+80	-80+150	-150+200	F. Sand	Silt	Clay
201851	10N on Pegmatite Feldspar Zone	0-5"	200	208	168	216	232	280	920	1720
201853		5-10"	216	168	208	192	208	208	1000	1720
201854		10-17"	320	248	300	240	296	328	1280	1680
201855		17-26"	256	220	192	192	260	300	920	1600
203785	Over schist	5-10"	92	128	120	112	92	96	92	60
204577	Over granite 2Mi. from Pegmatite	0-5"	88	60	64	80	92	96	300	480
204578		5-12"	80	56	48	52	52	44	128	320
204579		12-24"	64	68	64	44	64	72	120	320

Because of the large difference between the fluorine content of soils over granites and pegmatites it is unlikely that granites will offer any interference when using the element in reconnaissance surveys.

The fluorine content of various size fractions of soils taken over pegmatite, schist and granite is presented in Table 3.1D. For soils over the schists there is little variation in the fluorine content of the size fractions from -10 mesh to clay, with perhaps a depletion in the clay size fraction. There is, therefore, no preferential enrichment of the element in these soils due either to absorption in clays or concentration of fluorine-bearing resistant minerals.

Over pegmatite and granite the highest concentrations of fluorine are observed in the silt and clay size fractions with the latter containing almost twice as much as the former. The enrichment of fluorine in these two size fractions is largely related to the fact that for both these rock types the micaceous minerals (biotite, muscovite, etc.) are the principal fluorine-bearing minerals and their decomposition will, therefore, produce clays rich in fluorine. For the coarser size fractions there is little variation in fluorine content, and hence no preferential enrichment factor can be invoked for the -10 mesh to fine sand material. Also for these soils there is no systematic variation in the fluorine content of the size fractions with depth.

Over the pegmatite the amount of fluorine in soils which can be extracted by 0.01 M HCl is of the order of 2-8 ppm (Fig. 3.23), which when compared with the total amount of fluorine (500-10,000 ppm) indicates that little of the element is dispersed in the ionic form. The fluorine in the clay minerals is, therefore, present almost entirely as absorbed or structurally reordered fluorine.

There is little difference between the fluorine content of the -80 mesh fraction of soils over schist and granite, both being approximately 100 ppm F (Fig. 3.21). If one wishes to differentiate between these rock types the use of a silt-clay fraction will produce anomalously different results (approximately 80 ppm F over schists and 400 ppm F over granites (Table 3.11).

The dispersion of total, acid-diffusible and cold-extractable (0.01M HCl) fluorine (cxF) along a soil traverse over the Bepe pegmatite is shown in Figs. 3.22 and 3.23. For purposes of correlation the dispersion of P is presented in Fig. 3.24.

The most striking point of interest in these data is the fact that the cxF method produces a very erratic anomaly of low contrast. Fluorine is undoubtedly bound in minerals resistant to attack by 0.01M HCl such as micas, apatite and tourmaline. For this reason the cold-extractable method is unacceptable for detailed surveys.

The dispersion pattern for acid-diffusible fluorine is almost identical to that for total fluorine, and it is interesting to note that the acid-diffusion method extracts, almost consistently, 10% of the total fluorine in these soils. This means that almost 90% of the fluorine is in a mineral form or forms resistant to attack by orthophosphoric acid (tourmaline, quartz, feldspars and to a lesser extent the micas). Based on the observed P levels in these soils (Fig. 3.24) and the fact that 2.5 ppm P is equivalent to 1 ppm F if all the P is present as fluorapatite, almost 30% of the fluorine extracted by the acid diffusion method can be accounted for by apatite. The remaining 70% is extracted from clays, primary micas, fluorite and possibly feldspar. Provided large amounts of apatite are present in the types of

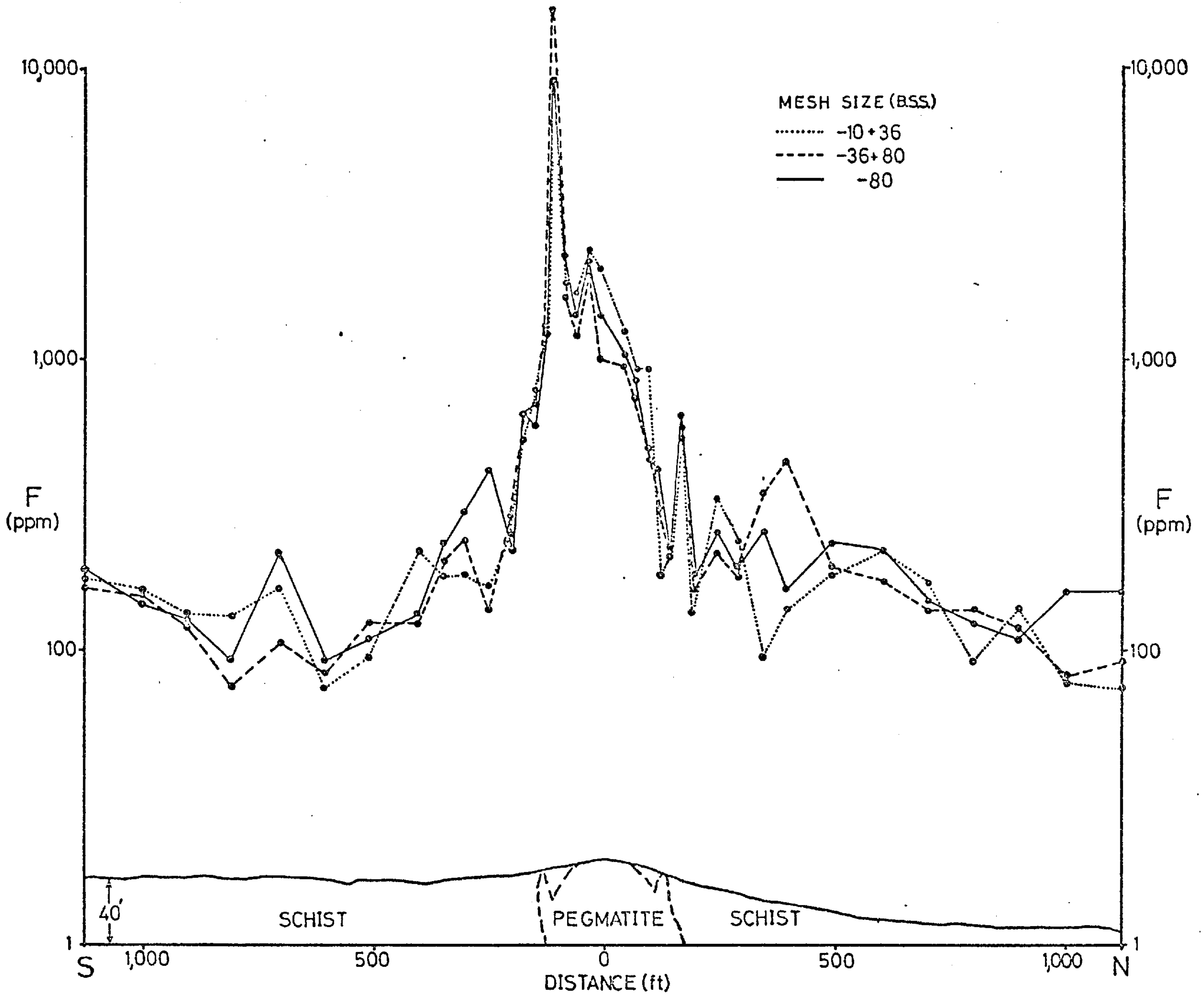


FIGURE 3.22 DISTRIBUTION OF TOTAL FLUORINE IN VARIOUS SIZE FRACTIONS (200u) OF SOILS OVER THE BEPE 2 PEGMATITE, RHODESIA (samples taken by Debnam, 1961)

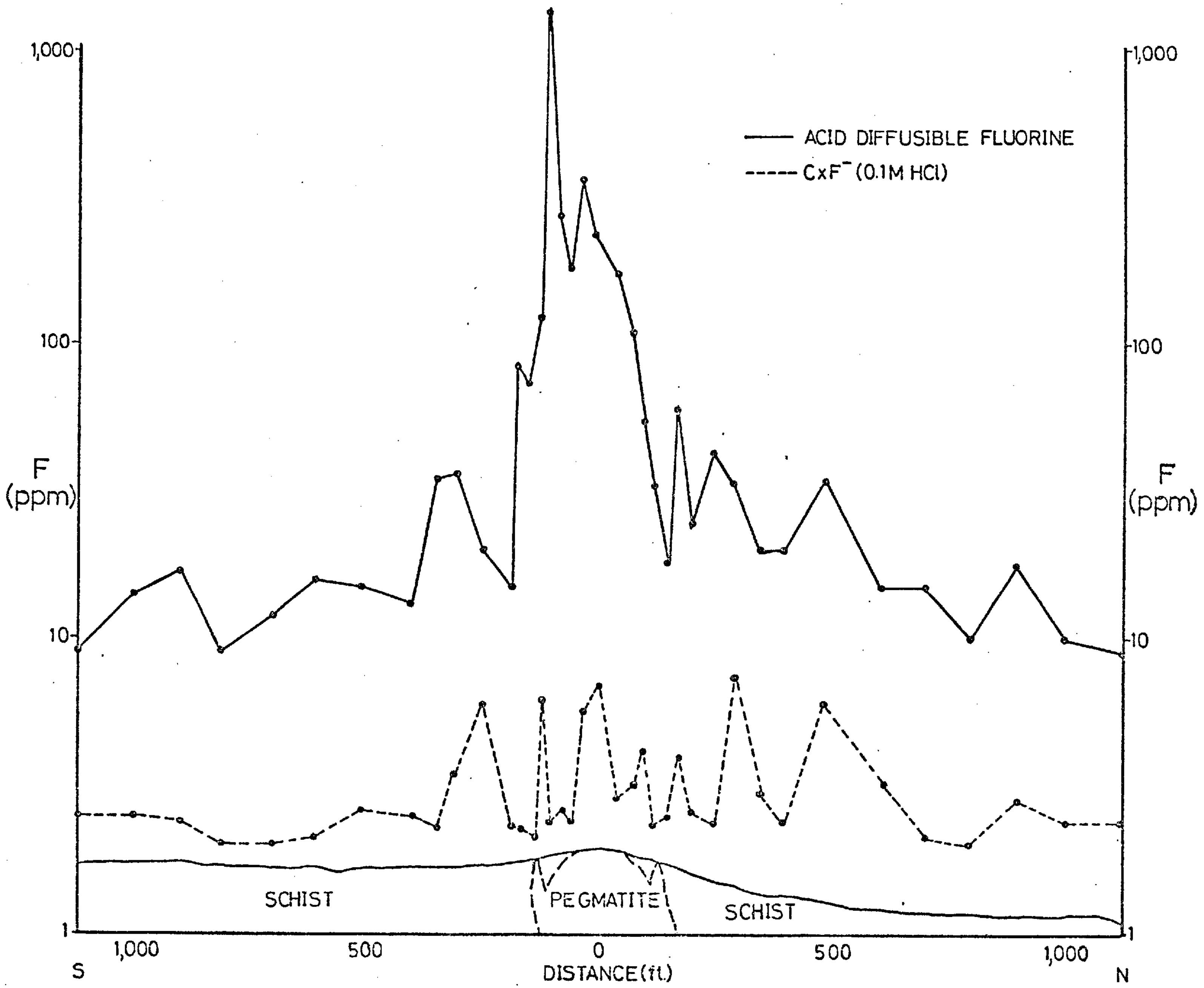


FIGURE 3.23 DISTRIBUTION OF ACID DIFFUSIBLE AND CxF (0.01M HCl) FLUORINE IN SOILS (-80 mesh, <200u.) OVER THE BEPE 2 PEGMATITE, RHODESIA (samples taken by Debnam, 1961)

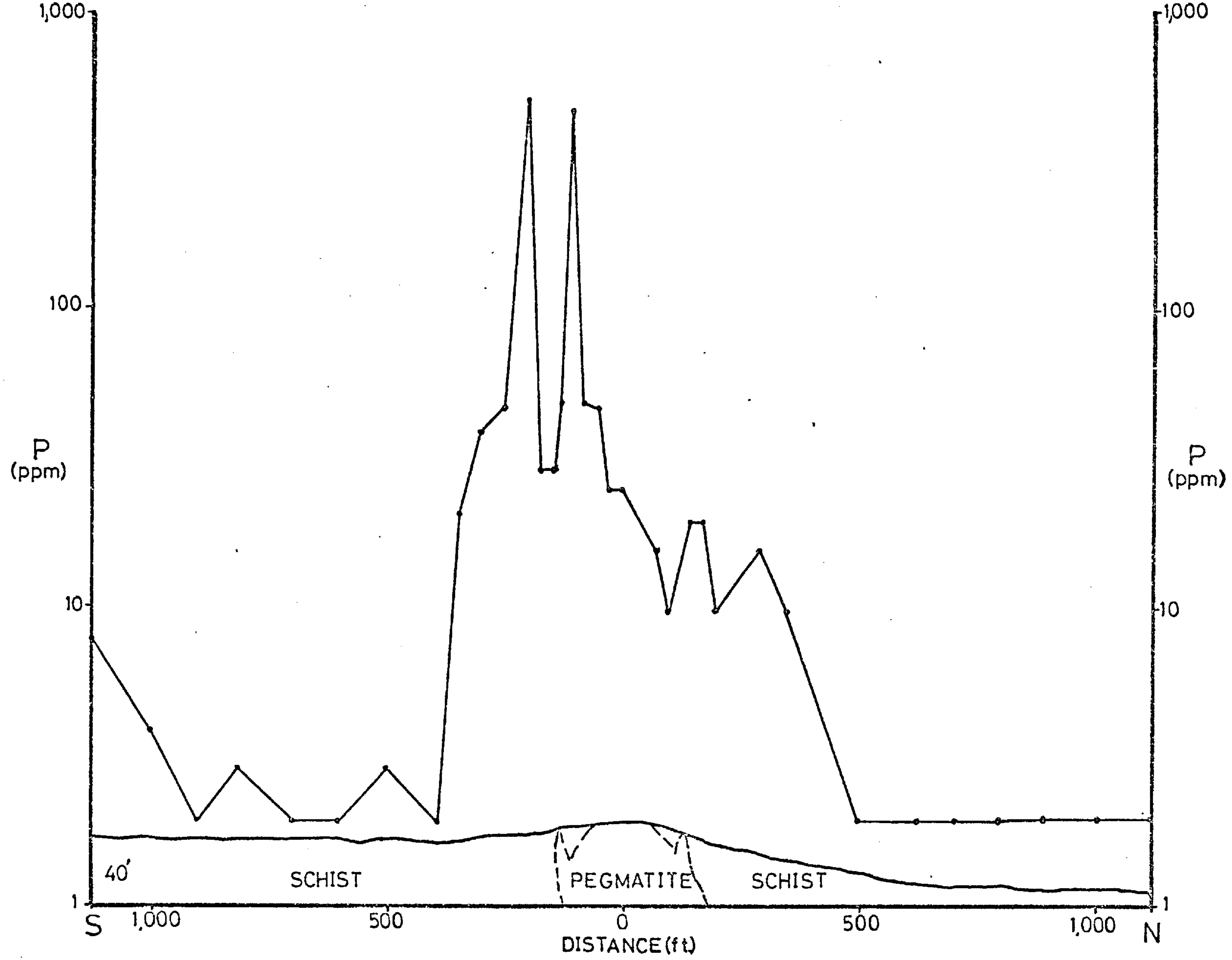


FIGURE 3.24 DISTRIBUTION OF PHOSPHORUS IN SOILS (-80 mesh, 200μ) OVER THE BEPE 2 PEGMATITE, RHODESIA (samples taken by Debnam, 1961)

pegmatites under consideration the acid-diffusible method should be adequate for detailed investigation. Bearing in mind the selectivity of this method and the great heterogeneity in mineral content observed for pegmatites, the analysis of total fluorine would, however, be a more preferable method.

For total fluorine (Fig. 3.22) the analysis of coarse (-10+36 and -36+80 mesh) and very fine sand-silt-clay (-80 mesh) size fractions gives identical results with an anomaly contrast of about 10-fold. The -80 mesh fraction can be used in most cases but, when greater anomaly contrast is desired, the results of Table 3.11b, indicating fluorine enrichment in the silt-clay fraction, suggest that a finer fraction should be used (e.g. -200 mesh).

3.2.5.3 Richardson Uraninite-Fluorite Pegmatite, Bancroft Area, Canada

3.2.5.3.1 Introduction

The Richardson pegmatite deposit is situated in the Bancroft area of Ontario in the Grenville metamorphic province of the Canadian Shield (Fig. 3.25). The area is characterized as a metallogenic uranium province, the uranium occurring mainly as uraninite and uranothorite in complex pegmatites (generally uneconomic), simple pegmatites (Richardson and a number of other deposits), pegmatitic granite and syenite bodies (economic deposits at Bicroft and Faraday) and metasomatic deposits in marble and metamorphic pyroxenites (uneconomic). Although only the simple pegmatite deposit at Richardson has been studied, it should be noted that fluorine, as fluorite and/or apatite, is an abundant constituent of all these deposit types. Detailed descriptions of the geology of the Bancroft deposits are given by

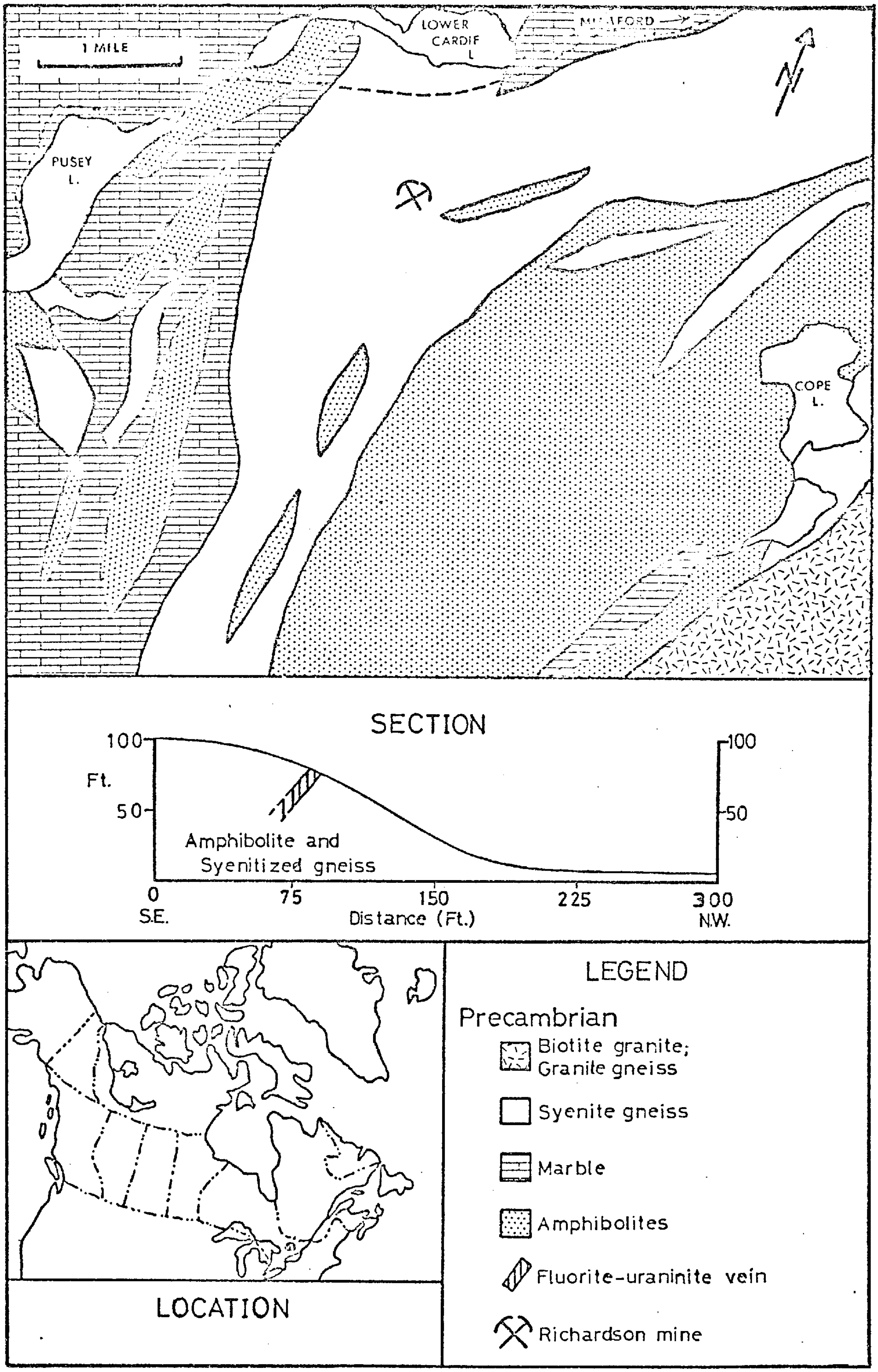


FIGURE 3.25 GEOLOGY AND LOCATION OF THE RICHARDSON PEGMATITE AREA, BANCROFT, ONTARIO, CANADA (Geology after Ontario Dept. of Mines Map 1957-1)

Rowe (1952), Heinrich (1958) and Lang et al (1962). The entire area is now the subject of intensive exploration for uranium and will no doubt continue to be so for some time. For this reason the author collected samples during a short visit to the Richardson deposit to obtain information on the dispersion characteristics of fluorine in the vicinity of the uraniferous deposits of the area. Soil profiles were taken along a traverse over the deposit. There is no drainage system associated with the deposit.

The Richardson pegmatite is a 10-20 feet wide dyke-like feature intruded into syenite gneiss and amphibolite. As with all the pegmatites of this area, it is spatially associated with one of three granitic complexes to the east (Cardiff plutonic complex). The deposit is situated on the side of a gentle hill and exhibits no topographic expression.

The pegmatite is composed mainly of calcite (about 70%), fluorite (10-20%), apatite (10-15%) and uraninite (about 0.1%), with lesser amounts of biotite, hornblende, sphene, zircon and tourmaline. Although it has a relatively simple mineralogy (hence its classification as a simple pegmatite) weakly defined zones are present in places (Heinrich, 1958).

The deposit can be traced for almost 3,000 feet, and although assessment, mainly in the form of trenching and bulk sampling, was carried out during the latter part of the present century it is not yet considered to be economic. The southern section of the pegmatite where the soil traverse was taken is undisturbed.

Vegetation in the area is typified by a well-developed deciduous forest. The soils are typically podzolic with pronounced differentiation into an organic-rich A horizon, an Fe-rich B horizon and a C horizon of decomposed bedrock. Although the area was glaciated, till and other glacial deposits are sparse, and the soils are largely residual in origin.

3.2.5.3.2 Dispersion of Fluorine in Soils

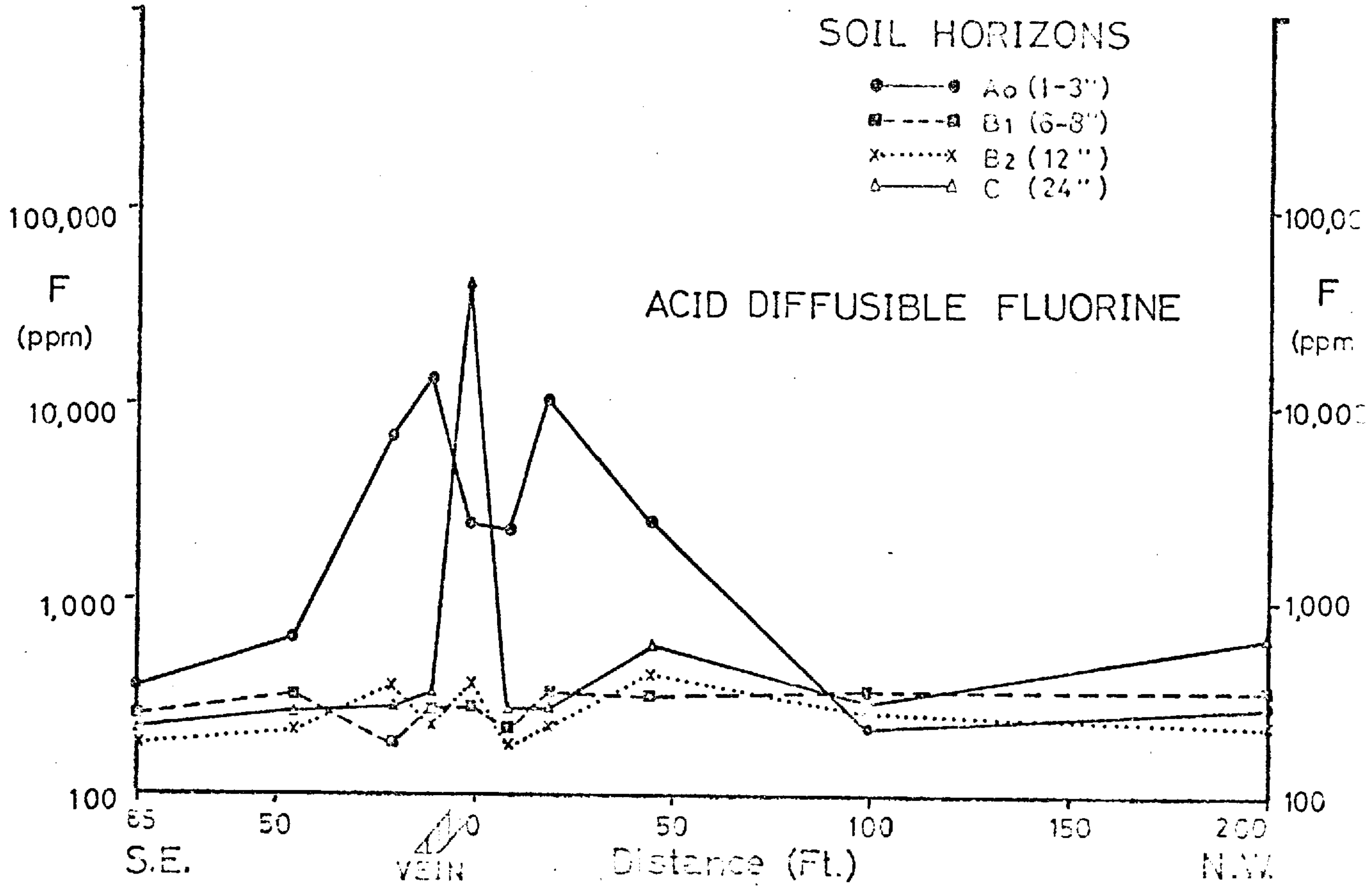
The dispersion of total, acid-diffusible, and cold-extractable (0.01 M HCl and 0.01 M NaOH) fluorine in soils over the Richardson pegmatite is presented in Figs. 3.26 and 3.27. For comparison, the dispersion of Ca, P, U and Th is also given (Figs. 3.28 and 3.29).

The most remarkable feature of the data is the complete lack of a fluorine anomaly in the B horizon whereas the organic-rich A horizon exhibits a strong anomaly with high contrast extending almost 50 feet on either side of the pegmatite. For the C horizon, only the sample taken directly over the pegmatite is anomalous. This is an unusual phenomenon since even when the A horizon exhibits stronger anomalies than the B horizon for a number of elements, as shown in several cases (Boyle and Dass, 1967; Lalonde, 1974) there is still a significant anomaly in the latter horizon. Two hypotheses can be suggested to account for this phenomenon.

a) Disintegration of apatite, fluorite and other fluorine-bearing minerals by rootlets of the vegetation cover, with subsequent uptake of the element and concentration in organic-rich horizon.

b) Gaseous diffusion of fluorine, as HF, through the B and C horizons and concentration by adsorption processes in the organic horizon.

Although the hypothesis of gaseous diffusion cannot be entirely ruled out since fluorine is known to diffuse from fluorite (See the section on Vapour Geochemistry in this Chapter), the fact that Ca and to a lesser extent P also exhibit the same pattern as fluorine suggests that a process of biologic uptake and organic sequestration is probably the most operative



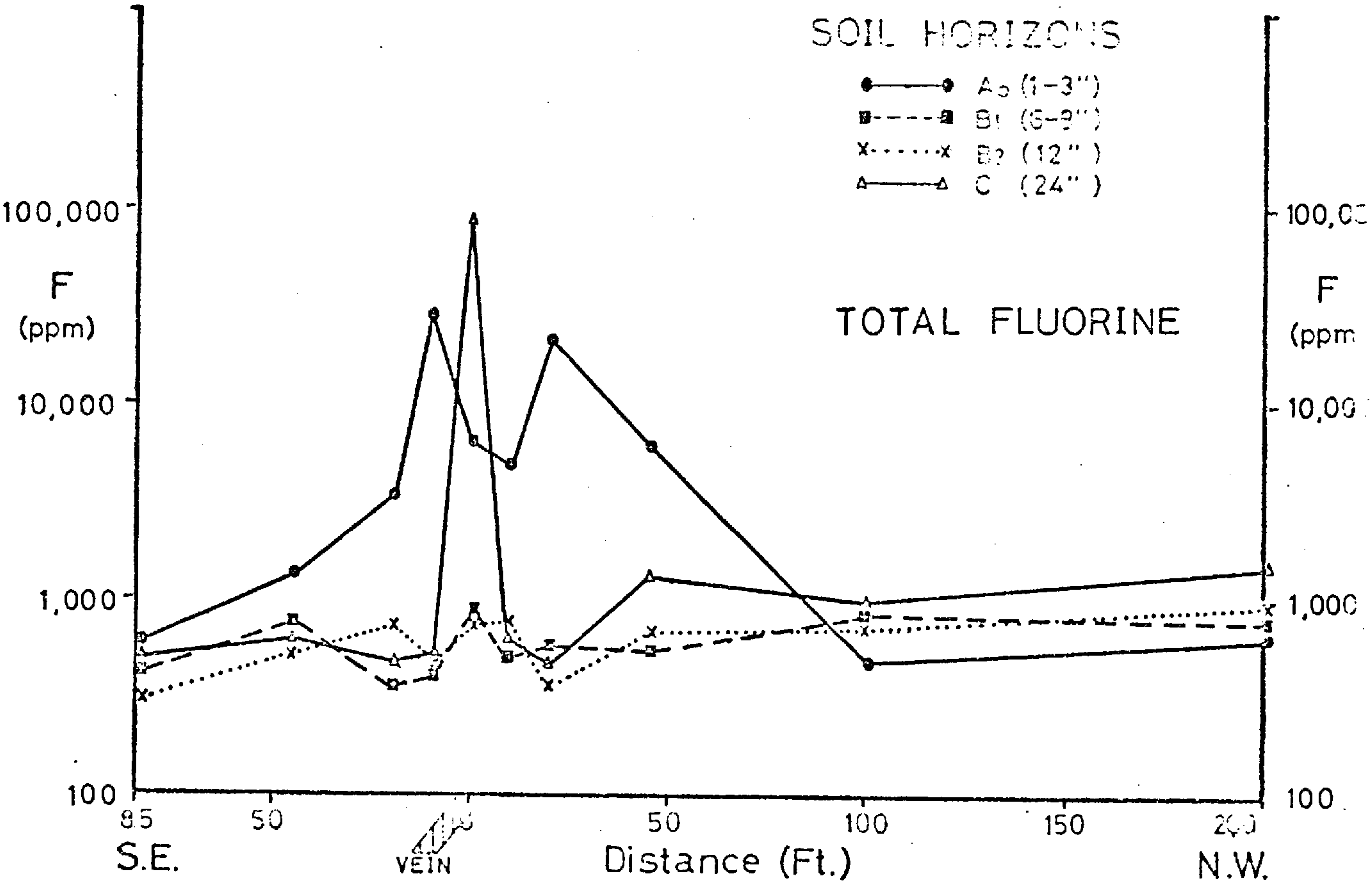


FIGURE 3.26 DISTRIBUTION OF TOTAL AND ACID DIFFUSIBLE FLUORINE IN SOILS (-80 mesh 200u.) OVER THE RICHARDSON PEGMATITE, BANCROFT AREA, ONTARIO CANADA

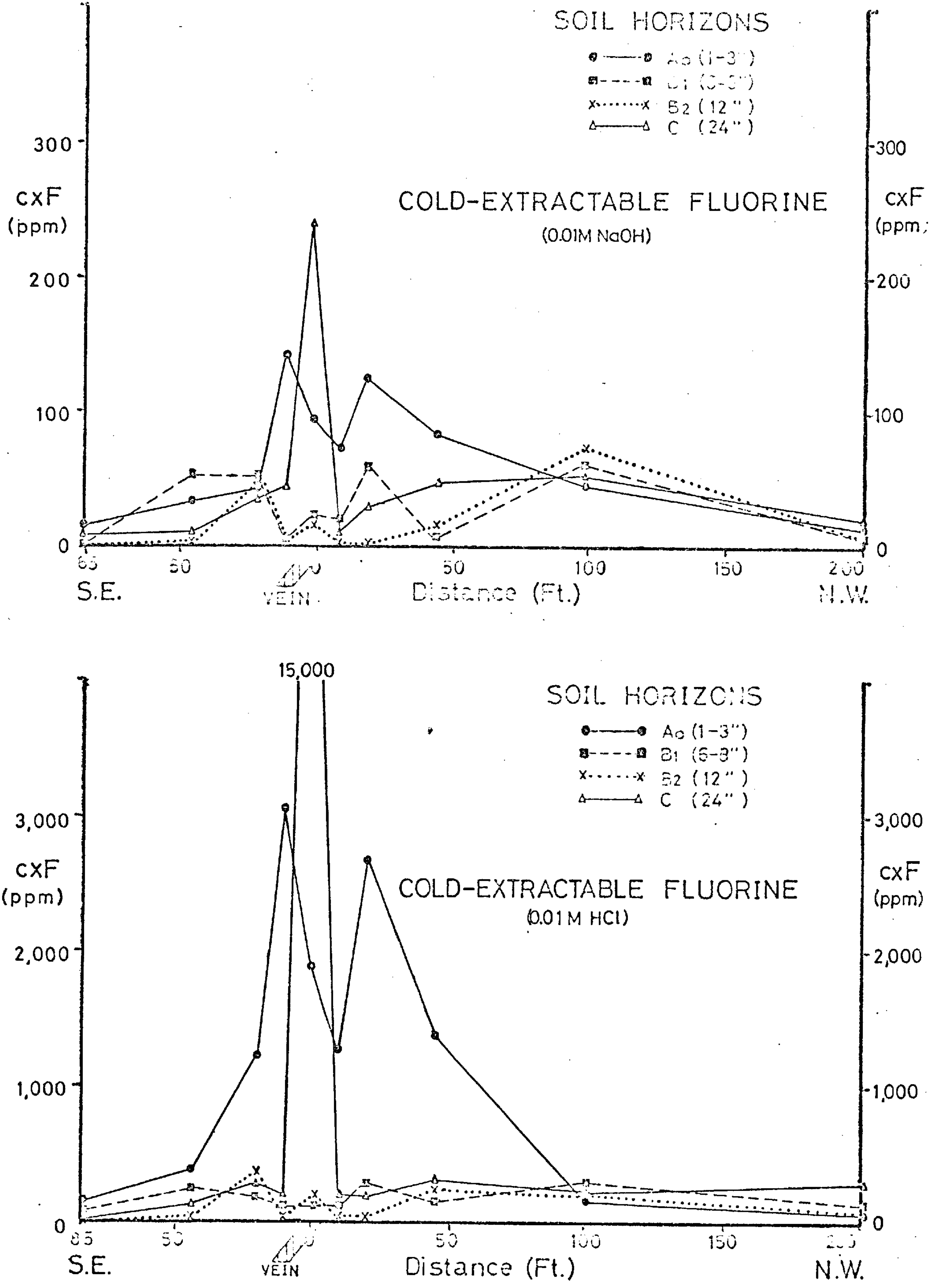


FIGURE 3.27 DISTRIBUTION OF CxF (0.01 M HCl and 0.01 M NaOH) IN SOILS (-80 mesh, 200 ft.) OVER THE RICHARDSON PEGMATITE, BANCROFT AREA, ONTARIO, CANADA

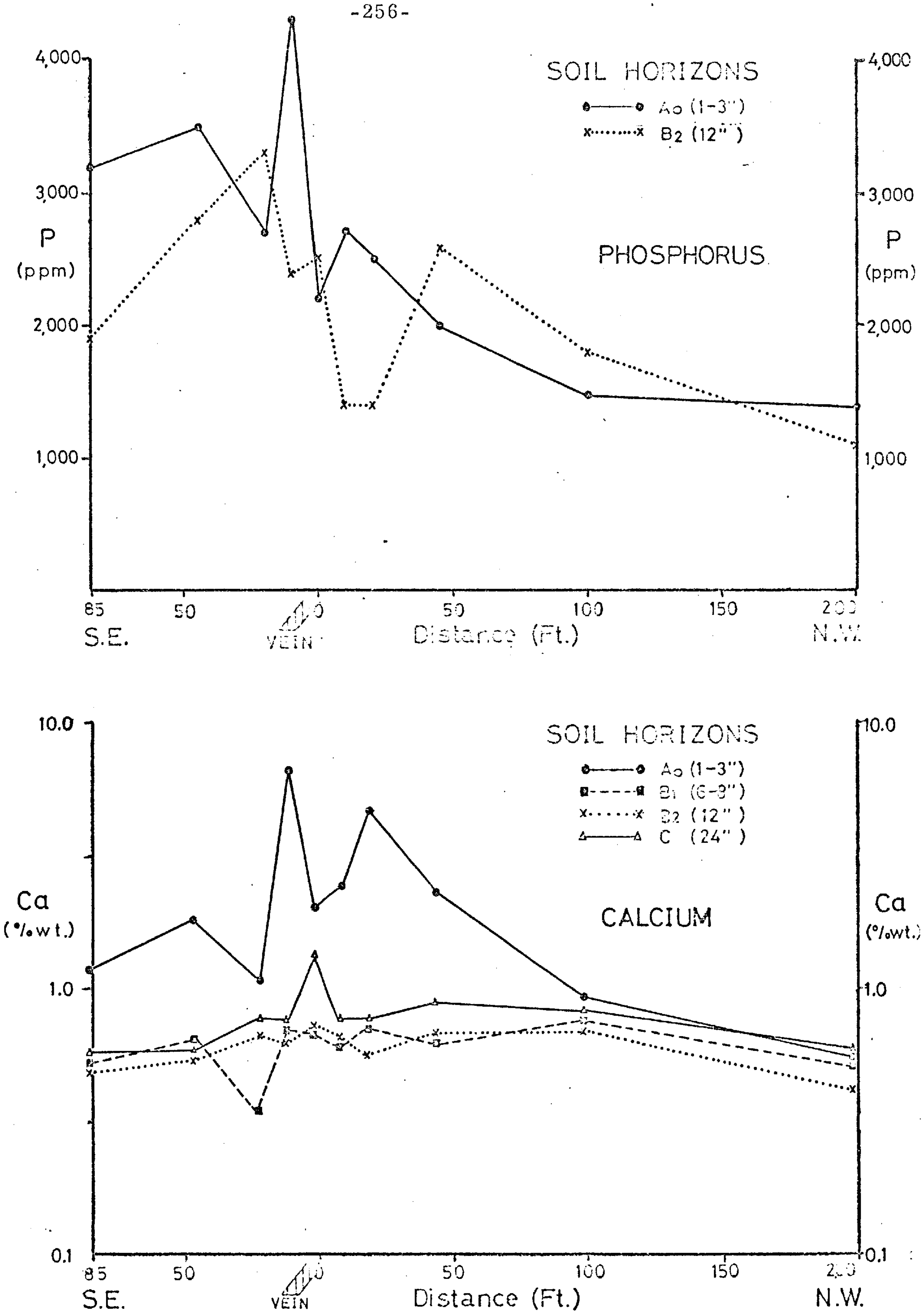


FIGURE 3.28 DISTRIBUTION OF CALCIUM AND PHOSPHORUS IN SOILS (-80 mesh, 200u) OVER THE RICHARDSON PEGMATITE, BANCROFT AREA, ONTARIO, CANADA

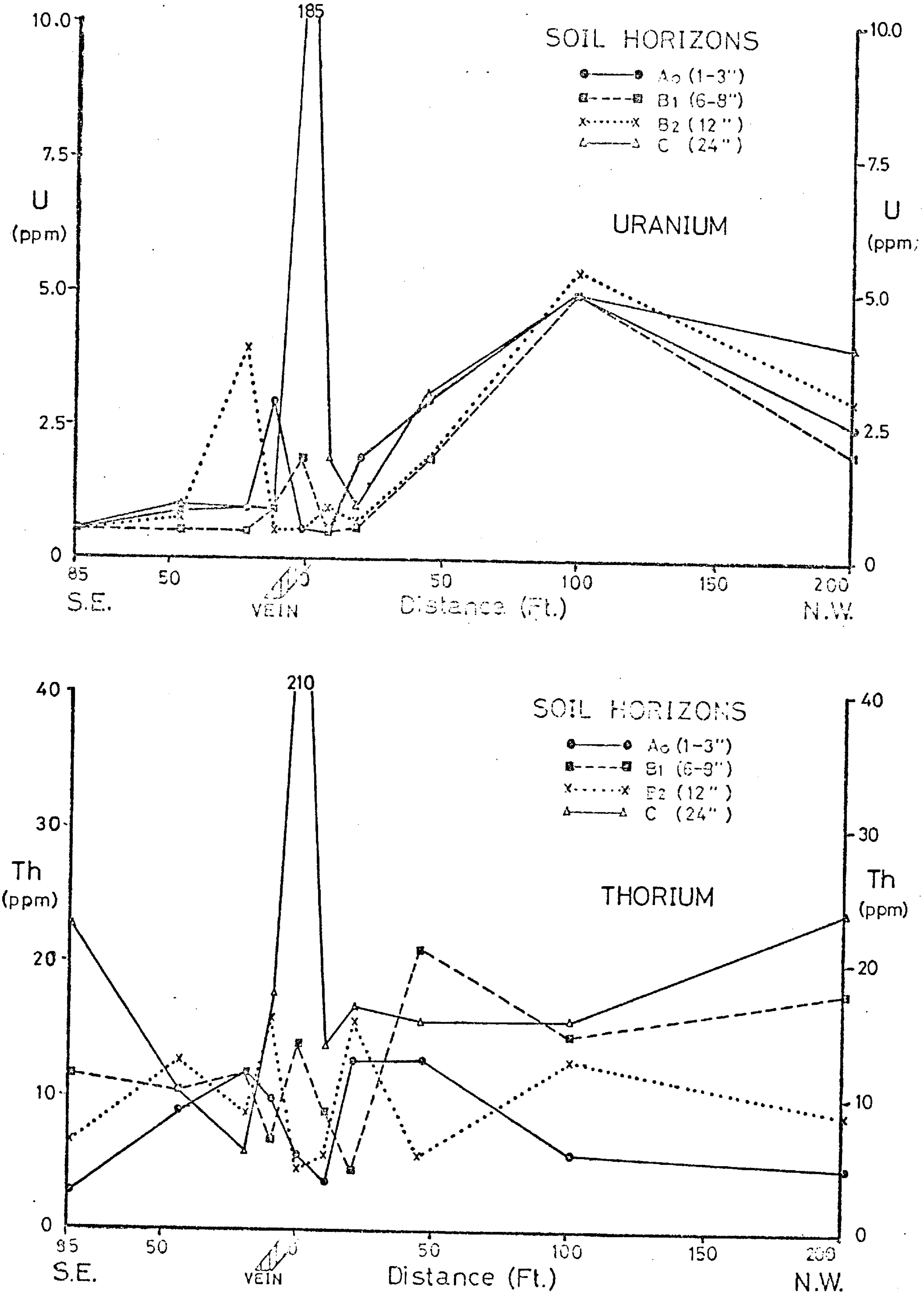


FIGURE 3.29 DISTRIBUTION OF URANIUM AND THORIUM IN SOILS (-80 mesh, 200u) OVER THE RICHARDSON PEGMATITE, BANCROFT AREA, ONTARIO, CANADA

mechanism of enrichment. Plants are known to have a high tolerance towards fluorine and can concentrate the element in large quantities without ill effects. This fact, coupled with the knowledge that soils in the area are relatively thin (less than 4 feet) permitting good root penetration, further supports the biogeochemical hypothesis. It is interesting to note that the dispersion of U and Th (Fig. 3.29) is not controlled by the biogeochemical process, and hence these two elements do not produce adequate anomalies in soils associated with these deposits and cannot, therefore, be used in detailed surveys. This statement does not, however, apply to scintillation and gamma ray spectrometry surveys.

Before comparing the various analytical methods used for fluorine, it is important to emphasize at this point that once an anomalous area suspected of containing a pegmatite deposit has been outlined by reconnaissance methods, only the organic soil horizon should be used during the detailed follow-up stage of exploration. It should also be noted that pegmatite deposits constitute small targets in geochemical exploration, the Richardson pegmatite having a width of about 10 feet gives rise to a soil anomaly of less than 100 feet in width. For this reason closely spaced soil sampling is required.

Of the analytical methods for fluorine used in this study, only the 0.01M NaOH cxF method produced an anomaly in the A horizon of unacceptable contrast when compared with the other methods. It is, therefore, of little use in exploration. The anomaly contrasts for the 0.01M HCl cxF, acid diffusible and total fluorine method are almost identical at 10-15 fold. Considering the percentages of extraction for the two partial methods, the 0.01M HCl cxF method extracts approximately 10% of the total fluorine present and the acid diffusible method extracts almost 100% of the total fluorine.

This should be contrasted with the Bepe pegmatite area where very poor percentages of extraction were obtained by these methods (less than 1% and about 10% respectively). Since most of the fluorine in the Bancroft deposits is present in fluorite and apatite, the more rapid methods of 0.01M HCl cxF and acid diffusible fluorine can be used both in reconnaissance and detailed surveys. The total method may, however, be more desirable if mapping of the underlying rocks is required.

The results presented for the Richardson deposit indicate that fluorine can be a valuable aid in prospecting for uraniferous deposits in the Bancroft area.

3.2.5.4 Conclusions on Prospecting for Pegmatites

The two examples given in this section emphasize the variety of dispersion patterns which fluorine may exhibit over pegmatite deposits. The characteristics of the secondary environment, as shown by the Richardson survey, and the mineral form or forms in which fluorine is present in the deposit have a significant effect on the pattern of dispersion for the element. It is, therefore, essential that effective use be made of the analytical methods available with full understanding of the various minerals that are attacked by each of the reagents employed. The 0.01M HCl cxF, acid diffusible and total methods may also be used to investigate the modes of occurrence of fluorine and to some extent the mineralogic composition of the pegmatite.

Pegmatites also contain high concentrations of elements such as Li, Cs, Rb, Be, Ta, Y, La, REE, P, U and Th, and it would be unwise to use F as the only pathfinder element since many of these other elements may also produce significantly anomalous dispersion patterns. A suitable selection of pegmatitic elements, of which fluorine should be one, can be used as indicators during prospecting for most types of pegmatite deposits.

Because of the small size of most pegmatites, dispersion trains in drainage systems tend to be small, mainly because the dispersion is essentially mechancial from the deposit. Of the minerals present the micaceous minerals generally have the longest dispersion from the source because of their small grain-size and low specific gravity. From this it follows that Li and F probably exhibit the longest dispersion trains in most places. Sampling intervals and pathfinder elements for drainage surveys should be chosen that take into account the restricted dispersion of most elements from pegmatites.

In pegmatite provinces, where an adequate drainage system is absent for stream sediment sampling, smaller areas for detailed soil surveys may have to be sleected on a geologic basis. Where this is the case the results presented for the Bepe and Richardson areas indicate that fluorine is a valuable prospecting aid.

3.3 Prospecting for Mineral Deposits of Pneumatolytic-Hydrothermal Origin

3.3.1 Introduction

Fluorine plays an active role in the formation of practically all types of pneumatolytic-hydrothermal mineral deposits and is one of the few 'gangue elements' which span the entire temperature range of these deposits. The element is ubiquitous in greisen (Sn, W, Be), skarn (W, Mo, Sn, Cu) and kaolin deposits and common in many types of hypothermal, mesothermal, and epithermal mineral deposits where it occurs mainly in fluorite, tourmaline, topaz, micas, humites, amphiboles, and apatite. Greisen, skarn and kaolin deposits are universally fluoriferous. Hypothermal deposits (e.g. gold-quartz veins) contain anomalous concentrations of fluorine only if tourmalinization, topazization and/or sericitization is present. Not all mesothermal and epithermal mineral deposits are fluoriferous, and it is important to establish that fluorite is a major gangue mineral in any metallogenic sulphide or gold (Cripple creek type) province before using the element in geochemical surveys.

The application of fluorine to prospecting for greisen, skarn, kaolin, hypothermal, mesothermal and epithermal mineral deposits is described in the following sections.

3.3.2 Prospecting for Greisen Deposits

3.3.2.1 Introduction

Greisenization is a collective term representing processes of tourmalinization, topazization, sericitization, fluoritization, silicification and chloritization. Some or all of these processes may have been operative to form greisen deposits. The principal mineral deposits which exhibit greisenization include veins, lodes, pipes and disseminations of Sn, W, Be, Cu and As in granitic terranes (e.g. Southwest England and Malaysian tin provinces), and stockworks and disseminations of Sn, W, Cu, Bi and Mo in rhyolite flows, quartz-feldspar porphyries and ignimbrites (e.g. the Mount Pleasant deposit in New Brunswick, Canada, and the Bolivian tin province).

Greisen deposits containing one or more of the suite of elements - Sn, W, Be, Cu, Bi and Mo - occur in albitic or coarse-grained granitic terranes or in hypabyssal volcanic provinces. For this reason fluorine can be used as a general pathfinder to outline areas of greisenization which may contain economic concentrations of one or more of the above ore-forming elements.

As an example of the application of fluorine to prospecting for greisen deposits the dispersion characteristics of the element in the tin province of south-west England were studied, the data being presented in the following sections.

3.3.2.2 Tin Province, South-West England

3.3.2.2.1 Introduction

Southwest England (Devon-Cornwall) is a well defined metallogenic tin sub-province from which, in addition to tin, elements such as W, Cu, Pb, Zn, U, As, Fe, Sb, Ag and Mn have been won at various times. The sub-province forms part of the large Paleozoic West European and Iberian tin province which also includes the Erzebirge (Germany), the Armorican Massif (France) and the Iberian Meseta districts. The geology of the deposits in the south-west England tin province have been described in some detail by Dines (1956), Webb (1947), Edmonds et al (1969) and Hosking and Shrimpton (1964).

Five large granitic intrusions of Variscan age, together with a number of smaller granitic bodies, are intruded into Devonian and Carboniferous sediments and volcanics (Fig. 3.30). The Devonian and Carboniferous rocks, consisting essentially of interbedded shales, sandstones,

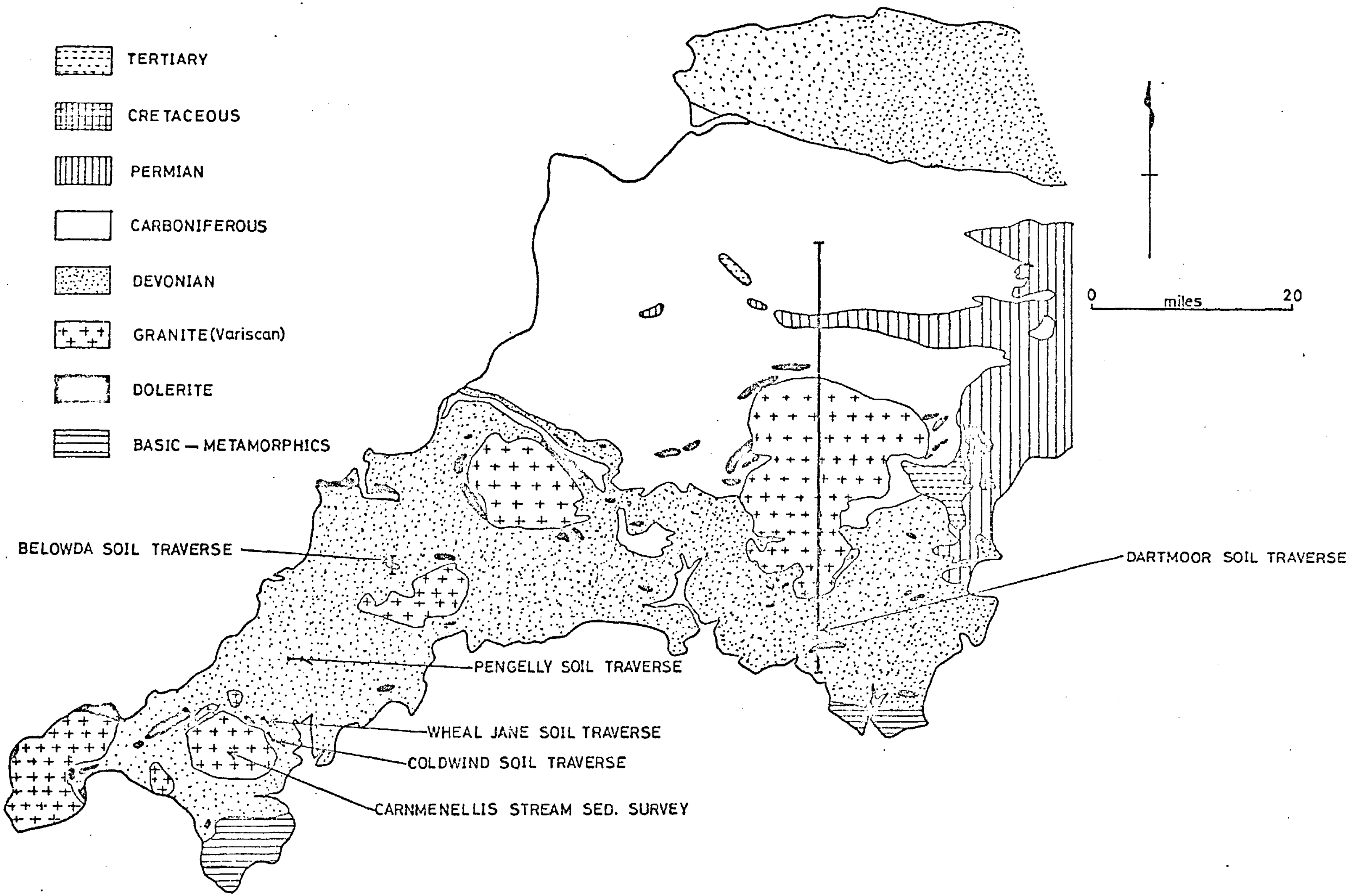


FIGURE 3.30 GEOLOGY OF SOUTH WEST ENGLAND AND LOCATION OF STUDY AREA

limestones, lavas and tuff, have been intensely folded and regionally metamorphosed. Locally these rocks are called killas. Intrusive rocks, other than the granites, include dolerites intruding the Devonian and Carboniferous rocks and quartz porphyry or 'elvan' dykes which are widespread throughout the entire area, occurring in both the granites and metamorphosed sediments and volcanics. The granitic intrusions as now exposed are considered to be the cupolas of a high level granitic batholith. Aureoles of thermal metamorphism are clearly defined around all of the exposed granites.

Tin mineralization consists of greisenized dyke swarms in the apices of granitic cusps and NE-SW and NW-SE greisen veins in zones peripheral to the granitic masses. Copper, arsenic and tungsten ores may accompany the tin mineralization. Occasionally the tin lodes or veins are associated with elvan dykes as at Wheal Jane, but more commonly they occur as steeply dipping veins in the 'killas' parallel to the main underlying granite ridge. Mesothermal deposits of galena, sphalerite, fluorite and siderite occur in N-S crosscourses some distance away from the main areas of Sn, W, Cu, and As mineralization. In addition to this lateral zoning, primary zoning in which Cu mineralization gives way in depth to tin mineralization is also clearly defined. In the metamorphic aureole surrounding some of the granites (e.g. Dartmoor granite), skarn deposits are present in places. These deposits are chiefly tungsten bearing.

A marine transgression at the end of the Miocene epoch has produced a landform in southwest England dominated by an erosional platform at about 430 ft. O.D. As a result of this erosional period considerable dispersion and concentration of alluvial tin took place in the valley bottoms.

The entire area is marked by a well developed dendritic drainage pattern and is, therefore, well suited for drainage sediment surveys.

Above the 430 O.D. mark the soils are residual and generally undifferentiated; below this mark the superficial deposits consist of mixed residual soils and Pliocene deposits.

A number of investigators have discussed the applications of geochemical methods of exploration in southwest England. Hosking (1971) has dealt with the problems associated with using such indicator elements as Sn, Cu, As and W. He has concluded that the main problems arise from contamination due to mining and allied work and agricultural activities. Fortunately, as regards fluorine these contamination problems are not as great as they are for the metals mentioned above. Slags used as fertilizers contain low concentrations of fluorine (less than 400 ppm). Effluents from smelting activities are not generally enriched in fluorine since this element is removed as topaz, tourmaline, and sericite prior to smelting. Problems of contamination, affecting the use of fluorine, may arise from the dumping of wastes during concentration of the ore, and hence careful consideration should be given to those areas where this type of contamination is suspect. Observations of the nature of the surficial deposits can often aid interpretation in this matter. Further geochemical investigations in southwest England have been concerned with the dispersion characteristics of tin (mainly detrital) below the 430 O.D. mark (Dunlop, 1974) and the regional distribution of arsenic in stream sediments and soils (Aguilar, 1974).

3.3.2.2.2 Primary Dispersion of Fluorine

A compilation of the fluorine content of the various rock types in south-west England is presented in Table 3.12. The two most common rock types in the area, unaltered normal granite and killas, contain an average of 1,516 and 790 ppm F respectively. Much higher concentrations are observed for the unaltered Li-mica and fluorite granites (18,143 and 12,514 ppm F respectively) but these rock types together with their kaolinized

TABLE 3.12

FLUORINE IN ROCKS OF THE SOUTHWEST ENGLAND TIN PROVINCE

Rock Type	F(ppm) Range	F(ppm) Mean*	Reference**
Unaltered normal granite	300-6700	1516(118)	1,2,3,4,5,7,8,10 11
Unaltered Li-mica granite	3800-30000	18143(14)	2,4,5
Unaltered fluorite granite	6000-13600	12514(7)	4,7
Kaolinized normal granite	800-4147	1685(15)	7,11,13
Kaolinized Li-mica granite	255-5000	2583(6)	4,7
Kaolinized fluorite granite	1200-12000	5021(8)	4,7
Greisenized granite	655-10700	4210(10)	10
Greisen	5900-23100	13100(14)	4,7,10,11,13
Granite pegmatite	5500-40000	28500(3)	2,3
China clay rock (kaolin)	1400-7400	-	12
Elvan(quartz porphyry dyke)	1200-1800	1590(9)	1,9
Metamorphic aureole			
- Hornfels	550-2950	1570(45)	2,6
- Alteredkillas	1400-7500	4335(15)	1,2
Killas (regionally metamorphosed)	400-1700	790(6)	1,2

*Number of Analyses in Brackets

** (1) Author's Data; (2) Brammall and Harwood (1932); (3) Bowler (1959); (4) Exley (1958); (5) Exley and Stone (1964); (6) Floyd and Fuge (1973); (7) Fuge & Power (1969); (8) Ghosh (1927); (9) Hall (1970); (10) Hall (1971); (11) Reid & Flett (1907); (12) Ussher (1909); (13) Fuge (1975).

counterparts (2,583 and 5,012 ppm F respectively) are almost exclusively confined to the St. Austell granitic mass. Kaolinized normal granites (1,685 ppm F) contain slightly more fluorine than unkaolinized normal granites; kaolin deposits, however, contain much higher levels of fluorine (1,400-7,400 ppm). Of the greisenized rocks, greisen deposits per se contain much higher concentrations than greisenized granites (13,100 and 4,210 ppm F respectively). Granitic pegmatites have the highest average fluorine composition (28,500 ppm), but these bodies are relatively rare in Cornwall and Devon. The quartz porphyry dykes or 'elvans' have a remarkably similar fluorine content (1,590 ppm) to that or normal granites (1,516 ppm) suggesting possibly that they are fine grained derivatives of the granites. In the metamorphic aureole around the granites two types of rock can be recognized, hornfels formed as a result of alteration of dolerites (1,570 ppm F) and altered killas (4,335 ppm F) formed where granites intrude the metamorphosed sediments. The latter type of aureole rock is the more common

The average fluorine content of granites from southwest England is about twice that of the grand mean for granites (850 ppm). Although high levels of fluorine are not exclusive to tin-bearing granites, the element may be included with other diagnostic elements such as B, Li, Rb, Zr, Sn and W to form criteria on which discrimination of barren and productive granites can be made.

The distribution of fluorine in the granite-metamorphic aureole-killas system of the Dartmoor granite is presented in Table 3.13. Well away from the contact the granite contains approximately 600-1,200 ppm F, but near the contact it exhibits fluorine concentrations of the order of 1,240-3,920 ppm. The contact rock (750 ppm F) contains much less fluorine

TABLE 3.13

FLUORINE CONTENT OF ROCKS IN THE GRANITE-METAMORPHIC AUREOLE-KILLAS SYSTEM, WEST DARTMOOR, CORNWALL

Rock Type	Location	F ppm
Granite	In granite 12 miles from contact	800 1200 600
Granite	In granite near contact	3920 3200 2320 2000 1240
Contact rock	At contact	750
Metamorphic aureole	At contact	2000 1680 1440
Metamorphic aureole	Two miles from contact	1000 560 216 560
Killas	Four miles from contact	840

relative to the granite and altered killas flanking it. In the metamorphic aureole, fluorine is enriched in the contact zone (about 2,000 ppm) and decreases gradually in concentration outward into the unaltered killas. This pattern of fluorine enrichment in the granite and altered country rock near the contact attended by a distinct depletion of the element in the immediate contact zone may be the result of fluorine migration to the peripheral zones of the granite during emplacement where, due possibly to a slow diffusion rate across the contact, the element is concentrated in these zones when the granite mass cools. The depletion of fluorine in the contact zone may be due to continued diffusion into the aureole zone when the granite was solidified but still reasonably hot. This would result in an increased concentration in the altered killas at some distance from the contact ('diffusion front'). In the contact zones of the New England granites of the USA, Seraphim (1951) has noted a somewhat different dispersion pattern for fluorine. The enrichment of fluorine in the country rock near the contact and its depletion in the immediate contact zone is still evident but in the granite near the contact there was either no change in the fluorine content or a slight depletion was noticed. Fluorine obviously had time to escape from the granite during the emplacement of the masses.

The results shown in Table 3.12 for the fluorine content of the various rock types in the Dartmoor area are of considerable importance when planning a geochemical survey using this element. Provided that some a priori information is available on the nature of the granites (i.e. normal or other types of granite present) lithogeochemical surveys of granitic masses within a tin province should be reasonably effective in outlining greisen zones. In the killas type of environment the only interference affecting the lithogeochemical application of fluorine would come from the high concentration in the aureole zones surrounding the granites. It will be noted however, that the fluorine contents in these rocks are still well below those for greisens.

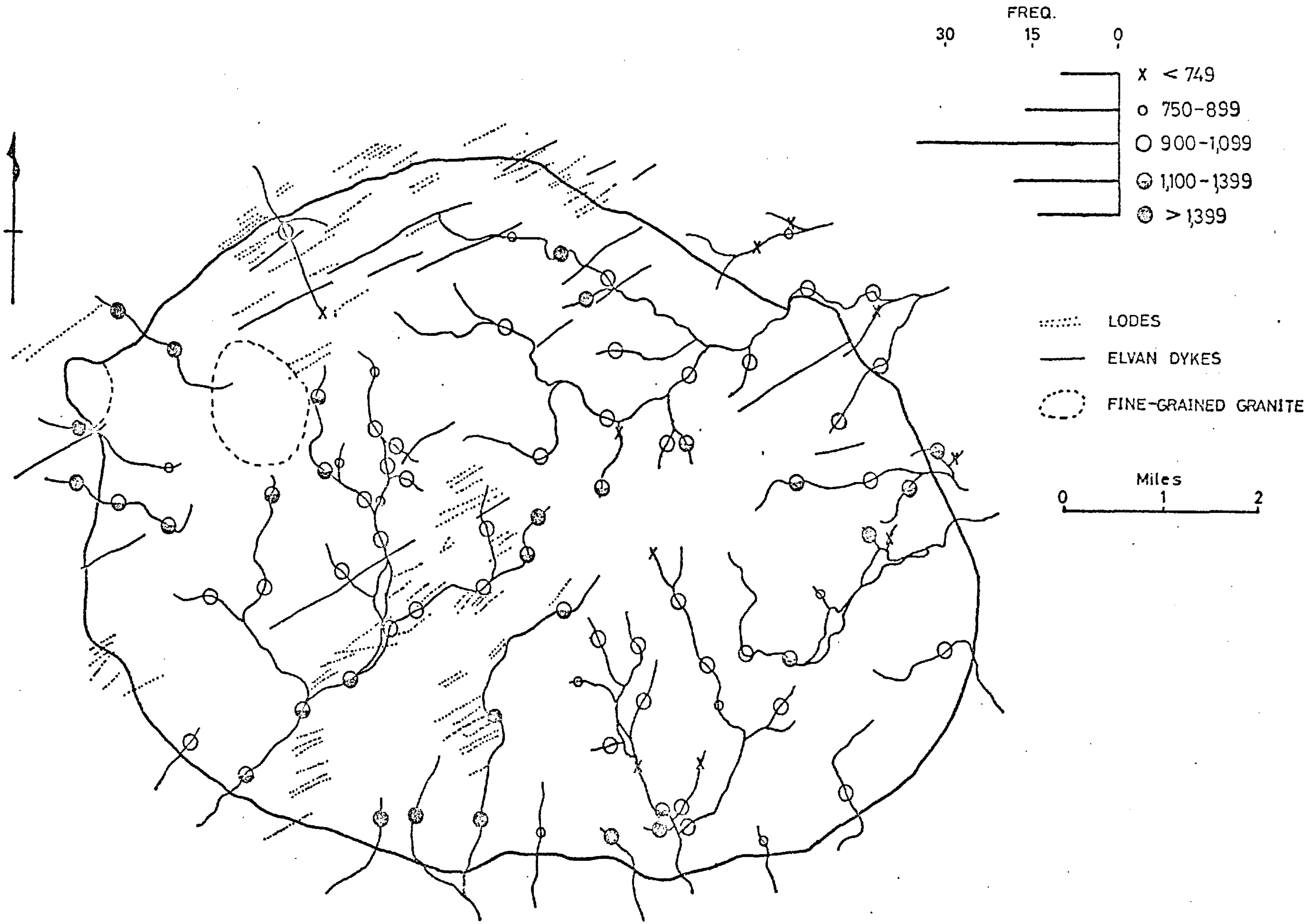


FIGURE 3.31 DISPERSION OF TOTAL FLUORINE IN STREAM SEDIMENTS (-80 mesh, 200u.) DRAINING THE CARNMENELLIS GRANITE, CORNWALL, ENGLAND

Non-mineralized zones exhibiting enrichments of fluorine in tin provinces will also affect soil and stream sediment surveys; for this reason the element should be used in conjunction with those elements characteristic of the mineralization (Sn, As, Cu).

3.3.2.2.3 Dispersion of Fluorine in Stream Sediments

The distribution of fluorine in stream sediments draining the Carnmenellis granite is shown in Fig. 3.31. This granite mass is characterized by a number of greisenized tin lodes located in swarms and trending NE-SW. Many of these deposits have been mined, and a number of streams in the area have been worked for alluvial tin. The nature of the contamination in this area and the lack of a strong co-relation between fluorine anomalies and areas of mineralization would seem to mitigate against using drainage surveys in south-west England. This is not a problem confined to the use of fluorine alone, since Hosking et al (1964, 1965) and Dunlop (1974) have also found similar erratic distributions for Sn, Cu, Zn and As in this province. There is little doubt that man's activities in this area have almost completely negated the possibility of using large-scale drainage surveys. A more effective form of exploration would involve the use of pedogeochemical and lithogeochemical surveys in areas considered to be geologically favourable for mineralization.

In tin provinces where there has been little mining activity, fluorine can be a valuable indicator in drainage surveys. If fluorite is not present in the deposits to produce hydromorphic anomalies the formation of anomalies in stream sediments is conditioned largely by the weathering of the greisen lodes and mechanical transport of the fluoriferous minerals topaz, tourmaline and sericite into the streams. For this reason it is advisable to use a total method of analysis (NaOH fusion) in order to ensure a high anomaly contrast.

3.3.2.2.4 Dispersion of Fluorine in Soils

The distribution of fluorine in soils over various rock types in south-west England is represented by a soil traverse over the killas-metamorphic aureole-Dartmoor granite system (Fig. 3.32). The distinct anomaly over both the north and south aureole zone supports the results obtained for the primary dispersion (Table 3.12). Over the Devonian rocks in the south and the Carboniferous and Devonian rocks in the north the fluorine content varies from 300 to 600 ppm. Over the granite, levels of 500 to 700 ppm F are indicated. In areas where alluvium is present the fluorine content of the soils may be suppressed.

The distribution of total, acid-diffusible and cold-extractable fluorine in soils over the Wheal Jane tin lode located east of the Carnmenellis granite (Fig. 3.30) are shown in Figs. 3.33, 3.34 and 3.35. For purposes of comparison the boron and phosphorus distributions over this lode are also presented (Figs. 3.36 and 3.37). The Wheal Jane deposit consists of a greisen tin lode localized along the contact zones of a series of elvan dykes which are up to 80 feet thick and dip northwest at 35^{o}. The deposit which extends approximately 2 miles along strike in an ENE direction is situated in the Devonian Mylor series of the killas. Mineralization consists of cassiterite, tourmaline, arsenopyrite, chalcopyrite and pyrite. Sericitic wallrock alteration extends up to 100 feet from the footwall (Rayment et al 1971).

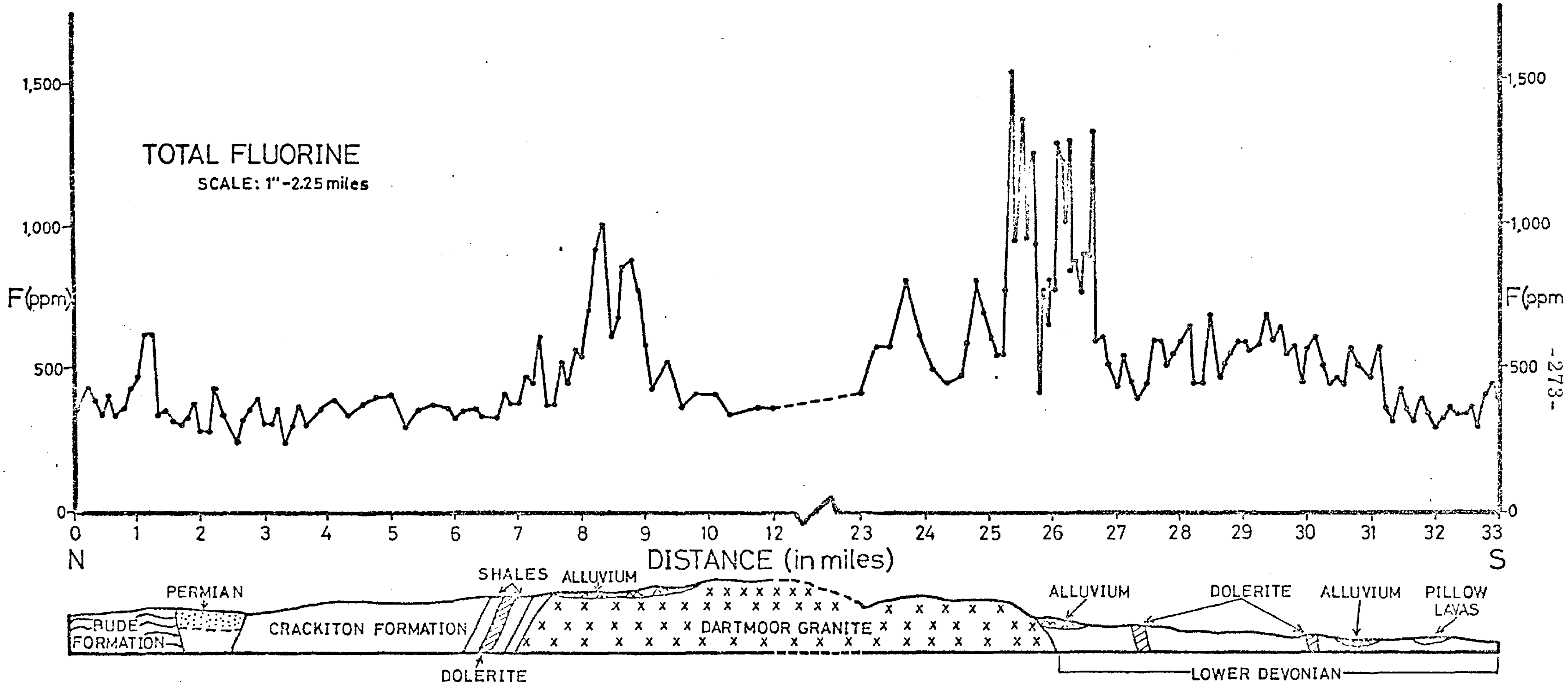


FIGURE 3.32 DISTRIBUTION OF TOTAL FLUORINE IN SOILS (6-8", -80 mesh, <200µ) OVER THE DARTMOOR GRANITE AND SURROUNDING COUNTRY ROCKS (see Fig. 3.30 for location of soil traverse; samples taken by Aquilar, 1975)

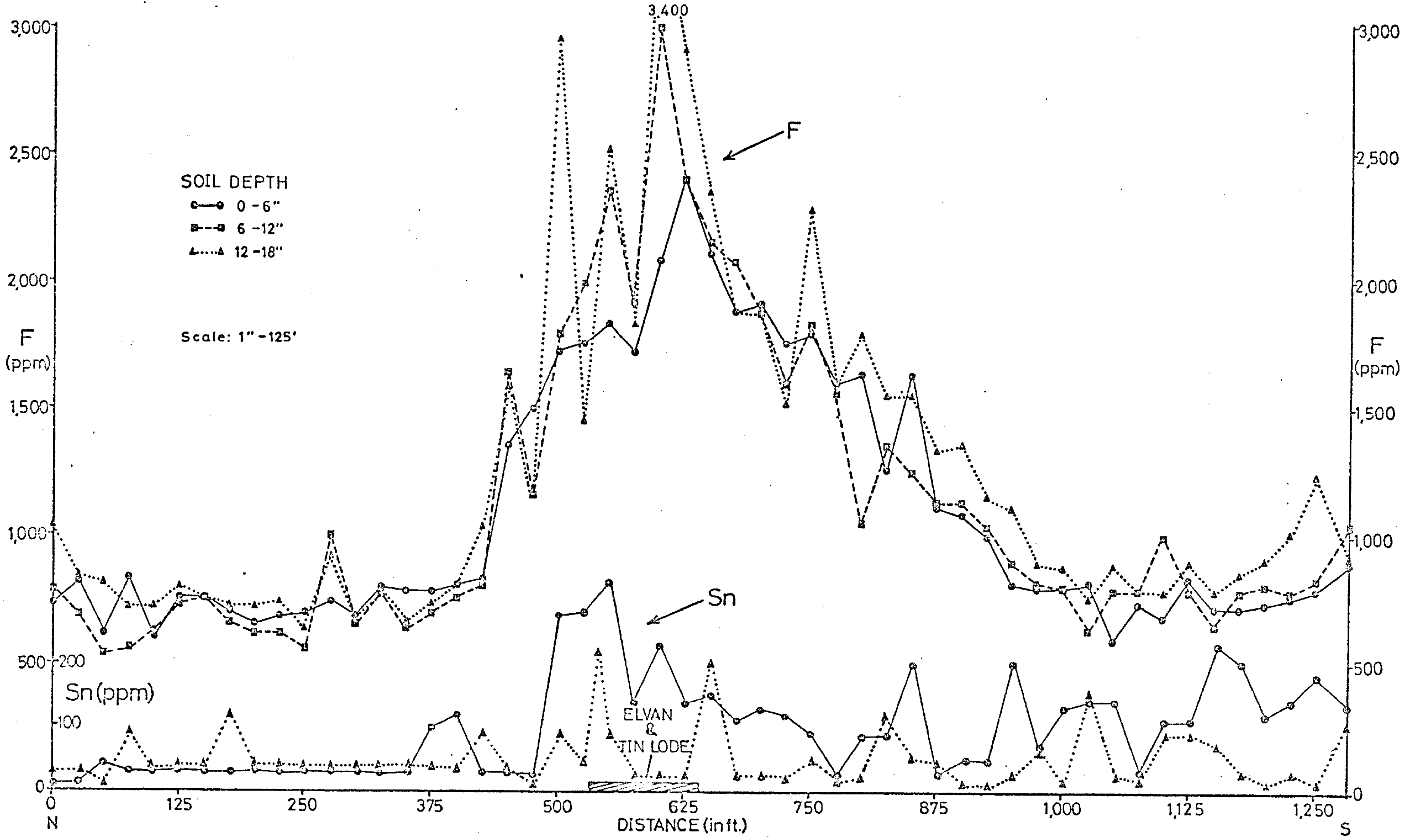


FIGURE 3.33 DISTRIBUTION OF TOTAL FLUORINE AND TIN IN SOILS (-80 mesh, ≡200µ) OVER THE WHEAL JANE TIN LODE, CORNWALL (see Fig. 3.30 for location of soil traverse; Sn analyses after Dunlop, 1973)

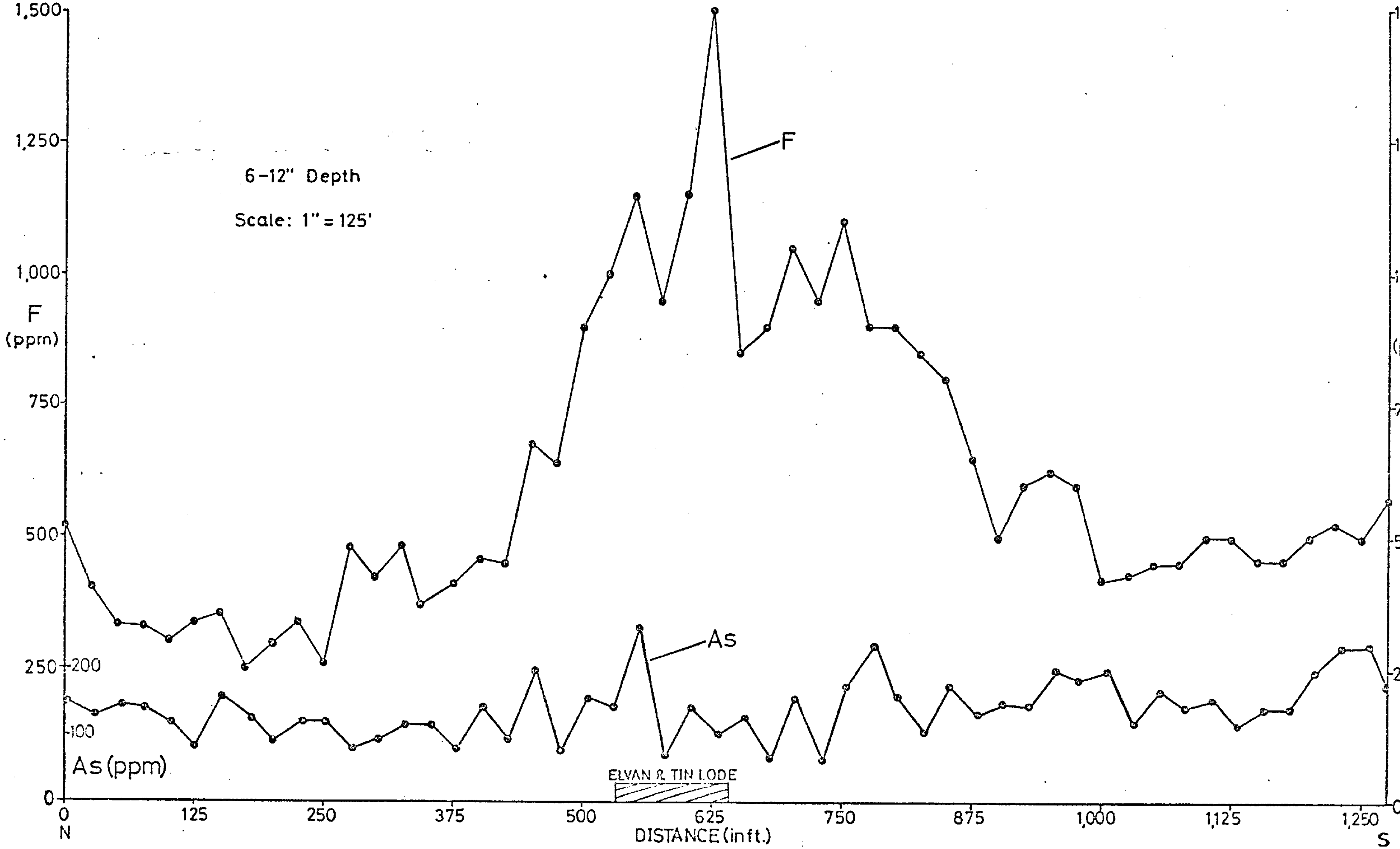


FIGURE 3.34 DISTRIBUTION OF ACID DIFFUSIBLE FLUORINE AND ARSENIC IN SOILS (-80 mesh, 200µ.) OVER THE WHEAL JANE TIN LODE, CORNWALL (see Fig. 3.30 for location of soil traverse; As analyses after Dunlop, 1973)

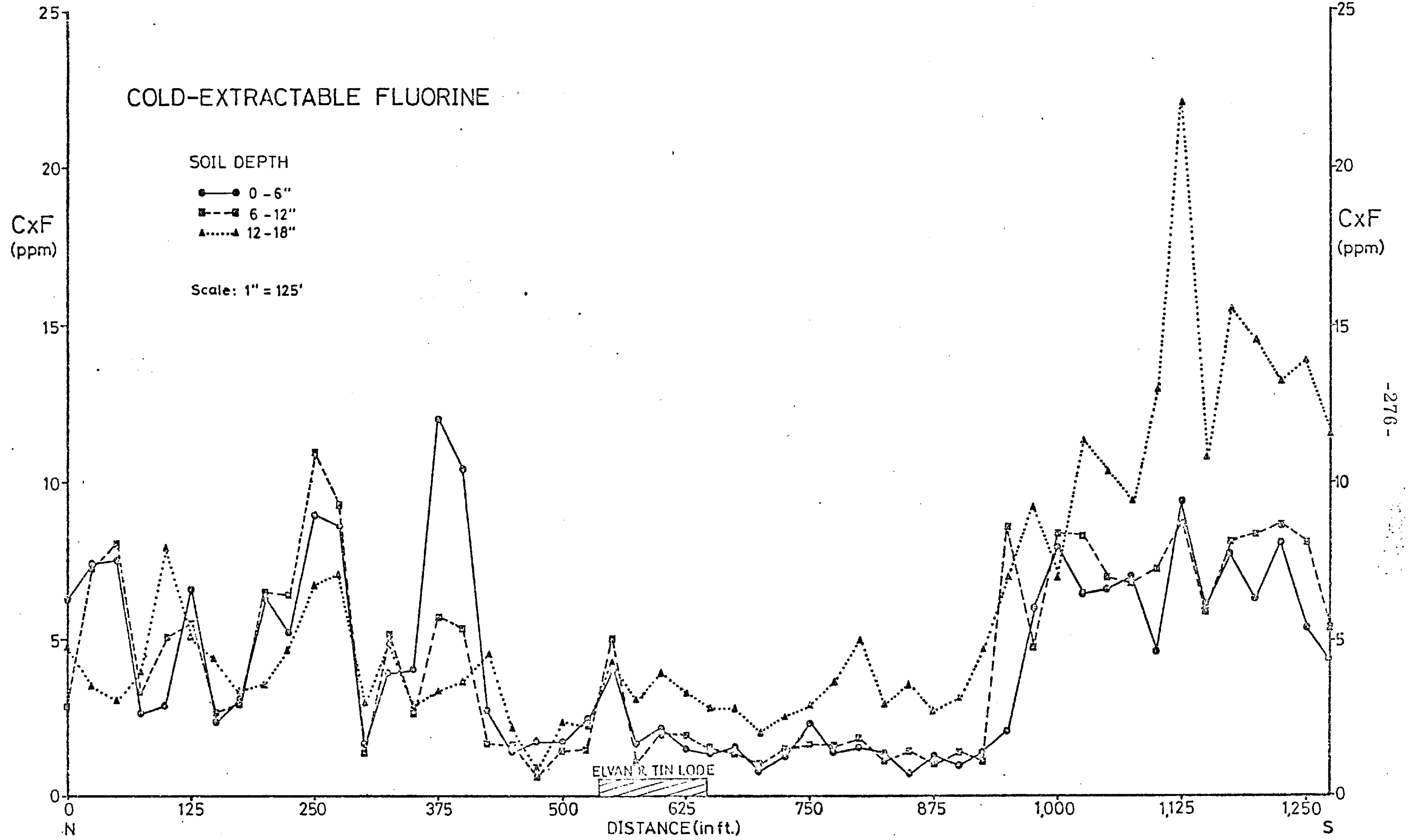


FIGURE 3.35 DISTRIBUTION OF CxF (0.01 M HCl) IN SOILS (-80 mesh, 200u.) OVER THE WHEAL JANE TIN LODE, CORNWALL (see Fig. 3.30 for location of soil traverse)

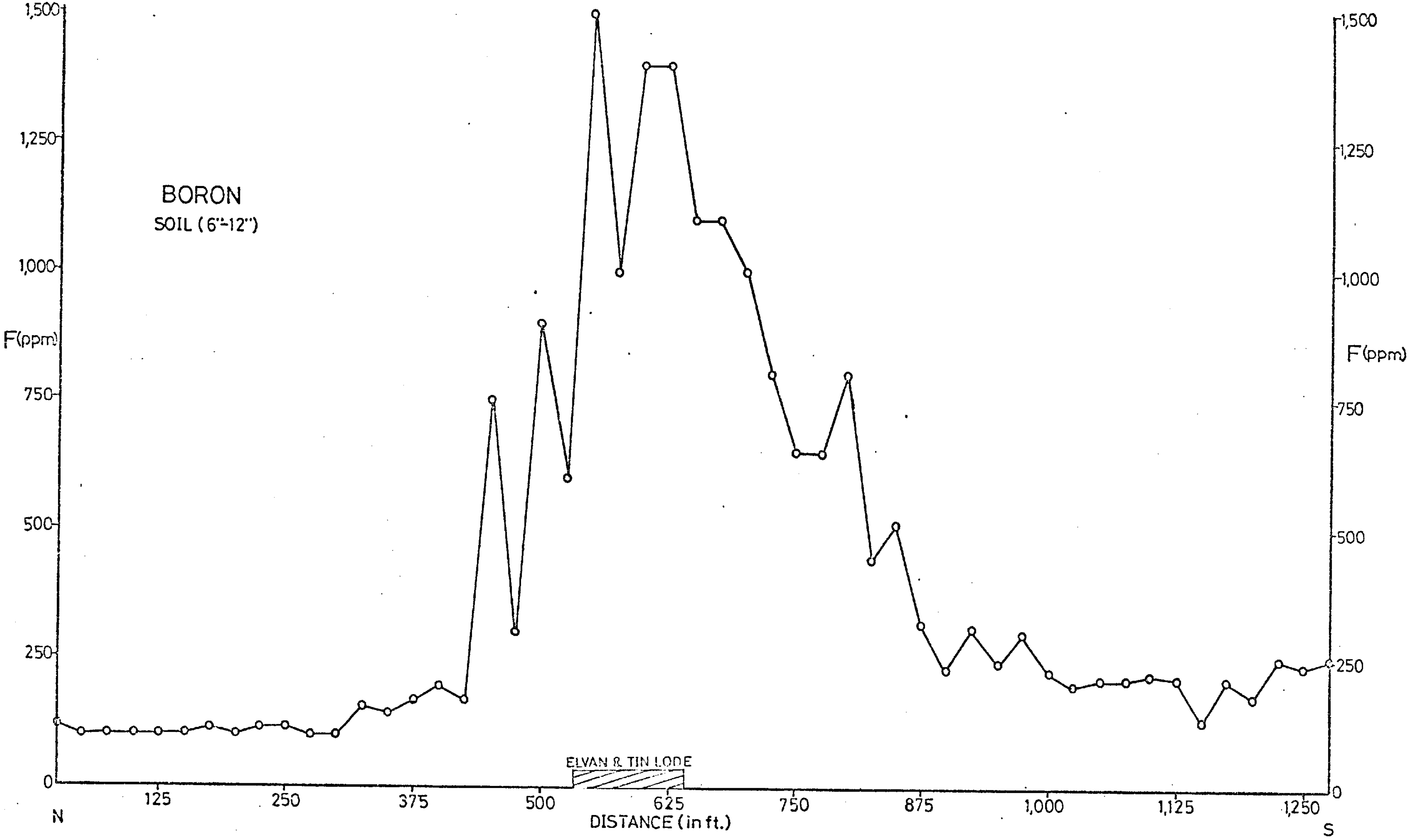


FIGURE 3.36 DISTRIBUTION OF BORON IN SOILS (-80 mesh, 200μ) OVER THE WHEAL JANE TIN LODE, CORNWALL (see Fig. 3.30 for location of soil traverse)

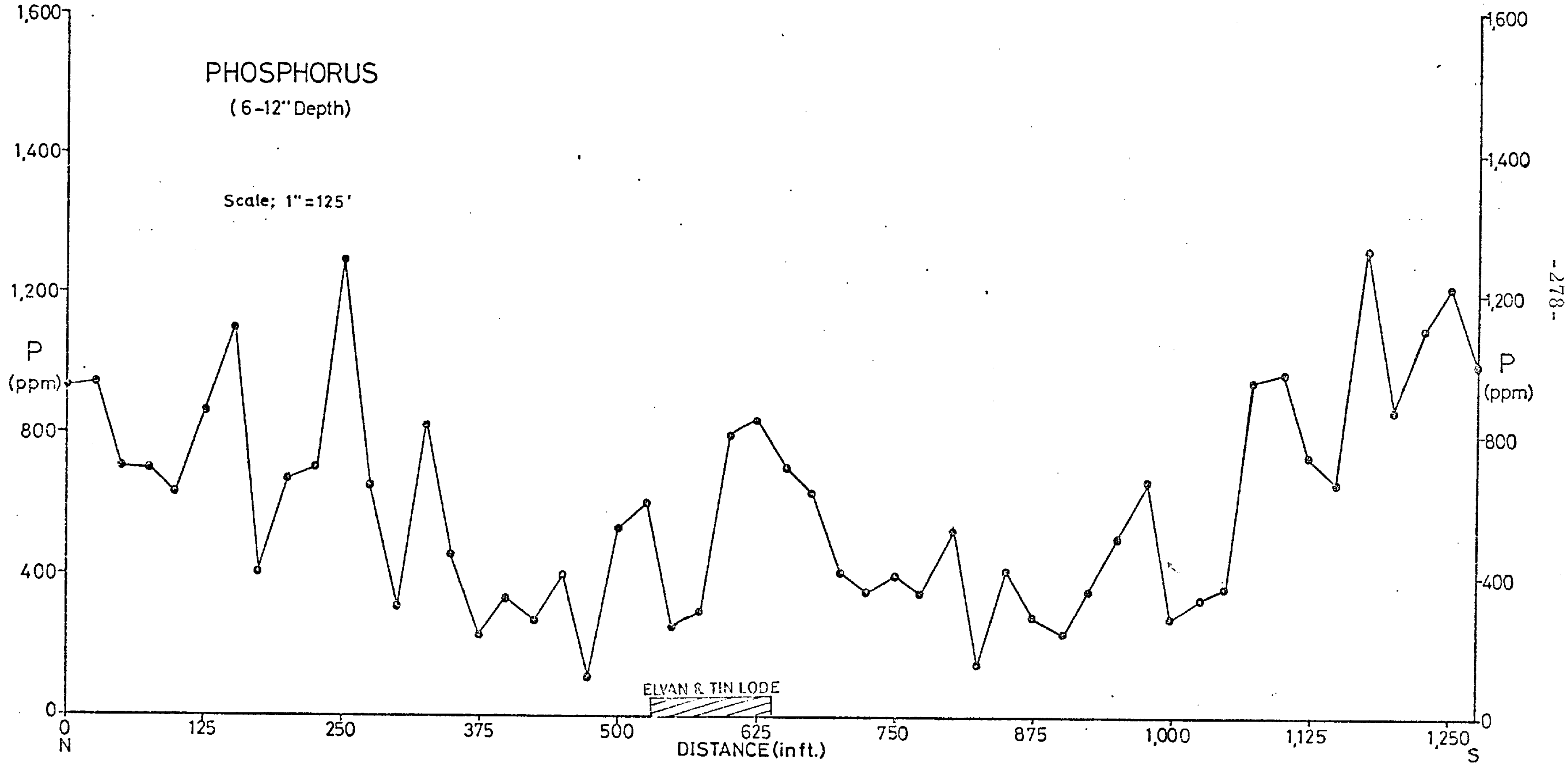


FIGURE 3.37 DISTRIBUTION OF PHOSPHORUS IN SOILS (-80 mesh, -200u.) OVER THE WHEAL JANE TIN LODE, CORNWALL (see Fig. 3.30 for location of soil traverse)

The results for the total fluorine in soils over this deposit clearly indicate the presence of a large anomaly of high contrast and good lateral extent. A comparison of the dispersion patterns observed for soils taken at different depths indicates that a greater anomaly contrast can be obtained by sampling the subsoil horizons (6"-12" and 12"-18"). Samples taken at 12"-18" produce a much greater erratic distribution pattern than those taken at 6"-12". For this reason the latter depth is preferred.

The distribution pattern of acid diffusible fluorine in the Wheal Jane soils (Fig. 3. 34) reflects that for total fluorine. Approximately 50% of the fluorine can be extracted by the diffusion method.

The (0. 01M HCl) cxF method (Fig. 3. 35) produces a distinct negative anomaly over the Wheal Jane mineralization. This is particularly accentuated by soils taken at depths of 12"-18". The fluorine in soils over the mineralized zone is obviously held in minerals extremely resistant to attack by 0. 01M HCl. Over the killas most of the fluorine is probably held by clay minerals in an adsorbed form, hence the positive cxF anomaly over these rocks.

The patterns observed for total, acid diffusible and cold extractable fluorine give a positive indication as to the forms in which fluorine is present in the soils over the Wheal Jane mineralized zone. The partial extraction of fluorine by the diffusion method (approximately 50% of total fluorine) and the negative anomaly exhibited by the cxF method suggest that the fluorine is incorporated in relatively resistant minerals, namely tourmaline, topaz and sericite. Apatite cannot be included in this group since phosphorus (Fig. 3. 37) is not anomalous over the mineralized zone. The anomaly observed for acid diffusible fluorine can be attributed mainly to sericite since this mineral is relatively susceptible to attack by orthophosphoric acid, whereas tourmaline and topaz are relatively resistant.

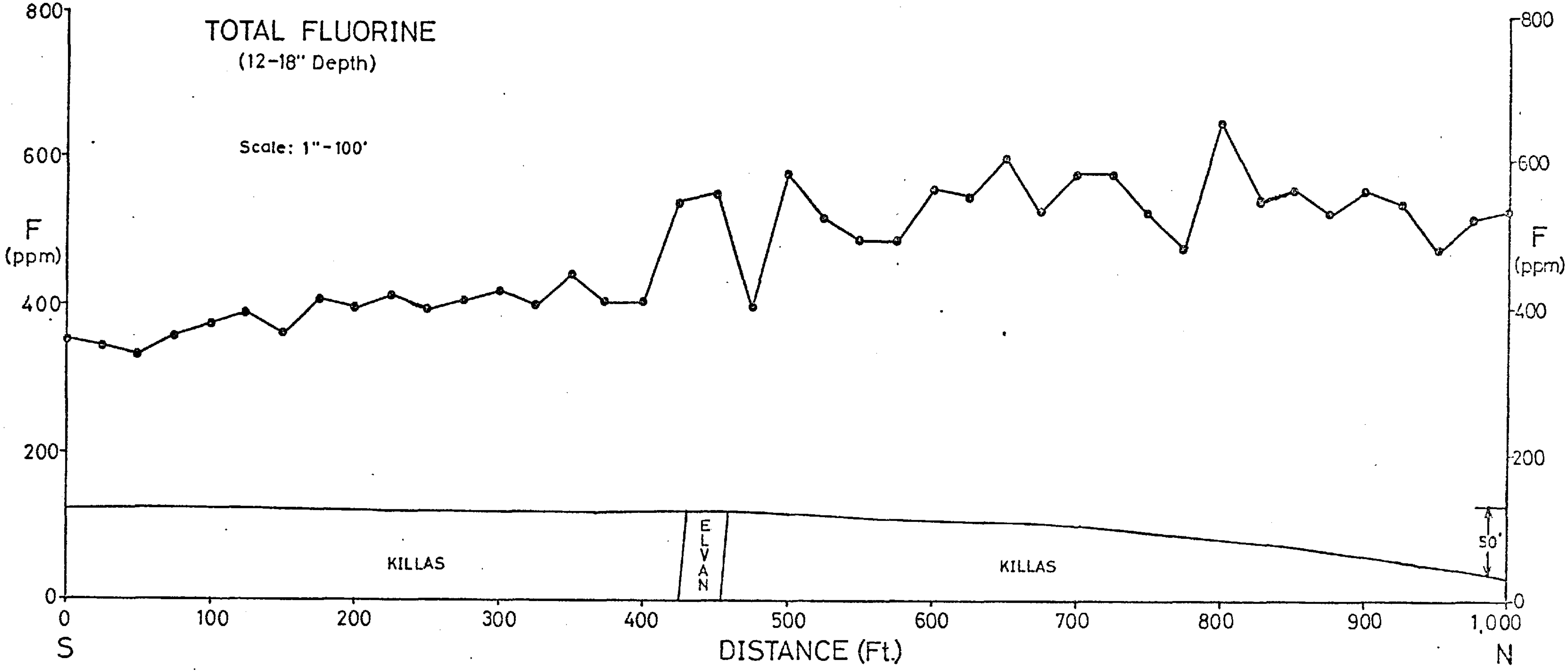


FIGURE 3.38 DISTRIBUTION OF TOTAL FLUORINE IN SOILS (-80 mesh, 200 µ) OVER THE COLDWIND ELVAN DYKE, CORNWALL (see Fig. 3.30 for location of traverse)

The dispersion pattern of boron in the Wheal Jane soils (Fig. 3.36) is remarkably similar to that for total fluorine, and hence much of the fluorine not extracted by the diffusion method can be attributed to tourmaline. Because of its common association with greisens, topaz, in minor amounts, is undoubtedly also present.

The results shown for the dispersion of fluorine over the Wheal Jane tin lode indicate that the choice of analytical method is extremely important. Cold-extractable methods are unacceptable, and the acid-diffusible method relies principally on the presence of sericite, the minerals tourmaline and topaz not being attacked by this method. For exploration, the total method is, therefore, preferred.

Since the Wheal Jane tin lode is associated with a quartz porphyry dyke ('elvan') a soil traverse was conducted over a barren elvan dyke (see Fig. 3.30 for location of Coldwind Elvan) to determine what the contribution, if any, of the Wheal Jane elvan is to the observed fluorine anomaly. The results for the traverse (Fig. 3.38) clearly indicate that very little of the anomalous fluorine expression over the Wheal Jane lode can be attributed to the presence of the elvan. The possibility still exists, however, that anomalies may occur over some elvans since these rocks on average contain more fluorine than the killas (1,590 and 790 ppm respectively). Anomalies of this type may be readily detected, however, by the lack of an anomalous expression in the overlying soils of elements such as Sn, B, As and Cu.

For soil surveys carried out over granites, regard should be given to the increased background levels that may be observed for fluorine. In this respect the use of a total method of analysis is strongly recommended if suitable anomaly contrasts are to be achieved.

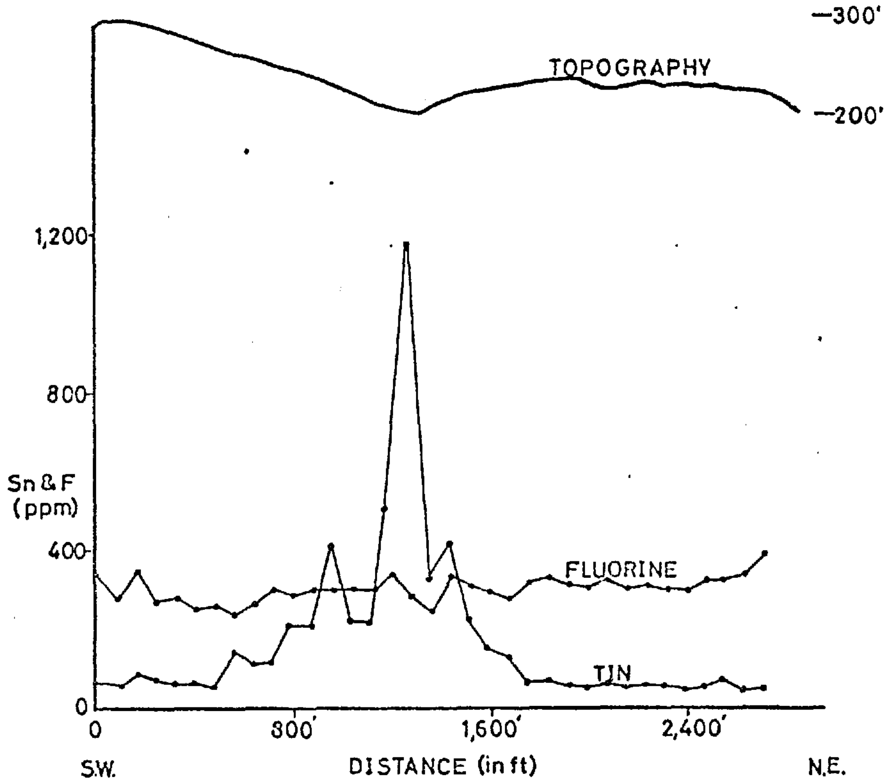


FIGURE 3.39 DISTRIBUTION OF TOTAL FLUORINE AND TIN IN SOILS (-80 mesh, 200µ.) OF THE PENGELLY TOPOGRAPHIC DEPRESSION BELOW THE 430 ft. O.D. (samples and tin analyses after Dunlop, 1973)

A further application of fluorine in prospecting for tin deposits in south-west England is the detection of tin anomalies associated with detrital tin accumulations in topographic depressions below the 430 feet O. D. During the marine transgression at the end of the Miocene epoch an erosional platform was present above this elevation, and considerable dispersion of detrital cassiterite into topographic depressions occurred. Many of these depressions have been investigated in detail by Dunlop (1973), who found that tin anomalies in the soils were not supported by Cu and As anomalies. Although As and Cu are often associated with Sn mineralization these two elements do not always give an anomalous response over mineralization (e. g. Wheal Jane lode described earlier); they are not, therefore, conclusive indicators of the presence of detrital tin anomalies. On the other hand fluorine is strongly associated with tin as one of the major elements in greisens. It produces strong anomalies over primary mineralization but does not correlate with detrital tin anomalies as evidenced from the traverse over the Pengelly depression (Fig. 3. 39). It may, therefore, be used to confirm the type of tin anomaly formed in soils.

The results described above for the dispersion of fluorine in the vicinity of tin mineralization indicate that the element is a much better pathfinder for tin deposits than Cu or As. This is due mainly to the fact that, unlike greisens, Cu and As mineralization is not always associated with tin deposits. Studies by Teh et al (1975) in the Malaysian tin province confirm the present author's results; these investigators found fluorine to be a better and more reliable pedogeochemical pathfinder for tin than arsenic. When prospecting for tin deposits it is advisable, therefore, to use both fluorine and tin as indicators at all stages of geochemical exploration.

3.3.3 Prospecting for Hypothermal Mineral Deposits

3.3.3.1 Introduction

Hypothermal or high-temperature hydrothermal mineral deposits represent a transition phase between pegmatites and mesothermal mineral deposits. The principal gangue minerals in these deposits are quartz, topaz, tourmaline, pyrite and apatite, and the economic mineralization if present is invariably gold and silver although occasionally Mo, W, Sn, Sb, and As may also occur in economic amounts. The wallrock alteration associated with these deposits is mainly sericitic but carbonatization, chloritization, topazization and tourmalinization may also be present.

The detection of these deposits by geochemical means is troublesome since most methods rely on an abundance of one or more of the gangue minerals. The pathfinding qualities of As, for instance, depend solely on the presence of arsenopyrite, sulphosalts, or arseniferous pyrite which do not always occur in large quantities in many of these deposits. Likewise, the use of fluorine requires the presence of topaz, tourmaline, fluorite and apatite, and these minerals are not always present. The more direct indicators such as gold and silver exhibit extensive dispersion haloes around mineralization but the analysis of these elements is quite expensive thus mitigating against their use in large reconnaissance surveys. They have their best application when specific target areas have been located.

3.3.3.2 Gold-Quartz Veins, Sierra Leone

These deposits are situated in the Sula Mountains-Kangari Hills area of central Sierra Leone. They occur mainly in a series of Precambrian

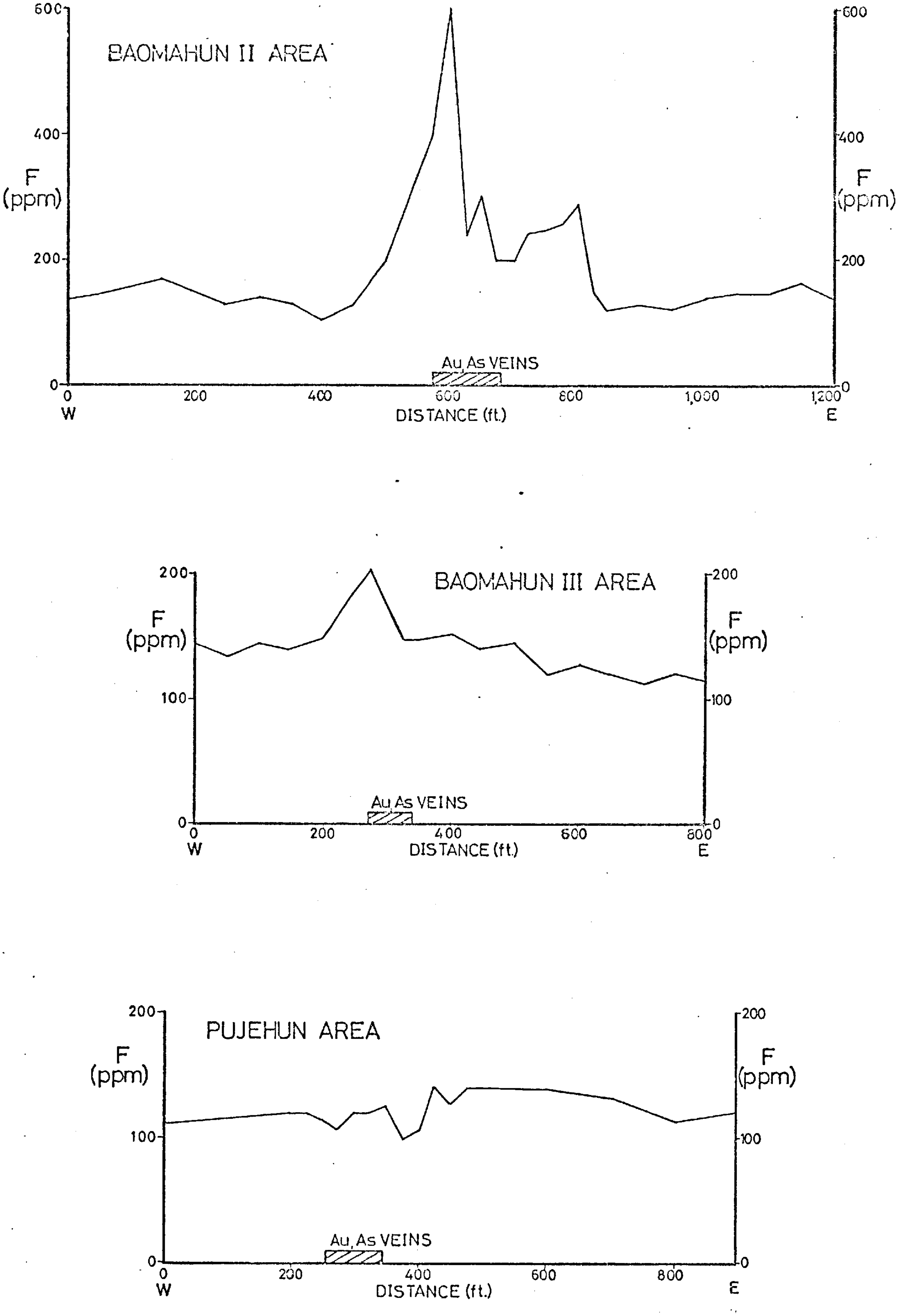


FIGURE 3.40 DISTRIBUTION OF TOTAL FLUORINE IN SOILS (-80 mesh, 200 ft.) OVER GOLD-QUARTZ VEINS IN CENTRAL SIERRE LEONE (samples taken by James, 1965)

crystalline basement rock (gneissis, schists, granulites, etc.). The mineralization as described by James (1965) consists mainly of quartz veins containing gold and arsenopyrite. Some of the deposits are tourmalinized. James (1965) has studied the dispersion of As in the residual soils over these deposits, and found the element to be a good indicator of the quartz veins in the underlying bedrock. Complications during the interpretation phase with respect to this element did, however, occur in areas where there was arsenic mineralization but no gold.

The distribution of fluorine in soils over three of these gold deposits is illustrated in Fig. 3.40. As can be seen from these data fluorine is not a universal indicator of their presence, but for those deposits which are tourmalinized such as the Baomahun II deposit the element is a good indicator.

In view of the fact that arsenopyrite and arseniferous pyrite is not always associated with gold-quartz deposits and interferences affecting the use of As may arise in areas of arsenic or sulphide mineralization, the use of both As and F to detect these deposits may be a more viable approach. Certainly, coincident As and F anomalies are a good indication of the presence of gold-quartz veins. Individual As and F anomalies, as well as coincident anomalies of these two elements, would have to be assessed by the aid of gold analyses. In the crystalline basement complexes in which gold deposits of this type generally occur, pegmatite deposits may also be present and fluorine anomalies in stream sediments or soils may be related to these types of deposits. They may, however, be easily differentiated from gold-quartz deposits by the anomalous dispersion of such pegmatite indicators as Be, Li, Ze, P, Nb, Ta, U and Th.

Fluorine is also a valuable aid in lithogeochemical surveys for gold-quartz veins. Shear zones, faults, breccia zones and fracture systems should be routinely sampled and the rock samples analysed for the element to outline areas manifested by processes of sericitization, tourmalinization and/or topazization. Such zones may be the loci for gold deposits.

3.3.4 Prospecting for Mesothermal and Epithermal Mineral Deposits

3.3.4.1 Introduction

In mesothermal and epithermal mineral deposits the principal fluorine-bearing mineral is almost exclusively fluorite. This mineral occurs in fluorite veins in both carbonate and granitic terrains, in vein and stratiform sulphide deposits in limestone environments, and in vein deposits carrying Hg, Sb and Mo. Numerous studies have indicated that fluorine is a good indicator of these types of deposits when used in geochemical surveys (Krainov et al 1967; Friedrich and Pluger, 1971; Prkorny, 1971; Schwartz and Friedrich 1973; Michael et al, 1973; Farrell, 1974; Carlson et al, 1974; Lalonde, 1974, 1975; Graham et al, 1975; and Tilsley, 1975). It is an abberation of nature, however, that fluorite is not always associated with these particular deposits; some metallogenic sulphide provinces, such as the base metal deposits of Ireland, are noted for their lack of fluorite while others, such as the Derbyshire ore province of England, are characterized by mineral zonation in which fluorite may be present in only one or two zones.

In view of the advanced research mentioned above on the application of fluorine in prospecting for fluorite-bearing hydrothermal ore deposits, the author turned his attention to the study of the dispersion of this element in the vicinity of hydrothermal ore deposits which do not contain visible amounts of fluorite. The reasoning behind this approach lies in the possibility that fluorine may have played a role in the hydrothermal processes and may be enriched in these deposits in a cryptic manner (i. e. camouflaged in micas and other minerals in the wallrock alteration and primary haloes).

To assess adequately the dispersion characteristics of fluorine in the vicinity of non-fluorite-bearing deposits of the types mentioned above, studies were carried out over the Tynagh Pb-Zn-Cu deposit of Eire and the Halikoy mercury and Ivrindi antimony deposits of western Turkey.

3.3.4.2 Tynagh Pb-Zn-Cu Deposit, Eire

3.3.4.2.1 Introduction

The Tynagh sulphide deposit (Fig. 3.41) occurs in limestones of Carboniferous age and is situated on the Tynagh fault. The geology of the deposit has been described in detail by Morrissey (1970). Essentially the deposit consists of galena, sphalerite, chalcopyrite and barite with minor amounts of other sulphides and no visible fluorite. The orebody is marked by zones of both secondary and primary sulphides (see Fig. 3.41). It is representative of the Pb-Zn-Cu-barite deposits which occur in the large metallogenic sulphide province in the Carboniferous limestone district of Eire. None of these deposits contain fluorite.

The secondary dispersion of Pb, Zn, Cu and Hg in the surficial cover over the Tynagh deposit has been studied in detail by Donovan (1965). His results indicate strong soil anomalies for these elements over the mineralized zone.

The distribution of fluorine in the secondary ore zone of the Tynagh deposit is represented by Fig. 3.42. Three zones of high fluorine content, seemingly unrelated to any particular type of secondary ore (oxide, black sulphide, or grey sulphide), occur in this section of the ore deposit. In two

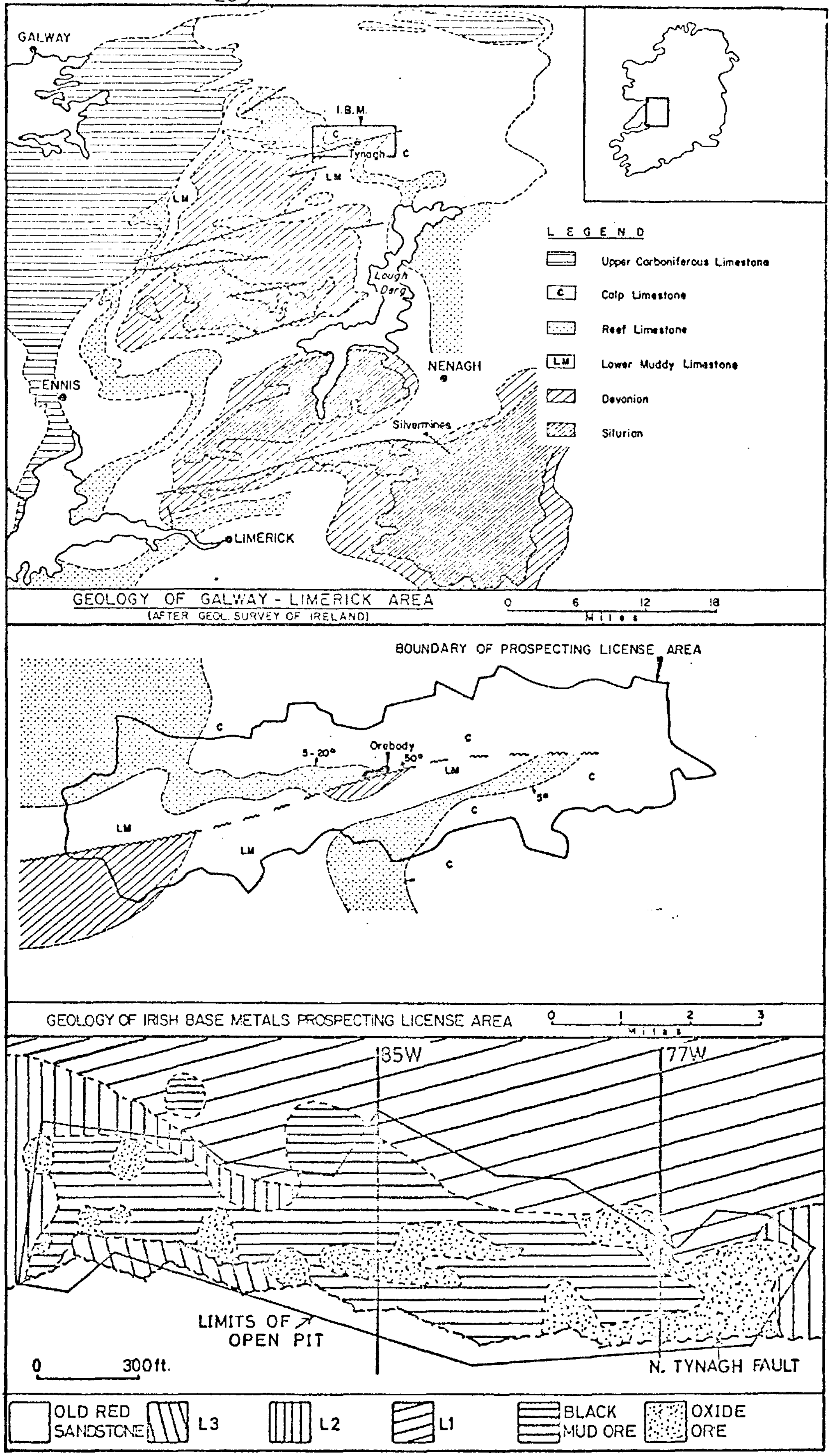


FIGURE 3.41 GEOLOGY AND LOCATION OF THE TYNAGH Pb-Zn-Cu DEPOSIT, COUNTY GALWAY, EIRE (Geology after Derry et al, 1965; L1, L2 and L3 units are limestones)

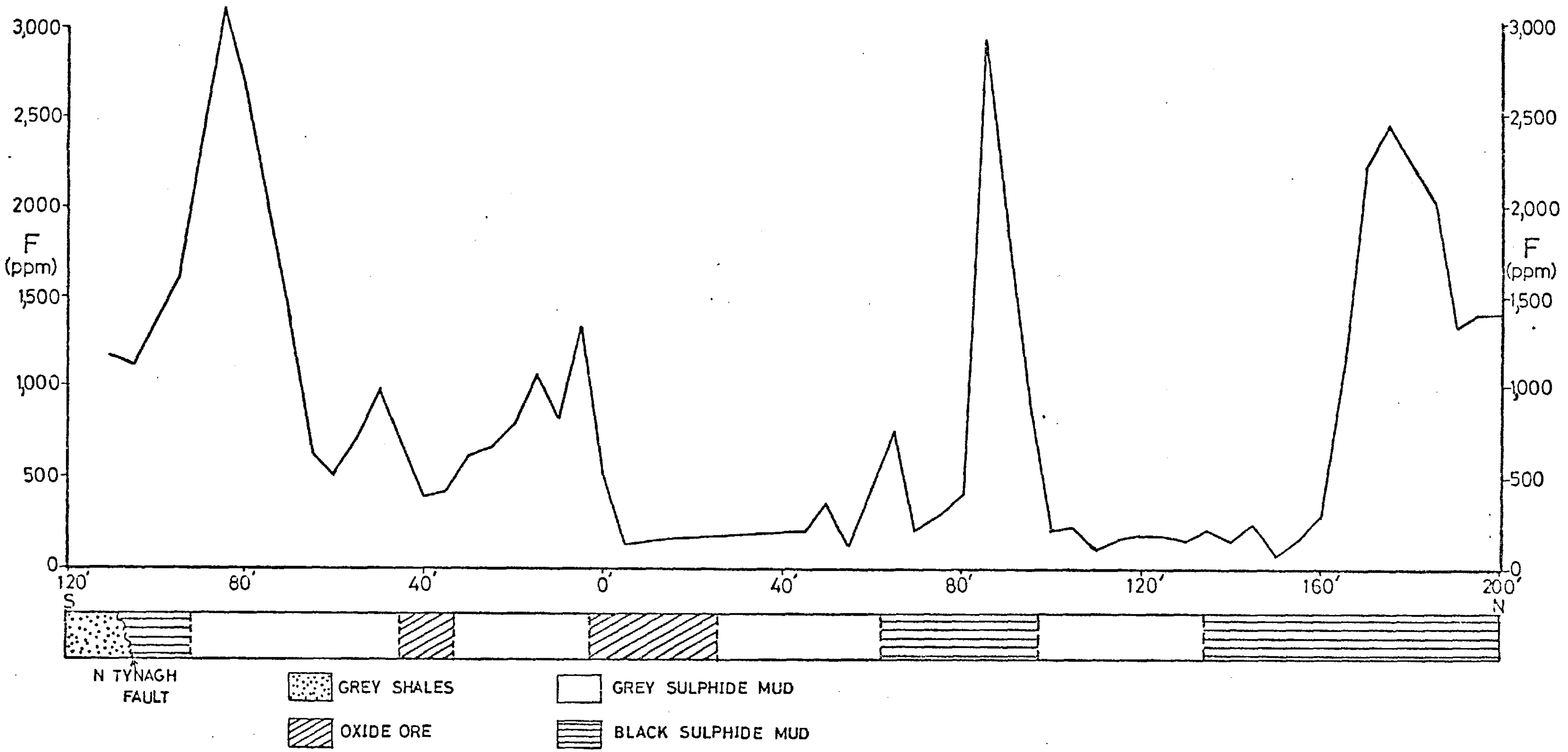


FIGURE 3.42 DISTRIBUTION OF TOTAL FLUORINE IN THE SECONDARY ORE ZONE, TYNAGH Pb-Zn-Cu DEPOSIT, EIRE. (Samples and geology after Donovan)

areas of the secondary ore zone the fluorine content is relatively low (100-200 ppm). The anomalous concentrations of fluorine may represent local enrichments of micro-crystalline fluorite since no visible fluorite has been noted in these deposits. Assuming that they can be related to the presence of fluorite, the fluorine values as a whole indicate that this mineral is present in concentrations of 0.04 to 0.6%.

3.3.4.2.2 Dispersion of Fluorine in Soils

The surficial deposits in the area of the Tynagh deposit are essentially freely-drained soils, peaty gleys and peat, the last two types being the most abundant. The depth of overburden generally varies from 1 to 3 metres.

Since samples are generally available and readily obtained from the A horizon during soil surveys in the area, materials from this horizon were chosen initially to study the distribution of total fluorine over the Tynagh deposit. These results are presented in Fig. 3.43. Although the Old Red Sandstone can easily be detected by the low fluorine content of the overlying soil, the fluorine values over the mineralized zone do not exceed the upper threshold value for soils over the limestone formations (L1 and L3). The data shown also indicate that considerable background fluctuation is present over the limestone areas. These large fluctuations appear to be related to the type of surficial material over which the A horizon sample was taken.

In order to ascertain whether background fluctuation could be suppressed and any anomalous concentrations of fluorine over the ore deposit enhanced, it was decided to analyse the B horizon soils using cold-extractable (0.01M HCl) analysis to extract only the hydromorphic component of the fluorine

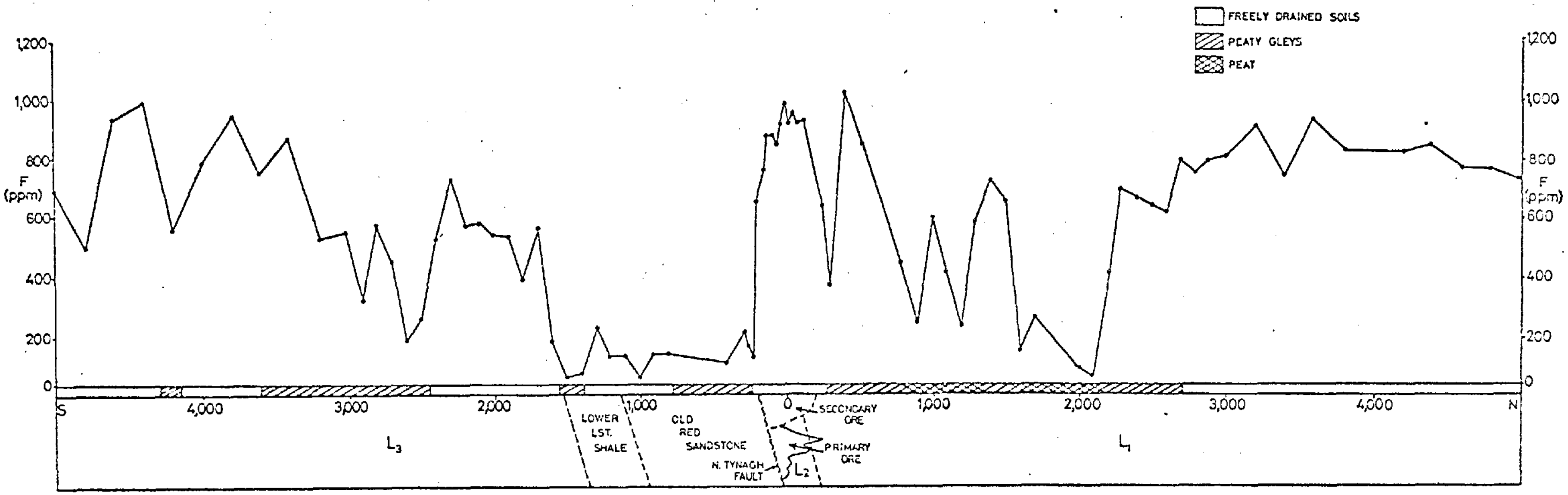


FIGURE 3.43 DISTRIBUTION OF TOTAL FLUORINE IN A HORIZON SOILS (-80 mesh, 200u ; line 77W) TYNAGH Pb-Zn-Cu DEPOSIT, EIRE (samples taken by Donovan, 1965)

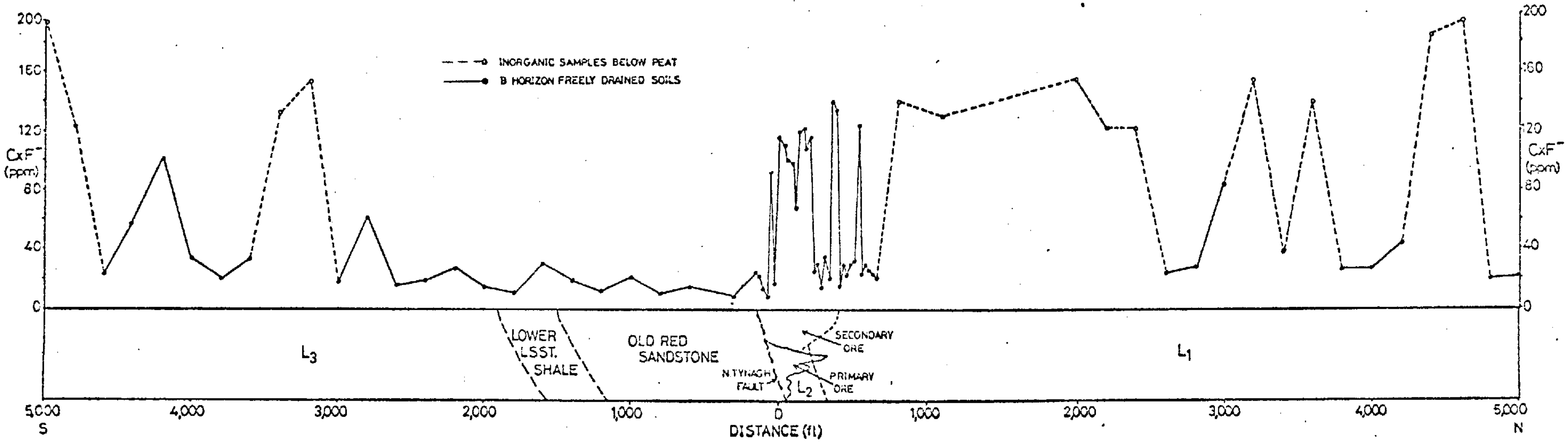


FIGURE 3.44 DISTRIBUTION OF CxF (0.01M HCl) IN B HORIZON SOILS (-80 mesh, 200µ , line 85 W) TYNAGH Pb-Zn-Cu DEPOSIT, EIRE (samples taken by Donovan, 1965)

dispersion. These results are presented in Fig. 3.44. For the B horizon soils taken over freely drained areas there is a distinct anomaly over the mineralized zone with a contrast of 3 to 4-fold. Those soils taken below peat, however, exhibit fluorine concentrations similar to the freely-drained soils over the ore deposit. The increased concentrations of loosely bound fluorine in the soils below peat may be related to the movement of water into these areas and the gradual build-up of ion concentrations.

The results of the present study indicate that provided due regard is given to the kind of material samples and the analytical method used, fluorine anomalies can be obtained over deposits of the Tynagh type. It is improbable, however, that fluorine will have a major application in Eire for two principal reasons

a) the base metals generally display much stronger anomalies over these deposits (Donovan, 1965) and

b) the sampling of freely drained soils is not a viable approach to exploration in an area largely covered by peat.

Regardless of its ineffectiveness as an exploration tool in the base metal province of Eire these results suggest that fluorine is enriched in base metal deposits occurring in limestone environments notwithstanding the fact that fluorite is not a characteristic gangue mineral in these deposits. The element may, therefore, be a useful indicator of these deposits in areas where the secondary environment does not have a strong modifying effect on the formation of anomalies. In particular, fluorine may be a good lithogeochemical indicator of concealed deposits of this type.

3.3.4.3 Halikoy Mercury Deposit, Turkey

3.3.4.3.1 Introduction

The Halikoy mercury deposit is located in the Paleozoic metamorphic complex of western Turkey (Fig. 3.45). The local geology (Fig. 3.46)

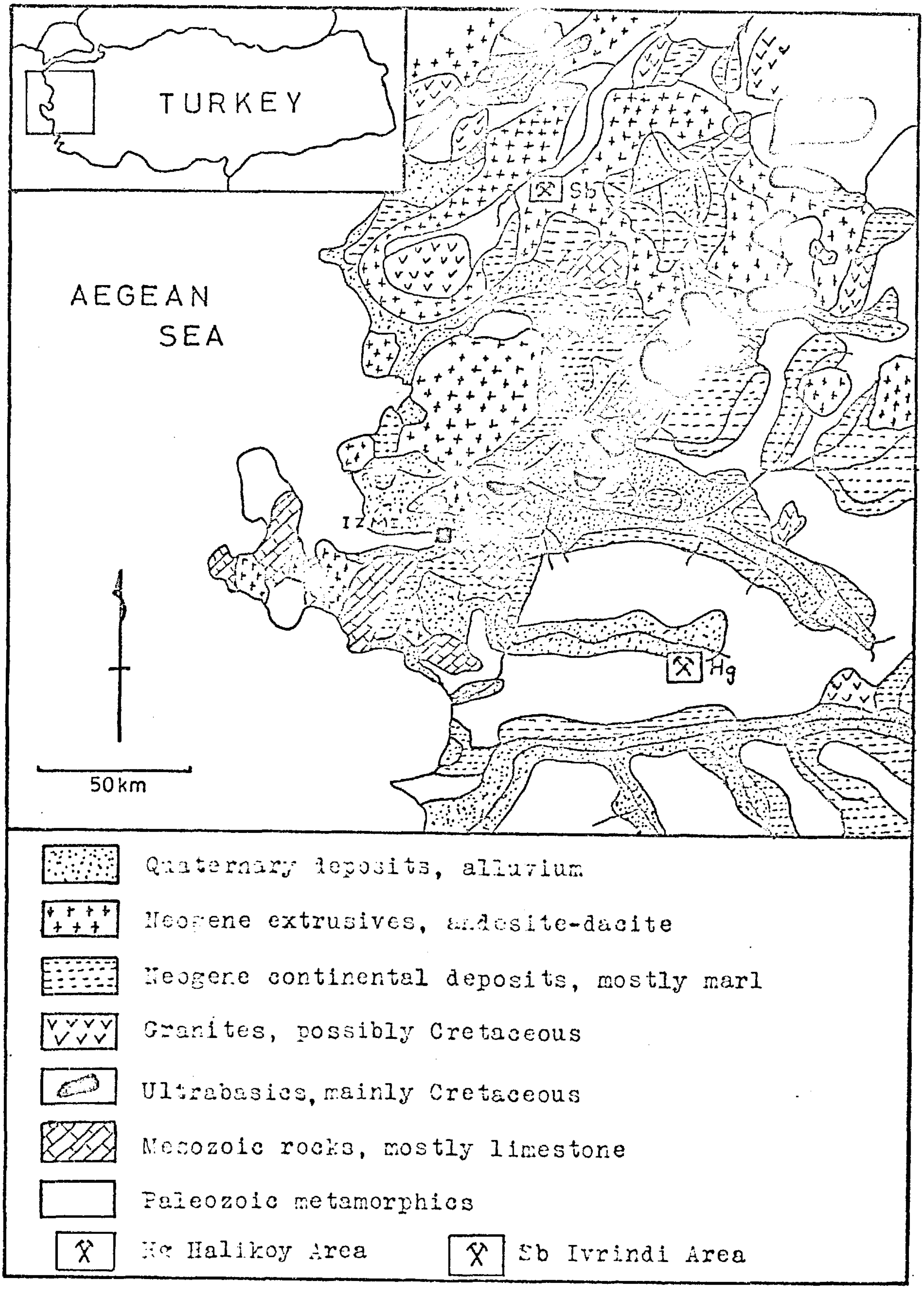


FIGURE 3.45 GENERAL GEOLOGY OF WESTERN TURKEY AND LOCATION OF HALIKOY (Hg) AND IURINDI (Sb) AREAS (Geology after Koksoy, 1967 from Maden Tetkik Arama geologic maps).

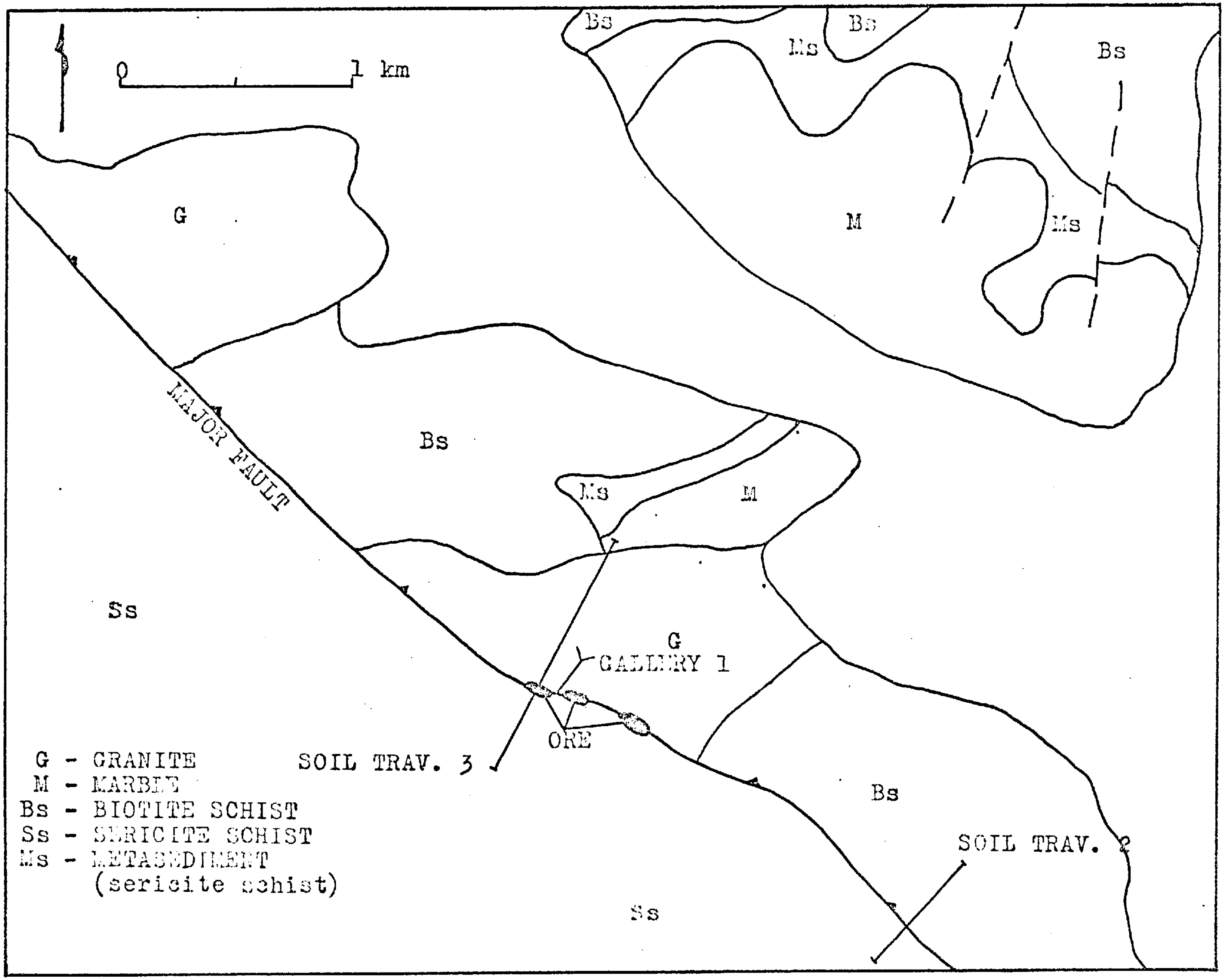


FIGURE 3.46 LOCATION OF ROCK AND SOIL TRAVERSES, HALIKOY, TURKEY (Geology after Koksoy, 1967)

consists mainly of granites, marbles, biotite and sericite schists and metasediments. The mineralization, which consists of cinnabar and quartz gangue with some pyrite and chalcopyrite, occurs as pods in dilatant zones along a major NW-SE fault zone. The hangingwall (granite) is intensely kaolinized and the footwall (sericite schist) has undergone silicification.

Underground mining of the deposit extends down to approximately 60m.

A detailed description of this area together with a study of the primary and secondary dispersion of Hg in the vicinity of this deposit has been given by Koksoy (1967).

3.3.4.3.2 Primary Dispersion of Fluorine

The dispersion patterns of fluorine and mercury in the footwall and hangingwall zones of the deposit are presented in Fig. 3.47. In the footwall zone (sericite schist) fluorine shows a slight enrichment in the vicinity of the ore, whereas mercury, although still at very high concentrations, shows a general decrease in concentration as the ore zone is approached. In the hangingwall (granite) mercury increases slightly as the ore zone is approached, but fluorine shows a distinct depletion in the gouge zone next to the ore. Away from the gouge zone the fluorine content increases rapidly in the granite to a level of about 800 ppm. The distribution patterns of mercury and fluorine in the granite next to the gouge zone are remarkably similar, suggesting perhaps that these two volatile elements have migrated into the hangingwall zone in the same manner. It should be noted that the gallery traverse in Fig. 3.47 is still well within the primary dispersion halo of this deposit and, although mercury is undoubtedly anomalous, it is difficult to determine

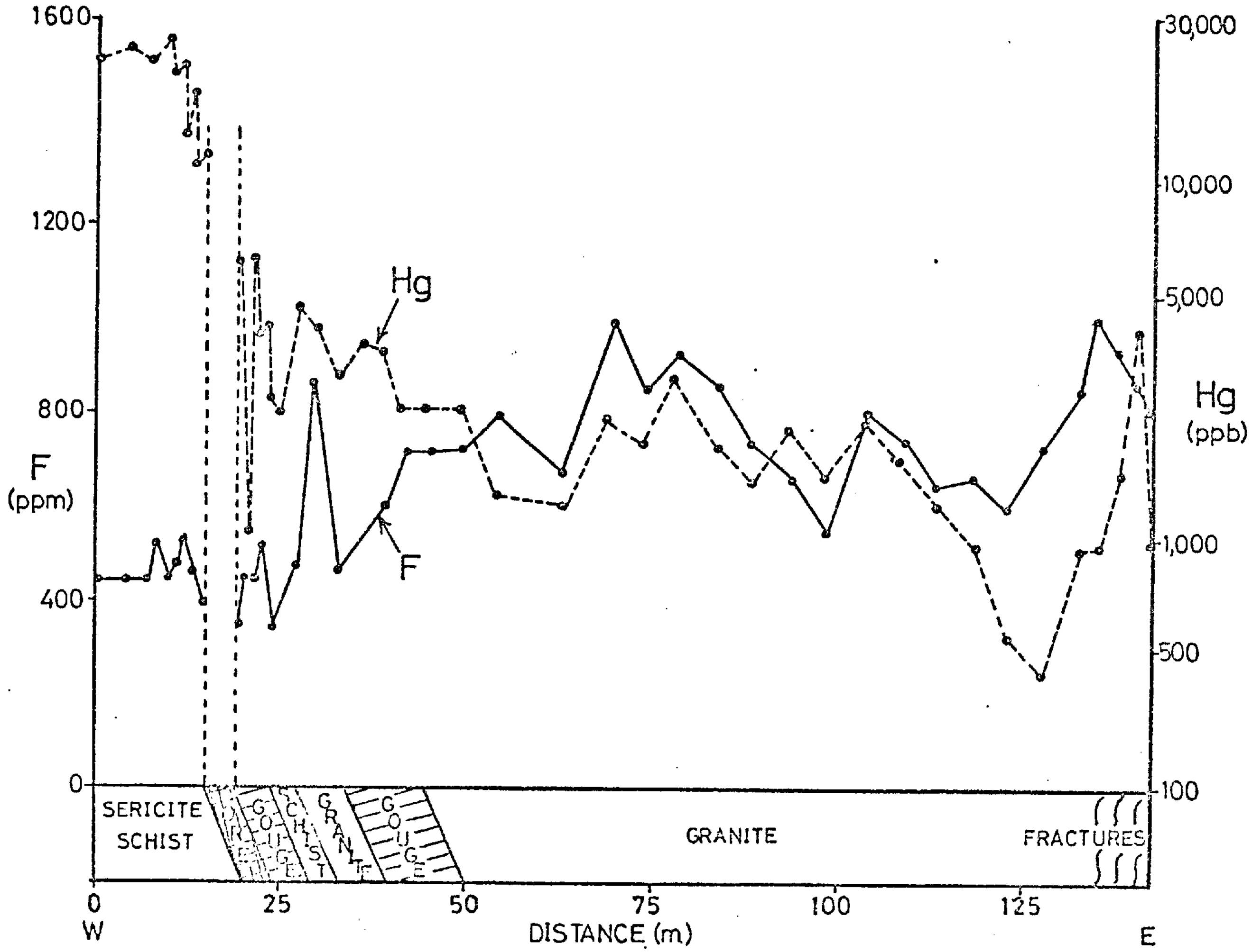


FIGURE 3.47 DISPERSION OF TOTAL FLUORINE AND MERCURY IN THE WALL-ROCK OF THE HALIKOY MERCURY MINE (Gallery 1) TURKEY (Geology and mercury analyses after

whether fluorine is also present in anomalous concentrations in the absence of data from background samples taken some distance from the ore. The results given in the following section for the distribution of fluorine in the overlying soils indicate that fluorine is however, anomalous in the hangingwall zone next to the deposit.

3.3.4.3.3 Dispersion of Fluorine in Soils

The soils in the Halikoy area are undifferentiated, residual, immature mountain soils ranging in thickness from 5 to 60 cm.

The distribution of fluorine and mercury for two soil traverses, one over the ore deposit and the other over the south-eastern extension of the fault zone (Fig. 3.45), are presented in Figs. 3.48 and 3.49 respectively. For the traverse over the ore deposit, mercury exhibits a strong anomaly directly over the ore zone (note log scale), but fluorine displays a broad anomaly stretching about 400 meters from the deposit. Fluorine has apparently accumulated in a large hangingwall zone next to the mineralisation. The anomaly contrast for mercury is greater than that of fluorine by orders of magnitude, and there can be little doubt that mercury is the best indicator of its own deposits in this case.

For the traverse over the fault extension, both fluorine and mercury have peak values over the fault zone; the mercury anomaly being considerably smaller than that over the ore zone.

Although these results indicate that mercury is obviously a better indicator of its own deposits than fluorine (this may not necessarily be so when fluorite is present in the deposit). They do show however, that fluorine

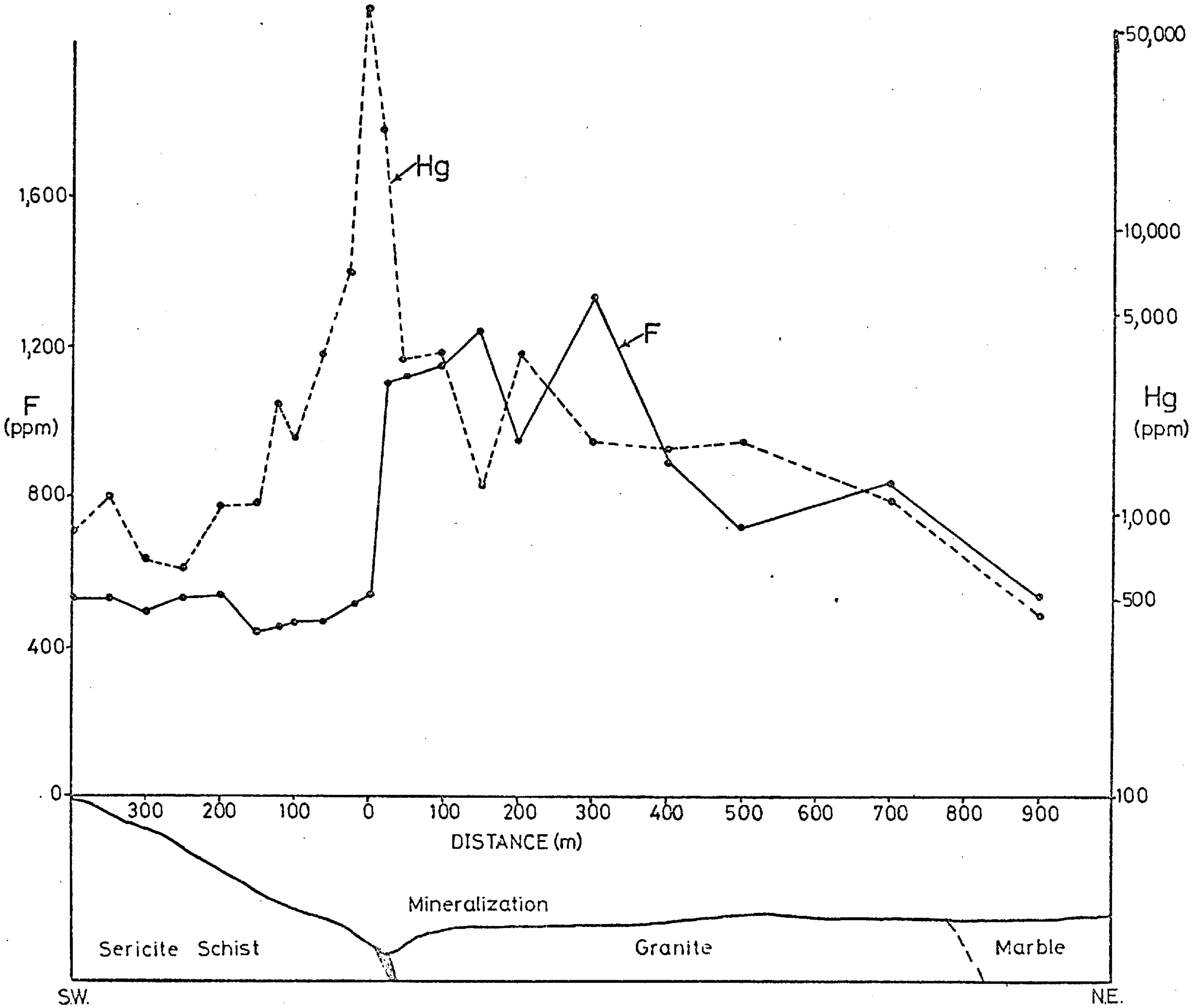


FIGURE 3.48 DISTRIBUTION OF TOTAL FLUORINE AND MERCURY IN SOILS (traverse 3, -80 mesh, <200u, 0-2cm), HALIKOY AREA, TURKEY (Geology and Mercury Analyses after Kelson, 1967)

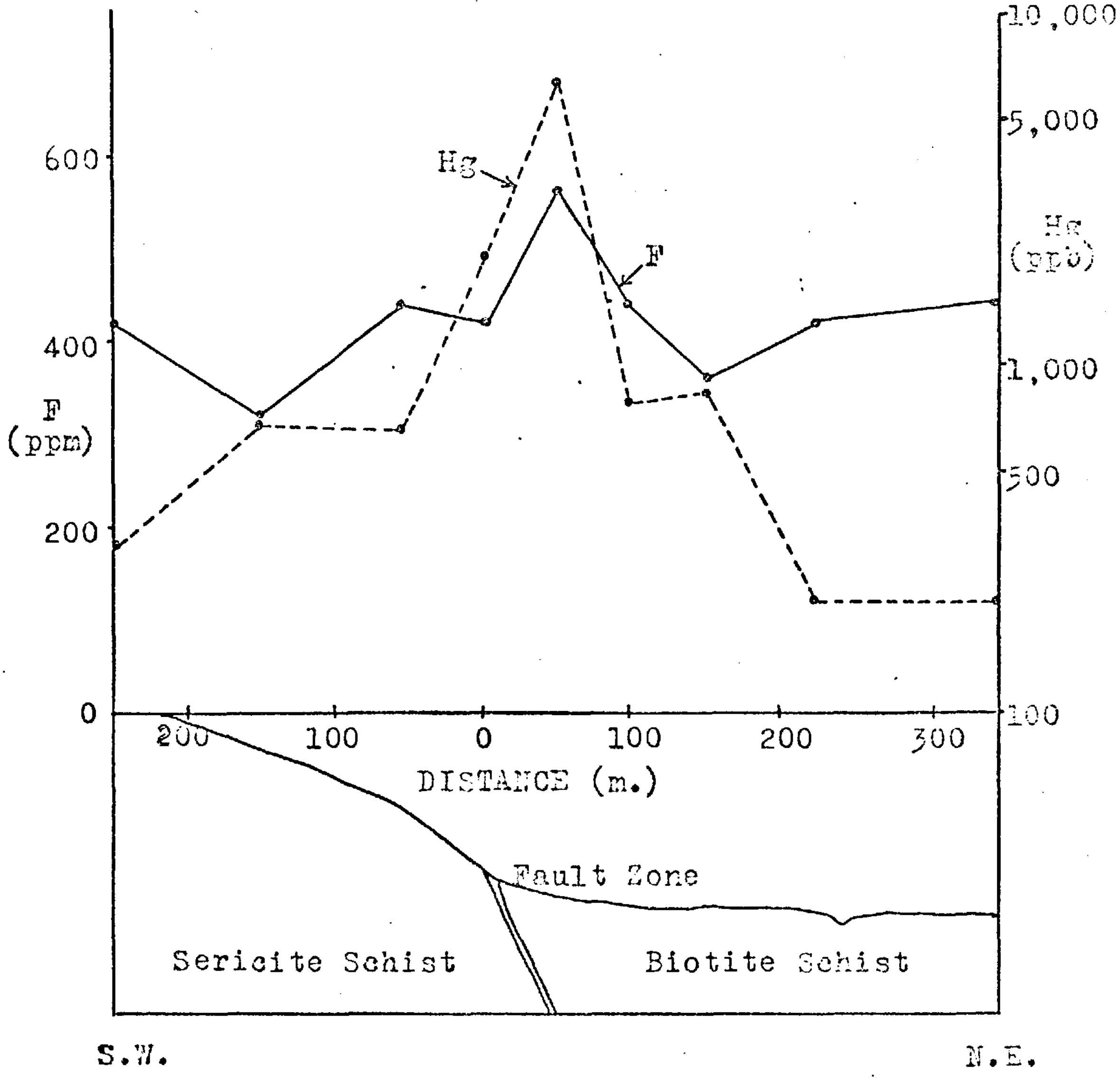


FIGURE 3.49 DISTRIBUTION OF TOTAL FLUORINE AND MERCURY IN SOILS (traverse 2, 80 mesh, $<200\mu$, 0-2cm) HALIKOY AREA, TURKEY. (Geology and mercury analyses after Koksoy, 1967)

may often be concentrated in the wallrock zones of mineralised faults. For deposits located along fault zones which do not contain mercury, fluorine, when used in rock and soil surveys, may be the only adequate indicator of the presence of mineralisation.

3.3.4.4 Ivrindi Antimony Deposits, Turkey

3.3.4.4.1 Introduction

These deposits are situated in the andesite-dacite Neogene extrusives of western Turkey (see Fig. 3.45). Mineralization consists of stibnite-quartz veins intruded into strongly propylitized andesites. Kaolinization is common in the vicinity of the veins.

3.3.4.4.2 Dispersion of Fluorine in Soils

The distribution of fluorine and mercury in soils over the Ivrindi deposits is presented in Fig. 3.50. Mercury displays a strong anomaly of good lateral extent over the main area of mineralization (note log scale); over smaller areas of mineralization it exhibits weaker but still well defined anomalies. Fluorine shows no anomalous expression over the areas of mineralization and the element is, therefore, not a good indicator of antimony deposits in this area. It is interesting to note that the formation of kaolin deposits in granitic intrusions is accompanied by the introduction of large amounts of fluorine in addition to the water required to alter the feldspars to kaolinite; this does not, however, appear to hold in the case of kaolinite formed as the result of propylitic alteration, as evidenced by the lack of anomalous fluorine concentrations in soils over the kaolinized zones of Ivrindi.

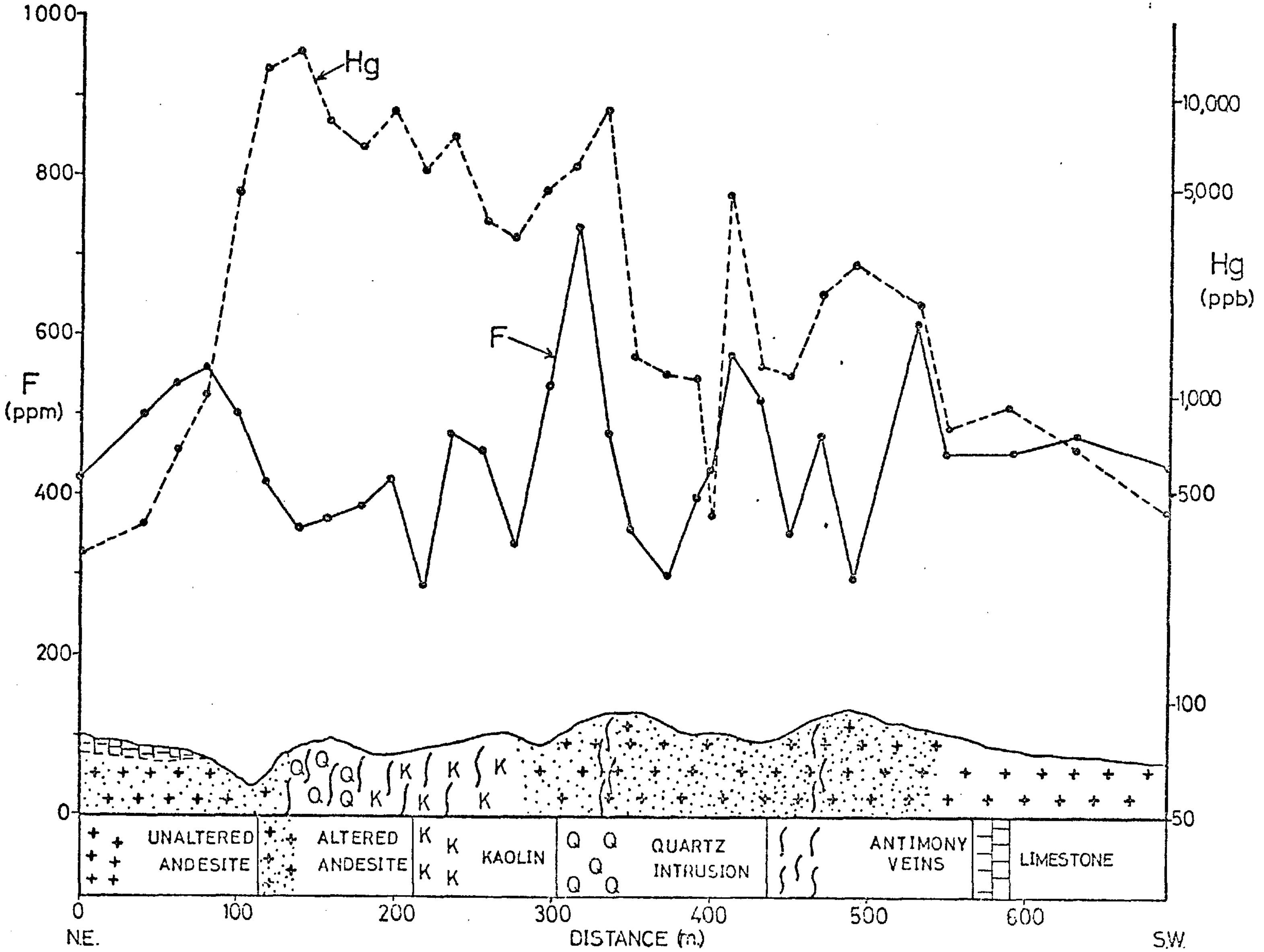


FIGURE 3.50 DISTRIBUTION OF TOTAL FLUORINE AND MERCURY IN SOILS (0-2 cm; -80 mesh, 200u) IVRINDI AREA TURKEY
[illegible]

3.3.5 Prospecting for Kaolin Deposits in Granitic Intrusions

The formation of kaolin deposits, such as those of southwest England involves the introduction of large quantities of super-heated water. In addition to water, considerable quantities of fluorine are also introduced. As a result, those intrusions which contain kaolin deposits exhibit a higher fluorine content (e.g. St. Austell granite - up to 20,000 ppm) than normal non-kaolinized granites (average of 1,500 ppm F for granites of southwest England). Fluorine may, therefore, be used in soil and rock surveys to outline areas of strongly kaolinized granite bodies. Fig. 3.51 represents the distribution of fluorine in soils over the Belowda Beacon kaolin deposit of southwest England. The kaolin deposit is clearly defined by a peak anomaly of approximately 2,400 ppm F; the largest anomaly contrast being obtained by sampling the lower soil horizons (12"-24" and 36"). These results also indicate that low-density soil sampling will effectively outline these deposits. It should be noted, however, that when using fluorine to prospect for kaolin deposits, greisen and pegmatite deposits may also be present in the same province. Secondary dispersion haloes over these deposits are generally much smaller than those over kaolinized granites. Greisens and pegmatites are also characterized by anomalous concentrations of elements found only in low concentrations in kaolin deposits such as Sn, W, As, Cu, Be, REE, U and Th; these elements may be used as discriminators.

3.3.6 Prospecting for Contact Skarn Deposits

Contact skarn deposits, together with deposits such as greisens, carbonatites, pegmatites and kimberlites, are universally fluoriferous. In contact skarns fluorine is concentrated in a veritable host of minerals of which fluorite, apatite, the micas, humites, tourmaline, topaz and amphiboles

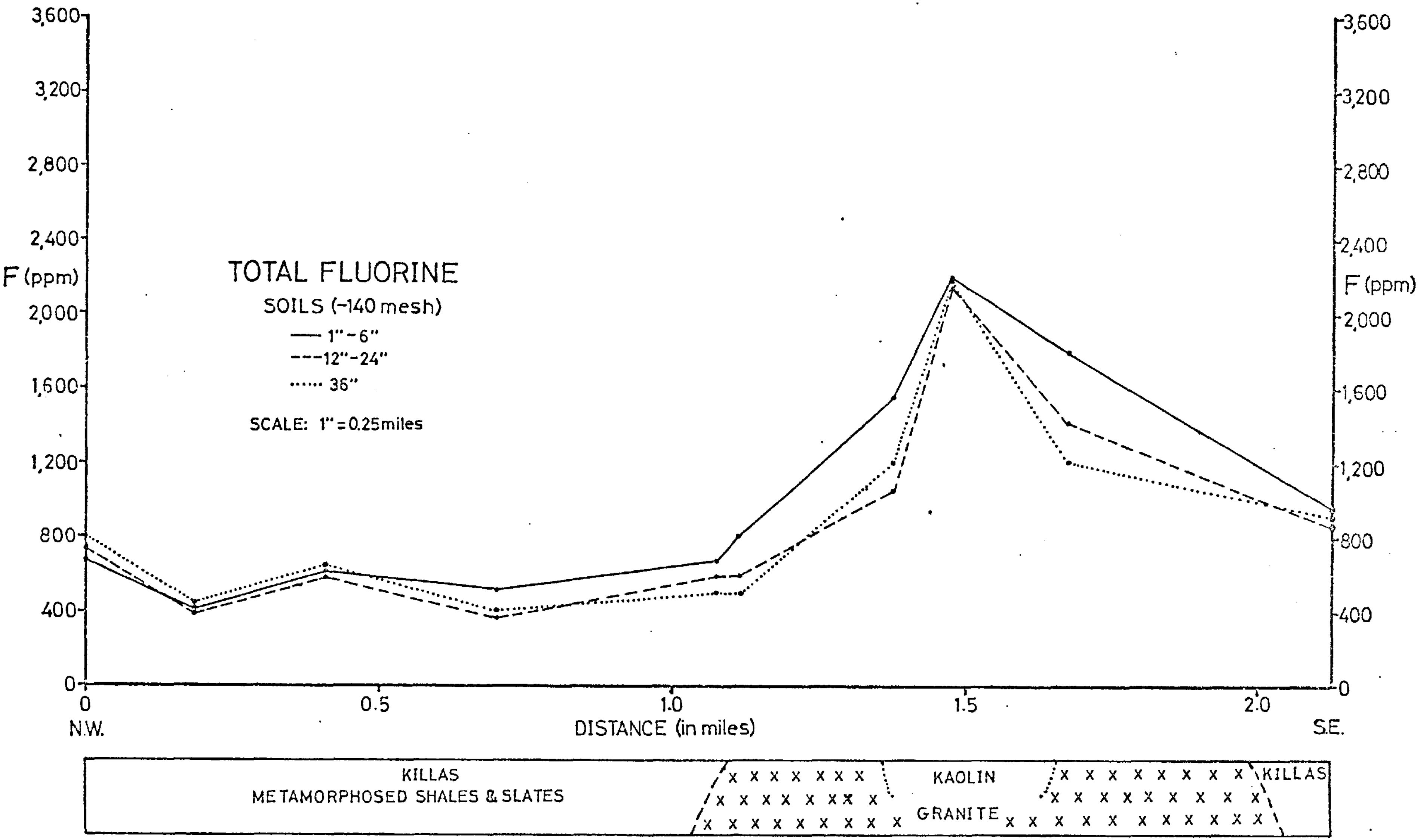


FIGURE 3.51 DISTRIBUTION OF TOTAL FLUORINE IN SOILS (-140 mesh, 200µ) OVER THE BELOWDA BEACON KAOLIN DEPOSIT, SOUTHWEST ENGLAND (see Fig. 3.30 for location of traverse).

are only a few. Ore deposits associated with contact skarns commonly occur as irregular pods, masses, and disseminated mineralized zones in the vicinity of the igneous contact. The deposits may contain economic quantities of Be, Sn, Cu, Mo, REE, Zn, Ti, U and Th, and are generally surrounded by a large zone of skarnification which is generally larger than the ore deposits by orders of magnitude. Unlike many of the ore-forming elements in skarn deposits, fluorine generally migrates in relatively high concentrations during ore formation to the farthest extremities of the skarnified zone and may in places form economic fluorite deposits some distance from the main focus of skarnification. Effectively, this means that fluorine anomalously represents the entire skarnified zone, and the element is, therefore, an ideal pathfinder for the deposits. In particular, fluorine should be a good indicator of blind skarn ore deposits where the only expression at the surface may be the unmineralized skarnified zone enveloping the ores. Both lithogeochemical and pedogeochemical surveys can be mounted in an attempt to outline these 'dome haloes'.

To date only two studies on the use of fluorine in prospecting for skarn deposits have been published (Krainov et al, 1967 and Cachau-Herreillat and Proulet, 1971); no doubt others will follow now that the analysis of this element is fast and inexpensive.

The study by Cachau-Herreillet and Proulet (1971) was conducted over the tungsten skarn deposits of the French Pyrenees. From a large drainage survey over areas of granitic intrusions in this area they obtained anomalies which were consistent with mineralization around the granitic masses and which increased in size in the order arsenic-phosphorus-fluorine. Furthermore soil surveys over one of these deposits indicated that the fluorine anomaly covered the entire skarnified zone whereas the W, Cu, As, Zn and Pb anomalies were limited to the area of mineralization. Clearly fluorine is the more useful pathfinder for detecting deposits of this type; the other elements in the deposits can be used effectively to assess mineral potential.

Krainov et al (1967) successfully outlined skarn fields in the USSR by measuring the fluorine content of groundwaters on a systematic basis. They obtained anomaly contrasts varying from 2 to 7-fold.

3.3.7 Prospecting for Volcanogenic Massive Sulphide Deposits

At present only limited work has been done on the application of fluorine to prospecting for massive sulphide deposits in volcanic terrains, more attention having been paid to the more common base metals in these deposits as well as to As and Hg.

Recently M.N. Cagatay (pers. comm.) in conjunction with the author has found that fluorine forms well-developed haloes in rhyodacitic intrusive rocks containing massive sulphide mineralization in the Eastern Black Sea volcanogenic sulphide province of Turkey. The fluorine haloes which are accompanied by incipient hydrothermal alteration are characterized by fluorine concentrations up to 2,000 ppm against a background of about 400 ppm. Furthermore, those intrusives containing only barren pyrite stockworks are not typified by the presence of a primary fluorine halo. It is possible, therefore, by systematically sampling rhyodacitic intrusive phases to outline those intrusions in which mineralization is present.

As yet no studies have been carried out on the primary dispersion of fluorine in the vicinity of volcanogenic sulphide deposits in ophiolite facies rocks.

3.3.8 Conclusions on Prospecting for Pneumatolytic-Hydrothermal Mineral Deposits

Greisen deposits (Sn, Be, W, Mo, Cu, Bi, etc.) containing the fluoriferous minerals fluorite, tourmaline, topaz and sericite can easily be detected with the aid of fluorine as indicator. The element can be used during all phases of exploration but is especially effective in detailed soil surveys and lithogeochemical surveys. Stream sediment surveys using fluorine depend essentially on the mechanical dispersion of tourmaline, topaz or sericite into stream channels. Groundwater surveys can be an effective method of detecting concealed deposits containing fluorite or other fluorine-bearing minerals susceptible to groundwater attack. It would appear from the data presented, that fluorine is a much better indicator of tin deposits than As or Cu. The element may also aid in the detection of anomalies due to detrital tin accumulations.

Contact skarn deposits are highly fluoriferous, and hence fluorine can be used in both reconnaissance and detailed (stream sediment, soil and rock) surveys to detect these types of deposits. Unlike the ore-forming elements, the presence of anomalous concentrations of fluorine in the entire skarnified zone surrounding the ores makes the element particularly useful in the detection of skarn ore deposits of which only the skarnified zone may be exposed. Systematic groundwater surveys using fluorine as the pathfinder may also be effective in outlining skarn-type deposits.

Fluorine plays an active role in the formation of kaolin deposits and the element can, therefore, be used in low density soil surveys to outline these deposits.

Hypothermal deposits (e.g. gold-quartz), provided they contain tourmaline or topaz, may be effectively located with the aid of fluorine as an indicator in soil surveys. In particular the element should be used to complement As, Sb and other indicators aimed at finding these deposits. Fluorine can also be used in lithogeochemical surveys to outline shear zones, faults, breccia zones, and fracture zones marked by sericitization, tourmalinization, and/or topazization which may be the loci for gold deposits (as well as greisen deposits).

The use of fluorine in prospecting for mesothermal and epithermal fluorite-bearing mineral deposits is well documented in the literature. The element can be employed at all stages of geochemical exploration and is particularly effective when used in systematic groundwater surveys. For mesothermal and epithermal deposits, which are not fluorite-bearing, the element would appear to be applicable only in the detection of sulphide deposits in limestone environments.

Volcanogenic sulphide deposits associated with acid intrusive rocks are characterized in places by the presence of pronounced primary fluorine haloes in the host intrusives. The element can, therefore, be used in systematic lithogeochemical surveys of rhyodacitic phases to outline intrusive bodies containing potential mineralization.

3.4 PROSPECTING FOR MINERAL DEPOSITS OF SEDIMENTARY ORIGIN

3.4.1 Introduction

Fluorine can be effectively used as a pathfinder for locating a number of types of mineral deposits formed as the result of bedrock weathering followed by concentration of the primary constituents essentially by gravity. The agents which govern concentration may be eluvial (residual), alluvial, glacial, eolian or biochemical in nature. The various fluoriferous sedimentary deposits may be broadly defined as:

a) Eluvial (residual) deposits (Nb, Ta, Sn, W, REE, Th, U, diamonds and other gems, fluorite, barite, etc.)

b) Placer deposits (Sn, W, Nb, Ta, REE, Th, U, Au, gems)

c) Phosphate deposits

The eluvial deposits are formed as the result of in situ weathering of parent rocks such as pegmatites (Sn, W), greisenized zones (Sn, W), acidic granites (Sn), carbonatites (Nb, REE, Th, U, fluorite, etc.), alkali granites (Nb, Ta) and kimberlites (diamonds). As these residual deposits are generally near their source and commonly constitute enrichments in the overburden the use of fluorine in their detection is analogous to that for locating the parent bodies. Methods of detecting pegmatites, greisen zones, carbonatites, kimberlites and disseminated deposits in alkali granites are discussed in previous sections to which the reader is referred.

3.4.2 Placer Deposits

Placer deposits are important sources of such elements and minerals as Sn, Nb, Ta, REE, Th, U, Au, gems (diamonds, topaz, etc.) and many other commodities. Since almost all of these elements and minerals are derived from fluoriferous deposits such as granites, pegmatites, carbonatites, kimberlites, and alkali granites and syenites, it is not surprising that fluorine can be a valuable aid in their detection. Pathfinder elements are extremely useful when prospecting for placer deposits because they obviate the need for time-consuming and expensive heavy mineral surveys. Only in those drainage systems where the pathfinder element (or elements) is anomalous is it necessary to carry out detailed panning surveys. Although a particular element may be a good indicator of a primary mineral deposit, a prerequisite for its application in prospecting for associated placer deposits is that it must 'travel' with the placer mineral or minerals of economic interest either as a constituent of the economic mineral or as a constituent of a non-economic mineral having similar hydrostatic equivalent and resistate characteristics. With few exceptions many of the fluorine-bearing minerals stand up well as indicators of the above mentioned types of placer deposits, the principal exceptions being diamond and gold deposits.

Although a good indicator of kimberlites, fluorine is probably not a good pathfinder for placer diamond deposits since most of the fluorine in the parent kimberlite is contained in phlogopite and serpentine, two minerals which do not have the same mechanical dispersion characteristics as diamond or the other heavy mineral indicators of these deposits (e. g. pyrope garnet, chrome-diopside, and picro-ilmenite).

Unless it can be established that the gold placer deposits of a particular area are derived principally from tourmalinized gold-quartz veins, fluorine would seem to have little application in prospecting for these deposits. If large amounts of tourmaline (up to 2% F) are present, stream sediment surveys using fluorine as a pathfinder, and total fluorine as the analytical method, can be employed.

Fluorine is an excellent pathfinder for placer deposits containing Sn, W, Nb, Ta, Y, La, REE, Th and various gems since it is often a principal constituent of the economic mineral in question or a constituent of 'fellow traveller' gangue minerals. Thus, in Sn placers the principal fluorine-bearing gangue minerals are topaz and tourmaline. Three types of Nb-Ta placers are recognized:

a) pyrochlore placers derived from carbonatites in which pyrochlore is the principal fluorine-bearing mineral;

b) pyrochlore-columbite-tantalite placers derived from alkali-granites and syenite pegmatites, pyrochlore and riebeckite being the principal fluorine-bearing minerals; and

c) columbite-tantalite placers derived from granitic pegmatites and albitic-granites, topaz and tourmaline being the principal fluorine-bearing minerals.

The elements Y, La, REE and Th are extracted from monazite, xenotime and thorite placers in which the rare earth fluorocarbonate minerals (bastnaesite, paresite, etc.), apatite and occasionally topaz are the major fluorine-bearing minerals. Fluorine is a good indicator of gem minerals found in pegmatite deposits (topaz, emerald, sapphire, ruby, etc.).

When prospecting for exposed (near-surface, non-buried), placer deposits, drainage surveys can be employed in the initial stages and the stream sediments analysed for fluorine and other indicator elements. It is important to carry out an orientation survey first to determine the optimum size fraction to be used, the more resistant indicator minerals generally being concentrated in the coarser fractions. For buried placers some form of overburden drilling should be employed in favourable areas. In this case direct analysis of the economic element may be desirable; on the other hand, bearing in mind the greater cost of analysis for elements such as Nb, Ta, Y, La, REE and Th, fluorine can be usefully employed to outline placer zones which can then be studied in more detail using the economic elements as indicators and heavy mineral studies. This approach is most effective where the mineral of economic concern is also fluorine-bearing (e. g. pyrochlore, bastnaesite, topaz, etc.).

3.4.3 Phosphate Deposits

The fluorine content of phosphorites varies from 10,400 to 42,000 ppm (average 31,000 ppm, Table 1.4, Chapter I). The element is therefore an excellent indicator of these deposits.

In oceanic prospecting for phosphorites, fluorine offers a means of assessing large areas of the ocean floors using regional sediment surveys. The fluorine content of non-phosphatic oceanic sediments is in the range 100-1,600 ppm (average, 640 ppm; Table 1.4 Chapter I). Phosphorites, therefore, contain 10-40 times more fluorine than any other type of marine sediment.

On land the initial reconnaissance stages of prospecting for phosphorites (rock (marine) phosphates, pebble phosphates, etc.) should employ fluorine as one of the indicators in drainage, lithogeochemical and water surveys. Because of the greater difficulty of analysis (especially for waters), phosphorus can be more usefully employed during the detailed investigation of areas found to be anomalous in fluorine. Limestones (220 ppm F), dolomites (260 ppm F), shales and siltstones (790 ppm F), and sandstones and greywackes (180 ppm F) offer little interference when prospecting for phosphate deposits in sedimentary environments.

3.5 VAPOUR GEOCHEMISTRY

3.5.1 Introduction

In addition to its strong lithophilic nature, fluorine exhibits a distinct atmophilic character. This is especially true of the primary environment where its presence as HF or other fluoriferous gases is observed in fumarolic and pneumatalytic processes. The occurrence of fluorine gases in the supergene environment, especially in the vicinity of fluoriferous mineral deposits has not been documented and is the subject of this section.

Research by the author concerning vapour geochemistry has followed four main directions. Firstly, as no information existed on the occurrence or evolution characteristics of fluorine gases in the vicinity of fluorine-bearing mineral deposits, experiments were set up in the laboratory to determine whether fluorine is evolved from fluorspar under normal atmospheric conditions.. Secondly, following affirmative results for the above requirements a more sensitive and precise method of analysis was required to determine fluorine gases, as fluoride (F^-), at the levels that might be expected in soil air. Thirdly, the author sought to develop a system of sampling soil air and analysing its fluorine content, and fourthly to carry out an initial assessment of this system in an area of known mineralization.

3.5.2 Laboratory Experiments

Studies were carried out in the larboratory to determine whether or not fluorine will diffuse as a gas from the surface of fluorspar under standard atmospheric conditions. Gaseous evolution tests were carried out on powdered and massive fluorspar specimens in both a dry and a wet state.

The experiments were conducted by placing the fluorspar sample (10 g for the powdered samples and a 200 g sample for the massive samples) in the bottom of a 100 ml polypropylene beaker, the top of which was covered with a filter paper to which was added 50 microlitres of 0.01M NaOH to trap any HF given off. To remove possible fluoride contamination the filter papers were successively rinsed in 0.1M HCl and metal-free water and then dried prior to use in the analyses. A second beaker was inverted over the sample beaker to ensure that the filter paper had no contact with ambient air, and the system was then placed in a bell jar for the required amount of time. A blank (empty beaker with filter paper) was run with each experiment. In all cases the blank was below the detection limit of the instrument (less than 0.02 mg F^-). For tests using wet fluorspar, water was added to the specimen until it was thoroughly moist. Diffusion was allowed to proceed for different periods of time, and in some cases a second test was made to determine reproducibility. After diffusion the filter papers were placed in 1 ml of TISAB buffer (See Analytical Section - water analysis), and the fluorine content was determined using the ion electrode system.

TABLE 3.14 EXPERIMENTAL INVESTIGATION OF THE EVOLUTION OF FLUORINE GAS FROM FLUORSPAR

Material	Diffusion time (hrs.)	Fluorine diffused (ug)	Rate of diffusion (ug/hr)
Powdered fluorspar (dry)	1	0.14	0.14
	24	1.30	0.05
	48	2.40	0.04
Powdered fluorspar (wet)	24(1st test)	7.10	0.29
	24(2nd test)	11.00	0.46
Massive fluorspar (dry)	24 (1st test)	0.92	0.04
	24 (2nd test)	0.72	0.03
Massive fluorspar (wet)	24	5.20	0.22

The results of these experiments are presented in Table 3.14. It is evident from these results that significant amounts of fluorine will diffuse into the surrounding air from the surface of fluorspar. Detectable amounts of gaseous fluorine were measured even after an hour's diffusion, and the amount of gaseous fluorine given off increases with increasing time. The decrease in the rate of diffusion over 48 hours is the result of carrying out the experiments in a closed system; in an open system however, such as occurs in soils a constant diffusion rate for a given set of physico-chemical conditions can be expected. A comparison of the amount of fluorine given off by massive and powdered fluorspar cannot be made because the area of surface exposure for the two types is not known. The results for the two are, however, similar. For moist fluorspar, the amount of gaseous fluorine released is greater than that for dry-fluorspar by a factor of 7 or more. From this it follows that the presence of water greatly increases the diffusion rate and that the process of gaseous evolution is primarily one of hydrolysis controlled by the following reaction:

$$CaF_2 + 2H_2O \rightleftarrows Ca^{++} + 2OH^- + 2HF$$

When just enough water is added to powdered fluorspar to make it thoroughly moist, the resultant pH is less than 3.0, and the formation of HF is, therefore, greatly enhanced (See Fig. 1.4 Chapter I). The dry fluorspar used in the experiments undoubtedly takes on enough water to promote hydrolysis.

Under natural conditions one can expect this process to give rise to the concentration of fluorine gases in the soil air above fluorspar deposits. If sulphides are also present in the environment the formation of H_2SO_4 during weathering promotes the formation of HF according to the reaction.

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

If, however, there is much carbonate material in the environment, as in some deposits and wallrocks, the carbonates will consume some of the H_2SO_4, possibly giving rise to more alkaline pH conditions and retarding or eliminating the formation of HF. Although detailed studies are required it would seem that the neutralising effect of carbonates would seriously affect the useful application of fluorine gas in detecting fluorspar mineralization in calcareous environments.

To date, only one study has indicated the possible formation of gaseous fluorine related to the presence of mineralization. Frederickson et al (1971) using a mobile mass spectrometer system measured the fluorine content of air at ground level over the gold-fluorspar deposits of Cripple Creek, Colorado. Although levels of concentration are not given, fluorine gas anomalies showing coincidence with mineralization were obtained. It is not known whether stronger anomalies existed in the soil air over these deposits, and as yet, no further research on this technique has been reported.

An indirect indication of the evolution of fluorine gases from mineral deposits comes from the work of Lalonde (1975) who analysed the fluorine content of snow over the Barvalee Zn-Cu sulphide deposit, Quebec, Canada and obtained anomalies over zones of known mineralization. He attribtued the anomalous concentration of fluorine in the snow to the attack of fluorine-bearing minerals by H_2SO_4 with subsequent evolution of HF. He further mentions that leaching of fluorine from the organic soil horizon, coupled with upward diffusion in the snow, may be another possible cause of these anomalies.

3.5.3 Analytical Development

The affirmative results obtained from the laboratory experiments indicated the possibility of utilizing fluorine gas as an indicator of mineralization and hence a definite need to develop an analytical method capable of measuring fluorine at the levels to be expected in soil gas.

The reported range for the fluorine content of air (residential and rural) is 3.0×10^{-5} to 9.0 to 10^{-4} ug F/1 (Marier and Rose, 1971). Since no evidence exists to suggest that soil air is either enriched or depleted with respect to these levels, it was felt that a method which had as low a detection limit as possible within this range would be acceptable for an initial assessment. Because most soils can be expected to yield a representative volume of soil air pumped from a single hole in the order of 10 to 20 litres without significant dilution or contamination from atmospheric air occurring, and because the theoretical detection limit of the fluoride ion electrode is 0.02 ug F^-/ml the volume of sample solution needed to measure fluorine in the lower part of the range mentioned above would have to be in the order of 20 to 100 microlitres. The efficient trapping of gases in volumes of these amounts is virtually impossible, a feature which led to the decision to trap the fluorine gas on a 13mm Whatman filter (purged of possible traces of fluoride with 0.1M HCl as noted above) to which was added 10 microlitres of 0.01M NaOH. This required the use of a citrate-acetate buffer capable of neutralising the NaOH. The lowest volume of working solution that could be used was 100 microlitres of TISAB buffer. The use of small volumes such as this necessitates a different electrode configuration than is normally used for fluorine analysis. To accomplish this an adaptation of a configuration

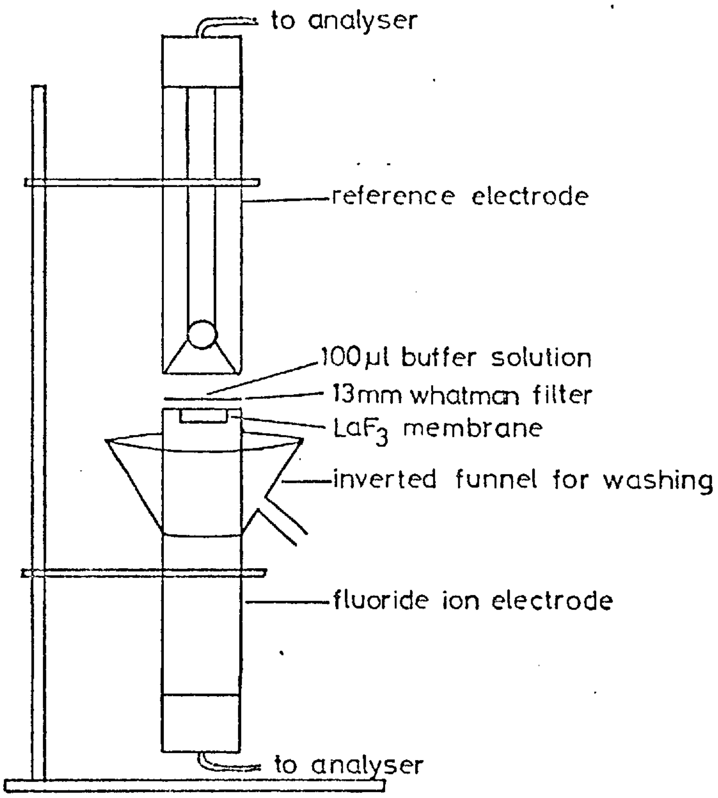


FIGURE 3.52 INSTRUMENTATION DESIGN FOR ANALYSIS OF GASEOUS FLUORINE (not to scale)

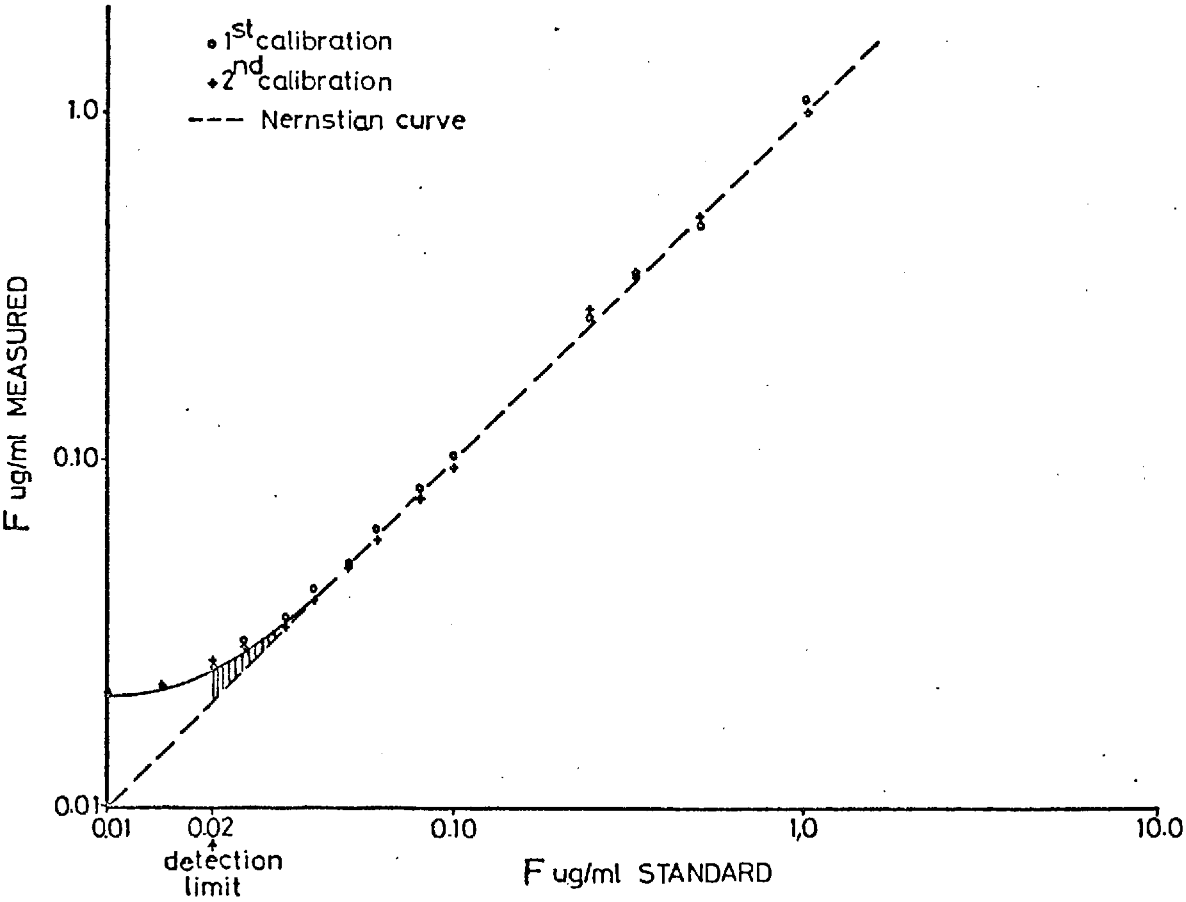


FIGURE 3.53 RELATIONSHIP BETWEEN MEASURED AND STANDARD FLUORIDE CONCENTRATIONS FOR GASEOUS FLUORINE ANALYTICAL METHOD (hachured area represents deviation from the theoretical Nernstian curve above the detection limit)

described by Durst and Taylor (1967) was adopted, the ion electrode being inverted and the reference electrode impinging on the membrane face as shown in Fig. 3.52. The filter paper and buffer solution are placed between the electrodes.

Calibration of this system resulted in the experimental curve shown in Fig. 3.53. The deviation (marked by hachuring) from the theoretical curve for concentrations above the detection limit is thought to be the result of citrate-acetate complexation of La from the membrane face and subsequent elevation of the fluoride levels in the buffered solution. Readings can, however, be made down to 0.02 ug/ml, but response is slow. Many workers have indicated that the theoretical detection limit for the ion electrode is too high, since it is based on the solubility product of LaF_3 and equilibrium is rarely achieved in the period over which a reading is taken. A number of researchers have taken readings down to 0.01 ug/ml as significant, but for an unbiased assessment in the present study the author considers only those readings above 0.02 ug/ml to be meaningful. As can be seen from the calibration curve in Fig. 3.53, good reproducibility is achieved when calibration is repeated.

3.5.4 Field Applications and Discussion of Results

Two methods of soil air sampling were used in the field. An active system was employed by hammering a steel tube (the centre of which contained a ramming rod) approximately two feet into the soil, extracting the rod and attaching a pump line containing a filter holder with a 13mm filter paper (10 microlitres of 0.01M NaOH added) and pumping the soil air with a small pump and battery at the rate of 3 litres/min. for 6 minutes. This gave a total sample volume of 18 litres. The system was initially tested in the laboratory by first sampling the laboratory air and then the air over a specimen of massive fluorspar. For these samples of air, concentrations of 1.25 x 10^{-4} ug/1 F and 4.25 x 10^{-4} ug/1 F respectively were obtained. To test the efficiency of extraction of the filter paper, two filter holders in series were employed. The scrubbing efficiency of the filter system was found to be better than 85%.

The second sampling system employed was a passive diffusion system in which the filter paper (10 microlitres 0.01M NaOH added) was suspended from the inside of a polythene cup, and the cup was then inverted over an augered hole. The cups were collected after 24 hours.

The area chosen for initial assessment of both methods was the Ball Eye fluorspar mine in the southeastern part of the Derbyshire fluorspar province. The mine has a fluorspar dump containing 30 to 40% fluorspar which has not been disturbed since mining in the early part of the present century. A description of the area and the location of sampling sites is given in Fig. 3.54. Soils within the area are well drained, and the weather at the time of sampling was cloudy with intermittent sun. A slight drizzle had prevailed during the preceding night.

The results of these investigations are outlined in Table 3.15. Sampling sites 1, 2 and 3 were located over the dump and sites 4 and 5 were located in a background field south of the mine.

Taking 18 litres as the sampling volume and 100 microlitres as the buffer volume, the lowest measurable level of gaseous fluorine for this system is 1.0 x 10^{-4} ug/1. It can be seen from the results of the sampling of the soil gas that the anomaly contrast for fluorine is extremely low, and with perhaps the exception of the result for Site 2, the values for soil air over the dump fall within the region of high analytical error (near the detection limit). Considering the high fluorspar content of the dump material, it is

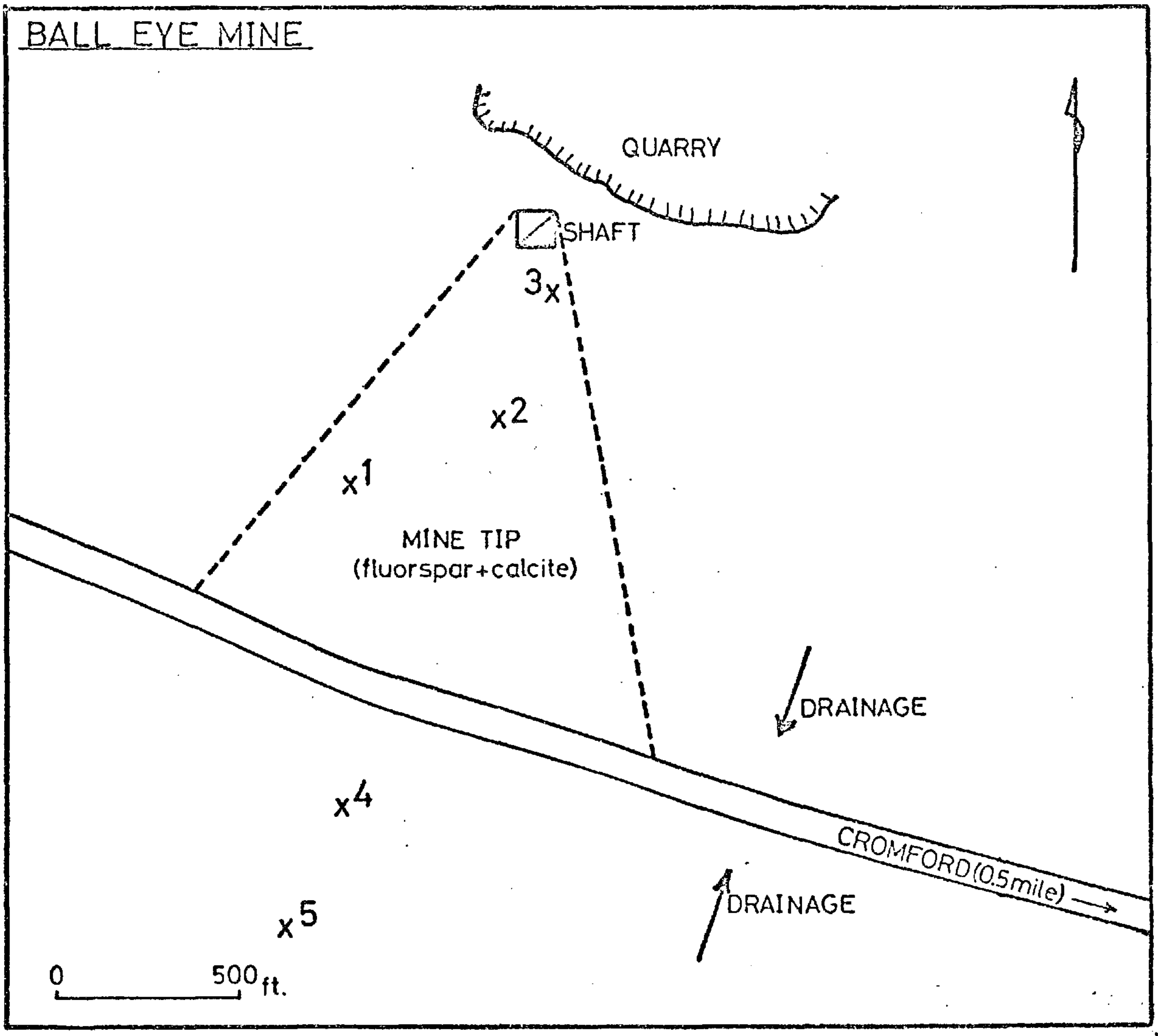


FIGURE 3.54 LOCATION OF SOIL GAS SAMPLING SITES, BALL EYE FLUORSPAR MINE, DERBYSHIRE

TABLE 3.15

FLUORINE IN SOIL GAS AND ATMOSPHERIC AIR, BALL EYE MINE, DERBYSHIRE

Sampling Site	Fluorine (ug/1)^1 Soil gas		Fluorine (ug/1)^1 Above ground	Fluorine (ug)^2 Diffusion Pots
	Day one	Day two		
1	$1.7x10^{-4}$	$2.0x10^{-4}$	$2.5x10^{-4}$	0.037
2	$2.3x10^{-4}$	$3.0x10^{-4}$	$2.4x10^{-4}$	0.020
3	$1.3x10^{-4}$	$1.5x10^{-4}$	$2.5x10^{-4}$	0.020
4	$1.0x10^{-4}$	$1.0x10^{-4}$	$2.3x10^{-4}$	0.020
5	$1.0x10^{-4}$	$1.0x10^{-4}$	$2.6x10^{-4}$	0.020

1. Pumping rate 3 l/min for 6 min.
2. Diffusion period - 24 hours.

doubtful if any noticeable anomalies would be detected by this system over zones of mineralization. The results for the second day's sampling of the same sites indicate that good reproducibility can be obtained with this method. The sampling of air at the ground-air interface gave similar results for mineralised and background areas. The data also indicate a possible dilution by a factor of about two for fluorine in soil gas with respect to atmospheric air, although the levels for site 2 are similar for both soil gas and air.

The use of passive diffusion pots gave negative results, with all but one site having non-detectable fluorine levels. The high result for Site 1 may be due to sampling or analytical errors. Considerable condensation occurred on the inside of the pots, and the filter paper was much wetter than at the start of diffusion, thus decreasing its ability to trap fluorine vapour. Considering the time element involved for collection and the above mentioned results and problems, it is doubtful whether this method would have any application in all but the most arid environments.

It is evident from the results obtained that, subject to further analytical development, fluorine vapour geochemistry cannot as yet be used with confidence in mineral exploration. Since 15 to 18 litres must be considered the maximum representative amount of soil gas that can be sampled, the only variable which can be adjusted to give a lower detection limit and greater analytical sensitivity, apart from adopting an entirely different analytical system, is the volume of buffer solution. With the electrode configuration shown in Fig. 3. 52, solution volumes as low as 20 microlitres can be used, but this also poses considerable buffering problems.

At present this system, together with other methods of gaseous fluorine analysis, are being investigated by the Applied Geochemistry Research Group as part of a larger vapour geochemistry programme related to mineral exploration. It is hoped that more positive results will derive from these investigations.

CHAPTER IV

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

4.1 SUMMARY AND CONCLUSIONS

4.1.1 INTRODUCTION

The present research on fluorine has been concerned with three main themes

a) the collation of information on the geochemistry of fluorine,

b) the development and investigation of analytical methods for fluorine which are acceptable to the exploration geochemist, and

c) an assessment of the application of the element in mineral exploration.

Based on these themes, the following conclusions can be drawn from the research.

4.1.2 GEOCHEMISTRY OF FLUORINE

Fluorine plays an active role in many of the geochemical processes of the primary and secondary environments.

In the lithosphere, it is the fourteenth most abundant element and is concentrated in such minerals as fluorite, apatite, amblygonite, topaz, pyrochlore, amphiboles, tourmaline, the micas, clay minerals and many rare earth fluorocarbonate minerals. The occurrence and factors affecting its concentration in these minerals has been discussed at length. Fluorine is incorporated in minerals in one of three ways

a) as an essential element (e.g. fluorite, topaz),

b) by isomorphous substitution of the OH^- ion under all temperature and pressure conditions (e.g. micas, amphiboles, etc.), and

c) by isomorphous substitution of the O^{2-} ion, generally under high temperature and pressure conditions (e.g. pyrochlore, magnetite, etc.).

In igneous rocks fluorine is concentrated in alkali - and/or silica-rich rocks. Thus, for alkali granites, -syenites and -ultramafics, the mean fluorine content is 5,500, 1,800 and 1,400 ppm respectively and for non-alkali granites, diorites, gabbros and ultramafics, the average content is 810, 665, 430 and 130 ppm respectively. For late differentiates and dyke rocks, the element exhibits high concentrations in carbonatites (8,100 ppm), pegmatites (4,320 ppm), kimberlites (1,410 ppm) and lamprophyres (1,500 ppm). As a result of degassing at the surface, extrusive rocks contain less fluorine than their intrusive counterparts; but the relationship to alkali and silica content still holds. Thus, phonolites, alkali-basalts and alkali-ultramafics contain on average 950, 925 and 2,015 ppm respectively, whereas rhyo-dacites, andesites and basalts contain an average of 610, 250 and 375 ppm F respectively.

In the sedimentary environment, fluorine is concentrated in rocks with a high micaceous and/or phosphate content (phosphate rock, 31,000 ppm F; shales, siltstones and mudstones, 790 ppm F). Rocks relatively poor in these constituents have much lower fluorine contents (sandstones, greywackes 180 ppm; limestones, 200 ppm; and dolomites, 260 ppm).

During regional metamorphism, fluorine is remobilized and may act as a mineralising flux. The average fluorine content of gneisses, amphibolites and schists is 1,030, 740 and 250 ppm respectively. During processes of metasomatic alteration, fluorine may be concentrated in greisens (9,800 ppm), contact skarns (9,780 ppm), kaolinised granites (4,500 ppm), hornfels (1,630 ppm) and fenites (560 ppm), all values being averages.

In the pedosphere, fluorine accumulates in surficial materials rich in colloids, clay minerals and phosphates; deposits poor in these constituents contain only minor amounts of fluorine. The fluorine content of residual soils is generally in the range 10 to 7,000 ppm, depending on the type of bedrock. Some soils may report as much as 2%F. For most soils, the fluorine concentration decreases gradually with depth; in podzolic soils, the organic horizon may exhibit a considerable enrichment in fluorine.

In the hydrosphere, fluorine is present mainly in the ionic state (F^-), but may form complexes with a number of cations (e.g. Al, Fe, B) under certain conditions. The fluorine content of natural waters is generally less than 8 ppm, but concentrations as high as 1% have been reported for some saline waters. Calcium and sodium are the major parameters limiting the concentration of fluorine in natural waters; calcium supresses the fluorine content and sodium enhances it. The element is extracted from natural waters by precipitation of fluorite or apatite, or as a result of adsorption by clay and organic-rich sediments.

In the biosphere, fluorine generally accumulates in plants as fluoracetate, fluor-oleic acid or fluor-palmitic acid. Such plants are extremely toxic to animals. On a dry weight basis, the fluorine content of plants is generally in the range 10 to 100 ppm, but a number of plants, of which the tea plant is one, may accumulate much higher amounts of the element (up to 8,000 ppm). No plants (i.e. geobotanical indicators) are known which specifically require high fluorine concentrations in their substrate.

The atmosphere receives fluorine as a result of the evaporation of water (especially sea water); from volcanic exhalation, exudation from the biosphere and from industrial activity. Soil gases, especially those over fluoriferous mineral deposits, may receive fluorine (as HF) from the hydrolysis of fluorite. The fluorine content of atmospheric gases varies from a trace to as much as 1 ug/m^3; in industrial areas it may be higher by an order of magnitude or more.

The role of fluorine in the formation of mineral deposits, with emphasis on elemental associations, controls to mineralization and alteration, has been discussed. Fluorine tends to accumulate in the late residual fractions of both acidic and alkalic magmas; hence it is concentrated in pegmatites and carbonatites. The element also plays an active role in pneumatolytic and hydrothermal processes and is concentrated, in a wide variety of mineral forms, in greisen, skarn and many types of hydrothermal deposits. In the marine environment fluorine plays an active part in the formation of phosphate deposits.

During processes of ore formation fluorine may form complexes with, and therefore contribute to, the transport and deposition of such elements as Li, Be, Y, La, REE, Nb, Ta, W, B, Ge, Sn, Th and U. Due to increased solubility of sulphides in fluoride solutions, fluorine may enhance the concentration of such elements as Cu, Pb, Zn and Ba, and as a result of its own extraction from the fluid system cause these elements to precipitate in large concentrations as sulphides or sulphates. Calcium, through the formation of fluorite, strongly controls the dispersion and concentration of fluorine during ore forming processes.

Fluorine is concentrated in the alteration zones of many types of magmatic and pneumatolytic-hydrothermal ore deposits. The principal types of alteration with which it is associated are greisenisation, topazisation, tourmalinisation, sericitisation, skarnification, fenetisation, carbonatisation, kaolinisation, serpentinisation and occasionally chloritisation and argillitisation. The main fluorine-bearing minerals in these alteration zones are fluorite, topaz, tourmaline, the micas, amphiboles, humites, serpentine and clay minerals.

4.1.3 ANALYTICAL GEOCHEMISTRY

A review of the analytical geochemistry of fluorine is given, including all methods prior to the development of the specific ion electrode. The availability of the fluoride ion electrode has permitted the author to develop analytical methods for fluorine which, for the purpose of exploration geochemistr meet the balanced requirements of speed, precision and low cost.

The analytical instrumentation, consisting of a fluoride ion electrode, a reference electrode, and a millivolt meter (Ionanalyser) can easily be adapted for use under both laboratory and field conditions.

Natural waters may be analysed without pretreatment by simply adding a known quantity of buffer solution (pH 6.5) to the water sample. Fluorine determinations using standards made up in a similar solution matrix can be carried out directly by the electrode-Ionanalyser system. Analytical precision over the concentration range 100 to 1,000 ppm F is better than ±10%.

For geochemical media other than natural waters, cold-extractable, acid-diffusible and total methods of fluorine analysis have been developed and investigated for possible interferences.

Of the extractants investigated for cold-extractable analysis (0.01M NaOH, 0.01M HCl, and TISAB buffer), 0.01M HCl gave the highest anomaly contrasts over areas of mineralisation. This extractant is capable of leaching adsorbed fluorine from clay minerals as well as partially attacking fluorite and apatite (approximately 12 and 2% respectively of the total fluorine can be removed from these minerals). It will not, however, remove fluorine from the more resistant fluoriferous minerals such as topaz, tourmaline, pyrochlore and the micas. The analytical precision at the 95% confidence level for this method is better than ±20% over the concentration range 5 to 100 ppm and better than ±10% over the range 100 to 1,000 ppm F. Approximately 200 determinations can be made per man-day.

The acid diffusion method extracts almost 100% of the fluorine from fluorite and apatite. In addition, it extracts a large proportion of the fluorine from minerals such as the amphiboles, amblygonite, monazite, samarskite, xenotime, columbite, the micas (but not phlogopite) and clay minerals. It will not extract fluorine from topaz, tourmaline, zircon, beryl, serpentine and phlogopite. The precision of this method at the 95% confidence level is better than ±20% over the concentration range 50 to 2,000 ppm F. Approximately 200 determinations can be made per man-day.

For total fluorine an NaOH fusion was found to be the most efficient method of analysis. In order to decrease analytical time and have a better control over the pH of the sample solution, a concentrated solution of NaOH, rather than dry pellets, was used as a flux. With the exception of beryl and tantalite, which generally contain only low levels of fluorine, all the naturally occurring minerals are completely digested by this method. Interferences occur only if the elements Be, Zr, Y, Th, U and Sc are present in concentrations greater than 1,000 ppm. The method has a detection limit of 8 ppm, and the precision at the 95% confidence level is better than ±10% over the range 100 to 10,000 ppm F. Comparison of published fluorine analyses of U.S.G.S. rock standards indicates that the method is also accurate.

4.1.4 APPLICATIONS IN MINERAL EXPLORATION

4.1.4.1 Introduction

Fluorine may be effectively applied in all types of geochemical surveys aimed at detecting the following types of deposits:

a) Carbonatites
b) Kimberlites
c) Pegmatites
d) Greisen deposits
e) Skarn deposits
f) Hypothermal deposits containing tourmaline, topaz or fluorite.
g) Mesothermal and epithermal deposits containing fluorite or fluoritized wallrocks.
h) Volcanogenic sulphide deposits in rhyo-dacitic intrusives.
i) Serpentinized ultrabasic and basic intrusions possibly containing Ni, Co, Cr, Cu mineralisation.
j) Disseminated deposits of fluorite, Nb-Ta, Sn, W, Be, REE, U and Th in granitic, syenitic and rhyo-dacitic intrusions.
h) Primary kaolin deposits
l) Phosphate deposits
m) Placer deposits containing pyrochlore, topaz, tourmaline, xenotime, monazite and a number of other fluoriferous minerals.

Many of these deposits (carbonatite, kimberlite, pegmatite, greisen, skarn, kaolin, phosphate and disseminated deposits) are universally fluoriferous while others such as the hypo-, meso- and epi-thermal deposits may not always contain significant amounts of fluorine-bearing minerals (e.g. non-tourmalinized and/or topazized gold veins; base metal deposits of Eire; and the Hg and Sb deposits of western Turkey). The use of fluorine to detect the latter types of deposits can only be an effective approach to exploration if it has been established beforehand that fluorine-bearing minerals are associated with deposits of this type.

For volcanogenic sulphide deposits in rhyo-dacites and sulphide deposits in serpentinized ultrabasic and basic intrusions, the effective use of fluorine as a pathfinder relies heavily on its association with alteration processes characteristic of these deposits; in the former case with kaolinization of the rhyo-dacitic host rocks (e.g. deposits of the Eastern Black Sea Cu province of Turkey) and, in the latter case, with both autometamorphic and hydrothermal alteration of the basic rocks to form serpentinite.

Placer deposits must contain a fluoriferous mineral or minerals of primary or secondary importance for the element to be an effective pathfinder. Fluorine should be a good indicator of alluvial placer deposits derived from the weathering of carbonatites, pegmatites, greisen and skarn deposits, and many types of disseminated mineral deposits in igneous rocks (e.g. Sn, Nb, Ta).

Examples of the application of fluorine in prospecting for carbonatites, kimberlites, pegmatites, hypothermal gold veins, mesothermal and epithermal sulphide deposits containing little or no fluorite, and primary kaolin deposits have been discussed. The use of fluorine in prospecting for fluoriferous deposits for which study areas were not available has also been discussed, in order to make a full appraisal of the efficacy of this element in geochemical exploration. A review of methods used prior to the present research is also given. The results from both the present research and previous studies form the basis for the conclusions given below, on such aspects as choice of analytical method and regional, litho-, hydro-, pedo-, bio- and atmo-geochemical surveys. Finally, some of the problems that may arise when using this element in geochemical surveys are discussed together with methods of verifying the type of fluoriferous deposit present.

4.1.4.2 Choice of Analytical Method

Examples of the use of cold-extractable, acid-diffusible and total methods of fluorine analysis, for the detection of a wide variety of mineral deposits, have been presented. It is evident from these results that the choice of analytical method, when using geochemical materials from the secondary environment (stream sediments, soils, etc.) is of critical importance.

The choice of analytical method will be governed chiefly by the form or forms in which fluorine occurs in the mineral deposit, the predominant type of dispersion (hydromorphic or mechanical) in the secondary environment and the obvious restrictions of cost and time; the cold-extractable and acid-diffusible techniques are both cheaper and less time-consuming than the total method. Thus, for greisens, pegmatites, hypothermal deposits, non-fluorite bearing disseminated deposits (mainly Nb, Ta, Sn, W, Be, etc.) and placer deposits, fluorine occurs mainly in resistate minerals such as tourmaline, topaz, pyrochlore and the somewhat less resistate micas; cold-extractable methods will therefore be unacceptable since these minerals are not readily attacked by weak acid (0.01M HCl) or weak alkaline (0.01M NaOH) extractants.

In addition, hydromorphic dispersion from these deposits is generally minimal and the stripping of adsorbed fluorine from clay minerals by cold-extractable leachates would not be possible.

The acid-diffusible method will produce adequate anomalies in stream sediments and soils associated with the above mentioned deposits, only if a significant amount of the fluorine present is contained in the micaceous minerals or apatite; the other fluorine-bearing minerals being relatively resistant to this attack. In most cases, the total method should be preferred for detecting these types of deposits.

For kimberlite deposits, in which fluorine occurs mainly in phlogopite and serpentine and to a lesser extent in apatite, the determination of cold-extractable and acid-diffusible fluorine will generally give much lower anomaly contrasts than the total method, since both phlogopite and serpentine are relatively resistant to acid attack. Any anomaly produced by the cold-extractable or acid-diffusible techniques would have to rely upon the extraction of fluorine from the small amount of apatite present and the stripping of adsorbed fluorine from montmorillonite, which is the major weathering product of phlogopite and serpentine. It should be noted, however, that the attack on montmorillonite will only be partial, since most of the fluorine will be lattice-held rather than adsorbed. The above statements also apply to the detection of serpentinized ultrabasic and basic intrusions which may contain Ni, Co, Cr, or Cu mineralisation.

For deposits which contain a large amount of fluorite and/or apatite, such as carbonatites, skarns, mesothermal and epithermal deposits, phosphate deposits and some pegmatite and disseminated deposits, cold-extractable and acid-diffusible attack may produce anomaly contrasts similar to the total method. Deposits of this type give rise to a substantial amount of hydromorphic dispersion and the (0.01M HCl) cold-extractable and acid-diffusible techniques have, therefore, been shown to give good anomalies in stream sediments and soils associated with these deposits. Detection of these anomalies is also aided by the fact that fluorite and apatite are completely attacked by the acid diffusion method and the determination of total fluorine may, therefore, give no further information. Where the total method may be more effective, is in the detection of carbonatites and skarns, since a significant amount of the fluorine in these deposits also occurs in the more resistate minerals such as pyrochlore (carbonatites) and topaz, tourmaline, amphiboles and the micas (skarns). If it is suspected, or proved by orientation work, that the largest component of dispersion is hydromorphic then the cold-extractable and acid-diffusion techniques will generally be more effective than the total method.

When studying the dispersion of fluorine in rocks, determination of total fluorine is generally preferred, although it should be stated that no research has been carried out to determine which of the methods available will be the most effective in outlining primary haloes associated with various types of deposits.

Although the above conclusions stress the preferred method to be used it is often advantageous if more information is required on the form of dispersion, to use more than one, and sometimes all of these analytical extraction procedures. Thus, by using all of the methods the author has been able to demonstrate the following points:-

a) For the anomalous streams draining the Kaluwe carbonatite, approximately 40% of the total fluorine in the sediments was found to be in a form resistant to cold-extractable attacks. Most of this fluorine is present in pyrochlore; the presence of a large Nb anomaly supports this statement. Approximately 60% of the total fluorine can be extracted by acid diffusion and most of this can be attributed to apatite and fluorite, with lesser amounts coming from pyrochlore and ionically dispersed fluorine. Only 10% of the total fluorine can be extracted by cold 0.01M HCl and the majority of this must be ionically dispersed fluorine adsorbed on clays.

b) For the soils over the Kaluwe carbonatite, these analytical methods have been used to identify the various facies within the deposit and the forms in which fluorine occurs in them. Thus, fluorite -, apatite-, and pyrochlore- rich facies have been identified.

c) For soils over the Wheal Jane tin lode, Cornwall, the cold extractable method produced no anomaly, whereas acid-diffusible and total fluorine indicated the presence of a large anomaly of high contrast and good lateral extent. Approximately 50% of the total fluorine was extracted by acid diffusion and, since phosphorous is not anomalous over this deposit, most of the fluorine can be attributed to sericite. The fluorine not released by the acid diffusion method can be accounted for by tourmaline and topaz; the presence of a large boron anomaly indicated that the former mineral is probably the most abundant.

d) For soils over the Bepe 2 beryl pegmatite, Rhodesia, the cold extractable method gave a poorly defined anomaly and the acid diffusion method, although producing a reasonable anomaly, extracted only 10% of the total fluorine. Therefore, most of the fluorine is present in resistant minerals such as tourmaline, quartz, feldspar and to a lesser extent the micas.

e) For soils over the Richardson uraninite-fluorite pegmatite deposit, Canada, nearly 100% of the total fluorine in the A horizon soils, which give the only anomalous expression over this deposit, can be extracted by the acid diffusion method. This fact, together with the presence of Ca and P anomalies in the organic horizon of these soils, suggests strongly that the most operative mechanism of dispersion is biologic uptake of fluorine from fluorite and apatite, with sugsequent sequestration in the humus horizon.

4.1.4.3 Regional Geochemical Surveys

In mineral exploration, broad-scale geochemical surveys, using a sampling medium suitable to the environment under investigation (e.g. stream sediments, lake sediments etc.), are generally carried out in order to

a) detect and outline new metallogenic provinces,
b) give better definition to existing metallogenic provinces and
c) supply information on the nature of the underlying geology, especially in areas of heavy residual overburden.

Due to the anomalous association of fluorine with a wide variety of mineral deposits (listed in section 4.4.1) and, since it generally demonstrates distinct levels of concentration in the various types of igneous, sedimentary and metamorphic rocks, fluorine is an ideal element to include in regional geochemical surveys.

4.1.4.4 Hydrogeochemical Applications

The greatest use of fluorine in mineral exploration has been in hydrogeochemical surveys, involving both stream sediment and water sampling, the latter is the most important method to date.

When planning stream sediment surveys, in which fluorine is to be used as a pathfinder, special attention must be paid to the predominant type of dispersion that may be expected in the vicinity of the mineral deposit; the choice of analytical method and sampling density will be dependant upon this a priori knowledge. Anomalies, formed as a result of saline dispersion, will be most predominant in the region of deposits containing significant amounts of fluorite and/or apatite, since these minerals are less resistant to chemical weathering than most other fluoriferous minerals. Deposits which may be characterised by saline anomalies are carbonatites, mesothermal and epithermal deposits, phosphate deposits, disseminated deposits containing fluorite and certain pegmatite and skarn deposits. Fluorine may also be ionically dispersed from primary haloes and alteration zones associated with a wide variety of magmatic, volcanogenic, metasomatic and hydrothermal mineral deposits; features which are often the only expression of these deposits at surface. If it is suspected that saline dispersion is the only form of dispersion operative in a particular environment, cold-extractable and/or acid-diffusion methods of analysis should be used, since the total method of analysis will create a significant background noise in which anomalies may be lost.

In the absence of extensive primary haloes and alteration zones, the detection of a number of fluoriferous deposits in which fluorite is not always present, such as kimberlites and certain pegmatites, greisen, skarn, hypothermal and disseminated deposits, will rely heavily on the mechanical dispersion of fluorine-bearing minerals from these deposits. When mounting drainage surveys aimed at the detection of these types of deposits, total fluorine analysis and a tighter sampling density should be used.

Often it is not possible to ascertain the predominant type of dispersion which will be present and, for this reason, the maximum amount of information can be obtained only if the cold-extractable or acid-diffusion method of analysis is used in conjunction with the total method.

Fluorine may also be used effectively in drainage surveys aimed at detecting alluvial placer deposits containing economic concentrations of pyrochlore, columbite-tantalite, cassiterite, scheelite and REE, Th and U minerals (monazite, xenotime, thorite, etc.). For many of these deposits, the mineral of economic concern is fluoriferous (e.g. pyrochlore, REE, fluorocarbonates) and for others, there may be significant concentrations of associated fluorine-bearing resistate minerals such as tourmaline and topaz in cassiterite deposits and topaz in columbite-tantalite and scheelite deposits.

The use of fluorine in groundwater and stream water surveys has been discussed. The element has been found to be an effective indicator of the presence of fluorite, pegmatite, skarn and many types of sulphide deposits with which it is associated. Aureoles or dispersion trains of up to 4 km have been noted, but the extent of anomalous dispersion is generally less than 0.5 km. Landscape has an effect on the observed concentration of fluorine in waters; the highest concentrations (2,000-4,000 ppb) occurring in saline desert environments and the lowest (100-450 ppb) in northern glacial and permafrost terrains. The highest anomaly contrasts (up to 10-fold) occur in groundwaters associated with fluorite deposits or deposits containing an appreciable amount of fluorite (e.g. skarn and some sulphide deposits). Lower anomaly contrasts (2-6 fold) occur in waters associated with mineral deposits in which fluorine is held in more chemically resistant minerals (e.g. pegmatite and Au deposits).

Studies of the mode of occurrence of fluorine in stream waters indicated that this element is dispersed predominantly in the ionic state (F^-). Both calcium and sodium will therefore have a modifying effect on the levels of fluorine which may occur; calcium because of the common ion effect, and the low solubility of CaF_2 (equivalent to 8 ppm F at 25°C) will suppress the fluorine concentration and sodium, because of the high solubility of NaF, will increase the solubility of fluorite and will also promote the extraction of large amounts of fluorine from rock formations. In this manner, legitimate anomalies may be suppressed by Ca and false anomalies may be created by the enhancing effect of Na. Therefore, it is advisable that waters be analysed for Ca and Na, in order to aid interpretation.

An investigation of seasonal variations in the fluorine content of groundwaters associated with fluorite mineralisation indicated that considerable errors in interpretation can occur as a result of the collation of data collected over an extended period of time, generally two or more seasons. Water surveys should be carried out over a short period of time. If this is not possible, some method of monitoring seasonal changes, such as repetitive sampling of control stations, should be employed.

4.1.4.5 Pedogeochemical Applications

The use of fluorine in pedogeochemical surveys, in areas of both residual and transported overburden, has been reviewed and examples of its application in outlining carbonatites, kimberlites, pegmatites, greisen tin deposits, primary kaolin deposits and hypothermal gold veins are given, together with an investigation of its dispersion in the vicinity of non-fluorite-bearing mesothermal and epithermal sulphide deposits. Previous workers have shown fluorine to be an excellent pedogeochemical indicator of the presence of fluorite and skarn deposits (not included in the present research).

In the soil regime overlying fluoriferous deposits, anomalies will be formed as a result of mechanical or hydromorphic dispersion (or a combination of both), depending on the type of deposit present and the principal fluorine-bearing minerals in it. Deposits containing a great deal of fluorite (carbonatite, skarn and fluorite-bearing hydrothermal deposits) are generally typified by hydromorphic anomalies. The detection of fluoriferous deposits, in which fluorine occurs chiefly in minerals resistant to chemical weathering (topaz, tourmaline etc.) or in minerals which give up their fluorine to clays with little or no release of the element into the aqueous phase, will rely chiefly on the concentration of these minerals in the overlying residuum. Total methods of analysis will be required to detect these anomalies.

Over the Kaluwe carbonatite, fluorine exhibits a well-defined anomaly and, therefore, can be used to outline sub-outcropping deposits of this type. For blind carbonatites, the element can be used to outline fenetized zones which are often associated with these deposits. In addition, the analysis of fluorine in soils over the Kaluwe deposit, using cold-extractable, acid diffusion and total methods, and the correlation of these data with those of Nb and P, permitted the delineation of certain diagnostic facies within the carbonatite (upper, middle and lower facies). For large intrusive bodies such as carbonatite complexes and mineralised multi-phase granites, syenites etc., fluorine can consequently be used as an aid in geologic mapping, especially when these bodies are covered by thick residual overburden. This attribute is of particular importance when prospecting for kaolin deposits in granitic massifs; deposits which are invariably fluoriferous.

For soils over kimberlites, fluorine generally exhibits anomalies of high contrast (depending on the type of host rock) but with little lateral dispersion. Hydromorphic dispersion from these deposits would appear to be insignificant; the element being entirely incorporated in the weathering products of phlogopite and serpentine (mainly montmorillonite). Because of the small size of most kimberlite deposits (5-200 meters in diameter), it is essential when using fluorine as a tracer in soil surveys to employ a very tight sampling grid.

In the tin province of south-west England, fluorine was found to be a better indicator of primary tin lodes than As and Cu. Over the Wheal Jane tin lode, fluorine exhibited a strong anomaly of good lateral extent, whereas As and Cu displayed barely discernable anomalies. Over this deposit, practically all of the fluorine is concentrated in tourmaline, sericite and topaz. Since these minerals are not attacked by weak acids, cold-extractable fluorine analysis is ineffective for detecting greisen deposits and, the acid diffusion method will rely heavily on the presence of sericite to produce an adequate anomaly. Consequently, it is advisable to determine total fluorine when prospecting for these deposits.

Fluorine was also found to be a valuable discriminant for primary and detrital tin deposits, the latter type of deposit, which occurs below the 430 O. D. level (accredited to a Pliocene marine transgression) is marked by a strong tin anomaly, but no supporting fluorine anomaly.

From a soil traverse over the Dartmoor granite - metamorphic aureole-killas system of South-west England, fluorine displayed a distinct anomaly of high contrast over the aureole zone. Hence, fluorine can be used in detailed soil surveys to map aureole zones around igneous intrusions, thus giving better definition to areas of exploration for skarn-type mineralisation.

Studies of the dispersion of fluorine in soils overlying pegmatite deposits (Bepe 2 beryl pegmatite, Rhodesia and Richardson uraninite - fluorite pegmatite, Canada), indicated the presence of distinct fluorine anomalies of high contrast over these deposits. In view of the variable composition of pegmatites, in terms of fluorine bearing minerals (some contain little or no fluorite and/or apatite), the total method of fluorine analysis should be used in soil surveys carried out in the vicinity of these deposits. Fluorine can also be used to map the various mineral zones which occur in the more productive complex pegmatites; for the Bepe 2 pegmatite, higher fluorine concentration occurs in the vicinity of the mineralised beryl-quartz zone.

In soil surveys aimed at the detection of hypothermal gold-quartz veins, fluorine may be used as a pathfinder for those deposits formed in conjunction with processes of tourmalinisation, topazisation and sericitisation of wallrocks. Since the element is not a universal indicator of this type of deposit, it is best used together with arsenic, which is generally considered to be a more specific pathfinder for gold-quartz veins (but by no means universal). Therefore, the two should be considered as compatible.

In the Halikoy district of Turkey, fluorine was found to be enriched in soils overlying both the mineralised (Hg) and unmineralised sections of a major fault zone. The fault zone has probably provided the channelway for the movement of volatiles or fluids containing fluorine; the fluorine entering the wallrocks and subsequently the soils, as a result of weathering. As with mercury, fluorine appears to show excellent potential as an indicator of fault zones, structures which form the domain for many types of mineral deposits.

For soils over nonfluorine-bearing mesothermal and epithermal sulphide deposits, fluorine displayed either anomalies of low contrast (Tynagh Pb-Zn-Cu deposit, Eire and Halikoy Hg deposit, Turkey), or no discernable anomaly whatsoever (Ivrindi Sb deposit, Turkey). Although fluorine may be concentrated in some of these deposits in a cryptic manner, it would appear that the presence of fluorite is a prerequisite to the element's application in geochemical surveys aimed at detecting these deposits. In many metallogenic provinces containing hydrothermal ore deposits, the presence of fluorite as a major gangue mineral is well established and therefore, these areas constitute better environments in which to use the pathfinding qualities of this element.

In mineralised areas, characterised by relatively undifferentiated soils, there is very little change in the anomaly contrast of fluorine with depth and a suitable sampling horizon can be adopted, for most surveys. In podzolic soils however, there is strong evidence to suggest that the organic A horizon is a more suitable horizon to sample, when using fluorine in soil surveys. Thus, for example, the podzolic soils over the Richardson urananite-fluorite pegmatite deposit (Bancroft area, Canada) display a strong anomaly of good lateral extent in the organic A horizon, but no anomalous expression could be detected in the B horizon; in the C horizon the anomaly is confined to the immediate vicinity of the deposit. Less extreme examples have also been noted for other podzolic soil environments and, it is, therefore, strongly recommended that, in these environments, consideration be given to the use of the organic horizon in soil surveys.

4.1.4.6 Lithogeochemical Applications

In lithogeochemical surveys fluorine may be used to delineate the following types of features, which may be indicative of the presence of mineralisation.

a) Environments Coeval with the Formation of Mineral Deposits:

For fluorine these are mainly of an igneous intrusive or sedimentary nature. Granitic bodies which either contain or represent the parent magma, from which Sn, Nb, Ta, Be and certain W deposits have formed, are invariably enriched in fluorine. Tin-bearing granites of Cornwall contain, on average, twice as much fluorine (1570 ppm) as the norm for granites (8 ppm); the Sn and Nb-Ta bearing granites of Nigeria are also substantially enriched in this element. Criteria, based on both the fluorine content and the content of other diagnostic elements (Li, B, Be, Sn, Nb, etc.), can therefore be adopted to discriminate between barren and productive granitic environments.

Although fluorine has proved to be useful in the above mentioned situation, this has not been the case for Cu-Mo porphyry deposits in granodiorite and monzonite intrusions. Extensive studies have shown that no discrimination can be made between barren and mineralised intrusions on the basis of their fluorine content.

In the sedimentary environment, fluorine can be used to detect formations which are rich in phosphate (3 to 4% F in apatite). These may be favourable host rocks for phosphorite and uranium deposits. In this respect, routine analysis of drill cores from petroleum exploration programmes may give valuable information.

b) Primary Haloes

Fluorine is often concentrated in primary haloes formed around carbonatites, skarns, pegmatites, greisens, hydrothermal veins and volcanogenic sulphide deposits in rhyo-dacites. Around carbonatites, the element is enriched as a result of fenetization of the host rock. During the formation of skarn deposits, the element generally migrates to the extremeties of the skarnified zone, which may be larger than the ore zone by orders of magnitude. Certain volcanogenic sulphide deposits in rhyo-dacites are characterised by primary fluorine haloes, formed as a result of hydrothermal alteration of the host rock. Haloes around pegmatite, greisen and hydrothermal vein deposits are generally not extensive and therefore constitute small exploration targets.

Fluorine may be used in both reconnaissance and detailed lithogeochemical surveys aimed at the detection of primary haloes associated with the above types of deposit. In particular, fluorine may be a useful indicator of blind mineral deposits, of which the only indicator at surface is a 'dome halo' of either a continuous or discontinuous nature.

c) Alteration

Fluorine is a constituent of many types of alteration associated with a wide variety of mineral deposits (greisenisation, fenetisation, skarnification, tourmalinisation, topazisation, sericitisation, serpentinization and chloritisation). The element, therefore, may be used as an aid in determining the presence or absence of particular types of alteration in a given geologic terrain, indicating also the potential for certain types of mineral deposits.

d) Fault Zones

Anomalous concentrations of fluorine were found to occur both in the mineralised (Hg) and unmineralised sections of a major fault zone in Western Turkey. Although more research along these lines is required, it is more than likely that fluorine is a good lithogeochemical indicator of potentially mineralised fault zones.

4.1.4.7 Biogeochemical Applications

The use of fluorine in biogeochemical surveys has been discussed in only the most cursory manner. It is known that plants possess a remarkable tolerance towards the presence of high concentrations of fluorine in soils and, are able to concentrate the element without any ill effects. It is therefore possible that fluorine may be particularly useful in this type of survey.

Due to the high tolerance plants have for this element, there are no morphological indications of the presence of fluoriferous mineral deposits, which can be used in geobotanical surveys. Likewise, there are no plants which seek areas of high fluorine concentrations in their substrates and, therefore, no geobotanical indicators of the presence of fluoriferous deposits.

4.1.4.8 Atmogeochemical Applications

Research concerning the evolution of gaseous fluorine from fluorite and methods of detecting fluorine vapour (at naturally occurring concentrations) have been discussed. It was found that significant amounts of fluorine were evolved from both dry and wet fluorite; the gteatest amounts coming from wet fluorite. It is thought that the process of gaseous evolution is primarily one of hydrolysis, with subsequent release of HF vapour. The pH of solutions in contact with fluorite has a controlling effect on both the quantity of vapour produced and the rate of diffusion. Highly acidic solutions provide the greatest evolution of HF.

Analytical instrumentation was developed to measure fluorine concentrations at the levels that might be expected in soil gases. A detection limit of 2.0×10^{-3} ug F was achieved, but, in field trials carried out over a fluorite dump in Derbyshire, the fluorine content of the soil gas was found to be at or below the detection limit for an 18 litre sample.

Although preliminary trials elsewhere have indicated that fluorine vapour can be detected over fluorspar mineralisation, using a mass spectrometer (Frederickson et al, 1971), it is evident from both the spectrometer study and the author's own research that, subject to further analytical developmen fluorine vapour geochemistry cannot as yet be used with confidence in mineral exploration.

4.1.4.9 Problems of Application and Methods of Verifying the Type of Mineralisation Present

Problems concerning the interpretation of fluorine anomalies will arise from the fact that the element is not, on its own, definitive of the type of mineral deposit present. In other words, it is a tracer of fluoriferous deposits, of which there are many types, both economic and uneconomic. Anomalies found during all phases of geochemical exploration need to be investigated, with the aid of other diagnostic elements, to determine specifically what type of mineralisation is present. This will require a sound knowledge of the elemental associations which characterise the various types of fluoriferous deposits. For example, a fluorine anomaly supported by anomalous concentrations of Ni, Cr, Co, Ti and Nb suggests the presence of kimberlite; an anomaly supported by high concentrations of Nb but not Ni, Cr, and Co suggests the presence of carbonatite, while anomalies supported by high concentrations of Li-Rb-Be-REE-U, Mo-W-Ti-V-Zr, Sn-B-Cu-As and Cu-Pb-Zn may indicate the presence of pegmatite, skarn, greisen and hydrothermal (sulphide-fluorite) deposits, respectively.

Significant fluorine anomalies may also be related to unmineralised bedrock enrichments of the element. Igneous rocks of high alkali content (alkali-granites, alkali-syenite, alkali-basalts, alkali-ultramafics, phonolites and lamprophyres), acidic granites containing large concentrations of disseminated fluorite, topaz or tourmaline and sedimentary rocks rich in phosphate will be the main sources of false anomalies. Therefore, careful consideration should be given to follow-up work when these sources are suspected, again, the use of other diagnostic elements will be required. It should be noted that, the presence of many of the fluoriferous rock types mentioned above is considered by most economic geologists to be indicative of the nearby occurrence of certain types of mineralisation. Thus, alkali-granites may signify the presence of Nb deposits, topaz-granites the presence of Nb-Ta and Sn deposits, greisenised granites the presence of tin deposits and phosphate-rich sediments the presence of phosphate deposits.

Finally, consideration must be given to the anomaly contrast that might be expected in different geologic environments. Since fluorine exhibits an extremely large overall concentration range for the major rock types (10-20, 000 ppm), the magnitude of anomalies associated with fluoriferous deposits will depend to a large extent on the type of host rock in which mineralisation occurs. For example, lower anomaly contrasts can be expected when pegmatites or griesen tin deposits occur in granites, as opposed to sedimentary formations. The same also holds true in cratonic shield areas, where carbonatite and kimberlite deposits may occur in basement (schists and gneisses), sedimentary or basaltic formations. It is important, therefore, to establish threshold values corresponding to each of the various rock types in a study area and, to interpret the data associated with each of these rock types on the basis of the threshold values obtained.

4.2 RECOMMENDATIONS.

No research can ever be considered complete and despite the present work many aspects of the geochemistry of fluorine and its application in mineral exploration have not been adequately investigated. The following suggestions for further research may be of interest to those wishing to carry out studies on the geochemistry of fluorine or employ it in exploration programmes.

a) Our knowledge of the geochemistry of fluorine in the primary environment is still very weak especially when considering the large abundance of this element in the lithosphere. This matter can only be rectified through detailed studies of the dispersion, mobility, concentration and elemental relationships of fluorine in the igneous, metamorphic and sedimentary environments. The role of fluorine in the formation of ore deposits is certainly a subject which needs much clarification.

b) Primary elemental haloes are often the only expression at surface of blind mineral deposits and in this respect fluorine exhibits excellent potential as an indicator of haloes associated with a wide variety of deposit types. Very little information on the use of fluorine to detect primary haloes has been forthcoming. This is, therefore, a field of application which requires concentrated research.

c) The factors affecting the dispersion and concentration of fluorine in the aqueous environment and methods of quantifying these effects must be studied in more detail if the element is to be effectively applied in drainage surveys utilizing both waters and sediments.

d) It has been shown in laboratory experiments that significant amounts of gaseous fluorine will evolve from fluorite. Analytical instrumentation for the measurement of extremely low levels of gaseous fluorine, that may be expected in soil gases, is not presently available. Research and development in this direction is badly needed if the potential of the element in vapour geochemical surveys is to be properly assessed. At the moment, gas chromatography and mass spectrometry (especially quadropole) systems show promise as vapour detectors in mineral exploration. Both these instruments are reasonably sensitive to fluorine and it is hoped therefore, that the element will be included in any research programmes using them.

e) Plants show a strong tolerance towards high levels of fluorine in soils and are able to concentrate the element with few ill effects. In this respect the possible application of fluorine in biogeochemical surveys should be investigated.

f) The geochemical analysis of fluorine is now relatively inexpensive and precise, but a separate analytical procedure is required and, unlike many other methods, additional elements cannot be included. The present trend in geochemical exploration is towards single-procedure multi-element analysis using such instruments as the inductively coupled plasma source direct reading spectrophotometer. Although a great deal of research will have to be carried out, the advantage of including fluorine in these multi-element methods is obvious.

g) Finally, the true worth of fluorine as a pathfinder in mineral exploration can only be determined through more detailed studies of its association with dispersion from mineral deposits of all types.

BIBLIOGRAPHY

1. AGUILLAR, A.N., 1974, The Regional Geochemical Distribution of A senic in South West England. PH.D. Thesis, Imperial College, Univ. London.

2 ALCARD, P., 1959, The Application of Geochemical Methods (Cr. and Ni) to Prospecting for Kimberlite Pipes. Annales Des Mines, P103-110.

3 ALMANN, R. and KORITNIG, S., 1972, Fluorine. In Data of Geochemistry, Sect. 9, Springer-Verlag.

4 BAKER, W.E., 1973, The Role of Humic Acids from Tasmanian Podzolic Soils in Mineral Degradation and Metal Mobilization. Geochim. et Cosmochim Acta, Vol. 37, P269-281.

5 BANDURKIN, G.A., 1961, Behavious of the Rare Earths in Fluorine-Bearing Media. Geochemistry, No. 2, P159-167.

6 BARSUKOV, V.L., 1957. The Geochemistry of Tin. Geochemistry, No. 1, P41-52, 1957 (Also in 20th Int. Geol. Congress, Mexico.

7 BARTH, T.F.W., 1947, On the Geochemical Cycle of Fluorine. Jour. of Geol., Vol. 55, No. 5, P420-426.

8 BARTOSEK, J., KASPERAC, I., and SKUTHAN, B., 1971. Location of Fluorite Deposits by Geophysical Methods with the Aid of Activation Analysis. Z. Agnew. Geol., Vol. 17, No. 8, P333-336.

9 BEUS, A.A., 1956, Geochemistry of Beryllium. Geochemistry, No. 5, P511-531.

10 BEUS, A.A., 1958, The Role of Complexes in Transfers and Accumulations of Rare Elements in Endogenic Solutions. Geochemistry, No. 4, P388-397.

11 BEUS, A.A., 1962. Transport of the Elements in the Form of Halides in Endogene Processes in Experimental Investigations of Deep-Seated Processes. (In Russ), Izd. Adad. Nauk. SSSR.

12 BEUS, A A., SOBOLEY, B.P., and DIKOV, YU.P., 1963. Geochemistry of Beryllium in High Temperature Postmagmatic Mineralization. Geochemistry, No. 3, P316-323.

13 BEUS, A.A., and SUBBOTIN, K.D., 1964. Lithium, Beryllium and Fluorine as Prospecting Indicators for Beryl Pegmatites (Russ.). Sov. Geol., Vol. 7, No 5, P50-57.

14 BEWERS, J.M., 1972. The Global Circulation of Halogens in Nature. Proc. 24. Int. Geol. Congress, Montreal, Section 10, Geochemistry, P273-81.

15 BLOOMFIELD, K., REEDMAN, J.H. and TETHER, J.G.G., 1971. Geochemical Exploration of Carbonatite Complexes in Eastern Uganda. In Can. Inst. Min. Metal. Spec. Vol. 11, (Boyle, R.W. and McGerrigle, J.I. Eds.) P85-102.

16 BLOSS, F.D., SHEKARCHI, E., and SHELL, H.R., 1959. Hardness of Synthetic and Natural Micas. AM. Mineralogist, Vol. 44, P33.

17 BOND, G.W., 1945, A Geochemical Survey of the Underground Water Supplies of the Union of South Africa. Geol. Surv. South Africa Mem. 41.

18 BORCHERT, H., 1952. On the Geochemistry of Fluorine (GER). Heidelberger Beitr. Miner. U Petrog., BD 3, H.1, P26-43.

19 BOVAY, E., 1969. Fluoride Accumulation in Leaves due to Boron-Containing Fertilizers. Fluroide Quart. Rept., V2, P222-228.

20 BOWER, C.A., and HATCHER, J.T., 1967. Adsorption of Fluoride by Soils and Minerals. Soil Sci., Vol. 103, P151-154.

21 BOWLER, C.M.L., 1959. The Distribution of the Five Alkali Elements and Fluorine in Some Granites and Associated Aureoles from the S.W. England. PHD. Dissertation, Univ. of Bristol.

22 BOYER, R.E., 1961. Occurrence of Radioactive Fluoritic Sandstone Wet Mountains, Colorado. Econ. Geol., Vol. 56, No. 4, P780.

23 BOYLE, R.W. and DASS, A.S., 1967, Geochemical Prospecting-use of the A Horizon in Soil Surveys. Econ. Geol., V62, No.2, P274-75.

24 BRAMMELL, A. and HARWOOD, H.F., 1932. The Dartmoor Granites their Genetic Relationships. Q. Jour. Geol. Soc. Lond., V88, P171-237.

25 BROWNELL, G.M., 1959. A Beryllium Detector for Field Application Econ. Geol., V54, P1103-1114.

26 BUTLER, J.R., 1953. The Geochemistry and Mineralogy of Rock Weathering (I) The Lizard Area, Cornwall, England. Geochim et Cosomochim Acta, Vol. 4, P157-178.

27 BUTLER, J.R., 1954, The Geochemistry and Mineralogy of Rock Weathering (I) The Lizard Area, Cornwall, England. Geochim et Cosmochim Acta, V6, P268-281.

28 CACHAU-HERREILLAT, F., and PROUHET, J.P., 1971. The Utilization of Metalloids (Arsenic, Phosphorus, Fluorine) as Pathfinders for Skarn Tungsten Deposits in the Pyrenees of France. Canadian Inst. Min. Spec. Vol II, P116-120.

29 CARLSON, E.H., MANUS, R.W. and PHUPHATANA, A. 1974. Application of the Fluoride Ion Electrode to Geochemical Prospecting (Abst.). Geol. Soc. America Abst. with Programs, V6, No.6, P496.

30 CARPENTER, R., 1969. Factors Controlling the Marine Geochemistry of Fluorine. Geochim et Cosmochim Acta, Vol. 33, No.10, P1153-1167,

31 CATTERMOLE, P.J. and FUGE, R., 1969. The Abundances and Distribution of Fluorine and Chlorine in a Layered Intrusion at Rhiw, Northern Wales. Geochim et Cosmochim Acta., Vol. 33, No. 10, P1295-1298.

32 CLARKE, F.W. and WASHINGTON, H.S., 1924, The Composition of the Earth's Crust. U.S. G ol. Surv., Porf. Paper 127.

33 COATS, R R., GOSS, W.D., and RADER, L.F., 1963. Distribution of Fluorine in Unaltered Silcic Volcanic Rocks of the Western Conterminous United States. Econ. Geol. Vol 58, No. 6, P941-951.

34 COLLET, G.F., 1969. Biological Effect of Fluoride on Plants. Fluoride Quart. Rept., V2, P22-235.

35 CORRENS, C.W., 1948. The Geochemical Balance. Naturwissenschaften, V35, P7-12.

36 CORRENS, C.W., 1956. The Geochemistry of the Halogens. Physics and Chemistry of the Earth, Vol. 1. P181-233.

37 CORRENS, C.W., 1957. The Geochemistry of Fluorine and Chlorine. (Ger.). Neues. Jb. Miner., ABH. BD. 91, P239-256.

38 DARLING, R., 1971. Preliminary Study of the Distribution of Minor and Trace Elements in Biotite from Quartz Monzonite Associated with Contact-Metasomatic Tungsten-Molybdenum-Copper Ore, California, USA. In Proc. 3rd Geochem Expl. Symp., Can. Inst. Min. Metall. Spec. Vol. 11, P315-322.

39 DAWSON, J.B., 1967. Geochemistry and Origin of Kimberlites. In Ultramafic and Related Rocks, Wyllie, P.J., ED., J. Wiley and Sons, New York.

40 DEBNAM, A.H., 1961. Geochemical Prospecting Studies for Beryllium in Central and East Africa. PH.D. Thesis Univ. London.

41 DELITSYNA, L. V., and MELENT, YEV, B.N., 1969. The Coexistence of Liquid Phases at High Temperatures. The System Nepheline-Villiaumite-Lithium Fluoride. Dokl. Akad. Sci. USSR Earth Sci. Sect., Vol. 189. P215.

42 DENISOV, A. P., DUDKIN, O. B., ELINA, N. A., KRAVCHENKO-BEREZHNOI, R. A., and POLEZHAEVA, L. I., 1961. Dependence of the Physical Properties of Apatite on the Admixture of Rare Earths and Strontium. Geochemistry, No. 8, P718-730.

43 DERRY, D. R., CLARK, G. R. and GILLATT, N., 1965. The Northgate Base-Metal Deposit at Tynagh, Co. Galway, Ireland. Econ. Geol. V60, No. 6, P1222-1237.

44 DINES, H. G., 1956. The Metaliferous Mining Region of South West England. Mem. Geol. Surv. Great Britain, 2 Vols. HMSO, London.

45 DODGE, F. C. W., and ROSS, D. C., 1971. Coexisting Hornblendes and Biotites from Granitic Rocks near the San Andreas Fault, California. Jour. Geol., Vol. 79, P158.

46 DONOVAN, P. R., 1965. Geochemical Dispersion in Relation to Base Metal Deposits in Glacial Terrain in West-central Eire. PH. D. Thesis, Univ. London.

47 DUNLOP, A. C., 1973. Geochemical Dispersion of Tin in Stream Sediments and Soils in South-West England. PH. D. Thesis, Univ. London.

48 DURNEV, V. V., KIM, E. K., and EGORENKOV, E. S., 1970. Spatial Relation of Molybdenum Hydrogeochemical Anomaly to the Ore Mineralization (in Russ.). Chem. Abstr., V72, No. 12, Item No. 1238W, P167.

49 DURST, R.A., and TAYLOR, J.K., 1967. Modification of the Fluoride Activity Electrode for Microchemical Analysis. Anal. Chem., Vol. 39, No. 12, P1483-1485.

50 DURST, R.A., 1969. Ion Selective Electrodes. Natl. Bur. Standards Spec. Publ. 314, 452P.

51 EDMOND, C.R., 1969. Direct Determination of Fluoride in Phosphate Rock Samples using the Specific Ion Electrode. Anal. Chem., Vol. 41, No. 10, P1327-1328.

52 EDMONDS, E.A., McKEOWN, M.C. and WILLIAMS, M., 1969. South West England. 3rd·Ed., British Regional Geology, 130p, HMSO, London.

53 EDMUNDS, W.M., 1971. Hydrogeochemistry of Groundwaters in the Derbyshire Dome with Special Reference to Trace Constituents. Inst. of Geol. Sci. Grt. Brit. Report No. 71/7.

54 ELVING, P.J., 1954. Analytical Chemistry of Fluorine-Containing Compounds. In Fluorine Chemistry (Simons, J.H. Ed), Academic Press Inc., Vol. 2, P53-212.

55 EVANS, P.A., MOODY, G.J. and THOMAS, J.D.R., 1971. Studies Concerning the Iorion 94-09A Fluoride Sensitive Electrode. Laboratory Practice, V20, No. 8, P644.

56 EXLEY, C.S., 1958. Magmatic Differentiation and Alteration in the St. Austell Granite. Q.J. Geol. Soc. of London, Vol. 114, P197.

57 EXLEY, C S., and STONE, M., 1964. The Granitic Rocks of South-West England. In Present Views of Some Aspects of the Geology of Cornwall and Devon (Hosking, K.F. and Shrimpton, G. J. Eds), Royal Geol. Soc. of Cornwall, P129-184.

58 FARRELL, B.L. 1974. Fluorine, A Direct Indicator of Flurotie Mineralization in Local and Regional Soil Geochemical Surveys Jour. Geochem. Expl., V3, No. 3, P227.

59 FEDERENKO, YU, D., 1964. Use of the Fluorine-Phosphorus Ratio in Geochemical Prospecting for Quartz-Fluorite Veins. Geochemistry International, No. 1, P29-32.

60 FERSMAN, A. E., 1939. Geochemistry Vo. IV - Geochemistry of Individual Elements. N.K.H.P. - USSR, Leningrad, (Translation R.W. Boyle, Geol. Surv. of Canada).

61 FICKLIN, W.H., 1970. A Rapid Method for the Determination of Fluoride in Rocks and Soils Using an Ion-Selective Electrode. U.S.G.S. Prof. Pap. NO. 700-C, P186-188.

62 FILIMANOVA, L.G., 1970. Possible Geochemical Prospecting for Phlogopite Deposits in the Aldan Shield (Russ.), Geol. Rud. Mestorozhd., Vol. 12, No. 2, P116-122.

63 FLANAGAN, F.J., 1969. U.S. Geol. Surv. Standards-2. First Compilation of Data for the New U.S.G.S. Rocks. Geochim et Cosmochim Acta, Vol. 33, No. 1, P81-120.

64 FLEISHER, M., and ROBINSON, W.O., 1963. Some Problems of the Geochemistry of Fluorine. In Studies in Analytical Geochemistry, Royal Soc. of Canada Spec. Pub. No. 6, P58-75.

65 FLOYD, P.A., and FUGE, R., 1973. Distribution of Fluorine and Chlorine in some Contact and Regionally Metamorphosed Cornish Greenstones. Proc. Ussher Soc., V2, No. 6, P480-481.

66 FOSTER, M.P., 1964. Water Content of Micas and Chlorites. U.S. Geol. Surv. Prof. Papers 474-F, P15.

67 FRANT, M.S., and ROSS, J.W., 1966. Electrode for Sensing Fluoride Ion Activity in Solution. Science, Vol. 154, P1553-1554.

68 FREDERICKSON, A.F., LEHNERTZ, C.A. and KELLOGG, H.E., 1971. Mobility, Flexibility Highlight a Mass Spectrometer-Computer Technique for Regional Exploration. Eng. Min. Jour., V172, No. 6, P116-118.

69 FRERE, F.J., 1961. Specific Microdiffusion Method for the Determination of Fluorine Based on the Lanthanum Alizarin Complexone Color System. Anal. Chem., Vol. 33, P644-645.

70 FRIEDRICH, G.H., and PLUGER, W.L., 1971. Geochemical Prospecting for Barite and Fluorite Deposits. Canadian Inst. Min. Spec. Vol. II, P151-156.

71 FUGE, R., and POWER, G.M., 1969. Chlorine and Fluorine in Granitic Rocks of Southwest England,Geochim et Cosmochim Acta, Vol. 33, P888-889.

72 GANEYEV, I.G., 1962. · On the Possible Transport of Matter in the Form of Complicated Complex Compounds. Geochemistry, No. 10, P1042-1049.

73 GAVRILIN, R.D., AGAFONNIKOVA, L.S., and SAVINOVA, YE.N., 1972. Behaviour of Fluorine in the Initial Stages of Granitization. Geochem. International. Vol. 9, No. 2, P180-185.

74 GERASIMOVSKII, V.I., SAVINOVA, YE. N., 1969. Fluorine Content in Volcanic Rocks of East African Rift Zone. Geochemistry International, Vol. 6, No. 6, P1124-1128.

75 GHOSH, D K., 1927. Petrology of the Bodmin Moor Granite, Cornwall. Mineralogical Mag., Vol. 21, P286.

76 GILLBERG, M., 1964. Halogens and Hydroxyl Contents of Micas and Amphiboles in Swedish Granitic Rocks. Geochim. et Cosmochim Acta, Vol. 28, P495.

77 GISINGER, L., 1968, The Solution of Various Fluorine Compounds in Soil Fluoride, 1, P21-26.

78 GLEVOB, M.P., MAKAGON, V.M., and MAKRYGIN, A.I., 1972. Halos of Pegmatitic Veins in Relation to the Search for Rare Metal Mineralization (In Russ.). Chem. Abstr. 79-81666.

79 GMELINS HANDBOOK OF INORGANIC CHEMISTRY., 1959. Fluorine (Ger). Verlag Chemie, GMBH, Weinheim/Bergstrasse, No. 5, 258PP.

80 GOLDSCHMIDT, V.M., 1954. Geochemistry. Oxford Press, 730P.

81 GORBATSCHEW, A.N., KARPUNIN, A.M. and MATUKANIS, L.F., 1974. Determination of Fluorine by Neutron Activation in the Search for Fluorite Deposits (in Ger.) Zeit. Fur. Angew. Geol., V20, No. 4, P157-8.

82 GORDON, C.C., 1970. Smelter Emissions at Columbia Falls, Montana. Report of the Dept. of Botany, Univ. of Montana, January.

83 GRAHAM, G.S., KESLER, S.E. and VAN LOON, J.C., 1975. Fluorine in Groundwater as a Guide to Pb-Zn-Ba-Fluorite Mineralizatior Econ. Geol., V70, No. 2 P396-98.

84 GREENLAND, L., and LOVERING, J.F., 1966. Fractination of Fluorine, Chlorine and other Trace Elements during Differentiation of a Tholeitic Magma. Geochim et Cosmochim Acta, Vol. 30, P963-982.

85 GREGORY, G.P., 1969. Geochemical Dispersion Patterns Related to Kimberlite Intrusives in North America. PH.D. Thesis, Univ. London.

86 GRIMALDI, F.S., INGRAM, B., and CUTTITTA, F., 1955. Determination of Small and Large Amounts of Fluorine in Rocks. Anal. Chem., Vol. 27, No. 6, P918-921.

87 HALL, A , 1970. The Composition of Cornish Quartz-Porphyry (Elvan) Dykes. Proc. Ussher Soc., Vol. 2, No. 3, P205.

88 HALL, J., and WALSH, J.N., 1962. A Rapid Method for the Determination of Fluorine in Silicate Rocks and Minerals. Anal. Chim. Acta., Vol. 45, No. 4, P341-342.

89 HALL, R.J., 1960. The Determination of Microgram Amounts of Fluorine by Diffusion. The Analyst. Vol. 85, P560-563.

90 HALL, R.J., and CAIN, R.B., 1972. Organic Fluorine in Tropical Soils. New Phytologist, Vol. 71, No. 5, P839-853.

91 HART, E.B., PHILLIPS, P.H. and BOHSTEDT, G., 1934. Relation of Soil Fertilization with Superphosphates and Rock Phosphate to Fluorine Content of Plants and Drainagewaters. Amer. Jour. Pub. Health. V24, P936-940.

92 HAYNES, S.J. and CLARKE, A.H., 1972. Distribution of Chlorine and Fluorine in Granitoid Rock and Associated Ore Deposits, Northern Chile (Abst) Econ. Geol., V67, ND.7, P1005.

93 HEINRICH, E. WM., 1958. Mineralogy and Geology of Radioactive Raw Materials. McGraw-Hill Co., 654P.

94 HEINRICH, E. WM., 1966. The Geology of Carbonatites, Rand McNally Co., 555P.

95 HEM, J.D., 1968. Graphical Methods for Studies of Aqueous Aluminium Hydroxide, Fluoride and Sulfate Complexes U.S.G.S. Water Supply Paper 1827-8, P81-833.

96 HOLLINGWORTH, R.P., 1957. Spectrophotometric Determination of Fluorine in Rocks. Anal. Chemistry, V29, PP1130.

97 HOLMAN, R.H.C., 1956. Applied Geochemical Studies in Uganda and Sierra Leone. Ph.D. Thesis, University of London.

98 HOSKING, K.F.G. and SHRIMPTON, G.J., 1964. Present Views of Some Aspects of the Geology of Cornwall and Devon. Royal Geol. Soc. of Cornwall.

99 HOSKING, K.F G., HOSKING, J.A., THOMAS, G.S., USMAN, H. and PISARSKI, J.B., 1964. The Distribution of Tin, Copper, Zinc, Beryllium and Phosphorus in the Stream Sediments of the Lands End Peninsula, Cornwall. Camborne School of Mines Mag., V64, P1.

100 HOSKING, K.F.G., OLINZE, S.K., LEE, J.Y., MITCHELL, D., and MUGENYI, Y.H.K., 1965. A Reconnaissance Survey of the Distribution of Tin, Copper, Zinc and Arsenic in the Sediments of the Rivers to the South of the St. Austell Granite Mass, Cornwall. Camborne School of Mines Mag., V65, P30-42.

101 HOSKING, K.F.G., 1971. Problems Associated with the Application of Geochemical Methods of Exploration in Cornwall, England. In Can. Inst. Min. Spec. Vol. 11, (Boyle, R.W. and McGerrigle, J.I. Eds.), P176-189.

102 HUANG, W.H., and JOHNS, W.D., 1967. The Chlorine and Fluorine of Geochemical Standards. Geochim. Cosmochim. Acta., V31, P597.

103 HUBNER, M., 1969. Geochemical Interpretation of Experimental Investigations of the Substitution of Fluorine for Hydroxyl Groups in Clay Minerals (In Ger.). Deut. Ges. Geol. Wiss. Ber. Reile. B., Mineral Lagerstatten Forsch, V14, No. 1, PP5-15.

104 INGRAM, B.L. and MAY, I., 1971. Determination of Fluorine in Silicate Rocks with a Specific Ion Electrode. US Geol. Surv. Prof. Pap. 750-B, P180.

105 ISKIV, B.M. and SAVADSKII, O.A., 1968. Role of Mineral Indiators in Evaluation of Secondary Dispersion Haloes of Rare-Metal Pegmatites in the Kalba Territory (In Russ.) Chem. Abstr. 75-99925.

106 JAHNS, R.H., 1955. The Study of Pegmatites. Econ. Geol., 50th Anniv. Vol. V2, P1025-1130.

107 JAMES, L.D., 1965. Regional Geochemical Reconnaissance in the Northern and Southern Sections of the Sula Mountains Schist Belt, Sierra Leone. Ph.D. Thesis. Univ. London.

108 JEDWAB, J., 1958. Looking for Kimberlite Diamond Pipes by Geochemical Prospecting. India, Madhya Pradesh.

109 JEDWAB, J., 1959. Prospection Geochimque de Kimberlite Diamantifera au Congo Belge. Soc. Belge. Geologie Paleontologie, et Hydrologie Bull.

110 JOHNSTON, W.B. and OLSEN, R.A., 1972. Dissolution of Fluorapatite by Plant Roots Soil Sci., V114, P29-36.

111 KESLER, S.E., VAN LOON, J.C. and BATESON, J.H., 1973(A). Analysis of Fluoride in Rocks and an Application to Exploration. Jour. Geochem. Expl., V2, No.2 P11-17.

112 KESLER, S.E., VAN LOON, J.C. and MOORE, C.M., 1972 (A). Evaluation of Ore Potential of Granodioritic Rocks using Water-Extractable Chloride and Fluoride. Can. Min. Metall. Bull. Feb. P56-60.

113 KESLER, S.E., ISSIGONIS, M. and VAN LOON, I.C., 1975(A). An Evaluation of the Use of Halogen and Water Abundances in Efforts to Distinguish Mineralized and Barren Intrusive Rocks. Jour. Geochem. Explr., V4, No.2, P235-245.

114 KESLER, S.E. ISSIGONIS, M.J., BROWNLOW, A.H., DAMON, P.E., MOORE, W.J., NORTHCOTE, K.E. and PRETO, V.A., 1975 (A). Geochemistry of Biotites from Mineralized and Barren Intrusive Systems. Econ. Geol. V70, P559-567.

115 KLUEV, O.S. and KONONKOV, N.A., 1971. Endogenous Geochemical Haloes of Pneumatolytic-Hydrothermal Beryllium Deposits, Compared with Mica Deposits (In Russ.), Chem. Abstr. 77-77867.

116 KOCHEMASOV, G.G., 1968. Endogenic Geochemical Haloes of Pegmatitic Tantalum Deposits (In Russ.). Chem. Abstr. 72-92171.

117 KOGARKO, L.N. KRIGMAN, L.D., and SHARUDILO, N.S., 1968. Experimental Investigations of the Effect of Alkalinity of Silicate Melts on the Separation of Fluorine into the Gas Phase. Geochemistry International, No.4, P782-790.

118 KOKSOY, M., 1967. Dispersion of Mercury and Ore Elements from Mineral Deposits in Turkey. Ph.D. Thesis, Univ. London.

119 KOKUBU, N., 1956. Fluorine in Rocks Proc. Fac. of Sci., Kyushu Univ., Ser C, V2, No. 3, P96-145.

120 KOMAROV, D.V., and NAKTINAS, E.U., 1965. Fluorine, Chlorine and Boron as Indicating Elements During Geochemical Prospecting (Russ.). Geology of Ore Deposits, USSR Acad. Sci., Vol. 7, No. 3, P65.

121 KOMAROV, P.V. and GLAGOLEV, A.A., 1969. Use of Fluorimetric Surveying in Prospecting for Mineral Deposits related to Alkaline-Ultrabasic and Alkaline Massifs (In Russ.) Chem. Abstr., V73, No. 6, Item No. 58022G, P117, Also Econ. Geol., V69, No. 4 1974, PP532-33.

122 KORITNIG, S., 1951. Investigations on the Geochemistry of Fluorine (Ger.). Geochim et Cosmochim Acta, Vol 1, P89-116.

123 KORITNIG, S., 1955. A Geochemical Study of the Element Fluroine. Der. Aufschlu., Vol. 6, No. 2, P20-24.

124 KORITNIG, S., 1963. On the Geochemistry of Fluorine in Sediments (Ger). Fortschritte in Der Geologie Von Rheinland Und Wesfallen, Band 10, St. 8, Krefeld, Okt. P231.

125 KORZHINSKY, D S., 1955. Outline of Metasomatic Processes (Russ). 2nd Ed. Moskwa, Akad. Nauk. USSR.

126 KOSALS, YA. A., 1968. Geochemistry of Be, B, Li, and F in the Process of Formation of Limestone Skarns, Gorny Altai. Geochemistry International, Vol. 5, No. 1, P131-140.

127 KOSTERIN, A.V., 1959. The Possible Modes of Transport of the Rare Earths by Hydrothermal Solutions. Geochemistry, No. 4, P381-387.

128 KOZLOVA, O.G., 1957. Rare Earths in Fluorites from Different USSR Locations. Geochemistry, No. 1, P53-68.

129 KRAINOV, S.R., 1967. Hydrogeochemistry of Fluorine in Regions of Fluroine-Bearing Deposits (Russ). Vyssh. Ucheb. Zaveb. Izv., Geol Kazved, No.12, P30-40.

130 KRAINOV, S R., RUBEIKAN, V.Z., KAPRANOV, S.D., and PETROVA, N.G., 1969. Highly Alkaline (pH 12) Fluosilicate Waters in the Deeper Zones of the Lovozero Massif. Geochemistry International. Vol. 6, No.4, P635-640.

131 KRAUSKOPF, K.B., 1969. Relative Volatilites of Fluorides and Chlorides of Ore-Forming Metals in Magmatic Gases. In Problems of Geochemistry. (Khitarov, N.I. Ed), Israel Prog. for Sci. Translation, P155-165.

132 KRIVONOV, V.F. and ROMANOV, N.N., 1971. Complex Methods in the Prospecting of Kimberlites in Yakutta (Russ.). Geol. Geofiz., V2, P146-150, Also Chem. Abstr. 76-61736.

133 LALONDE, J.P. 1974. Research in Geochemical Prospecting Methods for Fluorite Deposits., Madoc Area, Ontario, Geol. Surv. Canada Paper 73-38, 56P.

134 LALONDE, J.P. 1975. Fluorine - A Geochemical Indicator of Mineral Deposits. 77th Annual Gen. Program. Can. Inst. Min. Metall. Toronto.

135 LANG, A.H., GRIFFITH, J.W. and STEACY, H.R., 1962. Canadian Deposits of Uranium and Thorium. Geol. Surv. Canada, Econ. Ser. No.16, 324P.

136 LARSEN, E.S., and DRAISIN, W.M., 1950. Composition of the Minerals in the Rocks of the Southern California Batholith. Internt. Geol. Congr. 18th Session, Gt. Britain, Pt2, P66.

137 LARSEN, S., and WIDDOWSON, A.E., 1969. The effect of Fluoride on the Reactivity of Fertilizer Phosphate Soil. Phosphorus in Agriculture, Bull. DOC. No. 54, P11-16.

138 LEBEDEVA, K.W., 1969. Fluorine as a Hydrochemical Criterion during Prospecting for Tin Deposits (Russ.). Zap. Leningrad Gorn. Inst., Vol. 56, No. 2, P92-97.

139 LEWIS, H.P., 1931. A sandstone with Fluorspar Cement and Other Sandstones from West Cumberland. Geol. Mag., V68, P543-557.

140 LITINSKIY, V.A., 1961. The Amount of Ni, Cr, Ti, Nb and Some other Elements in Kimberlites and the Geasibility of Applying Geochemical Methods when Searching for Kimberlite Bodies. Geochemistry, V9.

141 LITINSKIY, V.A., 1963. Application of Metallometry and Kappametry in Prospecting for Kimberlite Bodies. Internat. Geol. Rev., V6, No. 11.

142 LUTZE, H., 1974. Ein Beitrag Znr Anwendung der Neutronenaktivierungsanalyse Bei der Flueriterkundun (In Ger.) Zeit. Fur. Angew. Geol., V20, P485-490.

143 LUTZENS, H. and ZIMMERMAN, G., 1974. The Use of Soil Geochemical Studies in the Prospection and Exploration for Fluorite Veins Covered by Loose Material in the Lower Harz Mntns, Germany, (In Ger.) Zeit Angew Geol. V20, No. 1, P1-8.

144 LYAKHOVICH, V.V., and BARINSKII, R.L., 1961. Characteristics of the Rare Earth Assemblages in the Accessory Minerals of Granitoids. Geochemistry, No. 6, P495-509.

145 MACINTIRE, W.H., 1942. Fluroine Content of Plants Fertilized with Phosphates and Slags Containing Fluorides. Indus. and Engin. Chem., V34, P1490-1499.

146 MACINTIRE W.H. SHAW W.M. and ROBINSON, B., 1955. Behavious of Incorporations of Potassium and Calcium Fluorides in a Siz Year Lysimeter Study, Jour. Agric. and Food Chem., V3, P772-777.

147 MANN, A.W., and TURNER, A.G., 1972. Excess Calcium Fluoride in Fluorapatite. Australian Jour. of Chemistry, Vol 25, No.12, P2701-2703.

148 MARIER, J.R., 1971. Fluoride in the Environment. In Internat. Symp. on Identification and Measurement of Environmental Pollutants, Ottawa, P404-406.

149 MARIER, J.R., and ROSE, D., 1971. Environmental Fluoride, Nat. Res. Council, Canada, Publ. No.12, 226, 35PP.

150 MARSHALL, H.L., JACOB, K.D. and REYNOLDS, D.S., 1935. Occurrence of Fluorine in Natural Phosphates, Ind. and Eng. Chem., V24, V01, P86-89.

151 MATUURA, S., KOKUBU, N , WAKIMOTO, S and KOGA, A., 1954. Fluorine Content in Plants. Mem. Fac. Sci. Kyushu Univ., Ser C. V2, No.1, P1-36.

152 McCONNELL, D., 1971. Crystal Chemistry of Phosphorite. Econ. Geol., Vol.66, P1085-1086.

153 McCONNELL, D., 1973. Apatite - Its Crystal Chemistry, Mineralogy, Utilization and Geologic and Biologic Occurrence. Springer-Verlag, 111P.

154 MESMER, R.E., and BAES, C.R., JR., 1969. Fluoride Complexes of Beryllium II in Aqueous Media. Inorganic Chem., Vol. 8, No. 3, P618-626.

155 MICHAEL, G. and BLUME, B., 1952. Ueber den Fluorgehalt Thuringer Bunsandstein und Muschelkaikboden und Dessen Bedeutung Fur Die Loslichkeit der Phosporsaure (In Ger.) Chem. Erde., V17, P27-48.

156 MICHAEL, S.S., MYERS, J.O. and YOUNG,' P.A., 1973 Geochemical Contamination and Fluorspar Prospecting in Derbyshire. Inst. of Min. and Metall. Sect. 3, Vol.82, P131-134.

157 MINEYEV, D.A., 1962. Geochemical Differentiation of the Rare Earths. Geochemistry, No.12, P1129-1149.

158 MISER, H.D. and ROSS, C.S., 1923, Diamond Bearing Peridotite in Pike County, Arkansas. US Geol. Surv. Bull. 735-I.

159 MISER, H.D. and PURDUE, A.H., 1929. Geology of the Dequeen and Caddo Gap Quadrangles, Arkansas, US Geol. Surv. Bull. 808.

160 MOGAROVSKII, V.V., 1971. Beryllium in Granites of the Pegmatite-Bearing Pamir-Shugnan Complex, Southern Pamirs (In Russ). Chem. Abstr. 76-48411.

161 MORISSEY, C.J., 1970. . The Mineralogy, Structure and Origin of the Lead-zinc-copper Residual Orebody at Tynagh, Co. Galway, Ireland. PhD Thesis, Imperial College, Univ. of London.

162 NACKOWSKI, M.P., 1952. Geochemical Prospecting applied to the Illinois-Kentucky Fluorspar Area. PhD Thesis, Univ. of Missouri, USA, 144PP.

163 NEMEC, D., 1968. Fluorine in Lamprophre and Lamproid Rocks. Geochim et Cosmochim Acta, Vol.32, P523.

164 NEMEC, D., 1969. Fluorine in Tourmalines. Contrib. Mineral. Petrology-Beitr. Mineral Petrologie, Vol. 20, No.3, P235-243.

165 NEY, C.S., ANDERSON, J.M., and PANTELEYEV, A., 1972. Discovery, Geologic Setting and Style of Mineralization, Sam Goosly Deposit, British Columbia, Canada. Can. Inst.Of Min. and Metall. Bull., Vol.65, No.723, P53-64.

166 NIXON, P.H. Ed., 1973. Lesotho Kimberlites. Lesotho Nat.Dev. Corp.

167 NOBLE, D.C., SMITH, V.C., and PECK, L.C., 1967. Loss of Halogens from Crystallized and Glassy Silicic Volcanic Rocks. Geochim et Cosmochim Acta, Vol. 31, No. 2, P215-223.

168 OKIKADAZE, G. L., 1971. Fluorine Distribution in Granitic Rocks of the Greater Caucasus and Dzhirul Crystalline Massif. Geochemistry International, No. 5, P314-323.

169 OELSCHLAGER, W. and HOHENHEIM, D.D.R., 1971. Fluoride Uptake in Soils and its Depletion, Fluoride, V4, P80-84.

170 OKAMURA, T. and MATSUHISA, T., 1967. The Fluoride Content of Favorite Foods of Japânese. Jap. J. Publ. Health, V14, P41.

171 ORION RESEARCH. 1971. Instruction Manual, Fluoride Electrode Model 94-09, Cambridge Mass. Orion Research Inc.

172 PARRA, P., 1974. Prospeccao Geoquimica de Quimberlitos Nas Bacias Fluviais do Lufule do Caculo. Bull. Servicos de Geolgia e Minas de Angola, No. 25, P35-59.

173 PARRY, W.T. and JACOBS, D.C., 1975. Fluorine and Chlorine in Biotite from Basin and Range Plutons, Econ. Geol. V70, P554-558.

174 PERELMAN, A.I., 1967. Geochemistry of Epigenesis (Russ. Trans.). Plenum Press, N.Y., 266PP.

175 PETERS, M.A., and LADD, D.M., 1971. Determination of Fluoride in Oxides with the Fluoride-ion Activity Electrode. Talanta, Vol. 18 No. 7, P655-664.

176 PLUGER, W.L., and FRIEDRICH, G.H., 1972. Determination of Total and cx-Fluoride in Soils and Stream Sediments with an Ion-Sensitive Electrode. In porc. 4th Int. Geochem. Exploration Symposium, London, P421-428.

177 POKORNY, J., 1975. Geochemical Prospecting for Ores in the Bohemian Massif. Czechoslovakia. In Geochemical Exploration 1974 (Elliott, I.L. and Fletcher, W.K. Eds.) Elsevier Sci. Publ. Co., P77-84.

178 RABINOVICH, YA. I., 1973. Fluorine as an indicator of Nickel Sulfide Mineralization in the Ultramafic Rocks of Pechaga, Geochem. Int., V10, No. 3, P716.

179 RAYMENT, B.D., Davis, G.R. and WILSON, J.D., 1971. Controls to Mineralization at Wheal Jane, Cornwall, Trans. Inst. Min. Metall. V80, P224-237.

180 REEDMAN, J.H., 1974. Residual Soil Geochemistry in the Discovery and Evaluation of the Bütiriku Carbonatite, South East Uganda. Trans. Inst. Min. Metal., V83, PB1-B12.

181 REID, C. and FLETT, J.S., 1907, Geology of the Lands End. Mem. Geol. Surv. Grt. Brit.

182 RIMSAITE, J., 1967. Studies of Micas from Uncommon Rocks. 1. Micas from Nepheline Syenite, Blue Mountain, Ontario and from Carbonatite, Oka, Quebec, Canadian Mineralogist, Vol. 9, P304.

183 RIMSAITE J.H.Y., 1967, Studies of Rock Forming Micas. Geol. Surv. Canada Bull, 149. P1.

184 RIMSAITE, J.H.Y., 1970. Structural Formulae of Oxidized and Hydroxyl-Deficient Micas and Decomposition of the Hydroxyl-Group. Beitr. Mineral. Petrog., Vol. 25, P225.

185 ROBINSON, W.O., and EDGINTON, G., 1946. Fluorine in soils. Soil Science, Vol. 61, No. 5, P341-353.

186 ROEDDER, E., 1972. Composition of Fluid Inclusions. US Geol. Surv. Prof. Pap. 440JJ, 164.

187 ROMNEY, E.M., and WOOD, R.A., 1969. Radioactive Fluorine 18 in Soils and Plants, Soil Science, Vol.108, P419-423.

188 ROMO, L.A., and ROY, R., 1954. F-OH Exchange in Layered Silicates (Abstr.) In Proc. of the 3rd National Conf. on Clays and Clay Minerals, P402.

189 ROWE, R.B., 1952 Petrology of the Richardson Radioactive Deposit, Wilberforce, Ontario. Geol. Surv. Can. Bull. 23.

190 SAHAMA, Th. G., 1948. On the Chemistry of the East Fennos Canadian Rapakivi Granites. Bull. Comm. Geol. Finlande, No.136.

191 SALISH, L.I., 1969. Fluorine Primary and Secondary Dispersion Haloes in Aurakmat Ore Field, Chatkal Area (Russ.) Nauch Tr. Tashkent. Gos. Univ., No.325, P138-144.

192 SALISH, L.I., 1969. Fluorine Primary and Secondary Dispersion Haloes in the Deposits of the Chatkal-Kurama Area (Russ.) Nauch. Tr. Tashkent. Gos. Univ. No.325, P128-137.

193 SAMSON, H.R., 1952. Fluorine Adsorption by Clay Minerals and Hydrated Alumina. Clay Minerals Bull., Vol 1, P266-270.

194 SAVCHENKO, G.S., and TANANAEV, I.V., 1951. About the forms of Complex Fluorine-Aluminates in Water Solutions (Russ.) Zhurn. Obshch. Khim., Vol.21, No.12.

195 SCHERBA, G.N., ZAMYATINA, G.M., KALININ, S.K. and MUKHLYA, K.A., 1966. Germanium in some Greisens in Kazakhstan, Geochemistry, No.11, P1091-94.

196 SCHWARTZ, M. O., and FRIEDRICH, G. H., 1973. Secondary Dispersion Patterns of Fluoride in the Osor Area, Province of Gerona, Spain. Jour. of Geochem. Exploration, Vol. 2, No. 2, P103-114.

197 SCWARTZ, M. O. and FRIEDRICH, G. H., 1973. Secondary Dispersion Patterns of Fluoride in the Osor Area, Province of Gerona, Spain. Jour. Geochem. Explr. V2, No. 2, PP103-114.

198 SEN GUPTA, J. G., 1968, Determination of Fluorine in Silicate and Phosphate Rocks, Micas and Stony Meteorites. Anal. Chi. Acta., Vol. 42, P119.

199 SERAPHIM, R. H., 1951. Some Aspects of the Geochemistry of Fluorine. PhD Thesis, Mass. Inst. of Tech., USA 96P.

200 SHAPIRO, L., 1967. A simple and Rapid Indirect Determination of Fluorine in Minerals and Rocks. U. S. G. S. Prof. Paper 575-D, PP233-235.

201 SHCHERBINA, V. V., 1959. Factors Determining the Geochemical Distribution of Scandium. Geochemistry, No. 8, P882-886.

202 SHCHERBINA, V. V., 1963. Occurrence of Elements as Chlorides and Fluorides in Nature Depending on the Position of the Elements in the Periodic Table. Geochemistry, No. 8, P751-755.

203 SHEPHERD, E. S., 1935. Volatile Constituents of Rocks - Fluorine. Carnegie Inst. Wash. Year Book, No. 34, P98-100, 1934-35.

204 SHIPULIN, F. K., GENKIN, A D., DISTLER, V. V., KOMAROV, P. V., MALINOVSKI, E. P., OZEROVA, N. A., PERELMAN, A. I., REKHAVSKII, V. I., ROZANOV, YU. A., FILIMONOVA, L. G., CHEMYSHEV, V. F., and ELINSON, M. M., 1973. Some Aspects of the Problem of Geochemical Methods of Prospecting for Concealed Mineralization. Jour. of Geochemical Exploration. Vol. 2, No. 3, P193-236.

205 SKVORTSOV, V V., and PRIKAZCHIKOV, L.A., 1970. Possible Use of Geochemical Prospecting for Pegmatites in the Korosten Pluton (In Russ.) Chem. Abstr. 74-114331.

206 SRINIVASAN, K. and RECHNITZ, G.A., 1968. Activity Measurements with a Fluoride Selective Membrane Electrode Anal. Chem. V40, No. 3, P509.

207 STAVROV, O.D., and BYKOVA, T.A., 1961, Distribution of Some Rare and Volatile Elements in the Rocks and Pegmatites of the Koroster, Skii Pluton. Geochemistry, No. 4, P370-374.

208 STRUBEL, G., 1965. Quantitative Untersuchungen Uber Die Hydrothermale Loslichkeit Von Flubspat (CAF2) Neues JahrB. Mineral. Monatsh., V83.

209 STUART, J.L., 1970. A Simple Diffusion Method for the Determination of Fluoride. The Analyst, Vol. 95, P1032-1038.

210 TABORSZKY, F.K., 1972. Geochemie Des Apatites in Tiefengesteinew am Beispiel des Odenwaldes. (In Ger.) Beitr. Mineral.Petrog. V8, P354.

211 TAGEEVA, N V., 1943. Geochemistry of Boron and Fluorine (Russ.) Priroda, Akad. Nauk. SSSR, Vol. 32, No. 6, P25-35.

212 TAUSON, L.V., 1967. Geochemical Behaviour of Rare Elements during Crystallization and Differentiation of Granitic Magmas. Geochem. Intern., Vol. 4, No. 6, P1067.

213 TEH, G.H., FUNG, K.W. and HOSKING, K.F.G., 1975. Use of Fluorine to Trace Sub-outcropping Tin Deposits at Tedda Hill in Perak, Malaya in Newsletter of Commonwealth Geological Liaison Office, Sept.

214 TERASHIMA, S., 1974. Spectrophotometric Determination of Chlorine and Fluorine in the Standard Silicate Rocks. Bull. Geol. Surv. Japan, V25, No. 4, P29-34.

215 TILSLEY, J.E., 1975. Application of Geophysical, Geochemical and Deep Overburden Sampling Techniques to Exploration for Fluorspar in Glaciated Terrain in Prospecting in Areas of Glaciated Terrain, Inst. Min. Metall. Publ., (Jones, M.J. Ed.), P126-133.

216 TUTTLE, O.F , and GITTINS, J., 1967. Carbonatites. Wiley Interscience Publishers, 591 PP.

217 UNDERWOOD, E.F , 1962. Trace Elements in Human and Animal Nutrition. Academic Press, N.Y., 429PP.

218 USSHER, W.A.E., BARROW, G., and MACALISTER, D.A., 1909. The Geology of the Country Around Bodmin and St. Austell, Mem. Geol. Surv. Gt. Brt.

219 VAN ALSTINE, R E., 1965. Geochemical Prospecting in the Brown Canyon Fluorspar District, Chaffee County, Colorado. U.S.G.S. Prof. Pap. 525-D, P59.

220 VAN LOON, J.C., 1968. The Rapid Determination of Fluoride in Mineral Fluorides using a Specific Ion Electrode. Anal. Letters. Vol. 1, No. 6, P393-398.

221 VAN WAMBEKE, L., 1970. Geochemical Prospecting and Appraisal of Niobium-Bearing Carbonatites by X-ray Methods. Econ. Geol., V55, No. 4, P732-758.

222 VINOGRADOV, A.P., 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau Inc., New York.

223 VLASOV, K.A., KUZMENKO, M V. and ESKOVA, E.M., 1966. The Lovozero Alkali Massif (Trans of Russ. 1959) Oliver and Boyde, 625P.

224 VOROSHILOV, YU. I., 1966. Geochemical Behaviour of Fluorine in the Ground Waters of the Moscow Region. Geochemistry International. No. 2, P261.

225 VOSKRESENSKAYA, N.T., 1959. Geochemistry of Thallium and Rubidium in Igneous Rocks. Geochemistry, No. 6, P599-611.

226 WAGNER, P.A., 1914. The Diamond Fields of South Africa. Transval. Leader, Johannesburg, 347P.

227 WALSH, J., 1969. Mineral and Thermal Waters of Kenya. 23rd Inter. Geol. Congress. Procc. Sympos. 2, Prague.

228 WARREN, L.J., and KITCHENER, J.A., 1972. Role of Fluoride in the Flotation of Feldspar. Adsorption on Quartz, Corundum and Potassium Feldspar. Trans. Inst. Of Min. and Metall. Sect C.

229 WATTS, J.T., 1960. The Secondary Dispersion of Niobium from Pyrochlore Carbonatites in the Feira District, Northern Rhodesia. PhD Thesis, Univ. London.

230 WATTS, J.T., TOOMS, J.S. and WEBB, J.S., 1962. Geochemical Dispersion of Niobium from Pyrochlore-Bearing Carbonatites in Northern Rhodesia. Trans. Inst. Min. Metal. V72, Pt. 2, P729-747.

231 WEBB, J.S., 1947. The Origin of the Tin Lodes of Cornwall. PhD Thesis, Imperial College, Univ. London.

232 WEBB, J.S., 1956. Observations of Geochemical Exploration in Tropical Terrains. Exploration Geoquimica Symposium, Primer Tomo, Mexico, P143-172.

233 WHITE, D.E. and WARING, G.A., 1963. Volcanic Emanations. In Data of Geochemistry 6th Ed. U.S.G.S. Prof. Pap. 440K, 27P.

234 WHITE, D.E., HEM, J.D., and WARING, G.A., 1963. Chemical Compositions of Subsurface Waters. U.S.G.S. Prof. Pap. 440-F, P1-67.

235 WILLARD, H.H. and WINTER, O.B., 1933. Volumetric Method for the Determination of Fluorine. Ind. Engng. Chem., Analyt. Edn. V5, P7-10.

236 WILLIAMS, A.F., 1932. The Genesis of the Diamond, Ernest Benn Ltd. Vol 1 and 2.

237 WYLLIE, P.J., and TUTTLE, O.F., 1961. Experimental Investigation of Silicate Systems Containing Two Volatile Components. Part II. Am. J. Sci., Vol. 259, P128.

238 WYLLIE, P.J., 1967. Ultramafic and Related Rocks. John Wiley and Sons. Publ., 464.

239 YOSHIDA, M., TAKAHASHI, K., and YONEHARA, N., 1971. Fluorine Chlorine, Bromine and Iodine Contents of Volcanic Rocks in Japan. Bull. Chem. Soc. Japan, Vol. 44, No. 7, P1844-1850.

240 YOUNG, E.G., and LANGILLE, W.M., 1968. Sea Occurrence of Inorganic Elements in Marine Algae of the Atlantic Provinces of Canada. Can. J. Bot., Vol. 36, P301.

241 YUSUPOV, S. SH., 1973. Fluorine Negative Anomalies in Granites Surrounding Chamber Pegmatites. Inter. Geol. Revs., Vol. 15, No. 3, P320-327.

242 ZAGORSKII, V.E., TESTOV, V.I., ZAGOSKINA, E.I. and SHIMANSKII, A.A., 1971. Biogeochemical Methods for Prospecting Mica-Bearing Pegmatites. (In Russ.) Chem. Abstr. 79-33589.

243 ZAGORSKII, V.E., 1972. Mineral and Element Haloes Near Mica-Bearing Pegmatite Bodies of Different Types (In Russ.) Chem. Abstr. 79-81667.

APPENDIX I

REFERENCES FOR TABLE 1.1

1. Allman and Koritnig, 1972, In Data of Geochemistry, Sec. 9, Springer-Verlug, Berlin.
2. Altschuler et al, 1959, U.S. Geol. Surv. Prof. Tup. 314-p, p.45-90.
3. Borneman-Starynkeviel and Myasnikov, 1950, In Deer et al, 1967, See Ref. 17.
4. Bouvier, 1970, In Allman, R. and Koritnig, S., Data of Geochemistry, Sec. 9, Springer-Verlag, Berlin.
5. Buddington, 1952, Amer. Jour. Sci., Bowen Vol., p.37.
6. Buddington and Leonard, 1953, Amer. Mineral., V.38, p.891.
7. Carpenter, 1969, Geochim. et Cosmochim. Acta, 733, No.10, p.1153-1167.
8. Cerna et al,1972, Canadian Mineral., VII, p643-659.
9. Cerna et al, 1973, Amer. Mineral., V58, p.291-301.
10. Cerny and Fovandra, 1972, N. Jb. Miner. Mh., V.9, p.400-406.
11. Coasts and Fakey, 1944, In Deer et al, 1967, See Ref. 17.
12. Compton, 1958, Amer. Mineral., V.43, p.890.
13. Cooray, 1970, Amer. Mineral., V.55, p.2038-2041.
14. Correns, 1956, In Physics and Chemistry of the Earth, V.1, p.181-233.
15. Deans, 1966, In Tuttle and Gittens, 1966, Carbonatites, Wiley Interscience Publ., 591p.
16. Deer, 1937, In Deer et al, 1967, See Ref. 17.
17. Deer et al, 1967, Rock forming minerals, London, Longmans Publ., Vols. 1-5.
18. Dietz et al, 1942, Bull. geol. Soc. Amer., V.53, p.815.
19. Dimitriyev et al, 1962, Geochem. Inter., No.3, p.248-266.
20. Drever, 1936, In Deer et al, 1967, See Ref. 17.
21. Engel. 1959, Bull. Geol. Soc. Amer., V. 70, p.951.
22. Engel and Engel, 1960, In Deer et al, 1967, See Ref. 17.
23. Engel et al, 1961, US Geol. Surv. Prof. Pap. 424-C, p.313-316.
24. Engel and Engel, 1960, Bull., Geol Soc. Amer., V. 71, p.1.
25. Exley and Stone, 1964, In Present Views of Some Aspects of the Geology of Cornwall and Devon (Hosking, K. F. and Shrimpton, G. J. eds.) Royal Geol. Soc. Cornwall, p.129-184.
26. Foit, 1973, Canadian Mineral, V.11, p.940-951.
27. Frank-Kamenetskii and Veselskii, 1961, Geochem. Inter. V.11, p.1158-1159.
28. Grelin, 1959, Handbook of Inorganic Chemistry, Verlag Chemie, GMBH, Weinheim/Bergstrasse, No. 5, 258 p.
29. Gerasimovskiy et al, 1966, Geochemistry of the Lovozero Alkaline Massif, Trans Australian Univ. Nat. Press, 2 parts.

30. Ghent, 1972, Canadian Mineral., V.11, p. 526-530.

31. Ginzburg and Yukhnevich, 1962, Geochem. Inter., No. 1., p.31-36.

32. Glass et al, 1944, In Deer et al, 1967, See Ref. 17.

34. Grigorev, 1939, Amer. Mineral., V. 22, p.169-177.

35. Groves, 1972, Econ. Geol., V. 67, p.445-457.

36. Gulbrandsen, 1966, Geochim. et Cosmochim. Acta, V.30, p.769-773.

37. Hallimond, 1943, Min. Mag., V.28, p.230.

38. Hamaguchi and Shimoda, 1953, Jour. Chem. Soc. Japan, Pure Chem. Soc., V. 74, p.879-884.

39. Harken, 1954, In Deer et al, 1967, See Ref. 17.

40. Haynes and Clark, 1972, Econ. Geol., V. 67, No. 7, p.1005.

41. Heinrich 1953, In Correns, 1957, N. Jb. Miner., Abh. Bd. 91, p.239-256.

42. Howie, 1955, Trans. Roy. Soc. Edinburgh, V. 62, p.725.

43. Hunter, 1972, Trans. Geol. Soc. South Africa, V.75, pt.3., p.293-294.

44. Hurlbut, 1955, Amer. Mineral., V.40, p.118.

45. Hutton, 1947, In Deer et al, 1967, See Ref. 17.

46. Invantshin et al, 1964, Geochem. Inter., No. 2., p.372-387.

47. Kind, 1938, Chem. d. Erde., V.12, p.50.

48. Kokubu, 1956, Kyushu Univ. Ser. C., No. 2, p.95-149.

49. Koritnig, 1951, Geochim. et Cosmochim. Acta, V.1, p.89-116.

50. Kosals and Maxurov, 1968, Geochem. Inter., No. 5., p.1024-1034.

51. Kostekskaya, 1968, Geochem. Inter., No. 3, p.519-524.

52. Kostetskaya and Mordvinova, 1965, Geochem. Inter., No. 5, p.927-936.

53. Kostetskaya and Mordvinova, 1968, Geochem, Inter., No. 5, p.519-524.

54. Kostetskaya et al, 1969, Geochem. Inter., No. 1, p.72-79.

55. Kunitz, 1924, N. Jb. Miner., Bd.50, p.365.

56. Lambert, 1959, Roy Soc. Edinburgh, V.63, pt.3, p.557-588

57. Larsen and Draisin, 1948, In Deer et al, 1967, See Ref. 17.

58. Larsen and Draisin, 1950, Int. Geol. Congress, 16th Session, pt. 2, p.66.

59. Leake, 1968, Jap. Jour. Geol. Geogr., V.33, p.1.

60. Lee and Van Loenen, 1970, US Geol. Surv. Prof . Pap. 700-D, p.296-306.

61. Leelandam, 1969, N. Jb. Miner., No. 8, p.461-468.

62. Lellandam, 1970, Jour. Petrol., V11, p.475.

63. Lisitsina et al, 1965, Geochem. Inter., No.3, p.463-475.

64. Litvin et al, 1964, Geochem. Inter., No.5, p.1003-1005.

65. Lokka, 1950, Bull. Comm. Geol. Finlande, V.151, 75p.

65 a) Lyons, 1972, Amer. Mineral, V.57, p.1404-1412.

66. Mackenzie, 1953, In Deer et al, 1967, See Ref. 17.

67. Mathes, 1950, N. Jb. Miner., p.29.

68. Meen, 1939, In Deer et al, 1967, See Ref. 17.

69. Muthuswam, 1958, In Deer et al, 1967, See Ref. 17.

70. Mysanikov, 1950, In Deer et al, 1967.

71. Nash, 1972, Geochim. et Cosmochim. Acta, V36, p.1313-1319.

72. Nash, 1972, Bull. Geol. Soc. Amer., V.83, p.1361-1382.

73. Nel, 1946, Amer. Mineral., V.31, p.51-57.

74. Nemec, 1968, Geochim. et Cosmochim. Acta, V32, p.523.

75. Nemec, 1969, Geochem. Inter. No.1., p.58-68.

76. Nemec, 1969, Contrib. Mineral. Petrol.-Beiter. Mineral Petrol., V.20, p.235-243.

77. Nemec, 1968, Geochem. Inter. No. 1, p.141-147.

78. Okikadze, 1971, Geochem. Inter., No.3, p.314-323.

79. Perrault, 1968, Canadian Mineral., V.9, p.381-401.

80. Quensel and Gabrielson, 1939, In Deer et al, 1967, See Ref. 17.

81. Rabbitt, 1948, Amer. Mineral., V.33, p.263.

82. Rankama, 1938, In Deer et al, 1967, See Ref. 17.

83. Ribbe and Rosenberg, 1971, Amer. Mineral., V.56, p.1812-1821.

84. Rimsaite, 1967, Geol. Surv. Canada Bull. 149.

84 a) Rinaldi et al, 1972, Canadian Mineral. V.11, p.690-707

85. Roegge et al, 1972, Econ. Geol. V.67, p.1009.

86. Rosenzweig and Watson, 1954, Amer. Mineral., V.39, p.581.

87. Sahama, 1946, In Deer et al, 1967, See Ref. 17.

88. Sahama, 1953, In Deer et al, 1967, See Ref. 17.

89. Seki and Yamasaki, 1957, Amer. Mineral., V.42, p.506.

90. Seraphim, 1951, Ph.D. Thesis, Mass. Inst. Tech., 96p.

91. Shaw et al, 1963, Canadian Mineral., V.7, p.578-616.

92. Shaw et al, 1965, Can. Jour. Earth sci., V.2, p.577-595.

93. Shmakin and Shiryayeva, 1968, Geochem. Inter., No. 5, p.796.

94. Solovyev et al, 1967, Geochem. Inter., No.4, p.278

95. Stevens, 1938, Amer. Mineral., V.23, p.607.

96. Stewart, 1942, Min. Mag., V.26, p.260.

97. Taborszky, 1962, Beitr. Mineral. Petrog., V.8, p.354.

98. Tilley, 1957, Amer. Mineral., V.42, p.412.

99. Troger, 1935, In Correns, 1956, See Ref. 14.

100. Tschirwinsky, 1929, Z. Krist., V. 70, p. 249-282.

101. Ukai, 1956, Min. Jour. Japan, V. 2, p. 27.

102. Vlasov et al, 1966, The Lovozero Alkaline Massif, Oliver and Boyd, Publ., 625p.

103. Volkov et al, 1962, Geochem. Inter., No. 6, p. 561-570.

104. Winchell, 1942, Amer. Mineral., V. 27, p. 114.

105. Zabavnikova, 1957, Geochem. Inter., No. 3, p. 271-278.

106. Paul et al, 1976, Chem. Geol., V. 17, p. 125.

107. Fairbairn and Robertson, 1966, Clay Minerals, V. 6, p. 351.

108. Carswell, 1975, In Physics and Chemistry of the Earth, V. 9, p. 423, (Ahrens et al eds.)

APPENDIX II

REFERENCES FOR TABLES 1.2, 1.3, 1.4, 1.5

1. Akaiwa and Aizawa, 1973, Japan Geochem. Jour., V.7, No.1., p.1-10.

2. Berth and Brun, 1945, Norsk, Vid. Akad. Skr., No.8, p.5-12.

3. Bowden, 1966, Geochem. et Cosmochim. Acta, V.30, p.555-564.

4. Bowler, 1959, PhD. Dissertation, Univ. of Bristol, England.

5. Bradford, 1957, Min. Eng., V.9, p.78-79.

6. Brogger, 1921, Videnek.-Skk. Kristiania, No.9, p.408.

7. Burturlinov and Zaritskii, 1965, Dopovidi, Akad. Nauk Ukr. RSR, V.9 p.1203-1205.

8. Cattermole and Fuge, 1969, Geochim. et Cosmochim. Acta, V.33, No.10, p.1295-1298.

9. Correns, 1956, Physics and Chemistry of the Earth, V.1, p.181.

10. Danilova, 1949, In Gerasimovskii, 1963, See Ref. 21.

11. Du Bois, 1963, J. Geophys. Res., V.68, p.267-278.

12. von Eckerman, 1948, Sveriges Geol. Undersok., V.36, p.176.

13. Erickson and Blade, 1963, US Geol. Surv. Prof. Pap. 525.

14. Exley, 1958, Q.J. Geol. Soc. London, V.114, p.197.

15. Exley and Stone, 1964, In Present views of some aspects of the geology of Cornwall and Devon, Royal Geol. Soc. Cornwall (Hosking, K.F. and Shrimpton, G.J. Eds), p.129-184.

16. Fleischer and Robinson, 1963, In Studies in analytical geochemistry, Royal Soc. Canada Spec. Pub. No.6, p.58-75.

17. Floyd, 1966, Nature, V.212, p.676.

18. Floyd and Fuge, 1973, Proc. Ussher Soc., V.2, No.6, p.480-481.

19. Fuge and Power, 1969, Geochim. et Cosmochim. Acta, V.33, p.888-889

20. Garsen, 1966, In Tuttle and Gittins, 1966, Carbonatites, Wiley Interscience Publ., 591p.

21. Gerasimovskii, 1963, Geochem. Inter. No.3, p.253-260.

23. Gmelin, 1959, Handbook of Inorganic Chemistry (Fluorine), Verlag Chemie, GMBH, Weinheim/Bergstrasse, No.5, 259p.

24. Kogarko, 1962, In Gerasimovskii, 1963, See Ref. 21.

25. Hall, 1971, Econ. Geol., V.66, p.1267.

26. Holmes and Harwood, 1936, Geol. Surv. Uganda, Mem. No.3, 298p.

27. Kakra, 1971, PhD. Thesis, Univ. Wales, Aberyswyth.

28. Kokubu, 1956, Kyushu Univ., Ser. C2, p.95-149.

29. Koritnig, 1951, Geochim. et Cosmochim. Acta, V.1, p.89-116.

30. Larsson, 1932, In Correns, 1956, See Ref.9

31. Lebedev, 1969, Metacolloids in endogenic deposits, Plenum Press, 298p.
32. Murata and Richter, 1966, U. S. Geol. Surv. Prof. Pap. 537-A.
33. Nemec, 1968a, Geochem. Inter., No. 1, p. 141-147.
34. Nemec, 1968b, Geochim. et Cosmochim. Acta, V. 32, p. 523.
36. Okikadze, 1971, Geochem. Inter., V. 8, No. 3, p. 314-323.
37. Orville, 1960, Bull. Geol. Soc. Amer., V. 71, p. 1467-1490.
38. Pecora, 1956, Bull. Geol. Soc. Amer., V. 67, No. 11, p. 1537.
39. Reid and Flett, 1907, Mem. Geol. Surv. Gt. Britain.
40. Reynolds, 1935, In Gmelin, 1959, See Ref. 23.
41. Rimsaite, 1969, Contrib. Mineral Petrol., V. 23, p. 340.
43. Saito, 1950, Sci. Repts. Fac. Sci., Kyushu Univ., No. 1, p. 121.
44. Seraphim, 1951, PhD. Thesis, Mass. Inst. Tech., USA, 96p.
45. Shiskina, 1966, Geochem. Inter., No. 1, p. 152-159.
46. Stavrov and Ukhanov, 1971, Geochem. Inter., No. 8, p. 168.
47. Stavrov and Bykov, 1961, Geochem Inter., No. 4, p. 370-374.
48. Stueber et al, 1967, Geochim. et Cosmochim. Acta, V. 32, No. 3, p. 353-358.
49. Troger, 1935, Chem. Erde., No. 9, p. 286.
50. Uspenskii, 1959, In Gerasimovskii, 1963, See Ref. 21.
51. Vlasov et al, 1966, The Lovozero Alkali Massif, Oliver and Boyd Publ.
52. Jahns, 1953, Econ. Geol., 50th Anniv. Vol., p. 1025-1130.
53. Heinrich, E. W., 1966, The geology of carbonatites. Rand McNally Press, Chicago, p. 222
54. Kosals, 1968, Geochem. Inter., V. 5, No. 1, p. 131-140.
55. Altschuler et al, 1959, US Geol. Surv. Prof. Pap. 314p. p. 34-90.
56. Dietz et al, 1942, Bull. Geol. Soc. Amer., V. 53, p. 815.
57. Gulbrandsen, 1966, Geochim. et Cosmochim, Acta, V. 30, p. 769-778.
58. Ussher, 1909, Mem. Geol. Surv. Gt. Britain.
59. Marshall et al, 1935, In. Eng. Chem., V. 24, No. 1, p. 86-89
60. Yoshida et al, 1971, Bull. Chem. Soc. Japan, V. 44, p. 1844-1850.
61. Fuge, R., 1975, Proc. Ussher Sco., V. 3, pt. 1, p. 156.
62. Dawson, 1960, PhD. Thesis, Univ. Leeds.
63. Fairbairn and Robinson, 1966, Clay Minerals, V. 6, p. 315.
64. Grantham and Allen, 1960, Overseas Geol. and Mining Res., V. 8, p. 5.
65. Paul et al, 1976, Chem. Geol., V. 17, p. 125
66. Author's data, this thesis
67. Bushinskii, G. J., 1969, Old phosphorites of Asia and their genesis. Israle Prog. for Sci. Trans., 265p.

APPENDIX III

REFERENCE FOR TABLE 3.2

(for Kimberlites and carbonatites the elements and number of analyses are given after each reference)

ULTRABASICS, BASALTS, INTERMEDIATE, GRANITES, SYENITES, CLAYS and SHALES:

Turekian, F.J. and Wedepol, K.H., 1961, Bull. Geol. Soc. Amer., V72, p175-192.

Vinogradov, A.P., 1962, Geochemistry, p641-664.

CARBONATITES:

Barth, T. and Ramberg, F., 1967. *In* Carbonatites, Tuttle, O.F. and Gittins, J. eds, Wiley Interscience C1-(3).

Garson, M.S., 1967. *In* Carbonatites, Tuttle, O.F. and Gittins, J. eds., Wiley Interscience. C1-(2)

Gold, D.P., 1963, Econ. Geol., V58, p988-991. Sc, Co, Ni, Cu, Ga, Y, Zr, Nb, Mo, Sn, La, Ce, Cr - (5 to 31).

Heinrich, E. Wm., 1966. The geology of carbonatites. Rand McNally Publ., 555p. Major, Mn, Ba, Sr, F, S - (84-129).

Jeffery, P.G., 1959, Geochim Cosmochim Acta, V16, p278-295, W-(7)

Khristianov, V.K. *et al*, 1960, Geochemistry, No. 2, p113-121 B-(200)

Schofield, A. and Haskin, L., 1964, Geochim Cosmochim Acta. V28, p437-446. REE-(2)

KIMBERLITES:

Akimov, A.P. and Semonov, G.S., 1969. Doklady Akad. Nauk SSSR, V190, p.205-208. Th, U-(18)

Burkov, V.V. and Podporina, Ye. K., 1966, Doklady Akad. Nauk SSSR, V171, p215-219. REE-(29)

Berg, G.W. and Allsop, H.L., 1972, Earth Planet Sci. Lett., V16, p27-30. Rb, Sr-(3)

Chevepanov, V.A., 1967. Doklady Akad. Nauk SSSR, V172, No. 3. B-(226).

Emelens, C.A. and Andrews, J.R., 1975. *In* Physics and Chemistry of the Earth, Ahrens, L.H., *et al* eds, V9, p179. Major, Mn, S, Ni, Cr, Co, V, Rb, Sr, V, Zr, Ba, La, Nb, Pb-(8)

Dawson, J.B., 1960, PhD thesis, Univ. Leeds. Major-(45); Li, Ga, Nb, La, Sr, Zr, Co, Ni, Y, Ba, Cr, Rb, Sc, Cu, Mn, Mo, Pb, V-(14).

Fairbairn, P.E. and Robertson, R.H.S., 1966. Clay Minerals, V6. Major, F, S, V, Rb, Li, Ba, Sr, Cr, Cu, Ni, Ca, Mn, Sc, Zr, -(2).

Fesg, H.W. *et al*, 1975. *In* Physics and Chemistry of the Earth, Ahrens, L.H., *et al*, eds, V9, p687 Major, Cr, Ni, Co, Sr, Ba, Rb, Cs, Th, U, REE-(58)

Gangadharam, E.V. and Aswathanurayana, U., 1969, Trans. Amer. Geophys. Union, V50, p341 Th, U, K, Na, Rb, Cs, Mn, Sc-(5)

Grantham, D. R. and Allen, J. B., 1960, Overseas Geol. and Mining Rev., V8, p5-25
Major, F, S, Mn, Ba, Sr, Zr, V, Cr, Ni - (1)

Gurney, J. J. and Berg, G. W., 1969 In Upper Mantle Project, Spec. Publ. Geol. Soc. S. Afr., No. 2, p. 417-427. K, Rb, Cs - (50)

Gurney, J. J. and Ahrens, L. H., 1973. Trans. Geol. Soc. S. Afr., V76, p301-307
Zn-(66)

Gurney, J. J. and Ebrahim, S., 1975. In Lesotho Kimberlites, Nixon, P. H. ed., Lesotho National Diamond Corp., p. 282 Major, S, Cr - (25)

Janse, A. J. A., 1975. In Physics and Chemistry of the Earth, Ahrens, L. H., et al eds., V9, p81
Major, Be, Co, La, Li, Mn, Mo, Nb, Ni, Pb, Rb, Si, Sr, V, Y, Zr - (4)

Kable, E. J. D. et al, 1975. In Physics and Chemistry of the Earth, Ahrens, L. H. et al eds., V9 p709
Ti, Nb, Ta, Zr, Hf, Sc, Cr, Y - (59).

Lee, H. A. and Lawrence, D. E., 1968. Geol. Surv. Canada Paper 68-22, 16p.
Major, Ge, Ag, Li, Cu, Sr, Ba, Sc, Y, La, Zr, V, Nb, Cr, Mo, Co, Ni - (2)

Litinskii, V. A., 1961. Geochemistry, No. 9, p813-821. Cu, Sc, Zr, V, Nb, Cr, Co, Ni - (459)

Ilupin, I. P. and Lutz, B. G., 1971. Sovetskaya Geol., V6, p61-73. Major, Mn, Cr, Ni - (623)

Murshintsev, V. K. and Sukneva, L. S., 1970, Geochem. Internat., V7, p1048-50.
Sc- (23).

Mitchell, R. H. and Crocket, J. H., 1971. Contr. Mineral. Petrol., V30, p277-290. Rb, Sr -(27)

Mitchell, R. H. and Brunfelt, A. O., 1975 In, Physics and Chemistry of the Earth, Ahrens, L. H. et al., V9, p671. REE, Co, Sc, Th, Hf, Ta - (13)

Paul, D. K. et al, 1975. Earth and Planetary Sci. Letters, V25, p151.
Major, Mn, REE, Hf, Ta, Th, Ba - (12)

Paul, D. K. et al, 1976. Chem. Geol., V17, p125. F, Cl-(22)

Robinson, D. N., 1975, In Physics and Chemistry of the Earth, Ahrens, L. H. et al eds., V9, p61,
Major, Mn, Ni, Cr, Sr - (3)

Stavrov, O. D., and Ukhanov, A. V., 1971. Geochem. Internat., No. 8, p168-178.
Li, Rb, F-(1).

APPENDIX IV

SAMPLE HANDLING AND PREPARATION

All soil and stream sediment samples used in this study were dryed and sieved using British Standard sieve sizes. Samples were generally sieved to -80 mesh (200 micron Nylon bolting cloth); in some cases different size fractions were taken for detailed studies. The organic Aoo horizon soil samples from the Richardson uraninite-fluorite mine area were macerated to -200 mesh B. S. S.

Rock samples were crushed using a jaw crusher and then ground in an agate Tema mill to -200 mesh B. S. S. Every precaution was taken to prevent cross-contamination. The mineral specimen used in the acid diffusion studies (Table 2. 11) were successively ground and sieved until a representative amount of -80+200 and -200 mesh material was obtained.

Water samples were collected in the field using polythene bottles, glass bottles not being used as fluoride is known to be absorbed on the surface of glassware. Acidification of the samples was not done as this may result in HF complexation. Analysis was carried out as soon as possible after collection.

APPENDIX V

SUPPLEMENTARY ANALYSIS

Phosphorus analysis of soils was carried out according to the procedure outlined in Technical Communication 52 of the Applied Geochemistry Research Group, Imperial College. A 0.20 gm sample was fused with potassium bisulphate, and this was then leached in a nitric acid solution. A 1 ml aliquot of this solution was added to a vanadate-molybdate solution and the phosphorus concentration measured spectrophotometrically. A precision of ±25% at the 95% confidence level can be obtained over the range 20 ppm to 10% P.

Calcium in soils was determined by atomic absorption after an HNO_3-$HClO_4$ acid attack. The analytical precision is approximately ±20% at the 95% confidence level.

Boron, uranium and thorium analysis of soils were carried out for the author by Bondar-Clegg and Co. Ltd., Canada. Boron analysis was done by emission spectrography using internal standardization and boron free electrodes. Thorium was analysed by x-ray fluorescence and uranium was analysed by a standard fluorometric technique.

Waters were analysed for Al, Fe and Mn by evaporating 500 ml of sample to dryness, taking the residue up in 6M HNO_3 and determining the concentration by atomic absorption.

Trace element analysis of kimberlites was done by direct reading emission spectrography and by atomic absorption (after an HF acid attack). Major element analysis of kimberlites was done by the analytical laboratories of the Geological Survey of Canada using standard x-ray fluorescent and wet chemical procedures.