Some aspects of the geochemistry of fluorine in metamorphic bocks

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Some Aspects of the Geochemistry of Fluorine in Metamorphic Rocks

A Thesis Submitted in Partial Fulfillment

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of Doctor of Philosophy

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by

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Preface

This work was carried out for the period October 1955 through June 1958 under a stipend provided by United States Public Law 550, 82nd Congress, and for the period July 1958 through September 1960 by a Research Assistantship tenable with the Durham Colleges in the University of Durham.

I am especially indebted to Prof. K.C. Dunham for his suggesting the topic of research. That this problem decides my investigations for as many years as I am able to contrive to devote to them, that he has always given encouragement and shown interest, and that his and his wife's hospitality to an overseas student has been so warm do cause me to add admiration to gratitude.

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Mr. H. Fettis and Mr. G. Martin are responsible for providing a steam distillation apparatus and an efficient steam generator for fluoride analysis.

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Chapter I -1

Abstract

The literature on the determination of fluoride is reviewed. Attention is given to its analysis in silicate materials, especially rocks and minerals; developments in method are traced from the first work, published in 1816, to the present. Special emphasis is given for the period 1951 through 1959, important methods and other pertinent work and findings being summarized chronologically by subject and without regard to systematic exposition of contradictions or their explanation: The summaries of some work are nevertheless detailed enough to make manifest some contradictions. Conflicting findings on the precision in the visual thorium titration and on the visual ratings of various indicators for this titration are thought merely to reflect individual skill and choice rather than superiority of method and (or) indicator. A strong case is thereby made for instrumental methods of analysis.

A method developed to determine fluoride in metamorphic rocks is described. A sodium peroxide decomposition, followed by a precipitation of silica and alumina and a steam distillation of the filtrates, gave quantitative isolation of fluoride. Aliquots of distillate were titrated spectrophotometrically in perchloric acid-sodium sulfanilate buffered solution in the presence of sodium 2-(p-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (SPADNS). The method was tested with synthetic rocks and soda feldspar, to which known amounts

of fluoride were added. Aliquots were titrated spectrophotometrically to within one microgram of fluoride. Results with G-1 and W-1 are compared with analyses reported by others. Replicate results for ten metamorphic rocks indicate a maximum proportional deviation of 2.0 percent. However, further replications have shown the error is somewhat greater, although nevertheless favorable: The standard deviation for 122 replicate determinations is ±0.0014 percent fluoride for rocks having up to 0.09 percent fluoride.

The applicability of the perchloric acid-sodium sulfanilate buffer for the thorium titration is examined. It is felt it is superior to the monochloracetic acid buffer commonly used.

The results of an interlaboratory standardization program conducted to check the validity of several methods and the comparability of results and to suggest possible superior methods of analysis are presented. Agreement is not favorable when all results are compared; possible matrix effects for pyrolitic and chemical methods are considered. Four of the eight procedures employed show favorable agreement, aspects of which are studied.

Work, carried out on synthetic solutions containing the elements commonly analyzed in the "main portion" of silicate rock analysis, is given and discussed. Minor modifications, mainly in technique, of the generally accepted methods are detailed. An important improvement in the examination of the calcium oxide and magnesium pyrophosphate precipitates for impurities such as strontium in the former and calcium and manganese in the latter has been developed. Considerable attention is given to the problem of determining "blanks" for this part of silicate rock analysis.

Chapter I -2

A Review of the Literature on the Analysis of Fluoride with Special Reference to Silicate Materials and to the Period 1951 through 1959

"Many methods have been devised for the determination of fluorine in solutions of pure fluorides. Only a few of these can be applied to the analysis of such complex materials as glasses and enamels, and none of them gives satisfactory results." Hoffman and Lundell in 1929 (113).

Historical Synopsis.- It was the mineral fluorite that figured in the discovery of the element, fluorine. Basilius Valentinus, towards the end of the 16th Century, mentioned some colored minerals which he termed "fluores." An artificer in Nurnberg was known around 1670 to have etched patterns on glass using mixtures of fluorspar and fuming sulfuric acid. Marggraf, observing the reaction between fluorite and sulfuric acid, reported "observations concernant une volatilisation remarquable d'une partie de l'espece de pierre, a laquelle on donne les noms de Flosse, Flusse, Flus-Spaht, et aussi celui d'hesperos; laquelle volatilisation a ete effectuee au moyen des acides." Then in 1771 the Swedish chemist, Scheele, distilling fluorite in glass vessels and observing the white residue that collected in the receivers, concluded correctly that it was silicic acid and regarded the fluorite as a mineral made of lime with a special acid bound to it: "als ein vorzuglich aus Kalkerde mit einer eigenen Saure verbundenes Mineral." In the face first of little interest and then of criticism, Scheele defended his discovery. He was aided by Wiegleb for one, who demonstrated that the silicic acid was derived from the glass vessel. In 1809 Gay-Lussac and Thenard, distilling fluorite with sulfuric acid in lead or silver vessels, succeeded in isolating an aqueous solution of hydrofluoric acid. By virtue of correspondence between Davy, who recognized the elemental nature of chlorine (1810), and Ampere, the latter termed the acid Fluorwasserstoffsaure; that is, the hydracid of the yet unknown element, fluorine. Both men considered there to be an analogy between hydrofluoric and hydrochloric acids. Ampere took the name "phtore" from the Greek meaning "to destroy" for the element. It was not until 1886 that Henri Moissan obtained elementary fluorine by electrolysis. See Gmelin (95).

And so with the discovery of the element by Scheele there came into the field of analytical chemistry on the one hand an element very difficult to look for and to determine and into the field of geochemistry on the other hand a minor element best characterized by its ubiquity.

Chemical Reactions of Fluoride.- Before entering the review of the literature it will be of value to examine the important reactions of fluoride upon which analytical methods are based: A. reactions of fluoride with certain other ions producing insoluble compounds;

1. $2F^- + Ca^{++} = CaF_2$

2. $3F^- + Bi^{+++} = BiF_3$

3. $3F^- + La^{+++} = LaF_3$

4. $3F^- + Ce^{+++} = CeF_3$

5. $3F^- + Y^{+++} = YF_3$

6. $F^- + Cl^- + Pb^{++} = PbClF$

7. $F^- + (C_6H_5)_3Sn^+ = (C_6H_5)_3SnF$

8. $4F^- + Th^{++++} = ThF_4$

9. $4F^- + Zr^{++++} = ZrF_4$

10. $H_2SiF_6 + Th^{++++} = H_2ThF_6 + Si^{++++}$

11. $5F^- + K^+ + U^{++++} = KUF_5$

B. reactions of fluoride with certain cations or complex ions producing stable fluoride complexes:

1. $xF^- + Al^{+++} = AlF_x^{3-x}$

2. $xF^- + Fe^{+++} = FeF_x^{3-x}$

3. $4F^- + Be^{++} = BeF_4^{--}$

4. $6F^- + Ti^{++++} = TiF_6^{--}$

5. $FeF_x^{3-x} + Al^{+++} = AlF_x^{3-x} + Fe^{+++}$ $x = 1\text{-}6$

6. $Fe^{++} + Fe^{+++} + xF^- = FeF_x^{3-x} + Fe^{++}$

7. $Fe(CNS)^{++} + xF^- = FeF_x^{3-x} + CNS^-$

8. $Al^\circ + xF^- = AlF_x^{3-x} + 3e$

9. $Zr^\circ + xF^- = ZrF_x^{4-x} + 4e$

The above equations are schematic only; the complete equation postulated for A.10, for example, is given by Wadhwani (235). The solubility of various compounds is given by the following: Mougnaud, CaF_2 (164); Hillebrand, Lundell, Bright, Hoffman, PbClF (110); Allen and Furman, $(C_6H_5)_3SnF$ (7); Wadhwani, ThF_4 and H_2ThF_6 (235). Domange states bismuth trifluoride is less soluble than calcium fluoride (60). Further information is given in the Handbook of Chemistry and Physics (104). The equilibrium constants of AlF_x^{3-x} complexes have been calculated recently by Kleiner (126), and Latimer and Jolly have measured the heats and, with the known equilibrium constants, calculated the entropies for the six stages of the aluminum ion and fluoride ion reactions (134). Kleiner cites dissociation constant data for the FeF^{++} and $Fe(SCN)^{++}$ complexes (126). The aluminum fluoride complexes are said to be more stable than the ferric ion ones (126, 147). The rate of association of ferric and fluoride ions has been determined by Smith (204). Interaction of aluminum and fluoride ions has been studied by Kleiner in the system aluminum nitrate-sodium fluoride-ferric nitrate-potassium thiocyanate in nitric acid solution (127).

The reactions outlined above are an oversimplification and can be misleading. For example, fluoride has never been determined gravimetrically as cerous fluoride; but titration of fluoride by cerous ion has been carried out on the basis of (1) hydrolysis of excess cerous ion producing a color change in methyl red indicator or adsorption by the precipitated cerous fluoride in the presence of excess cerium on the indicator (workers are not agreed on whether it is adsorption or hydrolysis) (24, 132), (2) change in redox potential in a system containing in addition to fluoride cerium ferrocyanide, potassium cerium ferrocyanide, and potassium ferricyanide (after precipitation of cerous fluoride with cerous titrant excess cerous ion represses the solubility of potassium cerium ferrocyanide, so the ferrocyanide/ferricyanide ratio decreases suddenly, effecting a jump in the potential) (8), and (3) chelation of excess cerous ion with murexide in alcoholic solution (41).

Indeed, gravimetric, volumetric, potentiometric, amperometric, polarographic, fluorometric, nephelometric, turbidimetric, and spectrophotometric methods are founded on the reactions cited schematically above. Spectrographic procedures are based on the emission of CaF or SrF band spectra (5). Silicate analysts, however, have only used gravimetric (and nephelometric) procedures involving calcium fluoride, lead chlorofluoride, and possibly triphenyltin fluoride; spectrophotometric procedures, involving the bleaching action of fluoride on thorium- and zirconium-dye systems and the peroxidized titanium complex; volumetric methods, usually with thorium nitrate in the presence of sodium alizarin sulfonate (Alizarin Red S); and spectrographic methods. The systems used for the spectrophotometric determination of fluoride in silicates are few; commonly employed systems are the thorium-sodium alizarin sulfonate-fluoride or the zirconium-sodium alizarin sulfonate-fluoride ones. The writer has decided to include in the following review some of the work done, albeit on pure fluoride solutions, for which many of the B group reactions listed above are the bases. The writer's reasons for their inclusion, apart from broadening the usefulness of this review, are presented in the discussion on the development of his method (cf. Chapter I -3, section a.).

Calcium Fluoride Method.- In 1816 Berzelius described the first procedure for determining fluoride in rocks (30); it is, indeed, with but two major modifications introduced by Hoffman and Lundell in 1929 (113) still used today when 10 milligrams or more of fluoride are present. The original method with modern refinement (110) is lengthy and involved, calling for (1) fusion of 2 grams of sample with sodium potassium carbonate and extraction of the cake, (2) precipitation of silica in the filtered extractate with ammonium carbonate, filtering, expulsion of ammonium carbonate by evaporation, (3) precipitation of remaining silica with ammoniacal zinc carbonate by boiling until excess ammonia is expelled and then filtration, (4) coprecipitation of calcium fluoride and calcium carbonate in the ammonium salt-free filtrate, filtration of the precipitate, (5) separation of the calcium fluoride from the calcium carbonate by treatment of these precipitates with dilute acetic acid solution and evaporation to dryness to render the former precipitate granular, and (6) filtering, ignition at 800° to 900°C of the washed precipitate, and weighing as calcium fluoride in platinum. The precipitate is likely to be impure, particularly if large amounts are involved, in which case it should be treated one (or more) times with acetic acid solution, refiltered, and reignited.

Calcium fluoride is apt to be colloidal, so several workers have directed their efforts to overcoming this, as well as the appreciable solubility. Coprecipitation techniques, first introduced by Rose (189) with calcium carbonate-calcium fluoride, have been carried out to overcome the former property. Yet neither of these numerous modifications, outlined by McKenna (147), nor the Berzelius method itself need be discussed further for numerous reasons, the key one being: "The result obtained by the Berzelius method is almost certain to be low and may even be negative if very little fluorine is present." (110). Hillebrand and Lundell (110) claimed 95 to 98 percent of the fluoride was recovered only provided both (1) the residue left from leaching the melt and the two batches of precipitated silica are refused and re-worked, and (2) filtrates from the coprecipitation of calcium carbonate and calcium fluoride are treated with more precipitants (sodium carbonate and calcium chloride).

Stevens took advantage of the colloidal property of calcium fluoride, which state he stabilized by the use of gelatin (216), to determine fluoride after its isolation by the Berzelius-Rose procedure as modified by Hoffman and Lundell (113). The colloidal calcium fluoride was developed in alcoholic solution and the turbidity measured with a nephelometer. Standards were prepared with sodium fluoride solutions. He claimed an accuracy of 1 percent, the lower limit of determination of fluoride in substances requiring fusion being 0.3 percent fluoride. He examined the effects of time and temperature and rate of addition of precipitant on the colloid. Sulfate and phosphate interfere, but can be removed by barium and ferric salts, respectively. However, the former precipitant must be added in slight excess only, for otherwise it forms barium fluoride. Ferric salts never completely remove phosphate. The method was unacceptable for high phosphate content materials, for the fluoride is never completely extracted. Results for a phlogopite, topaz, and National Bureau of Standards opal glass are given. He used the method for determining fluoride in lepidolites (217).

Lead Chlorofluoride Method.- To minimize time-consuming operations in the Berzelius-Rose method, Hoffman and Lundell turned to a lead chlorofluoride procedure (113) after separating silica in the leachate with zinc nitrate in a solution just alkaline, filtering, and precipitating the second lot of silica in the filtrate with zinc oxide dissolved in ammonium carbonate-ammonium hydroxide solution. The zinc nitrate-zinc oxide treatments did not prevent the complete isolation of fluoride. For the accurate determination the method gives good results when the fluoride content is between 0.01 to 0.1 gram; below 0.01 gram results tend to be low and above 0.1 gram they tend to be somewhat high. Kaufman's work is of interest in this respect

(125). For routine determinations of fluoride only the first precipitation of silica need be made; the lead chlorofluoride can be brought down in the first filtrate. When the Volhard titration is used, these authors' tests on synthetic solutions containing moderate amounts of ammonium nitrate, boric, chromic, sulfuric, or phosphoric acids show the results are acceptable. But the method cannot be used for phosphate rock, for leaching of fluoride from the fused sample is not complete. Hoffman and Lundell found that occasionally not all of the fluoride was extracted from the melt with water, filtering, and washing; however, only a very few residues showed as much as 1 milligram of fluoride. They accepted Hawley's recommendation (108) to boil the melt with sodium carbonate solution, although the treatment should be considered only a precautionary measure.

The precipitation of lead chlorofluoride, used by Hoffman and Lundell in rock analysis (above) was first described by Starck in 1911 (214). Since that time most efforts have been directed towards overcoming errors arising from the indefinite composition of the precipitate owing to coprecipitation of other lead salts. In general contamination from basic lead salts decreases as the pH does, but the solubility of lead chlorofluoride increases (103, 113); most workers seem now to agree that errors from either source are at a minimum for a pH range 3.6 to 5.6 (113, 125). The most significant improvement came in 1926 when Hawley suggested that fluoride, precipitated as lead chlorofluoride, should be determined by analysis of the chloride in that precipitate by the Volhard titration (108). This procedure is almost always used now (111, 112, 125), for it obviates errors due to coprecipitation of other lead salts, except lead phosphate, which entrains some chloride (72). Phosphate can be removed by a preliminary precipitation of silver phosphate (72). For the fusion of samples Hawley recommended that they be fused with 4 times as much silica as fluoride is present; if this ratio does not hold, pure, powdered silica must be added. He precipitated lead chlorofluoride in leachates from sodium potassium carbonate fusions without preliminary removal of silica.

However, Saylor, Deal, Larkin, Tavenner, and Vosburgh have found the composition of lead chlorofluoride varies with the method of precipitation, so that the method is not very reliable (193). But the errors they report from this cause would not be significant for rock analysis: 5 parts per thousand.

Fusion of ores and minerals with sodium hydroxide in an iron crucible followed by extraction, neutralization, and precipitation of silica with ammonium carbonate has been suggested by Popov (176). An aliquot of the clear, unfiltered solution is taken for determination of fluoride by the lead chlorofluoride-Volhard method (titration of excess silver with thiocyanate).

Lead Bromofluoride Method.- The precipitation of fluoride as lead bromofluoride has been discussed recently by Ehrlich and Pietzka (65). They have determined 70 to 100 milligrams of fluoride in a sodium acetate-nitric acid solution by dissolving the precipitate in acid, precipitating bromide with excess silver and titrating the latter with ammonium thiocyanate using ferric alum indicator. Cheburkova (47) used a very similar procedure for determining fluoride in welding fluxes after fusion of the samples with sodium carbonate-zinc oxide mixture and precipitation of silica by a simplified Berzelius method.

Barium Fluoride Method.- Three of the most interesting papers on analysis of fluoride in waters, living tissue, and minerals were published by Gautier and Clausmann in 1912 (87, 88, 89). They emphasized the inadequacy of methods then extant for determining accurately less than 1 milligram of fluoride in these substances, citing the principal limitation of the Berzelius-Rose, Wohler-Fresenius (76), Carnot (43), and Carles (42) methods as being their applicability only to large amounts of fluoride. Experiments on the concentration of the fluoride present in volcanic exhalations showed barium fluoride to be more insoluble than calcium fluoride; a further advantage for the use of barium was that its sulfate coprecipitated soluble fluoride. Based on this barium sulfate method of concentrating fluoride, they described a method applicable to rock analysis. Minerals not attacked by sulfuric acid are fused with fusion mixture plus silica, the melt leached, and silicate precipitated with ammonium carbonate and filtered off. To this filtrate, made faintly alkaline, is added sodium sulfate and then barium chloride, the solution taken to dryness, cold water added just to dissolve the soluble salts, an equal volume of hot alcohol added, the precipitate centrifuged and washed with alcohol to remove chloride, and then weighed. The precipitate is placed in the bottom of a 50 to 55 cc. capacity gold crucible above which is a tripod supporting a small basin of purified sulfuric acid, and above the latter a gold basket, supported from the crucible rim, containing a piece of moistened potassium hydroxide. The whole is sealed by a cover, convex side facing inside, the outside side being fitted flush with a cylinder serving as a water cooling system. After causing the acid content of the basin to pour onto the sample, the bottom of the crucible is heated in a metal block at 180° to 185°C for 2 hours after which time the fluoride is quantitatively expelled as hydrofluoric acid and (or) fluosilicic acid and taken up by the potassium hydroxide. The contents of the basket are dissolved, nearly neutralized, silica precipitated by ammonium carbonate, the solution evaporated to dryness, and fluoride again coprecipitated with barium sulfate and washed and dried and weighed as before. A small portion of this purified barium sulfate-barium fluoride precipitate is then tested qualitatively (89) to ascertain the approximate proportion of fluoride to sulfate, this information being necessary in order to regulate the quantities of precipitate and acid for the final determination: The remaining, major portion of this precipitate is weighed into the special apparatus already described except that the basket is lined with powdered lead glass (cristal optique contenant 42 pour 100 de plomb"). The system is heated to 140°C for 5 hours, at which temperature sulfuric acid is not volatilized. The hydrofluoric acid formed attacks the lead glass and forms lead fluoride in proportion to the amount of fluoride, this compound then being separated from the lead glass by washing with a potassium chlorate solution. The lead in this solution is precipitated, under special conditions, as colloidal lead sulfide and its amount determined nephelometrically. Known amounts of pure calcium fluoride are carried through the method starting with the acid attack in the gold crucible containing the lead glass. Curves relating the lead found nephelometrically to the fluoride taken are prepared. For the preparation of these curves these authors have shown that as little as 50 micrograms of fluoride can be determined. The method is ingenious but obviously very involved, time-consuming, and calling for a very delicate and specialized technique.

In their third paper (89) Gautier and Clausmann tested the method by adding known amounts of purified potassium fluoride to waters, dog brain, blood, and bone. The method was not suited to minerals having high amounts of fluoride (apatite, fluorite, topaz) unless a small sample was taken, which meant any error was multiplied by the aliquot factor. Nevertheless, on a topaz they obtained 15.1 percent fluoride by their method, 14.1 percent by the Berzelius-Rose procedure. They concluded that 0.1 milligrams of fluoride in a mineral can be determined with certainty by the above method, although they gave no data to support this claim.

In yet another paper these authors determined and discussed the fluoride content and the phosphorus/fluoride ratio in many plants and plant products, using an ashing procedure, calling for the use of lime, that they had evolved (90).

Thorium Tetrafluoride Method.- Another gravimetric procedure was introduced for silicates and fluoride-containing minerals by Pisani (174), involving precipitation of thorium tetrafluoride. For non-silicate minerals (apatite) he recommended fusion with sodium carbonate and silica and precipitation of fluoride in the filtered leachate neutralized with acetic acid; for amblygonite it was necessary to remove phosphate first. For silicates the procedure is the same, but silica need not be added for the fusion. Only 0.2 to 0.3 grams of sample are required. Certain precautions are necessary for the precipitation proper: The solution must be weakly acidulated with acetic acid to remove carbonate. If the amount of fluoride is not known, one must add some precipitant, decant a good portion of the liquor after letting it stand for some time, and test this liquor for completeness of precipitation. A rapid addition of a great excess of precipitant to a concentrated fluoride solution will redissolve some precipitate. When the fluoride content is known, one can precipitate in one operation. Settling of precipitates before filtering is necessary; it requires several hours. Before filtering, one must decant several times, let this liquid, collected in one container, stand for some time, then filter it, to avoid the fines in suspension from passing through the filter. It is best to ignite the precipitate to thorium dioxide and weigh as such.

Later Gooch and Kobayashi found the amount of thorium tetrafluoride recovered was sensitive to excess nitric or sulfuric acid, but some range of acetic acid was tolerated, and a slight excess necessary (97). To ensure a regulated excess of precipitant, they developed a method of estimating the fluoride present in the unknown by adding a portion of the latter dropwise into the precipitant solution until a distinct turbidity was produced, this condition representing a known ratio of thorium concentration to that of fluoride. Thus precipitation could be effected in one operation with a measured excess of thorium present. Rather than weigh the fluoride precipitate, Gooch and Kobayashi precipitated the excess thorium with oxalate and determined the latter permanganimetrically. Hoffman and Lundell (113) and Adolph (3, 4) have found that with alkali present sodium fluothorate (Na_2ThF_6) precipitates instead of thorium fluoride tetrahydrate.

Fluothoric Acid Method.- Wadhwani has recently described a gravimetric method (238): 30 to 90 milligrams of fluoride, as fluosilicic acid, are precipitated as fluothoric acid (H_2ThF_6) with excess thorium, which is then precipitated with oxalate, the latter being determined permanganimetrically.

Lanthanum Fluoride Method.- The formation of insoluble lanthanum fluoride is the basis of a method recently worked out by Popov and Knudson (175). Lanthanum fluoride has lower solubility than lead chlorofluoride and calcium fluoride, but the precipitate formed in dilute solution is gelatinous and becomes colloidal in an excess of lanthanum. However, a flocculent precipitate will form in the presence of dilute acetic acid. Popov and Knudson proposed to centrifuge the lanthanum fluoride formed on adding a measured excess lanthanum in the filtrate by precipitation and ignition of the cupferrate. The weighing of lanthanum fluoride leads to errors, for ignition converts it readily to an oxyfluoride. Lanthanum sulfate coprecipitates and, above pH 3, so do basic lanthanum salts. Tyndallometric investigation of the precipitation process of lanthanum fluoride and other metal fluorides has been carried out by Cernicki and Tizak (46).

Triphenyltin Fluoride Method.- Krause and Becker first reported the low solubility of triphenyltin fluoride in alcoholic, ethereal, and aqueous media (130); Allen and Furman developed a method, on the basis of experiments with pure sodium fluoride solutions, capable of determining from 0.05 to 40 milligrams of fluoride (7). For the higher amounts the average error was 0.10 milligrams, and for the microgram quantities it was less than 10 micrograms. Their experiments indicated absolute errors were at a minimum for 9 to 19 milligrams and for 0.05 to 1.0 milligrams of fluoride. These authors concluded that acceptable results can be obtained on a minimum of 0.05 milligrams, so that, as they suggested, it might be applicable to rock analysis. But they point out one difficulty arising from the fact that both precipitant and precipitate are appreciably soluble in alcohol, and that the former is not at all soluble in water: Too great an excess of the alcoholic solution of the triphenyltin reagent will effect coprecipitation of the reagent and certain inorganic salts with the precipitate. Indeed results on the analysis of fluorspar tend to be high, probably because of the coprecipitation referred to. On the other hand, although ageing of the precipitate requires a more elaborate technique than that for calcium fluoride and lead chlorofluoride procedures, the actual precipitation and subsequent operations are probably less involved than those for the precipitation and further treatment of the calcium fluoride precipitate; in addition, the precipitate has a low solubility and a low gravimetric factor, so it is suited to the determination of small quantities of fluoride. Also, it is stable so it can be weighed as such. It is readily filtered and washed. On the other hand, a very considerable objection to its use is that the fluoride must be separated from nearly every other element found in rocks for an accurate determination (cf. Appendix I, letter C).

However, recently Ballczo and Schiffner developed a microgravimetric method capable of good results (21), even in the presence of phosphate, borate, aluminum, and iron (20).

Thermogravimetric Methods.- Dupuis and Duval (61) have reported that triphenyltin fluoride, uranium oxyfluoride, lead chlorofluoride, bismuth trifluoride, calcium fluoride, lanthanum fluoride, thorium fluoride, and potassium fluosilicate give interpretable curves obtained by thermogravimetry, the first three precipitates above having the best curves. They gave recommended weighing forms, temperature limits for thermogravimetry, and precipitants.

Volatilization Methods.- In 1839 Wohler described a technique of analysis based on volatilization of fluoride on treatment of acid-soluble samples with sulfuric acid (253). His technique, perfected by Fresenius (76), applies only to minerals decomposed by sulfuric acid. For the Fresenius method the sample is mixed with pure powdered silica, a slight excess of acid is added, and the silicon tetrafluoride expelled on heating is caused to pass, by means of an air current, through a U-tube train, three tubes containing pumice-soda lime-calcium chloride mixtures. The increase in weight of these tubes is a measure of the fluoride evolved. Carnot modified this further by collecting the silicon tetrafluoride in potassium fluoride solution; potassium fluosilicate precipitates, which he determined gravimetrically (43).

Reynolds, Ross, and Jacob described a volatilization technique for phosphate rock (187). For pure compounds such as fluorite a coarse sample (pass 80 mesh) and 95 percent sulfuric acid heated to 200° to 250°C gave quantitative recovery of fluoride. But for phosphate rock 98 to 98.5 percent acid had to be employed and the sample had to be ground to pass 200 mesh. Recoveries were constant when the fluoride in the rock was 12.1 to 48.4 milligrams; higher amounts led to lower recoveries. The sample was treated in a reaction flask heated to 300°C in an electric oven. The flask was connected to a train of tubes, the principle being about the same as for the Fresenius method. Tubes with silver sulfate in sulfuric acid and chromic oxide in sulfuric acid removed chloride, sulfur dioxide, nitric acid, and oxides of nitrogen. Fluoride was caught in a tube containing dilute hydrochloric acid and the fluoride determined by sodium hydroxide titration after correcting for sulfur dioxide and sulfur trioxide. Duplicate determinations usually agreed to within 0.05 percent fluoride, but the recovery of fluorides was not much better than 92 to 94 percent, so that empirical corrections were necessary.

The volatilization technique has also been used by Sharpless and McCollum for the determination of fluoride in bones (198); silicon tetrafluoride is expelled when the sample is treated with silica and sulfuric acid. Two methods for the analysis of fluoride in fluorite and blendes, both involving the volatilization principle, have been described by Olivier (169).

Spectrographic Methods.-Papish, Hoag, and Snee were the first to describe an indirect spectrographic procedure for determining fluoride (171). They developed the CaF band spectra by arcing samples mixed with calcium carbonate at 8 to 10 amps, using anode excitation in the direct current arc. They ran qualitative tests on topaz, tourmaline, lepidolite, cryolite, etc., getting positive tests for each.

A quantitative spectrochemical method for rocks, minerals, and soils was given by Ahrens (6). Seraphim made some systematic studies on the determination of fluoride by the use of the CaF and SrF bands (197); he found that the detection limit is, for the direct current arc, 100 to 200 p.p.m. fluoride using the CaF 5291 Angstrom band, which limit can be lowered to around 50 p.p.m. if the more sensitive CaF 6036 Angstrom band is employed. However, the use of the latter requires a helium atmosphere to limit CaO interference and a relatively large dispersion spectrograph, such as a diffraction grating type. Seraphim found the relative deviation of his method, 15 to 20 percent, is comparable to that claimed by Koritnig for his chemical method (129). Seraphim prepared standards by adding either United States National Bureau of Standards phosphate rock or an amphibole with known fluoride to the standard diabase, W-1; either gave good working curves. Ahrens (5) has discussed the properties of the CaF band. The spectrochemical procedure has been used by Fuwa (82), who found high amounts of phosphorus necessitated isolation of fluoride (82). Fuwa also has used the CaF band method for the visual spectroscopic estimation of fluoride (0.001 to 0.05 percent) in sediments and soils (83); he has also claimed BaF bands can be used for spectroscopic analysis (84).

Smolyak should be consulted for another visual spectral method (209). Monnot claimed high amounts of silica diminishes CaF band intensity since silicon tetrafluoride forms from reaction of calcium fluoride and silica at high temperature; for high silica content materials, such as acid rocks, the effect of silica in preventing CaF band formation will be greatest (161).

A very sensitive spectrochemical method has been described by Gatterer (86). Methods for ceramics and porcelain enamel frits have been described (38, 212). The presence of fluoride in carbon electrodes has been looked into by Minami, Abe, and Takagi (158). The use of a copper line as an internal standard for the calcium fluoride band at 5298.6 Angstrom has been detailed for slags by Gillis, Hout, and Kemp (93), and Castro and Loude (45).

Peroxidized Titanium Method.- The first colorimetric method applied to rock analysis came in 1908 when Steiger applied the bleaching action of fluoride on the yellow color of peroxidized titanium solutions (215). Merwin showed that large amounts of alkali sulfates also bleached the color and that increasing temperature and free acid concentration intensified (restored) the color (153). He cited some difficulties in visual estimation and techniques to overcome these, and gave measurements on the effect of temperature on the fluoride-containing system (19 milligrams of fluoride bleached the color by 30 percent at 22°C, but heating this system to 70°C nearly restored the color), and the effect of aluminum, iron, and soluble silicate (the first two restore the color). The visual matching was done by adjusting the depth of solution of a standard until it matched the color depth of the unknown, each having the same concentration of acid, peroxide, and titanium; the ratio of thickness of unknown and standard giving the same color depth was approximately linear with respect to fluoride present. It was necessary to allow for the alkali sulfate present. He outlined a procedure for determining fluoride in rocks: (1) fusion of 2 grams with sodium potassium carbonate and leaching of residue, (2) precipitation of silica, alumina, and ferric iron with ammonium carbonate, (3) filtration (one only, residue and precipitates caught in one pass) and treatment of filtrate with color-developing reagents, and (4) matching of colors with standards. Later he provided more accurate data for optimum sensitivity to fluoride in the peroxidized titanium system (113).

Wichmann and Dahle examined the peroxidized titanium method of Steiger-Merwin to ascertain optimum conditions of fluoride determination and the effect of phosphate, aluminum, potassium sulfate, sodium chloride, and organic matter (243). The bleaching action, expressed as units per unit fluoride, is not always linear; it increases generally as the concentration of fluoride increases and that of titanium decreases. In a second paper (244) they utilized their findings for the determination of as little as 2 micrograms of fluoride in fruits and vegetables.

These authors preferred photometric measurement for the color, the instrument used for this purpose also being described (53).

Monnier, Vaucher, and Wenger studied the peroxidized titanium system more recently (160). They suggested the reaction, $Ti^{++++} + H_2O_2 = TiO_2^{++} + 2H^+$, which is endothermic, explained certain observations. A decrease of pH from 1.7 to 0.98 increased the optical density, measured in an absorptiometer, markedly and a further decrease from 0.98 to 0.65 only slightly; for a large excess of acid, the color weakens. The same relations applied, be the titanium present as chloride or sulfate. An increase of temperature to 40°C did not affect the optical density, but higher ones did. In studies on pure titanium-hydrogen peroxide-fluoride systems they found the sensitivity to fluoride, represented by the molecular extinction, was unchanged from pH 1.7 to 0.9 and that the Beer-Lambert law applied for this range. At lower pH sensitivity decreased and the Beer-Lambert law was not obeyed. In 50 cc. of solution containing 527 micrograms of titanium 0.15 grams of sulfate did not affect the optical density, but more than 5 milligrams of phosphate did. They proposed an ingenious method for determining fluoride in the presence of phosphate: In the above system they demonstrated that aluminum formed 1:1 complexes with fluoride that were more stable than the fluotitanate complex. Therefore, the increase of optical density effected by the addition of aluminum is in direct proportion to the fluoride present.

However, for consistent results the phosphate content for standards and unknowns must be adjusted to 100 milligrams per 50 cc. of solution.

Warren, Gimingham, and Page used the peroxidized titanium method for basic slag after fusion of a 5 gram sample with fusion mixture and treatment of the cake similar to that given by Merwin (240). Phosphate was removed prior to color development of the titanium complex in the filtrate. Determinations were done photometrically.

For fluoride determinations in minerals Koritnig fused them with sodium hydroxide in a nickel crucible, treated the melt with water, allowing it to stand for a time, filtered and washed the residue, precipitated silica and alumina with ammonium carbonate as in the Berzelius method after neutralizing the solution with sulfuric acid, filtered, acidified the filtrate, and developed the peroxidized titanium complex (129).

<u>Formation of Fluoferrate Complexes</u>.- A procedure that Fairchild claimed gave good results on rocks containing 5 to 60 milligrams of fluoride called for addition of a known excess of ferric iron to the fluoride solution, ferric fluoride (FeF_3) or fluoferrate ion (FeF_6^{--}) forming, the excess ferric ion then being determined iodometrically (71). Phosphate must be removed prior to the determination by precipitation with zinc ammonium phosphate. He fused samples with sodium carbonate, adding silica and alu-

mina in the form of feldspar if the sample was low in these oxides. He found the extraction of fluoride from the melt was more efficient if aluminum silicate was present in the leachate and if the sample was finely ground. After the usual fusion of common rock types, filtering of residue, precipitation of silica and alumina by repeated addition of ammonium carbonate with intervening evaporations, the phosphate was removed, and an aliquot taken for the titration. The filtrate was treated with potassium iodide, sodium chloride, zinc chloride, and allowed to stand for 30 minutes at 38°C to ensure completeness of reaction. The solution was then titrated with thiosulfate. Boruff and Abbott, however, found the method unacceptable, for the titrations were not reproducible, not even in solutions of pure fluorides (36); for best results a large excess of potassium iodide had to be added. Smith found organic complexes complexed the iron, thereby causing high results for fluoride (203); Foster said sulfate had the same effect (74).

Boruff and Abbott (36) and Smith (203) have provided careful and extensive critiques of methods extant at their time.

Foster developed a ferric-thiocyanate method capable of detecting 25 micrograms of fluoride in 75 milliliters of solution. The amount of iron withdrawn per amount of fluoride present was not linear. The system was very sensitive to sulfate and chloride, which also formed complexes with fluoride, although their effect could be counteracted by adding additional iron solution to complex these ions (73).

In 1939 Fahey described a ferron-ferric iron reagent suitable for the determination of 0.02 to 10 percent fluoride, the latter being the maximum percentage without the absolute error becoming considerable. The isolation of fluoride was effected by the Hoffman and Lundell procedure (113) and an aliquot of the filtrate was treated with ferron-iron solution (70). A comparison aliquot of the same volume, containing the same sodium chloride concentration and having the same pH, was also treated with the ferron reagent, and a standard sodium fluoride solution added until the color, tending towards yellow, matched that of the unknown solution to which was added equal increments of distilled water. With a Klett colorimeter (visual) differences of 0.05 milligrams of fluoride could be detected. In tests on many synthetic sodium fluoride solutions, one microcline-fluorite mixture, an opal glass, and a lepidolite his results differed by an average of 0.06 percent fluoride from the amounts calculated for 0.010 to 26.41 percent fluoride. For the determination of fluoride in waters the method was not sensitive to less than 1 p.p.m. of fluoride. To gain objectivity, Urech studied the system so as to adapt it to the spectrophotometer (230). He found color development was not reproducible; that is, new solutions of identical concentration would not give the same optical density, unless the system were heated for some time at 50°C. Solutions of sodium fluoride and sodium fluosilicate did not obey Beer's law, the change in absorbance per unit fluoride decreasing as the latter increased. Small amounts of perchloric acid that might be entrained in Willard-Winter distillations (251) caused a bleaching of the ferron reagent, but up to 5 milligrams of sulfuric acid per 100 cc. of distillate had no effect. He gave a procedure for determining fluoride in natural cryolites involving sodium carbonate fusion, double distillation, the second being from perchloric acid at 135°C, and color development of aliquots containing up to 6 milligrams of fluoride. For fluosilicic acid the best sensitivity was a change in per cent absorbancy of 7.3 for the corresponding change from 0.0 to 0.5 milligrams of fluoride.

Titration with Potassium Hydroxide.- In 1925 Guntz and Benoit advised fusion of lithium minerals with potassium hydroxide, precipitation of silica in solution by its precipitation with zinc hydroxide when ammonium hydroxide is added, and titration of the potassium fluosilicate formed with potassium hydroxide: $K_2SiF_6 + 4OH^- = 6F^- + 2K^+ + H_2SiO_3 + H_2O$ (100).

Titration with Thorium Nitrate.- With a paper presented by Willard and Winter in March 1932 there came a very significant advance in the analysis of fluoride: These authors proposed to titrate fluoride with thorium nitrate solution after its isolation from interfering elements by a steam distillation from a non-volatile acid media. With Willard and Winter's valuable development the steam distillation of fluoride and the thorium nitrate titration have each become the subject of an extensive literature, but since the two are often interdependent, the writer proposes to treat them concurrently, tracing some of the important developments since 1932. Both steps are used for some recent methods of rock analysis (99, 115).

To isolate fluoride from interfering ions, Willard and Winter devised a preliminary steam distillation of soluble fluorides with perchloric or sulfuric acid solution containing glass fragments so as to volatilize fluosilicic acid. They preferred perchloric acid media. For around 10 milligrams or less of fluoride they found collection of 50 to 75 milliliters of distillate sufficient, starting the steam distillation when the acid media reached 110°C and then maintaining it at 135°C by admitting water from a dropping funnel. Recovery was quantitative for temperatures ranging from 120° to 150°C. Gelatinous silica, boric acid, and aluminum salts retarded distillation; they removed the first and the last by the modified Berzelius procedure and distilled the filtrates, concluding this isolation step followed by the thorium nitrate titration was short and accurate (251).

Willard and Winter used an alcoholic solution, about 48 percent, for the titration of alkali fluoride and fluosilicic acid in the presence of zirconium alizarin sulfonate, since thorium fluoride that forms is quite insoluble in this media (251). Titration of 1.5 to 15.4

milligrams of fluoride with 0.1 normal thorium nitrate gave slightly lower average percent error but poorer precision than titrations of and with solutions having one-tenth the strengths. Results for all titrations, including a few unknowns done by two analysts, tended to give low results, but with titrations becoming progressively more quantitative as the milligrams of fluoride titrated diminished. For the more dilute titrant it was necessary to correct results for the amount of fluoride that combined with the zirconium of the indicator.

Armstrong introduced the first modification to the Willard and Winter method in 1933. He found the end point by the original method difficult to detect since the color change is faint, and found larger amounts of indicator added to improve the end point inadmissible, for the zirconium combines with the fluoride, as Willard and Winter reported. Armstrong suggested use of sodium alizarin sulfonate alone (13) and recorded best results on small amounts of fluoride since otherwise the "troublesome" adsorption of both dye and lake on the thorium fluoride formed is not so noticeable. He used a reference solution of the pink thorium alizarin sulfonate lake for ascertaining the end point. In tests on 0.050 to 0.400 milligrams of fluoride Armstrong obtained quantitative results.

Still later in 1933 Boruff and Abbott (36) studied the Fairchild method (71), that of Foster (73), that of Thompson and Taylor (225), and that of Steiger-Merwin (153) as modified by Wichmann and Dahle (243), recording objections to each, giving their reasons. Essentially, they confirmed the superiority of the Willard and Winter method, accepting Armstrong's recommendations (13) relative to indicator and the amount of fluoride to be titrated. They evaporated waters rendered alkaline in the distillation flask, distilled with sulfuric acid, and preferred collecting double the volume of distillate recommended by Willard and Winter. They then evaporated this solution, rendered alkaline, to a small volume prior to titration. In tests on synthetic waters they claimed quantitative results, although the data were not summarized in their paper.

One of the first thorough and systematic studies of this titration method was published by Hoskins and Ferris in 1935 (117). From studies on the distillation they found that below 110°C very little fluoride is volatilized; from 110° to 130°C volatilization becomes increasingly efficient, and above 130°C recovery of hydrofluosilicic acid is rapid and at optimum efficiency. They distilled at 140°C and collected 200 milliliters of distillate. Distillation of ashes from fruit and vegetables gave 96.7 percent recovery of fluoride per 150 milliliters of distillate. They, as did Reynolds (184), found siliceous coatings formed in the distillation flask retarded liberation of fluoride; they too removed these coatings with alkali. 1.785 milligrams of fluoride added as sodium fluoride to crushed apples was 97.3 percent recovered when the samples were ashed at 720°C for 20 minutes in a muffle. Lower temperatures and longer ashing times gave low results as did 820°C for 10 minutes. Lime was used as a fixative for fluoride. Such incomplete recoveries, often reported, are said to be due to loss during ashing or incomplete volatilization. Hoskins and Ferris preferred the former explanation, but they suggested high-temperature ashing may produce complex fluorides stable in hot acid; to obviate this error, they proposed to study ashing by combustion in oxygen.

The more important aspect of Hoskins and Ferris' work was on the titration phase (117): They (1) confirmed Armstrong's improvements (13), (2) developed an optimum concentration of sodium alizarin sulfonate (4×10^{-5} percent)-thorium (about 0.05 cc. of 0.001 molar solution) indicator solution, and (3) found a reference blank indicator should be freshly prepared, for the color intensifies with standing owing to the slowness of the reaction. Acidity affected fluoride results significantly, the "most desirable pH" being 3.5; pH values less than about 3.0 gave high results for fluoride and those above 3.7 gave low ones when the end point was taken by comparison with a thorium-indicator blank having the same pH as the unknown solution. But if the thorium-indicator blank had a constant pH (3.5), the range of pH values tolerated in the unknown solutions was greatly reduced. They demonstrated, moreover, that dropwise addition of 0.24 normal hydrochloric acid until the indicator appeared yellow did not give the pH control required, particularly for alcoholic solutions. They described the use of a half-neutralized monochloracetic acid buffer that gave the desired pH (3.5) in the alcoholic solutions called for by Willard and Winter (251) and Armstrong (13). For titration of 0.057 to 0.760 milligrams of fluoride Hoskins and Ferris also got a tendency towards low results (minus 1.0 percent average error compared with minus 2.2 percent reported by Willard and Winter for 0.154 to 0.77 milligrams of fluoride). They tabulated data on the interference of various ions in the titration: Effects by halides, nitrates, and perchlorates were appreciable at 0.1 molar, and by arsenate, sulfate, and phosphate at 10^{-6} molar. These authors were the first to recognize the effect of sulfate, which effect follows from Barre's findings (23) that even 0.001 molar thorium sulfate is not at all completely dissociated; they were also the first to recognize alcoholic media lessens the dissociation of thorium sulfate.

Not long after, in 1936, Armstrong made an important modification: He introduced titration in aqueous media, which media is now generally employed (14). His work arose from the need for a method capable of determining the microgram quantities of fluoride so common in "naturally occurring substances." For the 48 percent alcoholic solutions simple reduction of the volume of the fluoride-containing solution to 2 cc. and of the concentration of the titrant to 0.0004 normal gave both with and without the Hoskins and Ferris buffer (117) two thorium-to-fluoride titers, one for 0.5 to 1.25 micrograms of fluoride and another for 1.25 to 10.0 micrograms. In addition distillates gave high blanks for fluoride, equivalent to 20 micrograms and were ascribed to perchloric acid volatilized in amounts of about 2 cc. of 0.1 normal acid per 150 cc. of distillate when the distillation was run at 140°C. At 130°C the blank due to perchloric acid is equivalent to 8 micrograms of fluoride, but the fluoride was only 70 percent recovered. All in all, the distillation blank was so appreciable and variable that no reliable determination of microgram quantities of fluoride was possible, even when several expedients were tried. But by titration in aqueous media, the thorium-to-fluoride titer was constant for 0.5 to 10 micrograms of fluoride. The effect of perchlorate was much less in this media and its amount could be further reduced in the distillates by up to 50 percent by adding sodium perchlorate to the distilling flask. A formic acid-sodium formate buffer, giving a pH of 3.5, resulted in high values for fluoride less than 2 micrograms; with the Hoskins and Ferris buffer, having a pH of 2.8 in aqueous solution, the titer was exact for the 0.5 to 10 microgram range. Using distillation equipment like that of Willard and Winter (251), Armstrong distilled at 140°C and collected 150 cc. of distillate, these reported to provide optimum recovery of fluoride and minimal distillation of perchloric acid. He then evaporated the solutions, alkaline to phenolphthalein, to 5 to 10 cc., according as the amount of fluoride was less or greater than 5 micrograms. If less, he titrated 1 milliliter aliquots. A blank, amounting to over 0.2 cc. of 0.0004 normal thorium solution was found by graphical interpolation. A reference solution is used as a color standard for the determination of the end point. In titrations of 2 to 25 micrograms of fluoride Armstrong's average error was minus 1.3 percent for those fluoride solutions recovered by distillation and minus 1.0 percent for those carried through the post-distillation steps only, the comparison with the latter suggesting the former results were not quantitative through compensating errors. However, the writer considers that this conclusion cannot be justified by the comparison.

Rowley and Churchill, noting the success Armstrong claimed for the determination of microgram quantities of fluoride in aqueous solution, reported in 1937 a procedure for determining 1 to 50 milligrams of fluoride by titration with 0.1 normal thorium nitrate in the same media (190). They did, however, standardize the titrant with alkali fluoride in alcoholic media. For aqueous solution they demonstrated that the end point was distinct and occurred at the stoichiometric point when the pH was between 2.9 and 3.4; the "most sensitive end point" was at pH 3.0. For pH values less than 2.9 the volume of titrant exceeded that stoichiometrically required; for values greater than pH 3.4 the volume required was less. They found 1 milliliter of 0.5 normal monochloracetic acid-0.5 normal sodium chloracetate buffer per 100 cc. of fluoride-containing solution buffered the solution adequately; 0.5 cc. to 2.0 cc. of this buffer solution had no effect on the titration of 1.0 milligrams of fluoride in 100 cc. of solution. The authors concluded that use of aqueous media meant greater accuracy, because the end point was sharper than in 48 percent alcohol; they stated further, "Three analysts, who had had little, if any, experience with the method, had no trouble in observing the correct end point in the aqueous solutions, although they experienced considerable difficulty when they tried titrating the alcoholic solutions." They also concluded larger amounts of fluoride could be titrated in aqueous than in alcoholic solution and that titration of small amounts of fluoride with dilute thorium titrant (0.01 normal) is sensitive to the pH of the solution, the optimum pH for which not yet being established.

Rowley and Churchill suggested standardization of the titrant by distillation of pure natural cryolite or fluorspar or sodium fluoride; however, as mentioned above, they appeared to standardize also by direct titration of sodium fluoride. Rowley and Churchill (190), along with Willard and Winter (251) and Armstrong (14) considered the reaction of thorium with fluoride to be the same, be the fluoride present as alkali fluoride or fluosilicate; e.g., it forms "thorium fluoride." As a consequence, all these workers make no clear distinction between titrant standardized by and employed for either alkali fluoride or fluosilicic acid.

In the same year (1937) Churchill, Bridges, and Rowley (50), finding anomalously high results for fluoride in certain high phosphate content foods, which high results they concluded were due to interference by the phosphate in the thorium titration, recommended a double distillation of these ashed samples: The first distillation should be done from sulfuric acid, this distillate should be evaporated to low bulk after rendering it alkaline to phenolphthalein, and redistilled from perchloric acid at 135°C. They demonstrated that the double distillation method gave quantitative recovery of fluoride and its complete isolation from phosphate.

Early in 1938 Eberz, Lamb, and Lachele (64) dealt extensively with the errors involved in perchloric acid and sulfuric acid distillations of ashed tomatoes. They employed the alcoholic media of Willard and Winter (251), the sodium alizarin sulfonate indicator recommended by Armstrong (13), and the half-neutralized monochloracetic acid buffer of Hoskins and Ferris (117) for the titration of the fluoride in the distillates. They provided data on the effect of varying amounts of various anions on this titration: A given amount of sulfuric acid (0.10 to 0.25 milligrams added as the sodium salt into 30 milliliters total volume of alcoholic solution) causes increasingly higher titers according as the amount of fluoride increases; 5 to 10 milligrams of hydrochloric acid and up to 30 milligrams of perchloric acid had no significant effect on the titration of 0.15 milligrams of fluoride. In the absence of interfering ions the titer increased as the amount of fluoride increased up to about 0.05 milligrams, after which it was linear. Increases in volume of the fluoride-containing solution containing no buffer affected the titer appreciably; the data "illustrate the value of the buffer in greatly reducing the error arising from volumes of solution differing from the standard volume."

In 1939 Reynolds and Hill, finding that the volatilization method of Reynolds, Ross, and Jacob (187) and the fusion-acid extraction-lead chlorofluoride method of Reynolds and Jacob (186) gave low results, considered that the improved Willard and Winter method was the best (185). They found that:

1. a decrease or increase in the indicator concentration for small amounts of fluoride caused plus and minus errors, respectively, in the amount of fluoride found.

2. titration in either alcoholic or aqueous solution showed a linear relation up to 50 milligrams fluoride for each, essentially the same titer, but a larger blank for the latter media.

3. titration of less than 0.1 milligrams fluoride in aqueous media lead to progressively higher titers as the amount of fluoride diminished.

4. nitrate, chloride, and perchlorate, effecting low results in alcoholic solution, had about the same effect for the same concentration, indicating it was the alkali ion that was responsible for the negative effect.

5. using a common anion (chloride), the magnitude of negative error effected by the cation in alcoholic solution was in the order: K^+ Na^+ NH_4^+, and that the minus errors were due to the formation of insoluble compounds, of which potassium fluosilicate is the least soluble, as evidenced by the fact addition of these salts near the

end of the titration produced little effect.

6. in aqueous solution alkali chlorides, nitrates, and perchlorates had little effect up to 0.08 to 0.1 molar, or three times that tolerated in alcoholic solution, and that the effects of sodium and ammonium chlorides led to plus errors, unless the volume of solution was very low (10 milliliters instead of 50 milliliters).

7. orthophosphate was titrated quantitatively in alcoholic and aqueous solutions, but its effect was somewhat less in the latter media.

8. the effect of sulfate increased with the amount of fluoride in alcoholic media (1.0 milligrams sulfate effected an error of +0.14 milligrams fluoride for 1 milligram fluoride present and +0.32 milligrams for 3.8 milligrams present), but its effect nearly disappeared and was independent of the volume of solution in aqueous media (+0.015 milligrams of fluoride for 3.8 milligrams present).

In studies on the distillation Reynolds and Hill found sulfuric acid did not effect complete recovery unless the temperature was 150°C or more, at which temperature, however, sulfate was entrained in distillates. Phosphoric acid should be used in place of perchloric for distillation of organic matter, followed by redistillation with perchloric acid. In general, perchloric acid was the best media, but even with it phosphate will be entrained in distillates if the material is high in that element or if phosphoric acid was once used in the apparatus. In perchloric acid distillations chloride, nitrate, and sulfur compounds from pyritiferous samples were always entrained and boron and arsenic under certain conditions. Evaporation of distillates caused low results in the thorium titration, for reasons not determined. Blanks on perchloric acid varied with the lot of acid, inexplicably accumulated on double distillation, and when a blank distillate was added to a sodium fluoride solution and titrated, lowered the milliliters of titrant required, suggesting the blank was not due to fluorine in the acid. Recovery of fluoride from phosphate rock was complete when 150 milliliters of distillate was collected; preliminary fusion with sodium carbonate was not necessary, although Hoffman and Lundell reported this step improved recovery using sulfuric acid (114). Separation of sulfur from fluoride was effected with excess permanganate provided chloride was not present in more than traces. Ignition of phosphate rock to oxidize pyrite effected low fluoride results. They gave a procedure for phosphate rock analysis using the thorium titration of aliquots of distillate with sodium alizarin sulfonate and the Hoskins and Ferris buffer. Agreement was good with results obtained by the lead chlorofluoride method of Hoffman and Lundell (185).

In the same year McClure (146) reported lower precision in the microtitration of fluoride than Armstrong had claimed (14). In a visual titration in specially arranged lighting McClure found (1) that the "end point was scarcely sensitive to a variation of less than ... 0.15 to 0.25 micrograms of fluorine" owing to difficulty of end point determination and (2) that there was a high blank, equivalent to 1.8 micrograms of fluoride. He felt the blank should not exceed one-third the fluoride titrated. On titration of aliquots containing 1 to 10 micrograms of fluoride, his average error was 0.19 micrograms for an average 47.5 micrograms titrated. He reported low results for pure fluoride solutions after their evaporation in porcelain or glass; he could not offer an explanation. He followed Eberz, Lamb, and Lachele's procedure (64) for adding a silver salt to the distilling flask to prevent volatilization of chloride. In the analysis of biological materials he used small samples of ash to minimize the effect of interfering elements. He reported acceptable recovery for fluoride added to ashed samples, although his tests indicated a tendency for low results. His errors were ±1 to ±3 micrograms of fluoride for 60 to 110 micrograms titrated. However, he found the method unacceptable for samples having low fluoride but high ash contents; e.g., milk with less than 1 p.p.m. fluoride but high chloride and phosphate contents, for deviations on duplicate samples reached ±7 micrograms and recoveries of added fluoride were erratic.

Rempel described in 1939 a simplified procedure for determining fluoride in wine. He found that there was no loss of fluoride on evaporation of solutions in glass (182).

In 1940 Langer described a polarographic method of determining fluoride employing thorium nitrate solution (133). The method could not be carried out with calcium fluoride, lead chlorofluoride, or fluoferrate, fluoaluminate, and fluozirconate complex ions. He studied the effect of neutral salt concentration, temperature, and alcohol content, the latter producing higher titers in proportion to its concentration. The stoichiometric volume of thorium solution for polarographic determination was somewhat less than that indicated by gravimetric determination. For 560 micrograms of fluoride the standard deviation was equal to ±4 micrograms fluoride. By using more dilute solution of titrant he determined up to 38 micrograms fluoride to within a maximum error of about 1 microgram. Sulfate at 0.001 molar effected a plus error of 3.5 micrograms in the titration of 563 micrograms of fluoride. He reported lanthanum nitrate was also acceptable as the titrant for the polarographic method.

In 1942 Okuno, who published a very extensive review of the literature, carried out comparative studies on the Foster (73), Smith-Dutcher (205), Thompson and Taylor (225), and Sanchis (192) methods for water analysis, and concluded the Sanchis and Foster methods were superior to the others, preferring the latter, for it was more sensitive and more economic of time and reagents (168). Okuno found that in tests on pure solutions of sodium carbonate-sodium fluoride the Berzelius-Rose method gave progressively lower results as the fluoride decreased; 100 and 50 milligrams of fluoride was recovered 97 percent and 92 percent, respectively, and 50 milligrams and 1 milligram gave recoveries ranging from 70 percent to 30 percent. The Steiger-Merwin method, he claimed, had lower sensitivity compared to the more recent colorimetric methods mentioned above. For some water analyses he employed the Willard and Winter method as modified by Hoskins and Ferris (117) and Armstrong (13, 14), but further work showed an aluminum-hematoxylin system to be more sensitive than any other. It had a lower detection limit (0.001 milligrams fluoride per 100 cc. compared with 0.02 milligrams per 100 cc. for the "old method") and a superior sensitivity (differences of 0.005 milligrams could be distinguished by the aluminum-hematoxylin method, 0.01 milligrams for Sanchis' method). The tolerance of the system for salts was about the same as for others (Na^+ 700, K^+ 200, Ca^{++} 100, Mg^{++} 20, Cl^- 1000, SO_4^{--} 100 milligrams per liter for each); iron and aluminum in waters interfered. Okuno tabulated 58 complete analyses of mineral springs in Hokkaido and discussed their composition.

The next significant work on the thorium nitrate titration was carried out by Matuszak and Brown in 1945 (145). They confirmed Reynolds and Hill's finding that the optimum indicator strength for the visual titration was 0.025 percent. They used a color standard consisting of a sodium chromate-cobalt nitrate solution; the end point was taken as that thorium-alizarin color that matched this standard. They also confirmed the work of others on the effect of variations of pH on the titer, adding, however, that at a given pH the titer was not rectilinear. To compensate for this fact, they added acetic acid to the titrant so that the pH would decrease in proportion to the amount of fluoride titrated, thereby maintaining rectilinearity of titer. They proposed a procedure for correcting for the sulfate entrained with the hydrofluoric acid by titration of both acids with hydrochloric acid in the presence of sodium alizarin sulfonate, the sulfate being obtained by difference after the determination of the fluoride. They were of the opinion that the percent fluoride in the sample could be expressed to the fourth decimal place for amounts of fluoride up to 0.1 percent.

The first attempt to explain the effect of neutral salts such as sodium chloride on the titration came in 1946 in a paper by Williams (252). Previous efforts to obviate "salt errors" had involved titration of the acidity in the distillate as Matuszak and Brown had done (145), or back titration of thorium in a blank distillate by means of standard sodium fluoride or potassium fluosilicate, this step being in effect a standardization of the thorium at conditions approximating that of the distillation. The explanation of the effect of salts, acidity, and dilution of the solution lay, Williams suggested, in the degree of dissociation of the thorium tetrafluoride formed and of the indicator: (1) in dilute solutions thorium fluoride is never formed in stoichiometric equivalence to the fluoride present due to its dissociation; ThF^{+++}, ThF_2^{++}, and ThF_3^+ were formed instead in proportions governed by the amount of excess thorium, influence of hydronium ion, and other ions, (2) the fluoride ions derived from the dissociation of thorium tetrafluoride; e.g., $ThF_4 = ThF_3^+ + F^-$, are free to compete with thorium ions in the chelate, thus effecting a predominance of the yellow color of the indicator, and (3) increasing acid or neutral salt concentration increases the pH and consequently the degree of dissociation of the thorium tetrafluoride. However, relatively high concentrations of salts limit the degree of dissociation of the thorium tetrafluoride so that the titer decreases as the concentration of the former increase. This observation led Williams to develop a "high salt-acid" thorium nitrate titration of microgram quantities of fluorides (up to 150 micrograms). To obviate the indicator blank; that is, the titrant required to produce the color change in the indicator, Williams prepared a thorium-alizarin sodium sulfonate indicator whose color was equal to that taken for the end point, judged by either the temporary indicator system or a cobalt chloride-potassium chromate solution of identical color. He titrated distillates with hydrochloric acid-acidified thorium solution after adjusting the pH with hydrochloric acid, 2,5-dinitrophenol as indicator, and adding sodium chloride and indicator solutions. Williams claimed the use of the Hoskins and Ferris buffer decreased sensitivity and, like acetic acid buffers, resulted in high blanks. The Williams method is now often used, sometimes with modifications (206, 207).

The Williams (252)-Smith and Gardner (207) method has been studied by Adams and Koppe (1), who found the reaction was stoichiometric only between pH 2.9 to 3.2 and that titration at pH 2.9 was best, for the rate of change of titer was at a minimum to variations in pH around this value. They titrated unbuffered solutions of fluoride (less than 100 micrograms) adjusted to pH 2.90 with thorium nitrate solution of the same pH. To improve the precision, they calculated the fluoride after correcting the volume of titrant for the variation in pH from 2.90 at the end of the titration. The correction was taken from curves, prepared from titration of standard samples, relating variation of titer with pH. These authors claimed the use of this correction reduced the standard deviation for 20 to 80 micrograms of fluoride from 7.3 percent (without the correction) to 2.8 percent (with the correction). The pH for these titrations ranged from 2.83 to 2.94.

An important study of the use of the thorium nitrate titration for determining fluoride in soils was conducted by Hardin (105), who undertook a collaborative study of two methods, one involving ashing with calcium oxide and the other a direct double distillation, but both calling for a thorium nitrate titration for the final determination. Ten analysts did analyses of six soils by the two methods. The study showed not so much the relative efficacy of the two methods (the average fluoride reported for 9 analysts for each sample being quite similar for each method) but instead the very serious deviations among analysts for a given sample and method. Indications were that the poor agreement was "due to conditions inherent in the titration end-point phase, rather than to disparities in the recovery of the fluorine in the distillation step" and, further on, "It seems obvious that the titration phase of the procedure should be improved to assure greater accuracy and precision." In a subsequent paper Hardin confirmed that the personal factor in the titration, despite each collaborator's confidence in the method, was accountable for the poor agreement (106). Titrations were done by visual recognition of the end point. Bearing in mind that many conditions, such as methods, concentrations of titrant and indicator, etc., were constant for all collaborators, the writer finds Hardin's conclusions are discouraging indeed, all the more so since the results of one worker were so low that they were discarded. For method I only 44 percent of the results were within 10 p.p.m. fluoride of the averages for each of the six soil samples, for method II only 50 percent fell within 10 p.p.m., and the average deviation among collaborators for soil samples having an average of 32 to 415 p.p.m. fluoride, depending on method and soil, ranged from 8 to 27 p.p.m. Although there was this significant difference among collaborators, replications by the same collaborator agreed well. Again, depending on soil sample and method, standard deviations ranged from 9.8 to 41.2 p.p.m. fluoride. In a further study, however, a comparison of results obtained by visual and spectrophotometric titration showed agreement was good and that an experienced operator can complete a visual titration twice as fast (57).

An important series of papers was published by Wadhwani (235, 236, 237, 238), who gave convincing evidence that the reaction of alkali fluoride is different from that of fluosilicic acid in the thorium nitrate titration. His evidence was based on (1) the difference in stoichiometry for alkali fluoride and fluosilicic acid titrated by thorium solution of the same strength. For the same amount of fluoride two-thirds the volume of thorium solution is required for the element present as fluosilicic acid as against alkali fluoride; moreover, the average ratio of thorium to fluoride present as fluosilicic acid is different from that ratio in thorium tetrafluoride compound (2.053 against 3.054), (2) conductometric titration of the same quantities of fluoride, the end points for the two species of fluoride being again the two-thirds ratio, and (3) the fact that of three equations postulated for the fluosilicic acid-thorium reaction:

$$H_2SiF_6 + Th(NO_3)_4 + 4H_2O = Th(OH)_2SiF_6 + 4HNO_3 + 2H_2O \quad (A)$$

$$H_2SiF_6 + Th(NO_3)_4 + 4H_2O = H_2ThF_6 + 4HNO_3 + H_4SiO_4 \quad (B)$$

$$2H_2SiF_6 + 3Th(NO_3)_4 + 2H_2O = 3ThF_4 + 2H_4SiO_4 + 12HNO_3 + 4H_2O \quad (C)$$

equation (B) fitted the observations that (a) an insoluble compound is formed ($Th(OH)_2SiF_6$ is appreciably more soluble than H_2ThF_6), (b) the production of acidity measured on fluosilicic acid solutions containing thorium chloride in amounts less than an excess approximated that predicted by equation (B), and (c) the thorium content of the insoluble compound produced was found to be very close to that in the formula H_2ThF_6.

Wadhwani also observed (235) that dilution affected the equivalence of thorium to fluoride as fluosilicic acid less than for the latter element as alkali fluoride. In addition he observed distillation conditions affected the thorium to fluoride stoichiometry; gentle and slow distillations generally insured the stoichiometry was according to equation (B) above. He studied systematically the effect of pH on the titration of fluosilicic acid and interfering ions (235). He concluded that the pH did not govern whether this reaction was stoichiometric but rather the dissociation of the sulfonic acid group of the indicator. He obtained dissociation constant values at different pH values for the indicator and discussed explanations of the variation in stoichiometry based on equilibria between the various chemical species present; e.g., HIn (acid form of the indicator), H^+, In^-, F^-, and Th^{++++}. Only moderate amounts of fluoride could be titrated and that element is better determined as fluosilicic acid than as sodium fluoride, he concluded, giving reasons for this preference. He suggested an indicator whose dissociation was less affected by pH and salt concentration variations would lead to more accurate volumetric determinations of fluoride.

Other Thorium-Indicator Systems.- Indeed, recently some workers have examined new indicators for the thorium nitrate titration:

1. Ballczo and Kaufmann (19): 3 to 100 micrograms of fluoride in Willard and Winter distillates (perchloric acid) can be determined within 1 microgram by using an alizarin sulfonate-methylene blue mixed indicator for the visual titration with 0.001 normal thorium nitrate.

2. Willard and Horton (249): in a study of indicators giving a color change in the visual range, purpurin sulfonate was the best indicator, alizarin red S next best, and then eriochrome cyanine R. They gave optimum pH, amounts of fluoride that can be titrated accurately, and concentration of indicator data for each. They also rated fluorescence indicators.

3. Milton, Liddell, and Chivers (157): Solochrome Brilliant Blue B.S., the sodium salt of sulfo-dichlorohydroxy dimethylfuchsin dicarboxylic acid, has a sharp color change from pink to blue, is more sensitive than the color change given by alizarin, and the reaction is immediate. The solution must be buffered at pH 3.0. 2 to 100 micrograms of fluoride can be titrated; high amounts result in the precipitation of thorium tetrafluoride, although this can be avoided by a protective colloid. They gave a procedure for the visual titration of fluoride isolated by distillation.

4. Datta (56): Thorium nitrate titrations of small amounts of fluoride (down to 16 micrograms) can be carried out visually after a perchloric acid distillation by the use of 2-(p-sulfonaphthylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid (SNADNS), di-SNADNS, and nitroso-SNADNS dyes. The latter two dyes gave the sharpest end points, and all dyes worked best at pH 2 to 2.4, depending on the dye. The writer uses a related dye, SPADNS, for his rock analyses (115); Banerjee first described its preparation and use (22).

Instrumental Thorium Titration Methods.- The thorium titration has been followed oscillometrically (98, 102). Haslam and Squirrel (107) and Menis, Manning, and Ball (152) have carried out the titration with automatic titrimeters.

Titration with Zirconium Oxychloride.- Following the work of de Boer and Basart (32), who back titrated fluoride-containing solutions to which was added a measured excess of zirconium oxychloride octahydrate with potassium fluoride in the presence of sodium alizarin sulfonate, Millner and Kunos (156) found the method suitable for determining 1 milligram or less of fluoride only if the acidity was low and if phosphate were first removed by precipitation with silver. The method was used for sodium fluosilicate and cryolite.

Evaporation of Fluoride Solutions in Glass.- Evaporation of filtrates is commonly a step in fluoride procedures; some consider fluoride is lost if this step is carried out in glass, some do not. Specht found (211), on the basis of experiments with fluoride solutions in contact with ground borosilicate or soft glass that fluoride is either adsrobed or bound to the lattice; recovery of such adsorbed fluoride could be effected by dilute acid-ferric ion solutions followed by dilute alkali. Use of polyethylene containers did not result in loss of fluoride.

Distillation Apparatus.- The design of distillation apparatus has been given much attention. Smith and Parks devised a special steam tube that allows steam to escape just above the level of the solution, which is kept stirred by bubbles forming in a Markownikoff-type extension of the tube (208). To prevent entrainment of acid into distillate, Wadhwani (236) designed a special trap. Glass plates in the neck of the flask are said to accomplish the same purpose (227). An apparatus for a simultaneous double distillation has been designed by Fox and Jackson (75), who also examined the nature of the retarding effect of aluminum on fluoride recovery. One of the first semi-automatic distillation apparatus was published by Gilkey, Rohs, and Hansen (94); Huckabay, Welch, and Metler (118) improved the design considerably, theirs being used often, the writer included (115). Apparatus, often made automatic by a thermostatically-controlled heat regulator, are the subject of several papers (29, 59, 69, 123, 150, 195). Morris and Cerny have recovered fluoride from waters by an air-jet distillation (163). Pietzka and Ehrlich have examined the performance of a new distillation apparatus with pure sodium fluoride solutions and solutions containing aluminum and titanium ions (173).

Studies on the Steam Distillation.- The distillation step has also been examined. Remmert, Parks, Lawrence, and McBurney found that recovery of fluoride from ashed samples of grass and hay improved as the sample size decreased (181). Rowley, Grier, and Parsons reported a similar finding: Only small amounts of fluoride could be quantitatively recovered by a direct distillation of ashed vegetation samples (191). The only systematic studies on the distillation of fluoride were made by Wichmann and Dahle. In their first paper (246) they related effects on recovery to the following factors: (1) the amount of non-volatile acid used in the distillation flask, (2) temperature of distillation, (3) amount of distillate collected, (4) size of flask, and (5) effect of silica and aluminum salts and other retarding influences. In general the smaller the volume of acid used, the higher the temperature, and the smaller the flask the better was the recovery. Graphs expressing fluoride collected per unit volume of distillate showed an asymptotic relation. In a second paper (247) they found high amounts of aluminum, derived from ashing of certain foods with aluminum nitrate fixative (245), retarded distillation seriously unless distillation from sulfuric acid at high temperatures and collection of large amounts of distillate were employed. For the determination of fluoride impurity in alums, they used a double distillation from sulfuric acid, one at 162°C and the next at 137°C. The fluoride in the distillate was determined by the peroxidized titanium complex (244). In a third report on the distillation (248) examining the use of perchloric and phosphoric acids, these authors found that recovery per cc. of fluoride by these acids decreased with increasing volume of liquid in the distilling flask, increased temperature of distillation effected higher recoveries per cc., and that the above acid systems were more sensitive to conditions when distillations were made with perchloric and phosphoric acids than with sulfuric acid. Moreover, the addition of soluble salts or non-volatile acids to the usual contents in the distillation flask effected a decrease in the recovery rate greater than could be accounted for by the increase in volume of the contents caused by the addition of these salts. The recovery for these acids was also asymptotic.

Separation of Fluoride by Ion-exchange.- The separation of fluoride from interfering anions may also be done by the use of certain anion-exchange resins, Amberlite IRA-400 and IRA-410, under certain conditions (77, 80); these workers have removed phosphate, sulfate, and carbonate on a column, eluted fluoride, and determined it by aluminum titration with eriochrome cyanine R indicator or colorimetric methods with iron-salicylic acid or thorium alizarin red S systems. An acidimetric method based on titration of hydrofluoric acid formed on replacement of metal cation of a fluoride by hydronium ion is given by Aynsley (16). Separation of fluoride from phosphate and anionic metal chelates of ethylenediamine tetraacetic acid by use of a strongly basic resin has also been done (166). Fluoride in cryolites has been analyzed after ion-exchange by Ashratova (15).

Spontaneous Electrolysis Methods.- An inexpensive instrumental method that may merit further investigation is that of Baker and Morrison (18). A current, generated by the spontaneous electrolysis effected by fluoride in an Al°/CH_3COOH (0.2 molar)/Pt° cell is directly proportional to the fluoride present. A microammeter connects the electrodes which are quickly immersed in the fluoride-containing solution and the current is read exactly 2 minutes later. But as the method is empirical, exact adherence to operating conditions is necessary; moreover, frequent cleaning of the electrodes is necessary, followed by recalibration. Frequent checks are also necessary. See Megregian for a zirconium electrode for the determination of 2.5 to 20 milligrams per liter of fluoride by the same principle (149).

Spectrophotometric and Fluorometric Methods.- A number of spectrophotometric and fluorometric methods based on the bleaching action of fluoride ions in certain systems have been published in the last ten years. Below are some that might have or do have applicability to rock analysis.

Colorimetric procedures include:

1. a titanium-chromotropic acid system, Babko and Khodulina (17); a titanium-ascorbic acid system, linear from 0 to 50 p.p.m. of fluoride, Schall and Williamson (195). The work of Brownley, Jr. is also of interest (39).

2. a thorium-chrome azurol S system, Revinson and Harley (183). Up to 50 micrograms of fluoride in pure fluoride solutions can be determined to within an average of 0.8 micrograms of the amount present. The lake must be stabilized with gum arabic. Revinson and Harley concluded carbonyl and carboxyl group buffers reduced the sensitivity of thorium-dye systems for fluoride; they used a perchloric acid-o-toluidine buffer (pH = 4.0).

3. a thorium salt of N-(4-(o-arsonophenylazo)-1-naphthyl)

ethylenediamine reagent for the visual determination of small amounts of fluoride (0 to 2.7 micrograms), Liddell (136). The writer investigated the procedure and found determination inaccurate; the colloidal dispersion made it unadaptable to a spectrophotometric method. It was difficult for the writer to keep the solution colloidal for the visual method, as required; a precipitate formed readily.

4. a zirconium-eriochrome cyanine R system, Megregian (148). Of 7 dyes considered superior to nearly 200 organic reagents screened, Megregian chose the above dye, for its lake is soluble and stable, reactions in the zirconium-dye-fluoride system are rapid, and it has high sensitivity to fluoride. Megregian claimed the system was nearly ideal for successful colorimetric fluoride analysis; it was, however, subject to sulfate and phosphate interference, for which Megregian gave a turbidimetric correction procedure for the former anion. As with many systems of this sort, Megregian has found optimum conditions are essentially a compromise. Thus, at high pH the zirconium-dye system is stoichiometric, but it has increased sensitivity to phosphate and has low buffer capacity; at lower pH it is <u>vice versa</u>, but owing to lack of stoichiometric conditions, sensitivity to fluoride diminishes. In pure fluoride solutions ±0.5 micrograms fluoride can be detected in 50 milliliters. On replicate analyses of bone ash and urine, blanks for this method were about one-sixth of those for the thorium nitrate titration and the precision was better. Van Gogh has used the system to determine fluoride in cal-

cium acid phosphate (96).

5. a thorium-neothorin system, Emi and Hayami (66).

6. a thorium-thoron system, Horton, Thomason, and Miller (116). It has been used for the determination of up to 50 micrograms of fluoride after its separation by a steam distillation from perchloric acid.

7. a ferric-ferron system, Wadhwani (237). The system was more sensitive to the effect of fluoride ions than the thorium titration. The diminution of color by fluoride depended on whether it was present as alkali fluoride or fluosilicic acid. 1.7 to 170 micrograms of fluoride can be determined by the method, which is less accurate than the thorium titration although more rapid, free of personal factors, and requiring less experience.

8. a thorium-alizarin system, Icken and Blank (120). A spectrophotometric adaptation of the bleaching effect of fluoride on the thorium-alizarin red S lake, which these authors claimed was simpler, more rapid, and more objective than the titration method, was developed. A slightly modified procedure has been used by an analyst participating in the interlaboratory standardization program (cf. Chapter I -3, section b). 0 to 50 micrograms of fluoride are determined to within 1 microgram using a reference standard containing 500 micrograms of fluoride. Standards must be freshly prepared.

9. three organoferric complexes, Nichols and Condo, Jr. (167). Of 18 organoferric complexes screened for fluoride determination resoacetophenone, 5-phenyl salicylic acid, and beta-resorcyclic acid were the best. The first two are

stable and give good results for up to 6 p.p.m. of fluoride.

Fluorometric procedures include:

1. an aluminum-hematoxylin system, Hunter, MacNulty, and Terry (119). Later MacNulty and Hunter examined the reaction mechanism of this system (141). It has been used to determine fluoride in sewage effluent and waters (28).

2. an aluminum-oxine and an aluminum-morin system, Willard and Horton (250). The first is good for up to 20 micrograms of fluoride with 1 millimole aluminum employed. The aluminum-oxinate complex was extracted with chloroform at about pH 4.7 and the fluorescence in chloroform measured. Extraction seemed to introduce errors. The second system could determine up to 20 micrograms of fluoride in pure sodium fluoride solutions; the fluorescence is sensitive to pH, alcohol content (the morin is dissolved in alcohol), and the aluminum content (low amounts give best sensitivity to fluoride). AlF^{++} was not the only species present, hence the decrease in fluorescence of the system by fluoride does not obey Beer's law; an empirical curve must be prepared. The fluorescence for both systems was measured in a Klett fluorometer. The authors examined the effect of various ions. No complete data on the precision was given; it appeared to be about ±0.5 micrograms. Beck has adapted the method (26).

3. an aluminum-eriochrome red B and an aluminum-superchrome garnet Y system, Powell and Saylor (179). Compared to other fluorescent systems, these were less sensitive to pH variations and ion interferences; however, at pH 4.8 an

error of 1 microgram of fluoride in 25 micrograms will result from a pH variation of 0.03 unit for superchrome garnet Y and 0.08 unit for eriochrome red B. The systems also lose sensitivity with increase of temperature. One milligram of phosphate causes an error of 2 micrograms fluoride, which error, they claim, is less than that for other fluorescent and color systems. For replicate results on 50, 25, and 5 micrograms of fluoride the precision for both dye systems was ±0.04 to ±0.14 micrograms; for 50 to 75 micrograms the mean deviation was ±0.5 micrograms for superchrome garnet Y and ±0.2 for eriochrome red B. For 25 to 50 micrograms of fluoride as fluosilicic acid the relative error for both systems was 2.0 to 2.8 percent. Cu^{++}, Fe^{++}, Fe^{+++}, Ni^{++}, Co^{++}, SiO_3^{--}, Mn^{++}, Cr^{+++}, Be^{++}, Zr^{++++}, and Th^{++++} gave serious interference. In a study of several fluorescent systems White considered Powell and Saylor's systems most suitable for fluoride determination (242).

MacNulty, Hunter, and Barrett (142) adapted the aluminum-eriochrome cyanine R system, which Thrun (226) had first used for a visual estimation of fluoride in waters, to a spectrophotometric determination of up to 20 micrograms of fluoride with an error of ±0.6 micrograms. Similar precision for the same range of fluoride has been claimed for the aluminum-chrome azurol S system by MacNulty and Woollard (144). Interferences for these two systems are the same as for the aluminum-hematoxyline system (142).

The aluminum-superchrome garnet Y system has been used as a titrant for the amperometric determination of fluoride (44). A polarographic method based on the reduction of the aluminum-solochrome violet R.S. complex is good down to 0.001 p.p.m. of fluoride (143). Moelants used an aluminum-eriochrome violet BA system for the amperometric determination of fluoride, discussing also the principles involved (159).

Differential Spectrophotometry.- Since spectrophotometric and fluorometric methods for fluoride are indirect; that is, since fluoride forms no colored complexes of its own, a decolorization is measured instead of an intensification of color, Lothe has shown from theoretical considerations that best precision is obtained at low absorbance readings, where decolorization is nearly complete (138). By means of a differential spectrophotometric technique; e.g., absorbance readings of an unknown fluoride solution taken against a reference solution having similar amounts of all chemical species present in the unknown, precision is considerably improved (139). For the sodium alizarin sulfonate-thorium system he found pH affected the accuracy considerably; optimum sensitivity to fluoride increased as the pH decreased from 4.5 to 2.0, but the effect of pH on error increased. Studying the two variables, ratio of thorium to alizarin and pH, Lothe found that (1) the effect of pH on absorbance is linear for the pH range studied (2.6 to 3.0), (2) the effect of pH is independent of the thorium/alizarin red S ratio, (3) the change of absorbance with fluoride concentration depends on pH and this ratio, (4) the absorbance decreased with time for all but the lowest pH samples, (5) the stability was better at higher pH, and (6) all systems, whatever the pH, except the lowest studied, and whatever the ratio, had good reproducibility. He found an optimum ratio of thorium/alizarin, which was also that used by Icken and Blank (120) (0.2 grams alizarin red S and 0.1 gram thorium nitrate tetrahydrate per liter). A pH of 2.8 was chosen for measurements since it was at optimum buffer capacity for a monochloracetic acid buffer. He claimed superior stability than that of the Icken and Blank reagent to be due to use of dilute thorium-alizarin reagent; a stock was good for one month. Theoretical considerations showing the improved precision of the differential spectrophotometric technique were borne out by tests on fluoride standards: For 20 micrograms of fluoride determined against a reference standard of either 50 or 300 micrograms fluoride, the standard deviation is ±0.44 and ±1.11, respectively; for 50 micrograms fluoride against 50 micrograms, it is ±0.47; and for 200 micrograms against 300 micrograms, it is ±1.0. A pH error of ±0.01 unit has the effect of increasing the absolute error as the fluoride amount diminishes: For 20 micrograms, the error is 1.8 micrograms; for 50 micrograms, it is 1.1; for 200 micrograms, it is 1.0. Errors due to reading of the photometer scale are diminished considerably by use of the differential technique, particularly for low fluoride. Sulfate shows serious interference. Lothe points out (139), however, that the thorium-alizarin red S reagent is pH sensitive and is not as sensitive to small amounts of fluoride as the thoron reagent (116).

Hindrance of Extraction.- In three papers Szabo, Beck, and Toth have drawn attention to what they claim is enhanced sensitivity of colorimetric methods obtained by measuring the absorbance of a colorimetric reagent after extracting it into some organic solvent. Fluoride will prevent the extraction of iron in a ferric-thiocyanate complex, for example; the absorbance of the latter is measured after its extraction into n-amyl alcohol (220, 221, 222).

Pyrohydrolysis Methods.- A promising and straightforward procedure for rock analysis is a pyrohydrolitic method; one of the first procedures described has been for heavy metal and magnesium fluorides (239). Light metal and alkali fluorides can also be analyzed, but they are pyrohydrolyzed slowly so uranic oxide must be mixed with them, but the uranic oxide "accelerator" worsens the precision of the method (239). An inexpensive apparatus, substituting nickel for platinum and quartz, for this sort of analysis is given by Susano, White, and Lee, Jr. (219). Lee, Jr., Edgerton, and Kelley describe in detail the design of a pyrohydrolysis apparatus (135); they are, incidentally, the only workers in recent years to employ a spectrophotometric titration adaptation of the thorium nitrate-alizarin red S system. Rezac and Kubec have determined fluoride pyrohydrolitically in commercial aluminum fluoride and cryolite (188). Kinetics for pyrohydrolysis of calcium fluoride have been examined by Mikhailov (155). The method has been adapted to analysis of glasses and silicates (2); a temperature of 1000°C and a uranic oxide accelerator are employed, the pyrohydrolysis taking 30 minutes and the fluoride titrated with thorium nitrate. Gamble, Price, and Jones used pyrohydrolysis followed by thorium nitrate-alizarin titration for silica-alumina catalysts (85); agreement with chemical methods for the same samples was favorable. An apparatus made of a nickel reaction chamber is described in detail by Surak, Fisher, Burros, and Bate (218). They determined fluoride evolved and caught in alkaline solution either acidimetrically or spectrophotometrically with thoron reagent. Hibbits discussed precision in the determination of fluoride in simple compounds by pyrohydrolysis (109).

Pyrolitic Methods.- A method which has been used by a participant in the interlaboratory standardization program (cf. Chapter I -3, section b) has been described by Powell and Menis in two papers (177, 178). The writer has no doubt that this procedure or the pyrohydrolysis method (239) has features that will make it, with certain refinements, supersede existing procedures for determining fluoride in silicate materials. In one paper Powell and Menis analyzed clay minerals and other materials as follows: The sample was mixed with a fusion agent, sodium tungstate, and an accelerator, tungstic oxide, and moist oxygen was passed over the sample at 825°C. A flux-accelerator mixture was required to effect reaction of the fluoride and its subsequent pyrolysis. These authors tried the writer's sodium peroxide fusion step (115), followed by addition of tungstic oxide and then pyrolysis with no success (177). In the analysis of National Bureau of Standards opal glass number 91 and phosphate rock number 56b by the method, results agreed well with the accepted values when fluoride in the solution was determined acidimetrically. In the analysis of several clay minerals having 0.01 to 1 percent fluoride the coefficient of variation was 8 percent. They stated fluoride can be determined in "a considerably lesser period of time as compared to the method described by Hollingworth" (177).

Applications of Methods.- The application of various methods to a variety of materials is covered in the following references:

1. age determinations by analysis of bones: Weiner, Oakley, and Clark (241), Danilova and Alekseev (55), Bergman and Karsten (27), and van der Vlerk (233).
2. Miocene horse bones: Olsen (170).
3. cryolite: Bognar and Nagy (33, 34), Nagy (165), Shehyn (200).
4. fluorspar: Iliminskaya (121), Shehyn (200).
5. phosphate rock: Vigier (232), Shapiro (199).
6. soils: Jahn-Deesbach (122), Zemlyanitskaya (254).
7. slags: Kristoffersen (131), Bloch (31), Eberius and Kowalski (63), and Gericke and Kurmies (91).
8. waters: American Society of Testing Materials (10,

11), Anselm and Robinson (12), Demole and Held (58).

9. fumarolic products: Tonani (228).

10. glass: Allison (9), Vogel (234), and Proffitt, Hansen, and Cluley (180).

11. rocks: Danilova (54), Michael and Blume (154), Bear (25), Bøgvad (35), Spitzner (213), Comucci and Mazzi (52), and Demole and Held (58).

12. coals: Bradford (37).

A unique method of separating fluoride from silica by insolubilization of the latter with dilute nitric acid without loss of fluoride is given by Cioara, Popivici, and Musat (51).

An interesting standardization of thorium nitrate solution for fluoride determination is given by Venkateswarlu, Ramanathan, and Rao (231); it is standardized against oxalic acid with alizarin red S as indicator.

Recent Methods for Rocks and Minerals.- Chu and Schafer gave a detailed procedure for fluoride determination in silica and alumina catalysts after its isolation by first a precipitation of silica and alumina with zinc sulfate after a peroxide fusion and second a sulfuric acid distillation. They suggested its use for silicate analysis; the writer has adapted their fusion-precipitation step to analysis of rocks (49).

Shell and Craig used a zinc oxide-sodium carbonate fusion of silicates followed by leaching of the cake and a further precipitation of silica in the leachate with ammoniacal zinc oxide (201). Direct titration of the filtrate was useless, but after distillation good results were obtained with thorium nitrate titration using sodium alizarin sulfonate indicator. They studied the effect of various ions on the distillation step: Only aluminum, boric oxide, silica, and zirconium interfered seriously; certain amounts of 42 other elements had no effect. Up to 6 milligrams of fluoride could be recovered quantitatively in the presence of silica in the distillation, but higher amounts could not. For high amounts of fluoride the presence of both calcium and phosphate prevented complete extraction of fluoride and bulky precipitates from zinc oxide treatment sometimes contained up to 0.15 percent fluoride, expressed as percent of total.

Gericke and Kurmies (92) outlined a procedure for minerals calling for a sodium carbonate fusion, a single ammonium carbonate precipitation of silica and alumina, a removal of an aliquot of the unfiltered solution, and perchloric acid distillation of this aliquot. Analysis of fluoride in the distillate was effected by thorium nitrate titration with sodium alizarin sulfonate as indicator.

Emi, Hayami, and Takeda have analyzed rocks, feldspar, biotite, and quartz, these materials having a range of 0.008 to 0.5 percent fluoride (67). Their method calls for fusion with zinc oxide-sodium carbonate, leaching with sodium aluminate solution, distillation in phosphoric-sulfuric acid mixture, and determination of the fluoride in the distillate with neothorin. Kamada and Onishi have also given a spectrophotometric method for rocks (124).

A procedure for determining fluoride in rocks, described by Grimaldi, Ingram, and Cuttitta (99), has been used by the writer in the interlaboratory standardization program (cf. Chapter I -3, section b). After fusion of a one gram sample with a sodium carbonate-zinc oxide mixture, the melt is crushed and leached thoroughly, and the leachate filtered with washings directly into a steam distillation apparatus. These workers confirmed the findings of Brunisholz and Michod (40) that alumina has no retarding effect when a perchloric acid-phosphoric acid mixture is used for the distillation. They gave two methods for fluoride determination in the distillate: (1) a microtitration of fluoride, essentially that of Reynolds and Hill (185), the thorium solution being standardized by titrating known amounts of fluoride that have been carried through the distillation step, and (2) a spectrophotometric method using the thorium-thoron method (116). The writer used method 2. From the work of Grimaldi, Ingram, and Cuttitta it would seem that the thorium-thoron-fluoride color system at pH 1 tolerates relatively high amounts of phosphate. A calibration curve, relating decrease in absorbance to fluoride content, is made with alkali fluoride directly; it need not be carried through the distillation step.

Studies of Methods.- Comparative studies of various indirect colorimetric reagents for fluoride are given by Sen (196) and Longo (137). The former considers the ferric-sulfosalicylate method superior to zirconium-alizarin, ferric-tiferronate, and titanium-chromotropic acid systems; the latter finds eriochrome cyanine R superior to alizarin red S as indicator for the thorium nitrate titration of fluoride (chrome azurol S and azurol B follow in that order, according to this author).

For comparisons of methods Funasaka, Kawane, Tabuchi, and Kojima (81), Thom and Gribkoff (224), Funasaka, Kawane, Kojima, and Ishihara (79), Funasaka, Kawane, and Kojima (77, 78), and Tonani (229) should be consulted. The study of different methods for the analysis of soils and bauxites has been carried out by MacIntire, Hardin, and Jones (140) and Papp and Nagy (172), respectively. The work of Snow (210) and Zenin (255) is also of interest.

Reviews.- An excellent review on fluoride and fluorine methods of analysis has been published by McKenna (147). Epars has also reviewed fluorine analysis (68). A comprehensive treatise on fluorine chemistry has appeared under the Academic Press imprint (202); an addition to Mellor's series, on halogens, is also available (151). Other reviews are by Dyson (62) and Tada

(223). Reviews on analysis of fluoride in silicates and in mineral raw materials have been published by Morachevskii and Egorova (162) and Knipovich (128), respectively. Cholak has reviewed the occurrence of fluoride in air, food, and water and its analysis (48). Hackl has reviewed his own work on the determination of various elements, including fluoride, in silicates (101).

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Chapter I -3

The Procedure Employed for the Determination of Fluoride in Rocks

Section a

A Description of the Procedure: Spectrophotometric Determination of Fluoride in Rocks

> "No universal scheme can be set forth for the analysis of fluorine-containing materials. The amount of fluoride as well as the matrix must determine the analytical methods to be considered. In all cases the proficiency of the analyst with the method or technique adopted is of major importance. Certain contradictions ... as well as personal experience have indicated that all analysts are not equally adaptable to all of the techniques suggested in the literature." McKenna in 1951 (23).

A procedure must of course be precise and accurate. The writer's problem was in addition to develop a method that was relatively rapid and simple, for he had some 300 or more analyses to make; he feels the procedure given below meets these criteria rather well. Two major operations common in analyses of this sort require little supervision: (1) the decomposition of the sample and (2) the steam distillation.

In the following few paragraphs the writer outlines his reasons for the choice of certain steps in the analytical procedure. His thinking in developing the method was conditioned by his experience in the analysis of a phosphatic limestone by the method of Hoffman and Lundell (17), described by Groves (11). But some of the results from the interlaboratory standardization program (cf. section b of this chapter) indicate that some of the writer's thinking cannot now be regarded as valid.

The Fusion.- Some workers have reported low results for fluoride when samples are fused at high temperature with sodium carbonate; it is claimed alkali fluoride is volatilized (29). As a precaution in the analysis of the phosphatic limestone, the writer kept the temperature around 800°C, but found results for fluoride were erratic, ranging from 0.9 to 1.1 percent. As an expedient, the writer chose to use the maximum temperature of the burner, 1100°C, but to keep a platinum dish filled with water resting on the cover of the crucible. A single result for fluoride equalled 1.22 percent. Supervision of the fusion takes more time when high water content rocks as for example schists are involved, for if the fusion proceeds too rapidly, the sample effervesces and splatters. Not only supervision but also an extra step is involved with pyritiferous and carbonaceous rocks if sodium carbonate fusions are employed: The sample must be roasted to oxidize such matter prior to fusion. The writer considered that another disadvantage in the use of sodium carbonate flux was that quantitative separation of fluoride after fusion requires thorough crushing and leaching of the melt, the nature of which operations are likely to lead to negative errors through entrapment of fluoride in the residues. However, the results of the interlaboratory standardization program suggest now that the sodium carbonate fusion-leaching step does not seem to suffer from such negative errors to any greater degree than the writer's method does through entrapment of fluoride in precipitates.

But with the disadvantages in the use of the sodium carbonate fusion in mind at the time the writer decided to look for a fusion step that would (1) decompose the rock completely at low temperatures, (2) require little supervision, and (3) bring the sample into solution so no leaching would be necessary. A survey of the literature indicated a sodium peroxide fusion described by Rafter (26) would meet the above requirements. There was some danger of negative errors from incomplete fusion; however, the writer has had only a few such cases, readily detected, as part of a routine check on each sample, by the gritty sound or feel made by a flattened stirring rod on the bottom of the beaker and (or) the appearance of fragments, particularly dark minerals. Crushing of rock samples to 110 mesh and use of a pure, yellow sodium peroxide eliminated chances of incomplete fusion; a further step has been to hold the fusion at 480°C for 60 minutes or so. At this temperature, moreover, a frit forms that separates neatly from the crucible; the loss in weight of nickel crucibles used repeatedly has averaged 5 or 6 milligrams, most of this never entering the sample solution but being removed as the oxide on sponging out the crucibles before subsequent use. Preliminary treatment of pyritiferous and carbonaceous rocks is not necessary; the writer has analyzed black marine shales in the usual manner.

The Precipitation of Silica and Alumina.- The next problem was to look for a method of separating silica and alumina. As is evident from the review of the literature, most of the Berzelius methods and the like, using ammonium carbonate and (or) ammoniacal zinc oxide solutions, are involved, time-consuming, and require careful attention to conditions to ensure complete removal of these oxides. In fact, the problem was solved almost immediately the writer began to survey the literature: Chu and Schafer published a procedure for analysis of silica-alumina catalysts for fluoride after a single precipitation-filtration step at regulated pH to separate the first two elements (7); they claimed their separation was nearly complete. They also used a sodium peroxide fusion, which simplified things further for the writer.

The Steam Distillation.- It was of great importance that the distillation step also take care of itself, for each distillation requires 40 to 50 minutes (although doubtless a number of them can be run simultaneously). The writer was guided in the choice of apparatus by the criteria of Wichmann and Dahle (33, 34, 35), summarized in Chapter I -2. The apparatus described by Huckabay, Welch, and Metler (19) fitted the requirements admirably; these authors showed fluoride was distilled efficiently, even in the presence of moderate amounts of silica and aluminum salts. Compared to other distillation apparatus this device is quite efficient; the writer has recovered nearly 3 milligrams of fluoride from filtrates from peroxide-decomposed phosphatic limestone samples in 100 milliliters of distillate. At least 0.4 milligrams from rock samples have been recovered from the same volume. In addition to an efficiency explained by Wichmann and Dahle's studies (33, 34, 35), the writer suggests that an important factor is that nearly all glass surfaces of this apparatus with which acid solution and fluosilicic acid in the volatilized state are in contact are kept at 145° to 147°C by the boiling tetrachlorethane.

The Determination of Fluoride.- The final problem was to select a method for determining the fluoride once it had been isolated by distillation. There were two prime considerations: (1) The work of Hardin (13, 14) showed that, despite the claims by many workers that the thorium-sodium alizarin sulfonate titration method was capable of determining fluoride to within 1 microgram in the hands of the worker who described the method, in practice the average deviation among nine workers, experienced in the visual titration at that, was for one method nearly ±4 micrograms in the titration of about 60 micrograms in aliquots of distillate. Although it was possible Hardin's titration conditions were not optimum, as some collaborators observed (13), the work made it evident to the writer that the personal factor be eliminated in the determination. Studies comparable to Hardin's are not available for instrumental methods, but developments in the field traced in the review have indicated the superior sensitivity of these methods. The spectrophotometric adaptations of the titanium-hydrogen peroxide-fluoride (24) and ferric-ferron-fluoride (32) systems exemplify this gain in sensitivity. Of the possible instrumental methods the one available to the writer was a spectrophotometric one.

The writer has included in the review (cf. Chapter I -2) other instrumental methods and a considerable number of procedures for the analysis of solutions of pure fluorides, because these may well be worth examining for their applicability to rock analysis. A comparison of several instrumental methods and systems would be valuable. In addition systematic studies on sensitivity to fluoride, reproducibility, and tolerance to interfering ions would enable workers to select -- or tailor -- the system best suited to their needs. A case of interest to the writer is the use of the SNADNS dyes (8); he would like to determine whether these dyes will make possible more accurate spectrophotometric titration of fluoride, and whether, since their sensitivity is optimum at a lower pH than that used now by the writer for the SPADNS system, they would be less sensitive to sulfate or phosphate.

Of the spectrophotometric methods the titration kind should be more accurate than the measurement type, calling for the determination of the bleaching effect of fluoride, for, as Bricker and Sweetser have pointed out (5), an average slope is found from a number of optical density readings taken for the corresponding volume of titrant added, a line both before and after the end point being drawn (see figures 1-8 of this chapter). The disadvantage of the sodium alizarin sulfonate indicator for the thorium nitrate titration is that 1.00 micrograms of fluoride as fluosilicic acid is equivalent to 0.00876 milliliters of 0.00100 molar thorium solution, assuming the reaction takes place stoichiometrically according to the equation of Wadhwani (30). While the writer was considering the use of other systems, the problem was wonderfully solved by R.A. Chalmers, who apprised the writer of the work done by Banerjee (3) with a new indicator, SPADNS. In the presence of this indicator the thorium titration is not stoichiometric: more than twice the theoretical amount of titrant is required (18). This fact made possible the use of a smaller weight of sample, which is to be desired, for recoveries of fluoride are likely to be more quantitative (27). Some workers (36) have dismissed from further consideration indicators which give non-stoichiometric systems for no other reason than this. The work done by the writer, notably on the precision of this method, shows that such an objection is not valid.

The method described below has been modified in two important respects; e.g., the filtration and buffering of the distillate. The original procedure has been published (18). Most of the rock analyses (about 300 out of 420) have been carried out with the modified method, but both give comparable results. The following is in the main the writer's paper (18) with the descriptions of the modifications included.

Description of the Method: Introduction.- Usual methods for the determination of fluoride in rocks require a two-stage isolation. The first stage involves removal of silica, alumina, or both, commonly by the Berzelius method with an improvement introduced by Hoffman and Lundell (16). Grimaldi, Ingram, and Cuttitta (9) have described a zinc oxide-sodium carbonate fusion with direct distillation of filtrates in a phosphoric-perchloric acid medium. Shell and Craig (29) have reported a single precipitation-filtration removal of silica and alumina by a zinc oxide-sodium carbonate fusion with addition of ammoniacal zinc carbonate to the water leach. Chu and Schafer (7) have used a sodium peroxide decomposition for the determination of fluoride in catalysts containing silica and alumina. Their peroxide decomposition has three advantages for silicate rocks: Decomposition is complete (26), water solubility of the frit eliminates care over leachings, and a simple and rapid precipitation gives nearly complete removal of silica and alumina in a single step. In the second stage of isolation fluoride is recovered from the filtrates by some modification of the Willard and Winter distillation (37). A constant temperature steam distillation still designed by Huckabay, Welch, and Metler (19) was chosen for its semi-automatic operation.

Colorimetric methods for the determination of microgram amounts of fluoride were surveyed. A spectrophotometric adaptation of the Steiger-Merwin peroxidized titanium method, as desribed by Groves (10), has been reported by Monnier, Vaucher, and Wenger (24). With the instrument in this laboratory fluoride down to 5 to 7 micrograms can be determined to within 3 to 4 micrograms. A spectrophotometric adaptation of the sodium alizarin sulfonate-thorium method has been described by Icken and Blank (20). Their results suggest that fluoride in the range 0 to 50 micrograms can be determined to within 1 microgram. However, the method requires freshly prepared colored reagent and repeated use of standard solutions with the assays. Banerjee (3) described a colorimetric determination of pure solutions of alkali fluoride with a new dye, SPADNS, which is the sodium salt of 2-(p-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid. This dye forms a blue-violet lake with thorium ions; in the presence of alkali fluoride thorium tetrafluoride forms preferentially, the dye keeping its crimson color. According to Banerjee (3) this thorium-SPADNS-fluoride system has three advantages: The color change is marked from crimson to blue-violet at the end point, the reactions of thorium and fluoride in the presence of the dye are immediate, and the temperature coefficient is low. Moreover, the high titers required for titration of fluoride at pH 2.9 to 3.1 render possible semimicro titration of microgram amounts of fluoride.

Apparatus and Reagents.- The constant temperature distillation still designed by Huckabay, Welch, and Metler (19) for isolation of fluoride was modified by use of a

Davies double-surface condenser for collection of distillate and made of smaller dimension.

Pye Universal pH meter.

A 4-centimeter light path cuvette of total volume 45 milliliters and cuvette holder made of Perspex (Lucite) was used for the spectrophotometric titration. Its construction is illustrated in figure 9. A block mounted on top of the cover for the cell compartment has a flat surface, AB, on each side against which similar surfaces, A'B', on the cuvette fit securely. This arrangement ensures exact positioning of the cell in the light path. The cell is so marked that it has the same orientation in the light path for each determination. The cover and top of the cell are painted black, and the side surfaces are roughened with fine sandpaper.

Unicam SP. 600 spectrophotometer for the titration. The absorbance is checked at 580 millimicrons, where the difference in absorbance for the thorium lake and the dye is greatest.

Sodium peroxide. It must be pure, dry, and yellow.

Zinc sulfate solution. Dissolve 36 grams of zinc sulfate heptahydrate in 100 milliliters of distilled water.

Indicator. Dissolve 0.5 grams of malachite green oxalate in 50 milliliters of water.

Sulfuric acid, 1 to 3, 20 percent sodium hydroxide.

Sodium sulfate solution, 1 percent, made alkaline to phenolphthalein.

Concentrated sulfuric acid. Select a stock giving a low blank for fluoride (cf. the paragraph on standardization of the thorium nitrate solution).

Treated soda-lime glass. Place about 250 grams of glass powder in 200 milliliters of 1 to 2 sulfuric acid. Heat the mixture at 70°C for an hour. Cool, filter, wash with boiling hot distilled water, and dry at 150°C.

Perchloric acid, 0.5 normal, and sodium sulfanilate, 0.5 normal, for buffering aliquots of distillates to pH 3.2. Make certain the strength of each is as indicated; the sodium sulfanilate used here is not reagent grade. Also, as a further precaution, make certain 1.0 milliliters of sodium sulfanilate solution plus 0.50 milliliters of the acid buffer 25 milliliter aliquots of distillate to the pH specified.

Standard sodium fluoride solution. Dry sodium fluoride for 2 to 3 hours in an oven at 110°C. Cool in a desiccator. Dissolve 2.2108 grams in 1 liter of distilled water. Take a 10 milliliter aliquot and dilute to 500 milliliters. Store in polythene bottles. The latter solution contains 20 micrograms of fluoride per milliliter. It is best to check the purity of the sodium fluoride by converting samples into the sulfate; apply corrections to weighed samples.

Thorium nitrate, 0.001 molar (approximately). Dissolve 0.28 to 0.31 grams of thorium nitrate tetrahydrate in 500 milliliters of water. The titer should be 0.17 to 0.21 milliliters per 10.0 micrograms of fluoride. Store the solution, 0.001 molar in perchloric acid, in polythene. It is advisable to check the titer once every two weeks or so if it is in continuous use.

SPADNS, 0.020 percent. Synthesize the dye as directed by Banerjee (4). Dry a sample in an oven at 110°C for an hour and cool it in a desiccator. Dissolve 0.200 gram in 1 liter of distilled water. The solution is very stable; a stock solution has been in use for over 3 years without change.

Use reagent grade chemicals throughout. Make certain that the distilled water has negligible fluoride.

Analytical Procedure.- Grind a rock sample by percussion mortar and pestle to pass a 110-mesh per inch sieve. Analyze samples on an "air dry" basis (15). Weigh a 0.25 gram sample to within 1 milligram into a nickel crucible. Add eight to ten times the sample weight of dry, yellow sodium peroxide and mix thoroughly with the sample. Place the crucible and sample in a muffle furnace at 270° to 300°C. Bring the temperature up over 30 minutes to 480°

to 490°C, and hold at this temperature for 60 minutes. Cool to room temperature, dissolve the frit in 100 milliliters of distilled water, wash the crucible with a little hot water, and add the washings to the solution. Simmer the solution for 40 to 60 minutes to remove excess peroxide, and then boil for 1 to 2 minutes. Add slowly with stirring about 5.5 milliliters of zinc sulfate solution and 3 to 5 drops of the indicator solution, and adjust to pH 11 to 12 by dropwise addition of 1 to 3 sulfuric acid. At this pH the indicator has a faint green coloration. If the pH is too low, readjust by addition of 20 percent sodium hydroxide. Digest the bulky precipitate of zinc silicate, zinc aluminate, and hydroxides on a steam bath for about an hour. Digestion by partial immersion of the beakers, suitably protected from the steam bath vapor, in the boiling water is advisable, for it keeps the solution very hot for filtering.

Prepare a filter as follows: place a circle of Whatman 42 paper, 7 centimeter diameter, on a 6.5 centimeter diameter fine porosity sintered glass funnel, pressing the overlap on the sides of the funnel. Seal the filter paper-glass contact with a slurry of filter paper pulp, and place a fine layer of pulp over the paper-covered plate. Then place a small diameter circle of filter paper on top of this layer.

With gentle suction, a rate of 100 milliliters per 10 minutes being satisfactory, filter the solution, which should not be decanted but kept stirred for the entire filtration. To prevent disturbing the layer of pulp, allow the liquid to run down the stirring rod onto the small circle of filter paper. Wash the beaker and precipitate several times with boiling-hot sodium sulfate solution. Collect the filtrate and washings in a 250 milliliter beaker and evaporate to about 20 milliliters on the steam bath.

Place 20 to 23 milliliters of sulfuric acid with about 0.1 gram of the treated soda-lime glass in the distillation chamber of the still. Add the evaporated and cooled filtrate and rinse out the beaker into the chamber with hot water, policing the beaker with the last rinsing. Then rinse once with very dilute sulfuric acid. The total volume in the chamber should not exceed 45 to 50 milliliters. Mix the sample with the sulfuric acid by admitting air bubbles from the steam generator. When the _sym_-tetrachloroethane refluxes, admit steam to the distillation chamber and collect the distillate in a 100 milliliter volumetric flask at a rate of 1.5 to 2 milliliters per minute for the first 5 minutes. Then increase the production of steam so that distillate is collected at a rate of 2.5 to 3 milliliters per minute. Collect 100 milliliters of distillate.

Transfer into the Perspex cuvette an aliquot containing not more than 70 micrograms of fluoride (25 milliliters is usually a convenient aliquot), and add 2.00 milliliters of the 0.020 percent SPADNS solution, 1.0 milliliters of the sodium sulfanilate solution and 0.50 milliliters of the perchloric acid solution. The pH of the buffered distillate should be 3.2, although the writer has titrated many with good precision at pH 3.4. Titrate spectrophotmetrically with standard thorium solution. Note the change in optical density after each 0.050 milliliter increment of titrant. Determine the end point graphically by plotting optical density against volume of thorium solution. Draw the slopes of the two lines as described by Bricker and Sweetser (5). Take a second aliquot and titrate as described. Average the two results and calculate the percent of fluoride present. The two results should agree to within 0.017 to 0.021 milliliters of titrant. Figures 5 through 8 illustrate titration curves obtained on aliquots of distillate obtained from some rock samples.

Standardize the thorium solution as follows: Add known amounts of the sodium fluoride solution to the distillation chamber and carry through the procedure from there. A blank on the sulfuric acid used, 40, 100, and 200 micrograms charged to the still are a suitable range of standards for calculation of the thorium/fluoride titer. The average titer, expressed as milliliters of titrant per 10.0 micrograms of fluoride, should agree to within ±0.003 to ±0.005 of that titer calculated for each amount of fluoride. A sulfuric acid stock producing a low blank must be used; allow a maximum of 0.05 milliliters of titrant for a 25 milliliter aliquot of distillate. Such low-blank acid must also be used for the analyses. Standardization by carrying alkali fluoride through the distillation step is adopted for two reasons: (1) Distillation by the procedure described produces fluosilicic acid, the reaction of which with thorium nitrate is different from that of alkali fluoride (30), and (2) a constant amount of fluoride remains behind in the distillation chamber. Solutions of reagent grade fluosilicic acid, standardized by the lead chlorofluoride method (11), were titrated with the thorium nitrate both directly and after distillation; the ratio of the titer for solutions of distilled fluoride to the titer for solutions of the standardized fluosilicic acid indicated that recovery is 98 percent over the range 0 to 200 micrograms of fluoride for the distillation apparatus in use. Figures 1 through 4 illustrate titration curves obtained from titration of known amounts of fluoride.

Determine the blank on the reagents, and establish the sulfate interference for the conditions of distillation employed. The blank on the reagents is the sum of fluoride impurity and the effect of sulfate entrained in the distillation. Blanks have been from 0.06 to 0.12 milliliters of titrant. For a titrant of the same strength different blanks are obtained usually only when new stocks of sulfuric acid are introduced. Titration at pH values greater than 3.2 also tend to increase the blank. However, for a given set of conditions replicate determinations of the blank have given a maximum deviation of 0.004 milliliters of titrant.

Experimental.- The experiments were designed to establish the following:

1. The control of pH in the titration of fluoride as fluosilicic acid in buffered solution.
2. The range of fluoride that can be titrated without serious variations due to salt effects or changes of pH.
3. The recovery of fluoride added in known amounts to synthetic rocks carried through the procedure, and the volume of distillate required for acceptable recovery.
4. Interferences from elements expected in common rock types.
5. Comparison of results on standard rocks with results reported by other workers using other methods.
6. Reproducibility of the method.

pH is known to affect the titer when fluoride is titrated with thorium in the presence of a hydroxyazo dye. Wadhwani (30) has studied the pH effect on the stoichiometry for the thorium-sodium alizarin sulfonate-fluoride system. His explanations of the effect of pH on that system probably apply to the thorium-SPADNS-fluoride system as well. Moreover, Wadhwani has shown that the reaction of fluoride as fluosilicic acid with thorium is (30):

$$Th(NO_3)_4 + H_2SiF_6 + 4H_2O = H_2ThF_6 + 4HNO_3 + H_4SiO_4 \qquad (A)$$

Evidence given by Wadhwani (30) suggests that at the pH range 2.9 to 3.1 no further reaction between thorium nitrate and fluothoric acid (H_2ThF_6) to form thorium tetrafluoride takes place.

The production of acidity in this reaction will affect the stoichiometry of the system by lowering the pH (31). Consequently, a buffer was sought that would keep the pH within 0.2 unit or better, so that the titer would not be considerably affected. Following the observations of Revinson and Harley (28), the writer looked for non-carboxyl and non-carbonyl group buffers. The writer selected a perchloric acid-sodium sulfanilate buffer, whose optimum buffer capacity is at pH 3.1. (12). Tests with sodium fluosilicate in the presence of the usual amounts of sulfate found in distillates showed that 25 milliliter aliquots were buffered at the desired pH. See Table I. Further tests on actual distillates showed the fluoride-containing solutions were effectively buffered throughout the titration. See Table I. The higher pH values (3.4) for these solutions was probably due to impurities in the sodium sulfanilate and to incorrect values accepted for the perchloric acid stock. The writer decided, accordingly, in making up new stocks of buffer solutions, to adjust the strengths to give a pH of 3.1 to 3.2 in distillates.

The thorium-SPADNS-fluoride system does not obey the laws of chemical proportion at pH 2.9 to 3.4; theoretically, on the basis of equation (A), the volume of thorium required would be less than half of what is actually used. Such lack of stoichiometry, however, renders possible semimicro titration of microgram amounts of fluoride.

The recovery of fluoride from rocks was tested by adding known amounts of fluoride to synthetic rocks. A rock of granitic composition (AG) was made up from the oxides of silicon, aluminum, ferric iron, calcium, magnesium, titanium, phosphorus, and manganese and from sodium carbonate and potassium sulfate. The powders were thoroughly mixed and passed twice through a 120-mesh sieve. A rock of basaltic composition (AB) was similarly prepared. Blanks of each were made in duplicate, and found to be rather high. Determinations of the individual constituents showed that fluoride was present in the calcium oxide, magnesium oxide, and aluminum oxide, and all the fluoride in the synthetic rock could be accounted for by calculating the amount contributed by each constituent. The compounds used were not reagent grade. Fluoride was added to 0.250 gram samples as an alkaline solution. After careful evaporation, the samples were carried through the analytical procedure. Known amounts of fluoride as solid sodium fluoride were added to samples of Bureau of Standards soda feldspar sample number 99 by weighing the sodium fluoride on a microbalance. These were carried through the procedure also (SF). The results are given in Table II. With one exception the determinations are well within 1 microgram per aliquot. All the fluoride was recovered in the first 100 milliliters of distillate.

Ions forming a stable compound or complex with fluoride, thorium, or the dye will interfere. The effects should be similar to those reported for other thorium-azo dye-fluoride systems. Studies by Revinson and Harley (28), Lambert (21), and Shell and Craig (29) suggest that for normal rocks analyzed by this method ions causing interference are chloride, sulfate, phosphate, silicate, aluminum, and boron. Chloride can be removed by distilling in the presence of silver sulfate (19). The effect of sulfate is kept constant by establishing reproducible conditions of distillation (19). The writer has found that 0.3 to 0.5 milligrams of sulfate per 25 milliliters can be tolerated in the titration without significant change in the blank (Table III). Consequently, a reference solution containing 0.6 milligrams of sulfate and 1.0 milliliters of a saturated solution of barium chloride in 50 milliliters of water and another with 1.0 milligrams of sulfate plus the barium solution are used for comparison with distillates similarly prepared (1.0 milliliters of the barium chloride solution is added to the 50 milliliters of distillate remaining after titration of two aliquots). After the solutions prepared have stood for 15 minutes, the standards are held with the distillates against diffuse light to ascertain whether the amount of sulfate in the distillate is within these limits. In over 400 distillations only a few (less than 10) distillates contained sulfate in excess of 0.5 milligrams per 25 milliliters. However, no correction can be consistently applied to titrations in the presence of excess sulfate. The determination must be repeated. The sulfate present in distillates has never been less than 0.3 milligrams per 25 milliliters. If calcium and phosphate ions are both present, it can be expected that they will form fluorapatite, which will be precipitated with the silica and alumina. In order to study this possible effect a phosphatic limestone with 9.8 percent phosphorus pentoxide and 48.1 percent calcium oxide was analyzed by this method and the results were compared to those by the lead chlorofluoride method described by Groves (11). The data in Table IV suggest that there is no such interference and that the peroxide decomposition is more efficaceous. Forty milligrams of boric anhydride was added to samples of the synthetic granite and a metamorphic rock; the usual procedure was followed (Table IV).

Ahrens (2) has given data on the determination of fluoride by several workers on two standard rocks, G-1 and W-1. The agreement is not very good; however, his recommended value (the average of all determinations) is close to the duplicate results obtained by the SPADNS method (Table V).

As the recovery data indicated an error of about 2 percent for aliquots containing about 30 micrograms of fluoride, acceptable accuracy was expected for the microdetermination of samples with large amounts of fluoride (greater than 2.4 percent of fluoride). For this study Bureau of Standards sample opal glass, number 91, was analyzed in two ways: In procedure A the sample was, after peroxide decomposition, dissolved in about 50 milliliters of water, and silica and alumina were precipitated with 1 to 1 zinc sulfate solution. In procedure B the frit was dissolved in about 15 milliliters of water and the solution was added to the distillation chamber. The results for both methods are given in Table VI.

Replicate results for ten metamorphic rocks are given in Table VII. In the samples which were not run concurrently the analyses were effected with new thorium solution and new reagents. The maximum proportional deviation, defined as the maximum deviation divided by the arithmetic mean, is also presented for each of the replicate results. The actual maximum proportional deviation (Mpd) is compared with an Mpd calculated on the basis of an error of 1 microgram (Mpd'). Although Mpd is greater than Mpd' for four results, it is considerably greater in only one out of the ten analyses. The average Mpd is equal to the average calculated Mpd' for the ten analyses, suggesting that the method is capable of determining fluoride to within 4 micrograms per 0.25 gram sample.

Since the above tests on the precision of the method, carried out with the original procedure, the writer has run repeat determinations on 54 samples, including those above, some done in triplicate and quadruplicate, so that the determinations have totalled 122. In all cases repeat determinations were done without the writer's knowing the other results for the samples; in many cases repeat determinations were effected with thorium solution of different strength and with different stocks of reagents; and a few were done some four years later. From these data, summarized in Table VIII, the standard deviation was calculated to be $\pm 1.4 \times 10^{-3}$ percent fluoride for rocks having between 0.006 and 0.09 percent fluoride. The relative deviation, C, as defined by Ahrens (1), is, therefore:

$$C = \pm 1.4 \times 10^{-3} \times 10^{2}/0.040$$
$$= \pm 3.5$$

where 0.040 percent fluoride is the average amount of fluoride found by the method for the 54 samples. According to Ahrens, relative deviations of less than 10 percent indicate that the distribution of error is likely to be normal rather than lognormal (1). It follows from the standard deviation for this method that in the 95 percent confidence limit a single determination is to within ±0.003 percent fluoride of the arithmetic mean found by this method. The data in Table VIII also show that the original and modified methods give comparable results.

Modifications Employed.- Malachite green oxalate is used in the place of an alkaline blue-1,3,5-trinitrobenzene mixed indicator described by Chu and Schafer (7). The color change of the former was easier to see in the presence of the bulky, brownish-colored precipitates. Layers of filter paper and paper pulp on the sintered glass funnels have been the only means for ensuring a sharp separation of precipitates from filtrate; gentle suction and filtration of the stirred precipitates rather than by decantation also are important to ensure this separation. Otherwise, the analytical procedure given by Chu and Schafer (7) is followed.

Evaporation in Borosilicate Glass.- McClure (22) and Powell and Saylor (25) have reported low results when fluoride solutions are evaporated in porcelain or glass. The data herein indicate that the use of borosilicate glass for the evaporation of microgram amounts of fluoride is satisfactory. The beakers used must be scratch-free and are cleaned prior to use with hot chromic acid.

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FIGURE I

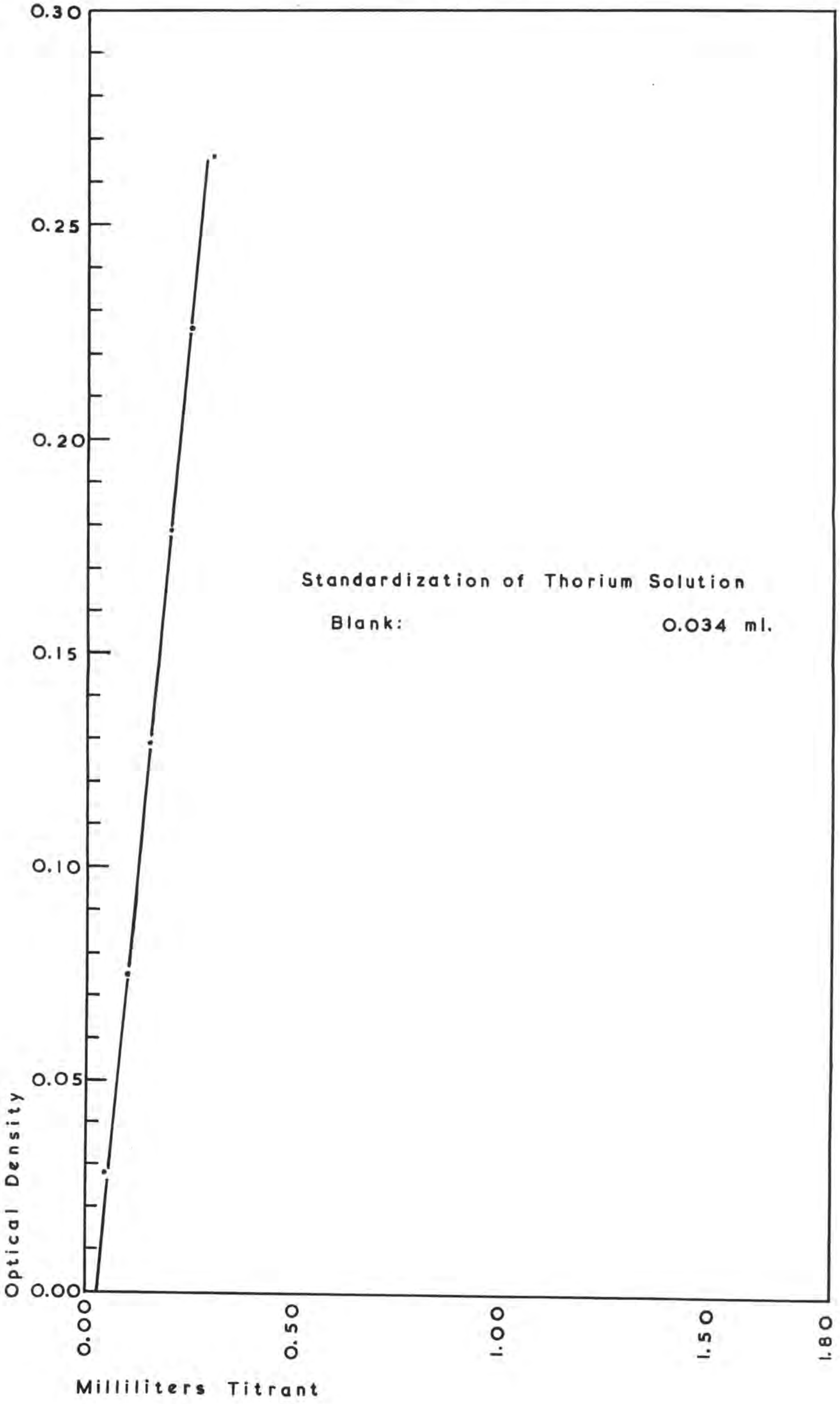
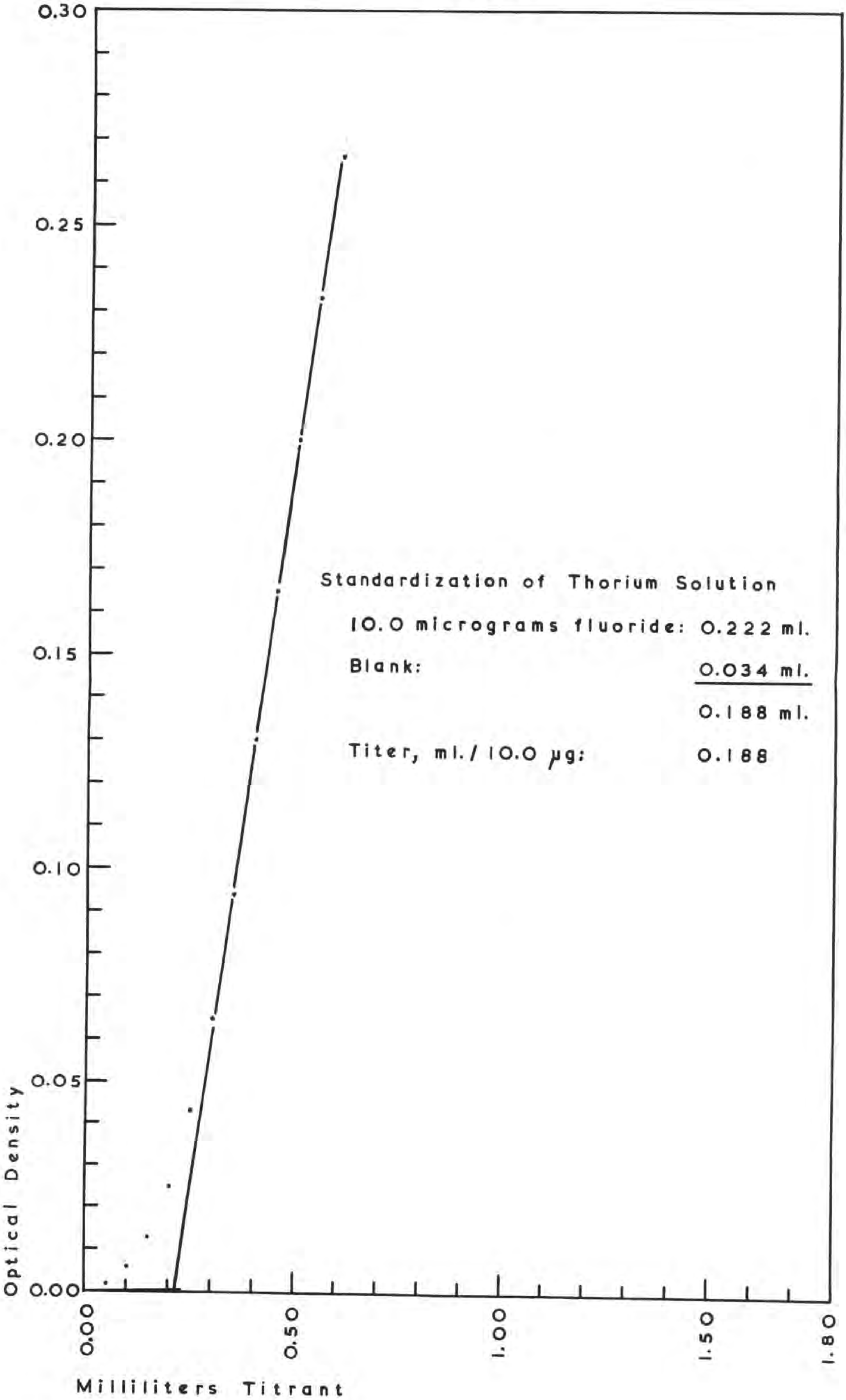

Standardization of Thorium Solution
Blank: 0.034 ml.
Optical Density
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.50
1.00
1.50
1.80
Milliliters Titrant

FIGURE 2



Standardization of Thorium Solution

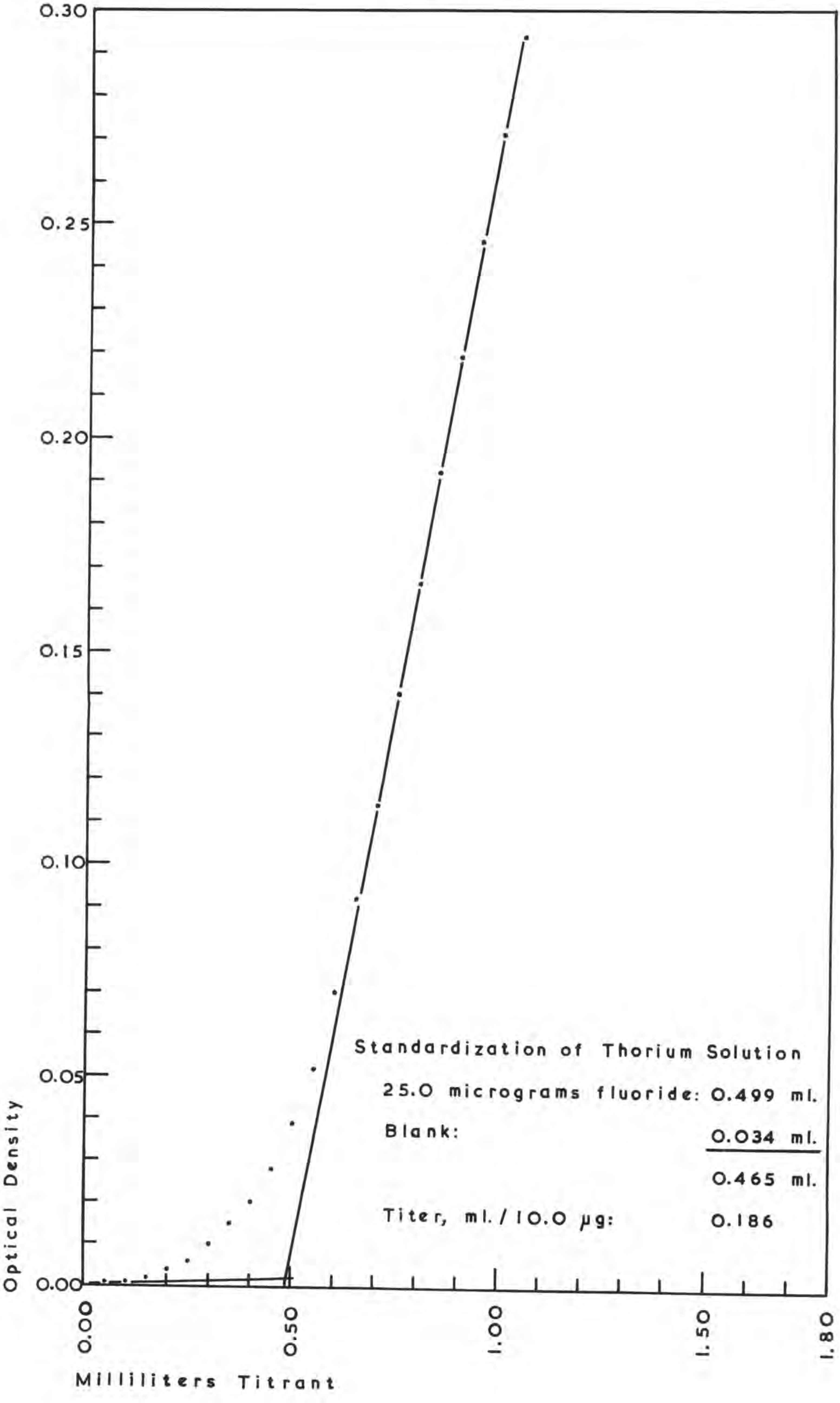
10.0 micrograms fluoride: 0.222 ml.

Blank: 0.034 ml.

0.188 ml.

Titer, ml./10.0 µg: 0.188

FIGURE 3


Standardization of Thorium Solution

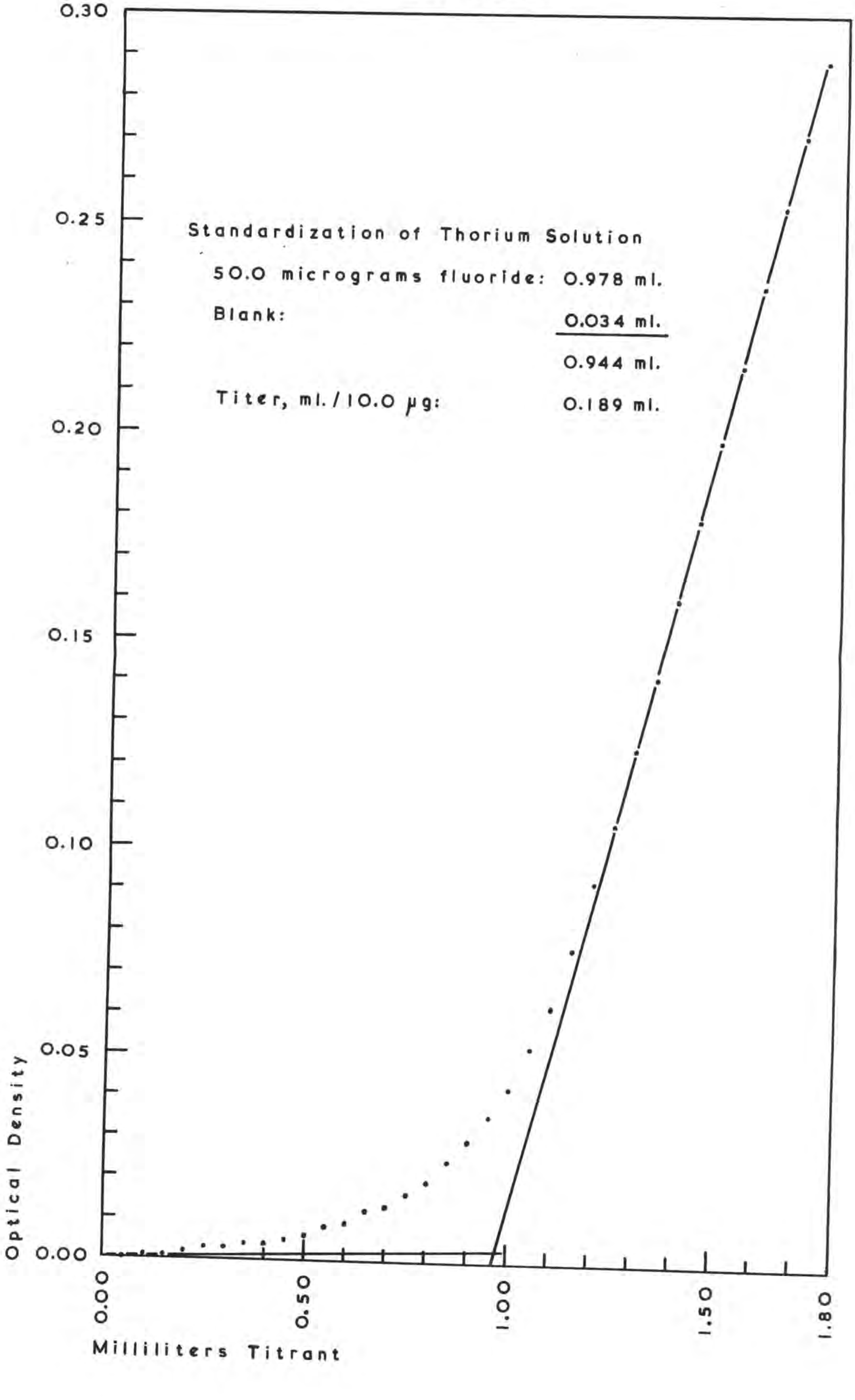
25.0 micrograms fluoride: 0.499 ml.

Blank: 0.034 ml.

0.465 ml.

Titer, ml./10.0 μg: 0.186

FIGURE 4



Standardization of Thorium Solution

50.0 micrograms fluoride: 0.978 ml.

Blank: 0.034 ml.

0.944 ml.

Titer, ml./10.0 μg: 0.189 ml.

FIGURE 5

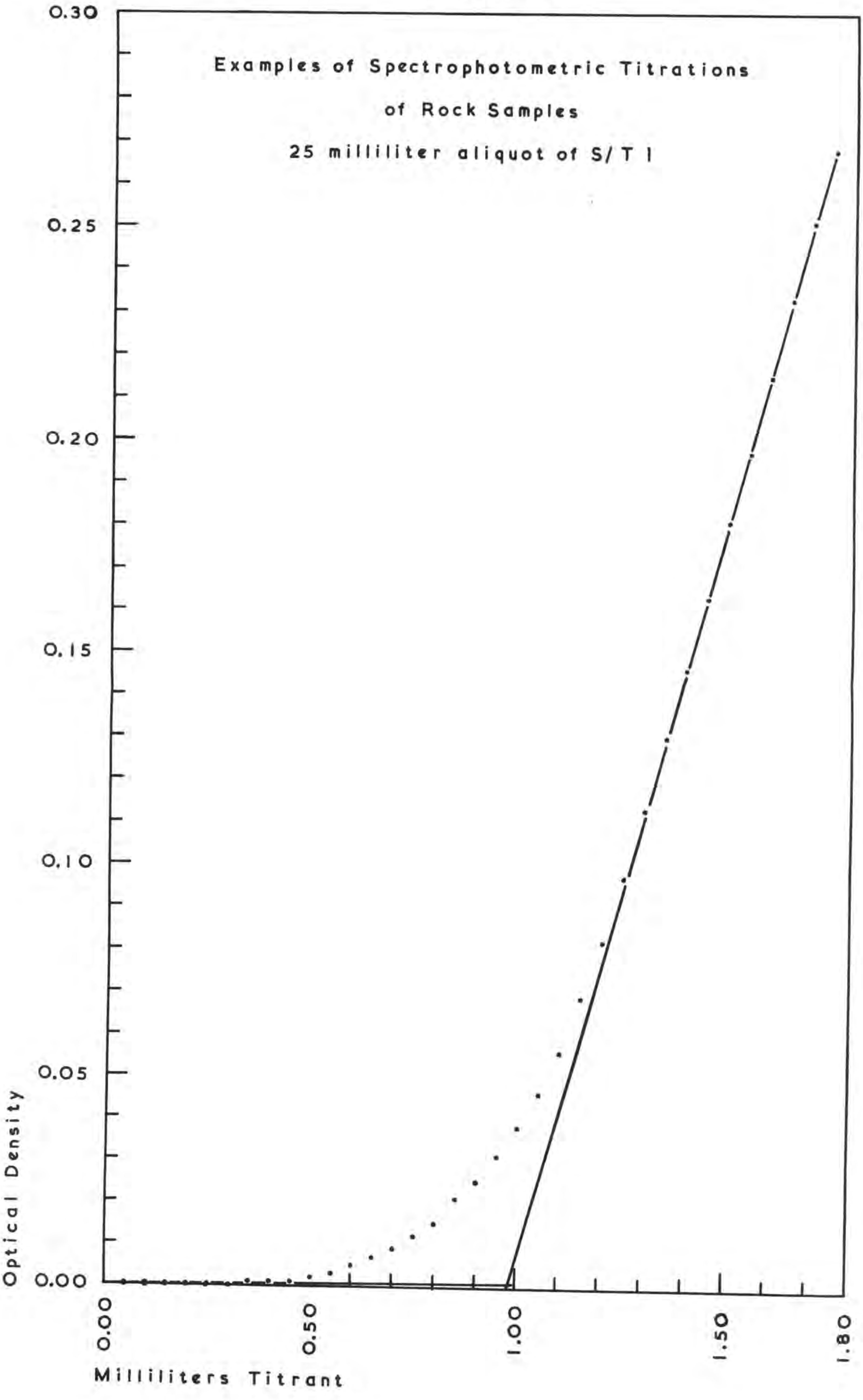
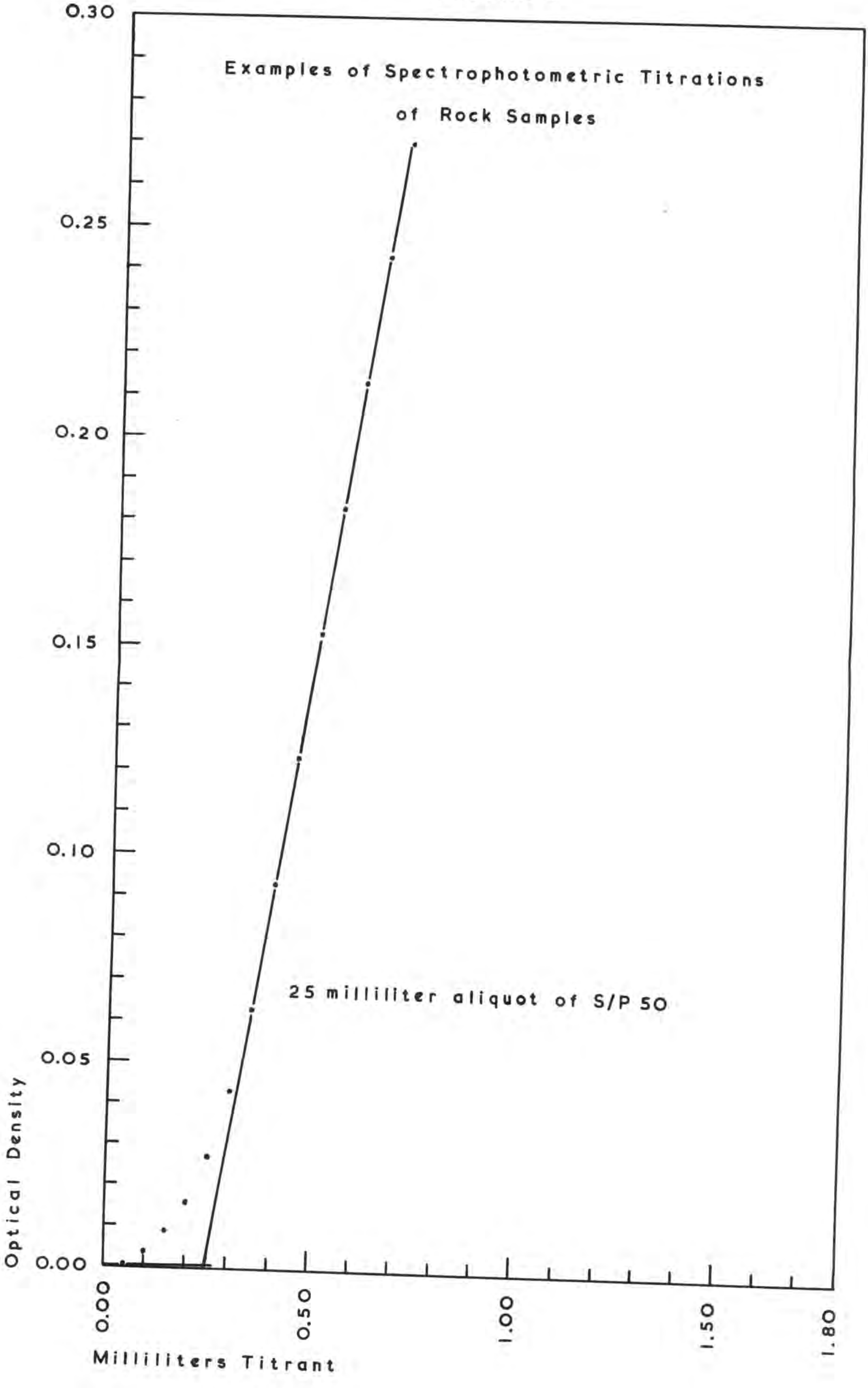

Examples of Spectrophotometric Titrations
of Rock Samples
25 milliliter aliquot of S/T 1
Optical Density
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Milliliters Titrant
0.00
0.50
1.00
1.50
1.80

FIGURE 6



Examples of Spectrophotometric Titrations of Rock Samples
25 milliliter aliquot of S/P 50
Optical Density
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Milliliters Titrant
0.00
0.50
1.00
1.50
1.80

FIGURE 7

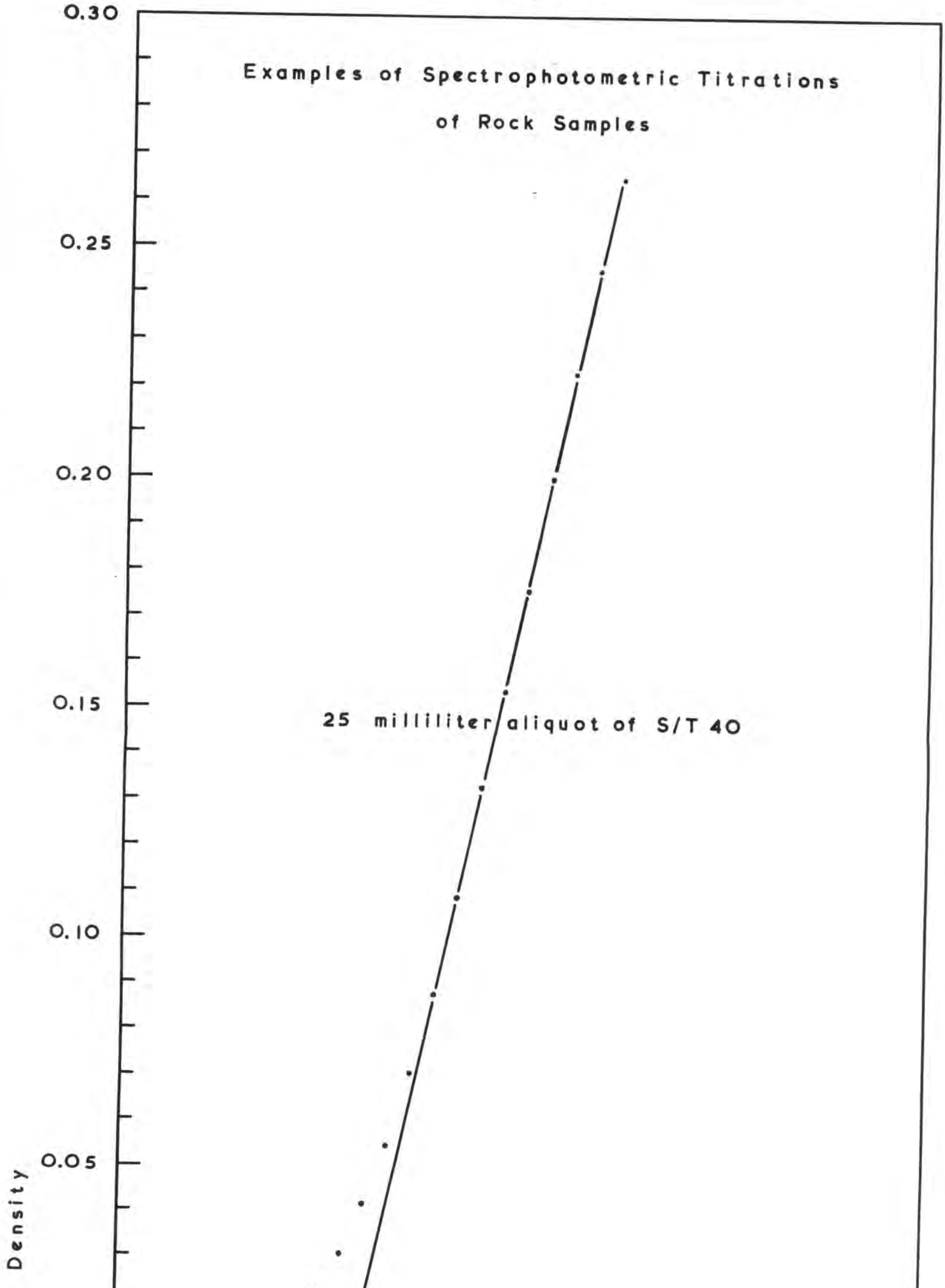

Examples of Spectrophotometric Titrations
of Rock Samples
25 milliliter aliquot of S/T 40
Optical Density
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Milliliters Titrant
0.00
0.50
1.00
1.50
1.80

FIGURE 8

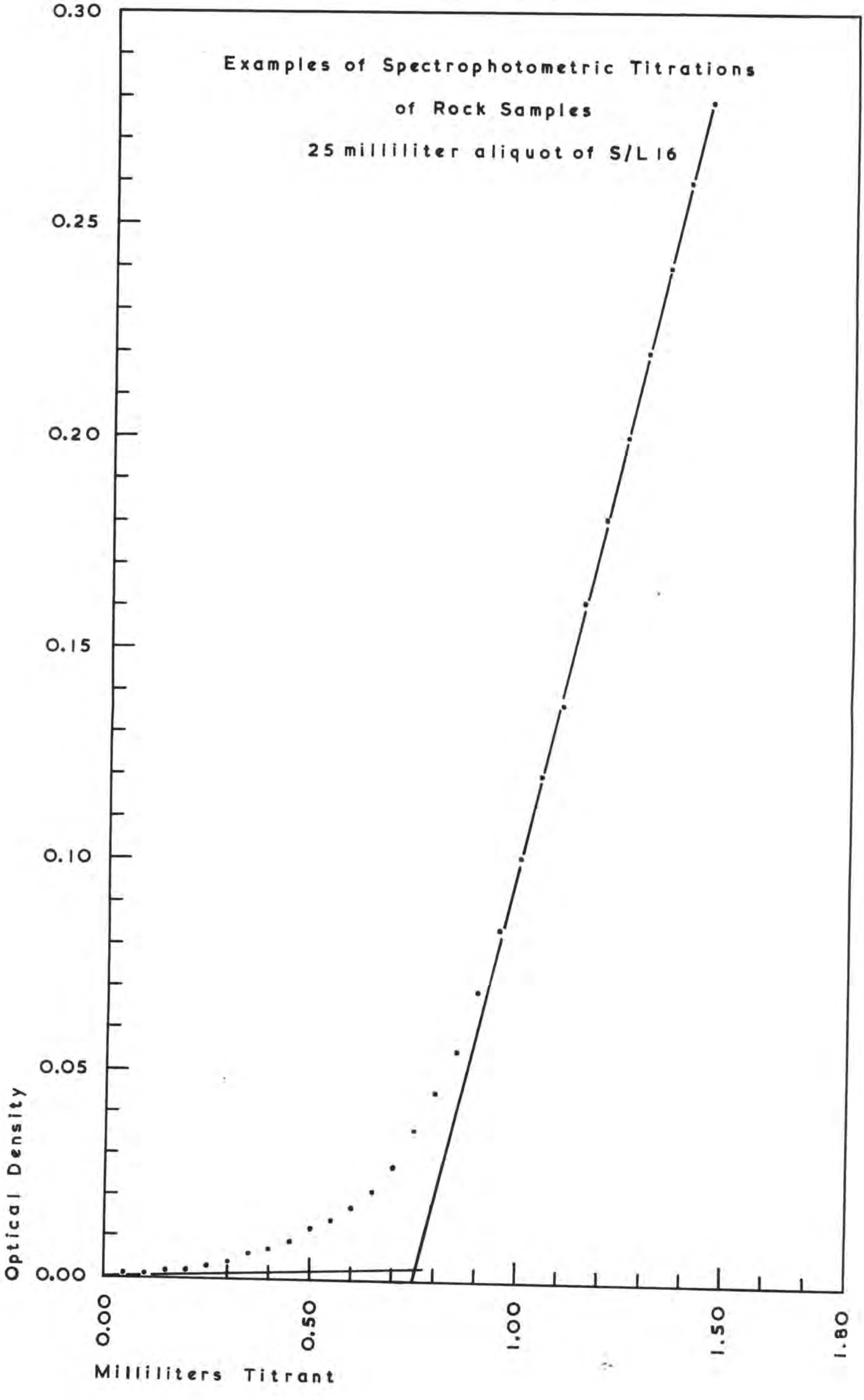
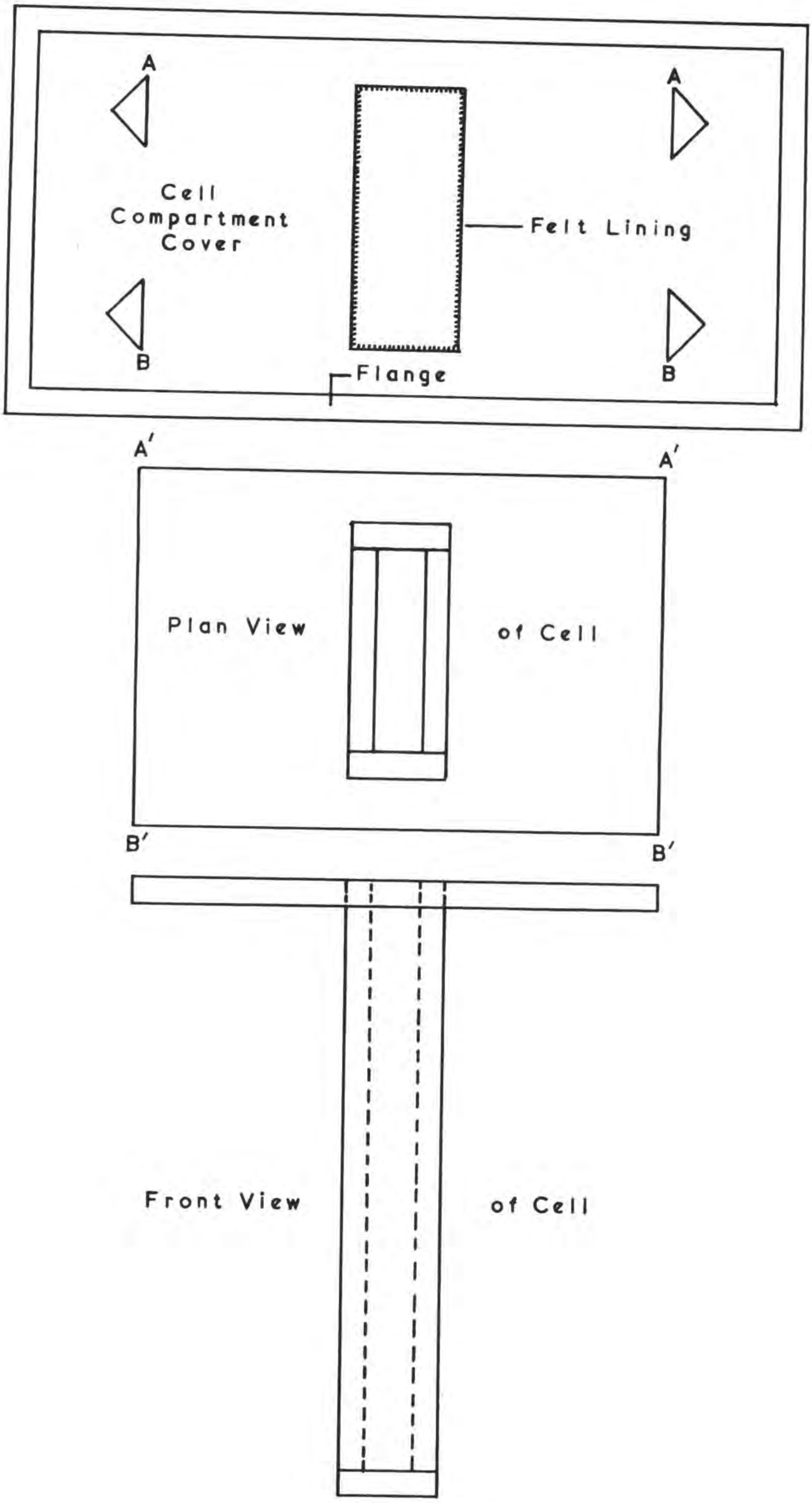

Examples of Spectrophotometric Titrations
of Rock Samples
25 milliliter aliquot of S/L 16
Optical Density
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.50
1.00
1.50
1.80
Milliliters Titrant

FIGURE 9



Titration Cell for Unicam SP. 600 Spectrophotometer

Drawn to Scale

pH Control by Perchloric Acid-Sodium Sulfanilate Buffer

ug/25 ml. aliquot	pH before adjustment	pH with buffer	pH at end of titration	titer, ml. Th/10.0 ug F
5	3.61	3.21	3.19	0.210
15	3.61	3.22	3.19	0.210
20	3.59	3.18	3.15	0.216
25	3.57	3.17	3.15	0.207
35	3.55	3.16	3.13	0.218
50	3.55	3.17	3.15	0.219
21, I/C 24[a]	3.61	3.42	3.38	0.189[b]
55, I/C 26	3.59	3.41	3.33	0.189
37, I/C 37	3.61	3.44	3.38	0.189
36, I/C 38	3.55	3.38	3.34	0.189
45, I/C S3	3.58	3.36	3.31	0.189
49, I/C H16	3.58	3.36	3.28	0.189
54, I/C 154	3.57	3.38	3.30	0.189
44, I/C 179	3.60	3.40	3.32	0.189
35, I/C 51	3.60	3.40	3.31	0.189
66, I/C 169	3.48	3.31	3.29	0.189
33, I/C 222	3.57	3.38	3.31	0.189
1, I/C 35	3.58	3.39	3.37	0.189
51, I/C 89	3.58	3.39	3.29	0.189
5, I/C 240	3.60	3.39	3.35	0.189
35, F/MC 21	3.59	3.37	3.30	0.189

a: Distillates from Rock Samples, code numbers given.

Fluoride Recovery from Synthetic Rocks and Bureau of Standards Soda Feldspar Sample No. 99

Sample No.	F added, ug	F, ug/25 ml.	F found, ug/25 ml.	% Error
AG-1	0.0 (blank)	0.0	11.8	---
AG-2	0.0 (blank)	0.0	12.0	---
AG-3	24.4	6.1	5.3[a]	13
AG-4	48.8	12.2	11.1[a]	9
AG-5	97.8	24.9	24.4[a]	2
AG-6	195.6	48.9	48.4[a]	1
AB-1	0.0 (blank)	0.0	22.1	---
AB-2	0.0 (blank)	0.0	22.7	---
AB-3	14.8	3.7	4.3[a]	16
AB-4	78.4	19.6	19.3[a]	2
AB-5	44.0	11.0	10.7[a]	3
AB-6	195.6	48.9	48.3[a]	1
SF-1	0.0 (blank)	0.0	17.7	---
SF-2	0.0 (blank)	0.0	18.3	---
SF-3	16.6	4.1	4.3[a]	4
SF-4	32.8	8.2	8.7[a]	6
SF-5	73.9	18.5	18.2[a]	2
SF-6	173.4	43.4	43.2	0

a: Reported as fluoride found in addition to average fluoride present in blank.

Table III

Effect of Certain Ions on Determination of Fluoride

(37.6 ug F added with 25 milliliters of water)

Ion	Amount added, mg.	Error, ug F
SO_4^{--}	0.1	0.0
	0.1	0.0
	0.2	0.0
	0.3	+3.6
	0.3	+4.1
	0.4	+3.4
	0.5	+3.5
	0.5	+4.1
PO_4^{---}	0.025	+1.5
	0.050	+3.6
	0.075	+11.3
	0.100	+18.7
	0.7	no end point
Cl^-	4.0	+3.4
BO_3^{---}	2.1	-3.7

NB: These studies were carried out on the original titration method.

Table IV

Recovery of Fluoride from Rocks Containing Certain Interfering Elements

Rock	% Fluorine	
	Expected	Found
AG-7 with 40 milligrams of B_2O_3 added	0.022	0.023
Chlorite schist with 40 milligrams of B_2O_3 added	0.051	0.052
Phosphatic limestone	1.22[a]	1.33

a: Fluoride determined by lead chlorofluoride method (11).

Comparison of Results on G-1 and W-1 by Different Workers and Methods

Rock	Method	Result, P.P.M.
G-1	Spectrographic	900
		800
	Chemical	450
		900
		900
		400
		800
	SPADNS	770
		800
	Grimaldi, Ingram, Cuttitta (9)	610
		580[b]
	Av. (Ahrens)[a]	740
	Av. (SPADNS)	790
W-1	Spectrographic	200
	SPADNS	200
	Grimaldi, Ingram, Cuttitta (9)	160

a: Data from Ahrens (2), except results reported by Grimaldi, Ingram, and Cuttitta (9).

b: Result obtained by the writer using the method of Grimaldi, Ingram, and Cuttitta (9).

Table VI

Microdetermination of Fluoride in Opal Glass and Zeophyllite

Procedure	% F found	Bureau of Standards Result	Range, Bur. of Standards Results
A-Opal Glass	5.67	5.72	5.65-5.80
B-Opal Glass	5.67	5.72	5.65-5.80
B-Zeophyllite	7.49[a]		

a: See Chalmers, Dent, and Taylor (6).

Table VII

Precision for Replicate Analyses of Some Scottish Metamorphic Rocks

Sample Code Number[a]	% Fluoride			Mpd	Mpd'
S/S 8	0.025	0.023[b]		4.2	3.3
S/S 10	0.042	0.039	0.035[b]	10.3	2.1
S/S 18	0.041	0.042		1.2	1.9
S/S 26	0.040	0.038		2.6	2.1
S/S 29	0.050	0.049	0.048[b]	2.0	1.6
S/S 34	0.057	0.057		---	1.4
S/S 46	0.029	0.030		1.7	2.7
S/S 51	0.024	0.023		2.1	3.3
S/S 87	0.037	0.034		4.2	2.3
S/S 94	0.058	0.058		---	1.4
			Average	2.8	2.2

a: See Part II of thesis for descriptions of samples.

b: Analysis not concurrent with other determination(s).

Table VIII

Precision of the SPADNS Method
for Determining Fluoride in Rocks

Sample Number	% F	% F	% F	% F	Avg. % F
S/S 4	0.007	0.010			0.009
S/S 7	0.006	0.007			0.007
S/S 8	0.025	0.023			0.024
S/S 10	0.042	0.039	0.035	0.036	0.038
S/S 12	0.011	0.013[a]			0.012
S/S 15a	0.047	0.046			0.047
S/S 18	0.041	0.042			0.042
S/S 24	0.040	0.042			0.041
S/S 26	0.040	0.038			0.039
S/S 29	0.050	0.049	0.048		0.049
S/S 34	0.057	0.057	0.059[a]		0.058
S/S 35	0.093	0.092			0.093
S/S 39	0.076	0.075[a]			0.076

____: Denotes different strength titrant and other reagents used from those used for non- or double-underlined results.

a: Analysis made four years later by modified method.

Table VIII
(continued)

Precision of the SPADNS Method
for Determining Fluoride in Rocks

Sample Number	% F	% F	% F	% F	Avg. % F
S/S 40	0.023	0.021			0.022
S/S 46	0.029	0.030			0.030
S/S 48	0.035	0.034			0.035
S/S 50	0.065	0.070	0.070	0.070[a]	0.069
S/S 51	0.024	0.023	0.022[a]		0.023
S/S 61	0.033	0.035	0.032[a]		0.033
S/S 65	0.058	0.059	0.056[a]		0.058
S/S 73	0.063	0.065	0.061[a]		0.063
S/S 86	0.026	0.025			0.026
S/S 87	0.037	0.034	0.037[a]		0.036
S/S 93	0.029	0.030	0.031[a]		0.030
S/S 94	0.058	0.058			0.058

____: Denotes different strength titrant and other reagents used from those used for non- or double-underlined results.

a: Analysis made four years later by modified method.

Table VIII
(continued)

Precision of the SPADNS Method

for Determining Fluoride in Rocks

Sample Number	% F	% F	% F	% F	Avg. % F
S/T 6	0.018	0.020			0.019
S/T 11	0.063	0.064[b]			0.064
S/T 18	0.069	0.069[b]			0.069
S/T 21	0.020	0.023[b]			0.022
S/T 26	0.044	0.043[b]			0.044
S/T 29	0.018	0.022			0.020
S/T 44	0.064	0.059			0.062
S/T 47	0.020	0.021[b]			0.021
S/T 49	0.063	0.069			0.066
S/T 52	0.007	0.010			0.009
S/T 62	0.017	0.019[b]			0.018
S/T 63	0.020	0.019			0.020
S/T 69	0.054	0.055	0.055[b]		0.055
S/T 76	0.067	0.063[b]			0.065
S/T 80	0.076	0.074			0.075

____: Denotes different strength titrant and other reagents used from those used for non-underlined results.

b: Examples of precision with different reagents. Non-underlined: blank = 0.063 ml. titrant, titer = 0.199 ml./10.0 ug F; underlined: blank = 0.117 ml. titrant, titer =

Table VIII
(continued)

Precision of the SPADNS Method
for Determining Fluoride in Rocks

Sample Number	% F	% F	% F	% F	Avg. % F
S/P 1	0.035	0.031			0.033
S/P 16	0.047	0.047			0.047
S/P 19	0.051	0.052			0.052
S/P 22	0.030	0.036			0.033
S/P 25	0.017	0.016			0.017
S/P 28	0.046	0.047			0.047
S/P 31	0.031	0.026			0.029
S/P 35	0.043	0.043			0.043
S/P 42	0.048	0.046			0.047
S/P 54	0.039	0.039	0.039		0.039
S/P 66	0.031	0.032			0.032
S/P 77	0.027	0.023			0.025
S/P 90	0.032	0.030			0.031
S/P 92	0.018	0.019			0.019

____: Denotes different strength titrant and other reagents used from those used for non- or double-underlined results

Chapter I -3

The Procedure Employed for the Determination of Fluoride in Rocks

Section b

A Comparison of Results Obtained by Different Methods and Workers on the Same Substances

> "There is a wide misconception, even among analysts themselves, as to the accuracy of the results obtained in analytical work, and many confuse precision with accuracy. It is a comparatively simple matter to establish the precision that can be expected if a certain method of analysis is applied to a given material. On the other hand, it may be extremely difficult to judge the probable accuracy of a result, for all results are matters of opinion rather than fact, and so the true result is never known. This is one of the most unsatisfactory aspects of chemical analysis. ... A fair question therefore is: 'How can the most probable value be established?' ... How the most probable value is established for standard samples ... is a long story that can be summarized by the statement that it is based on experience, on the work of others in the field, and usually on determinations made by as many fundamentally different methods as possible." Lundell in 1933 (12).

The sound opinion of Clarke and Washington (3) in the early years of geochemistry (1924) that most fluoride analyses were unreliable because of faulty methods, the even more recent (1954) poor agreement among workers analyzing G-1 and W-1 for fluoride (1) (cf. Table V, Chapter I -3, section a), the paucity of data on the geochemistry of fluoride, and the miniscule data on comparison of methods of analysis, particularly of post-1945 date and with specific reference to rocks, made it clear to the writer that an interlaboratory standardization program would provide useful data not only to check the validity of different methods (that of the writer's for the defence of his geochemical work, for one) but also to point the way to superior methods.

Accordingly, about 600 to 800 grams of ten rock types were prepared by the writer as described in Chapter II -2. The response to the writer's invitations to join the program was very encouraging; some participants took the time and trouble to analyze these samples by more than one method. It must be stressed that each has done the analyses without knowing the results obtained by any others.

To the best of the writer's knowledge this is the first extensive interlaboratory standardization program for the analysis of fluoride in rocks. Seeman in 1905 (19) tested all methods known in his time; Morachevskii and Egorova studied two methods (15), and other workers have tested their methods with standard samples.

Before examining this work it will be worth discussing briefly one principle. To know the true result for each of these rocks, it is necessary to determine fluoride by two or more reliable methods which differ greatly in principle, a criteria upon which Lundell has put such deserved importance (12). There are fluoride methods based on three different principles represented in this study: (1) chemical methods (A, B, D, F, G, H) calling for a fusion followed by a two-stage isolation of the fluoride (13) from interfering elements, the second stage being always a steam distillation; (2) spectrographic procedures (E) requiring admixture of carbon (or graphite) and some calcium or strontium compound, arcing in graphite electrodes, and measuring the intensity of CaF or SrF bands, and comparing the intensity of these bands with that of bands of standard samples (1), and (3) pyrolysis methods (C) calling for admixture of some "accelerator" such as tungstic oxide or uranic oxide, heating at 800° to 1000°C in a stream of moist oxygen, and collecting the gases evolved in dilute caustic solution (16, 17). The final determination of the fluoride isolated by the first and last methods is in general the same: a thorium nitrate titration in the presence of some dye that forms a colored lake with excess thorium (18). Now since the spectrographic procedures depend on standards prepared by chemical methods, the methods studied in this program which differ fundamentally in principle reduce to two.

The letters A through H in the paragraph above refer to the methods used by the participants; except for the writer's method, method D, these are described below. The descriptions are taken verbatim from the participants.

<u>Method A</u>.- The sample was fused with fusion mixture, leached with hot water and filtered. Alumina and silica were precipitated with ammonium carbonate and after standing overnight filtered off. The filtrate was evaporated to low bulk and a further precipitate filtered off. Finally the filtrate with powdered soda-glass added was distilled with steam

from sulphuric acid at 147°C and the distillate made up to 250 milliliters.

Method B.- The sample was sintered with sodium peroxide at 480-500°C for thirty minutes. After cooling the frit was dissolved in 100 milliliters of water and silica and alumina precipitated at pH 11.5 by the addition of zinc sulphate solution. The precipitate was filtered off and the filtrate evaporated to low bulk. Distillation was carried out as in method A.

Method C.- The pyrolitic method described by Powell and Menis (Analytical Chemistry, 30, 1546 (1958)) was applied. In this method the sample is mixed intimately with ten times its own weight of tungstic oxide and heated at 825°C in a silica tube furnace in a stream of moist oxygen and the exit gases absorbed in sodium hydroxide solution. It was found, however, that 825°C is not hot enough and it is necessary to heat the sample and tungstic oxide to more than 900°C and preferably 1000°C. The flow of gas through the furnace should be about 180 liters per minute and the pyrolysis should continue for thirty minutes.

In methods A, B, and C the fluoride in an aliquot of the final solution was determined titrimetrically using Alizarin red S as indicator and thorium nitrate as reagent.

Analyst for methods A, B, and C: Dr. H.N. Wilson, Research Department, Imperial Chemical Industries Limited, Billingham Division, Billingham, County Durham, England.

Method E.- Spectrographic procedure, no further details.

Analyst: Miss. Vertie C. Smith, Denver Rock Analysis Laboratory, United States Geological Survey, Denver, Colorado, United States of America.

Method F.- The method of W.D. Goss was used. Fluorine in these samples was determined by fusing the samples with sodium carbonate, leaching the fusion cake with water and filtering. Soluble silica was removed from the solution by precipitating it with zinc perchlorate (1). Fluorine was distilled by a modification of the Willard and Winter method (2) using perchloric acid and a modification of the procedures of Reynolds and Hill (3) and Matuszak and Brown (4). The temperature of the distillation was controlled by apparatus similar to that of Huckabay, Welch, and Metler (5). Color development and determination followed Icken and Blank (6) except that 20 milliliters 0.87 molar acetic acid was added to each solution after adjustment of pH to buffer the solution and stabilize the color.

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Analyst: Mr. L.F. Rader, Denver Rock Analysis Laboratory, United States Geological Survey, Denver, Colorado, United States of America.

Method G.- The method we use is that outlined by H.R. Shell and R.L. Craig in the Report of Investigations No. 5158, U.S. Bureau of Mines, January 1956. We follow this closely; our apparatus is similar to that described by Shell, with one or two slight changes. The sample (0.25 grams) was fused with 5 grams of sodium carbonate in a platinum crucible and allowed to leach overnight in the crucible; it was immediately transferred to the distillation flask with a minimum amount of water and the required amount of perchloric acid. Final distillation was done at 140°C, give or take 2°, and about 300 milliliters of distillate were collected. Evaporation was done in the platinum basins used to collect the distillate (fine sand was used during the distillation); the acid mixture from the distillation was saved until the final titration, but because of the low values no second distillation of the acid mixture was done. Titration was done according to Shell and Craig, using a pH meter to follow the changes in pH and adjustments made with dilute sodium hydroxide and perchloric acid. The same acid and flux, and sodium hydroxide, was used throughout the runs. I used G-1 (Minnesota value for this is 0.07 percent) as a control, and ran four blank runs as well. Titration blanks were determined before each series of titrations. I ran some of the samples by the zinc oxide fusion method described by Shell but was not very happy about it, since the procedure was entirely unsupervised by me and I did not like the high blank obtained (0.06 percent fluoride).

Analyst: Dr. J.A. Maxwell, Analytical Chemistry Section, Petrological Sciences Division, Geological Survey of Canada, Ottawa, Ontario, Canada.

Method H.- The method of Grimaldi, Ingram, and Cuttitta was employed, including use of their distillation outfit (Analytical Chemistry, 27, 918 (1955)). Two minor modifications in technique were adopted: (1) Fusion was done in a nickel crucible, the lid of which was cooled by nestling just in its recess a nickel vessel kept half-full with boiling water (the flame of the burner, which was kept at full blast, around 1100°C, soon makes the water boil), and (2) the thoroughly crushed residue was leached, not by boiling it with solution, but by immersing the beaker containing it plus sodium carbonate solution three times in boiling distilled water, made alkaline to phenolphthalein, for 3-5 minutes each time. Somewhat larger volumes of wash solution were used than those that the authors of the method employed, but to compensate 175 to 200 milliliters of distillate were collected at 135°C.

Analyst: Mr. R.P. Hollingworth.

Over-all Agreement.- Comparing all methods the agreement is not very good, for, taking the lowest results as an arbitrary reference, one finds others are 3.4 times higher, even omitting from consideration results for S/A 1. Comparing results obtained by method A, which commonly gives the lowest fluoride values, with those by method C, which gives with one exception the highest, one finds the latter average 2.2 times the results for the former method, omitting again results for sample S/A 1. Even when method C results are compared with a composite of method D, E, F, and H results (see the ensuing paragraphs) for all samples but S/A 1, the former are up to 1.8 times higher; they average 1.4 times the composite result for each sample, which factor amounts to an average difference of nearly 0.03 percent fluoride for the nine rocks, calculated from the composite above.

Possible Matrix Effects in Chemical Methods.- It follows from the considerations advanced by Lundell (12) that there is a region of doubt about the true result for these samples; in extreme cases as for example E/M 1 and E/H 1 we know only that the amount of fluoride for each is somewhere between 0.05 to 0.09 percent and 0.07 to 0.11 percent, respectively. That pyrolysis methods are not subject to the negative errors which usually accompany chemical methods (16) may be manifested in the higher fluoride values obtained by method C. Silicon (21, 22), aluminum (21, 22), and iron (22) might cause low results for fluoride when the usual two-stage chemical procedures are used, for these elements may entrap fluoride in the precipitation or retard it in the distillation. Both the small number of samples and the variables involved, as for example the indeterminate effect of the silica, alumina, and ferric oxide contents of rocks and other errors in the analysis, make it difficult to ascertain clearly whether one of these elements alone is responsible for erroneous results for fluoride. At any rate, there do seem to be such matrix effects when method C results are compared to those of method B and D. Taking the method B result minus the average result, C'', found by the pyrolitic method, as equal to X, one notes in Table X that the greatest absolute differences, X, are associated with the high silica content rocks. Similarly, if one makes like calculations with methods C and D, the greatest absolute differences, X', are associated with the high iron content rocks. On the other hand, when one expresses by what percentages methods B and D results are low (100X/C'' and 100X'/C'', respectively) compared to method C determinations, it is in both cases the high iron content rocks that are generally associated with the high relative differences.

To elucidate further these matrix effects, it would be valuable to compare rocks having different mineralogy and bulk chemical composition but the same fluoride content. The writer had hoped to run complete analyses for these rocks, but he found teaching himself silicate rock analysis more difficult than anticipated. See Chapter I -4. Nevertheless, the mineralogy for these rocks is known (Chapter I -4, Tables XII through XX), and the percent silica and ferric oxide may be estimated with the additional aid of analyses of like rock types. In Table XI are those samples which have like fluoride contents. The data suggest that, assuming the method C results are the accurate ones, the lower the ferric oxide content, the less the magnitude of negative errors in method D; compare F/MC 17 and I/C 2 results by method D with the others of each group (0.1 and 0.08 percent fluoride, respectively).

Possible Matrix Effects in Pyrolysis Methods.- However, the nature of reactions taking place with pyrolysis of silicate rocks, to the best of the writer's knowledge, is not fully understood. With the use of tungstic oxide and moist oxygen the fluoride is probably expelled either as hydrofluoric acid or fluorine oxide or a mixture of these gases.

Other halogens would also be expelled as their hydracids, although formation of tungsten hexachloride and tungsten hexafluoride, at least in the fluxing stage, may be a mode of expulsion of the fluoride. Possibly reactions of this sort take place:

$$WO_3 \text{ ("accelerator") } + \text{F-containing mineral} \underset{1000°C}{\overset{O_2,\ H_2O}{=}}$$

$$WF_6 + \text{decomposition products} \qquad \text{(A)}$$

followed by either:

$$WF_6 + 3H_2O \underset{1000°C}{=} 6HF + WO_3 \qquad \text{(B)}$$

or:

$$WF_6 + 3O_2 \underset{1000°C}{=} 3F_2O + WO_3 \qquad \text{(C)}$$

What is the behavior of tungstic oxide at high temperature? Treatment of tungstic oxide precipitates with hydrofluoric acid followed by heating to remove silica do not volatilize the former (9), but ignition of tungstic oxide precipitates above 900°C causes appreciable volatilization of that precipitate (9). But perhaps in pyrolysis of rocks either moist oxygen or the silicates prevent this loss.

Carbon present in any form in the rock would be converted to carbon dioxide and also expelled. Sulfide sulfur will also be converted to sulfate, and ferrous or ferric sulfate formed from pyrite would decompose with the formation of sulfur trioxide and ferric oxide (10). In fact probably most iron-nickel-copper-lead-zinc-cobalt sulfides in rocks would thus yield their sulfur (10). The presence of silica or ferric oxide is said to lower the decomposition temperature of calcium sulfate (10), although Wilson has reported this compound added to rock samples is without effect on results obtained by method C (23). In the writer's opinion the effect of pyrolysis on the phosphorus pentoxide content of rocks is yet to be established; apatite in particular may decompose with the formation of the phosphoric acid anhydride:

$$CaF_2 \cdot 3Ca_3P_2O_8 + 10WO_3 + H_2O \underset{1000\,°C}{\overset{O_2}{=}} 10CaWO_4 + 2HF + 3P_2O_5 \qquad (D)$$

However, Powell and Menis have determined fluoride in a phosphate rock, using a sodium tungstate-tungstic oxide mixture, and their result compares very favorably with the accepted analysis (17).

Thus procedures for which the fluoride is determined by thorium nitrate titration after pyrolysis of the sample may lead to plus errors, for the chloride and the carbon will be expelled with the fluoride and doubtless sulfur bound as pyrite (and other metallic sulfides) will also be brought over into the solution as sulfate, so that these elements will produce a "salt effect" or form insoluble thorium compounds. The amounts of chloride and carbon dioxide present in one gram rock samples will probably not cause much error, but sulfate even at 10^{-3} molar will (18); the effect of phosphate in the thorium nitrate titration in producing plus errors is sensible when it is 10^{-6} molar (18). Many of these rocks show sulfide in thin section; finely disseminated sulfide may be present in nearly all of them: "... rocks with hardly an exception and many minerals carry pyrite or pyrrhotite, or both, often in considerable amount, often in traces only. Sulfur can almost always be detected in 2 grams of rock powder" (11). Since for these ten rock samples the sulfide content increases approximately as the basicity, it is not at all unlikely then that the association of high differences in percent fluoride between method C and either method B or D with high iron content rocks (cf. Tables X and XI) is in large measure attributable to the higher sulfide present in them. The effect of pyrite would seem all the more convincing when one realizes that both E/M 1 and E/H 1, having the greatest amounts of this mineral, show, next to S/A 1, the highest absolute (X') (S/T 1 has slightly higher X' than E/M 1) and relative (100X'/C'') differences in fluoride given in Table X. Such matrix effects for the pyrolitic method may be clarified by assuming method D gives accurate results, so that for rocks having the same fluoride but different pyrite and (or) apatite content, pyrolitic results will be higher according as the pyrite and (or) apatite content increases. These relations are suggested in Table XII. That S/T 1 gives such X' and 100X'/C'' differences may be due to the volatilization of phosphorus postulated in equation (D).

To summarize, then, although the pyrolitic procedure, giving in this interlaboratory study of methods the highest results of all methods for fluoride as might be expected for a method free of those negative errors usually attendant with chemical methods, there is as yet no proof that the pyrolitic procedure is also free of the plus errors expected with the presence of chloride, sulfate, carbonate, and possibly phosphate in a solution whose fluoride content is determined by a thorium nitrate titration.

The above discussion should of course be regarded only as a guide for further work. The matrix effects are but adumbrated; they will remain obscure -- if they exist at all -- until further work establishes the nature of pyrolysis reactions. Of course, so will the doubt about the true results remain, so it is imperative that more investigations be effected to develop the applicability of method C for silicate rock analysis. But the features of this method (16, 23) make such investigations very worth while.

The Precision of Four Methods.- Having treated the unfavorable aspects in agreement, the writer now addresses himself to the encouraging ones. For a comparison of methods it will be useful to know the precision of which each method is capable. That for method D is given in Chapter I -3, section a, Table VIII. There is not sufficient data for a reliable calculation of the standard deviation for methods C and F; nevertheless, the limited data for these methods, in Table IX, can be used for a calculation: For method C the standard deviation is ±0.009 percent fluoride, or ±0.004 percent, omitting the results for E/P 1; for method F it is ±0.003 percent or, omitting the results for E/S 1 and E/P 1, ±0.0014 percent. On the basis of errors in spectrophotometric measurements alone for method H, the standard deviation for it should be about ±0.001 to ±0.002 percent fluoride, for even repeat spectrophotometric measurements on aliquots of test solution, a range of fluoride standards, aliquots of blank solution, and cell corrections should reduce the error at best to ±0.002 optical density, which is equivalent to ±1 microgram fluoride in a 20 milliliter aliquot taken from 250 milliliters. See the outline description of method H in the preceding pages. The reproducibility of method E is around 15 percent of the amount reported (4). Allowing, then, for the scanty data and for the somewhat lower precision of the spectrographic procedure, the standard deviation for methods D, F, and H should be set at ±0.003 to ±0.004 percent fluoride when comparing these methods and increased to ±0.01 percent fluoride when including method E results for comparisons.

Therefore, from the above considerations and bearing in mind the fact almost all results are single determinations by each method, it would seem that chemical and pyrolitic results that fall to within ±0.006 to ±0.008 percent fluoride of each other are in very good accord. From the data in Table IX it is seen that methods D, F, and H meet this criteria in the majority of cases. If the allowable range for E/S 1 and E/P 1 is increased to ±0.01 percent and ±0.02 percent fluoride, respectively, at least eight out of ten analyses by a given method, including method E results, agree to within about 10 percent of the amount of fluoride with results obtained by any one of the other three methods.

The Consensus Mean.- By calculating a consensus mean (5) for each sample further aspects of the agreement for these methods are brought to light. The consensus mean has been calculated in the following manner: After calculating the mean, M, for all determinations, using the average only for methods C and F (C'' and F'', respectively), values differing from this average by ±0.01 percent fluoride, which is somewhat more than the estimated 95 percent confidence limit for all methods but method E, were discarded and the consensus mean, CM, calculated from the results remaining. The difference between the result obtained by each method and the consensus mean was also calculated. All these data are presented in Table XIII, and one notes only four methods show deviations from the consensus means of ±0.01 percent fluoride or less for all ten rocks. Further data for these four methods showing the average deviation from the consensus mean, $\bar{D}_{cm}$, the average plus and minus deviations, $\bar{D}+_{cm}$ and $\bar{D}-_{cm}$, respectively, from CM, and the number of results higher and lower than the consensus mean, N^+ and N^-, respectively, are in Table XIV.

Further, using the difference between the result reported for a given method and sample and the corresponding consensus mean (cf. Table XIII) to calculate a standard deviation for each of the four methods, methods D, E, F, and H, one notes that approximately 9 out of 10 results for a given method will fall within ±0.006 to ±0.012 percent fluoride of the corresponding consensus means, depending on the method. In other words one is 95 percent certain that any one of the forty results is to within around ±0.01 percent fluoride of the corresponding consensus mean. See Table XV

No significance should be attached to the consensus mean; it is arbitrary (5), for there is no evidence that it represents the true result for each sample. Indeed, it is all the more difficult to consider it as the true result, for it is the mean of four methods that differ little in principle, two of which that have been carried out by the same analyst (the writer) and another two that have been done in the same laboratory. There is also, perhaps, a kindly coincidence: The consensus mean is often close to the mean, such proximity no doubt due to the fact that the relatively low results obtained by methods A and B are compensated for by the relatively high ones by methods C and G. Since the consensus mean is arbitrary, one is able only to cite the following, the significance of which can only be established with further work:

1. Allowing a variation from the consensus mean of ±0.004 percent for methods D, F, and H and ±0.01 percent fluoride for method E, the estimated standard deviation for these methods, one observes that 32 out of 40 analyses fall within these limits. See Table XVI. Somewhat higher limits should perhaps be allowed for analyses of E/P 1, say ±0.01 percent fluoride, in which case one notes that of the chemical methods method H falls within the assigned deviations for all analyses and method D follows with 9 out of 10 coming within these deviations.

2. Allowing for the lower precision of the spectrograph-

ic procedure, all analyses by method E come within ±0.01 percent fluoride of the consensus means.

3. The data in Table XIV show that methods E, F, and H have average plus and minus deviations of equal frequency; methods D, E, and F clearly give plus and minus deviations of equal magnitude; but method D has a greater number of minus deviations from the consensus means than plus ones.

4. Methods D, E, and H give the lowest average deviations from the consensus means; e.g., (D - CM)/10, etc. However, method D seems to give the narrowest dispersion about the consensus means. That is, 95 percent of all method D results would fall to within ±0.006 percent fluoride of the consensus means.

As implied above further work is required. It cannot as yet be demonstrated that the consensus means represent close approximations to the true results. The interlaboratory standardization program does on the one hand show the promise of pyrolitic methods for rock analysis and on the other hand reveal the sort of agreement that is possible with some methods. For example, compare the results for E/M 1, F/MC 17, and I/C 2 obtained by methods D, E, F, and H (cf. Table IX).

Summary.- To summarize the findings of this interlaboratory study of fluoride methods, the writer puts in an approximate order of importance the following conclusions:

1. The true result for these ten rocks is not yet established, for the average difference between the two methods

differing in principle is 0.025 percent fluoride when method C results, consistently having the higher values, are compared with the consensus means.

2. There is some evidence that either chemical or pyrolitic methods, or both, are subject to matrix effects. The evidence, though indirect and imperfectly correlated, is sufficient to warrant further study, particularly for pyrolitic procedures.

3. The higher results obtained by the pyrolitic procedure may make manifest the magnitude of negative errors so common in chemical methods. Yet the reworking of precipitates carried out by the writer for method D (see Appendix II) and of residues by Grimaldi, Ingram, and Cuttitta for method H (6) suggest recovery of fluoride by these procedures is at least 90 percent. In addition, other workers using the pyrolitic method on standard samples have reported results that agree well with the accepted values which are obtained by chemical methods (17).

4. Although the precision for some methods, such as method D, may justify the second decimal place for single determinations, particularly for comparison of results for different rocks obtained by the same method, the uncertainty about the true result for these samples and the standard deviations calculated from the consensus means show that single determinations, even by four methods showing good agreement, are comparable to no better than ±0.01 percent fluoride.

5. Four of the eight methods, three being chemical and one spectrographic, give close agreement with each other

and with an arbitrary mean, although it should be kept in mind that two methods (D and H) were employed by one worker and another two (E and F) were used by the same laboratory. It is of interest to note that the methods giving this close agreement all call for some instrumental method of determining the fluoride. The findings of Hardin (7, 8) on the thorium nitrate titration of fluoride should make obvious the necessity of using an instrumental method for determining minor amounts of this element. It follows that pyrolitic procedures can be developed so that, except for the weighings, the entire analysis is done instrumentally, as with spectrographic procedures.

Summary with Reference to Method D.- The order of importance of conclusions depends in part on the point of view. For the purposes of the geochemical work carried out by the writer, the following summary is critical:

1. Method D shows consistent favorable agreement with three other methods: methods E, F, and H, the first being a spectrographic procedure.

2. The precision of method D is rather good, although for lack of evidence it cannot be rated carefully with that of other methods. Nevertheless, a relative deviation (2), C, of ±3.5 percent for the average amount of fluoride in the metamorphic rocks studied and a dispersion in the 95 percent confidence limit of ±0.003 percent fluoride about the arithmetic mean are good, particularly in view of the small amounts of an element difficult to determine in silicates.

3. By use of an arbitrary statistical device; e.g., a

consensus mean, the frequency of method D results falling within an assigned deviation of ±0.004 percent fluoride of the consensus means is next highest to method H (cf. Table XVI). Method D results have the lowest dispersion about these consensus means, although its results tend to be low compared to the latter (cf. Tables XIV and XV).

The close agreement of method D with those used by the United States Geological Survey makes it possible for the writer to compare his results, for the purposes of the geochemical investigations, with those reported by Seraphim (20) and Kokubu (14), for these workers standardized their methods with the United States Geological Survey, using G-1 and W-1. However, from paragraph 4 of the general summary it is clear deviations of at least ±0.01 percent fluoride must be allowed when making such comparisons.

To sum up, the, the writer is able to demonstrate that at the least his results are no more doubtful than those obtained by three other methods!!

There are two criticisms of this work:

1. No one participant has done the analyses with any of the other seven methods.

2. Results for nearly all methods are based on single determinations only.

Had each participant done replicate determinations by each of the eight methods (perhaps the chemical procedures could have been halved), the data so obtained would doubtless not only strengthen the validity of some observations and conclusions but also make possible further scrutiny of methods. For example, more complete and by far more realistic data on the precision of these methods would be available, and tendencies for methods to be low or high compared with averages or arbitrary means would be more clearly revealed. But such a program would involve a great deal of time and training on the part of each participant and also a great array of equipment for each laboratory.

Criticisms notwithstanding, a feature of this interlaboratory program is that six methods (methods C through H) are ones described since 1955 and used by these participants with little or no modifications in the published procedures. These same methods are, moreover, the routine ones used by the participating laboratories. (13, outlines of methods on preceding pages). Thus workers in the field have a useful guide not only to the possible relations between method and result but also to the agreement that is possible in analyses of this element in rocks.

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Table IX

The Determination of Fluoride in Rocks by Five Analysts Using a Total of Eight Methods

Sample	A	B	C	C'	C''	D	E	F	F'	F''	G	H
E/S 1 quartz monzonite	0.072	0.082	0.138	0.140	0.139	0.117	0.12	0.12	0.13	0.13	0.11	0.114
E/P 1 tourmaline granite	0.156	0.162	0.275	0.220	0.248	0.242	0.23	0.23	0.24	0.24	0.53	0.227
G/G 1 nepheline syenite	0.032	0.044	0.070	0.068	0.069	0.047	0.05	0.056	0.057	0.057	0.06	0.053
S/T 1 tonalite	0.039	0.052	0.100	0.108	0.104	0.067	0.07	0.058	0.058	0.058	0.10	0.068
E/M 1 diabase	0.029	0.036	0.080	0.081	0.081	0.045	0.05	0.044	0.045	0.045	0.09	0.042
S/A 1 eucrite	0.002	0.008	0.019	0.016	0.018	0.000	0.00	0.004	0.003	0.004	0.02	0.000
F/MC 17 migmatite	0.050	0.058	0.110	0.118	0.114	0.088	0.09	0.089	0.092	0.091	0.10	0.091
I/C 1 semi-pelitic schist	0.048	0.056	0.090	0.102	0.096	0.070	0.08	0.070	0.064	0.067	0.12	0.078
I/C 2 hornfels	0.037	0.046	0.085	0.090	0.088	0.057	0.06	0.055	0.057	0.056	0.08	0.062
E/H 1 marine shale	0.044	0.048	0.110	0.112	0.111	0.069	0.08	0.066	0.068	0.067	0.07	0.072

Table X

Possible Matrix Effects Revealed by Comparison of Fluoride Results Obtained by Pyrolitic and Chemical Methods

Code Number	X	100X/C''	X'	100X'/C''
E/S 1	-0.057	-41	-0.022	-16
E/P 1	-0.086	-35	-0.006	- 2
G/G 1	-0.025	-36	-0.022	-32
S/T 1	-0.052	-50	-0.037	-36
E/M 1	-0.045	-56	-0.036	-46
S/A 1	-0.010	-56	-0.018	-100
F/MC 17	-0.056	-49	-0.026	-23
I/C 1	-0.040	-42	-0.026	-27
I/C 2	-0.042	-48	-0.031	-35
E/H 1	-0.063	-57	-0.042	-38

Table XI

Rocks Having Similar Fluoride Contents Obtained by Method C: Possible Matrix Effects in Method D Revealed by Comparison of Method C and Method D Results

Code Number	C''	D	% Fe_2O_3(est.)
S/T 1	0.104	0.067	6-8
F/MC 17	0.114	0.088	2-4
E/H 1	0.111	0.069	5-9
E/M 1	0.081	0.045	11-13
I/C 2	0.088	0.057	6-9

Table XII

Rocks Having Similar Fluoride Contents Obtained by Method D: Possible Matrix Effects in Method C Revealed by Comparison of Method D and Method C Results

Code Number	D	C''	% Fe_2O_3(est.)	% Ore[a]
G/G 1	0.047	0.069	9.7[b]	4.8[c]
E/M 1	0.045	0.081	11-13	7.8
S/T 1	0.067	0.104	6-8	0.9[d]
I/C 1	0.070	0.096	6-9	---
E/H 1	0.069	0.111	5-9	2-5[e]

a: See Chapter I -4, Tables XIV, XV, XVI.

b: Based on analysis. See Chapter I -4.

c: Includes biotite.

d: Volume percent figure for accessories, consisting of sphene, apatite, and zircon.

e: Estimated volume percent of pyrite.

Table XIII

Fluoride Results Obtained by Eight Methods Compared with Their Consensus Means

Sample	Mean (M)	Consensus Mean (CM)	(A-CM)	(B-CM)	(C-CM)	(D-CM)	(E-CM)	(F-CM)	(G-CM)	(H-CM)
E/S 1 quartz monzonite	0.111	0.118	-0.046	-0.036	+0.021	-0.001	0.00	+0.01	-0.01	-0.004
E/P 1 tourmaline granite	0.254	0.237	-0.081	-0.075	+0.011	+0.005	-0.01	0.00	+0.29	-0.010
G/G 1 nepheline syenite	0.052	0.052	-0.020	-0.008	+0.017	-0.005	0.00	+0.005	+0.01	+0.001
S/T 1 tonalite	0.070	0.066	-0.027	-0.014	+0.038	+0.001	0.00	-0.008	+0.03	+0.002
E/M 1 diabase	0.052	0.046	-0.017	-0.010	+0.035	-0.001	0.00	-0.001	+0.04	-0.004
S/A 1 eucrite	0.007	0.002	0.000	+0.006	+0.016	-0.002	0.00	+0.002	+0.02	-0.002
F/MC 17 migmatite	0.085	0.090	-0.040	-0.032	+0.024	-0.002	0.00	+0.001	+0.01	+0.001
I/C 1 semi-pelitic schist	0.077	0.074	-0.026	-0.018	+0.022	-0.004	+0.01	-0.007	+0.05	+0.004
I/C 2 hornfels	0.061	0.059	-0.022	-0.013	+0.029	-0.002	0.00	-0.003	+0.02	+0.003
E/H 1 marine shale	0.070	0.072	-0.028	-0.024	+0.039	-0.003	+0.01	-0.005	0.00	0.000

Table XIV

The Average Deviation and the Frequency of Plus and Minus Deviations from the Consensus Mean for Eight Fluoride Methods

Method	$\bar{D}_{cm}$	$\bar{D}^{+}_{cm}$	$\bar{D}^{-}_{cm}$	N^{+}	N^{-}
A	0.031	---	0.003	0	9
B	0.024	0.006	0.003	1	9
C	0.025	0.025	---	10	0
D	0.003	0.003	0.003	2	8
E	(0.003)	0.01	0.01	2	1
F	0.004	0.005	0.005	4	5
G	0.048	0.06	0.10	8	1
H	0.003	0.002	0.005	5	4

Table XV

The Standard Deviation Calculated from the Consensus Mean for Methods D, E, F, and H

Method	s	2s
D	±0.003	±0.006
E	±0.006	±0.012
F	±0.006	±0.011
H	±0.004	±0.009
Average	±0.005	±0.009

Table XVI

The Number of Analyses by Method Falling Within Assigned Deviations from the Consensus Means

Deviation Assigned	D	E	F	H	Total/40
±0.003	7	(7)	5	6	25/40
±0.004	8	(7)	5	9	29/40
±0.006	10	(7)	7	9	33/40
±0.008	10	(7)	9	9	35/40
±0.010	10	10	10	10	40/40

Chapter I -4

Some Procedures Adopted for the Analysis of the Ten Rocks Used as Fluoride Interlaboratory Standards

> "Even to those who are thoroughly familiar with the subject, rock analysis is a complex and often a trying problem. Although long practice may have enabled one to do certain parts of the work almost mechanically, perplexing questions still arise which require trained judgment to meet and answer properly, and there is yet room for important work in some of the supposedly simplest quantitative determinations. If the results are to have any decided value for purposes of scientific interpretation and comparison, they must be the outcome of the work of one who is able to find his way through the intricacies of an analysis in which 15 to 25 components are to be separated and estimated with close approach to accuracy, and this a beginner cannot hope to do. ... Too great stress cannot be laid upon the importance, especially for the analyst of limited experience, of consistently testing most of his final precipitates and filtrates as carefully as possible in order to be sure, on the one hand, that the substances reported by a given name are wholly such and, on the other, that all is reported. In no other way can an analyst so soon acquire the needed confidence in himself and his methods. Likewise methods should be checked with standard samples of like material whenever possible." Hillebrand, Lundell, Bright, and Hoffman in 1953 (11).

The writer planned to carry out complete analyses of the ten rocks selected for the fluoride interlaboratory standardization program (cf. Chapter I -3, section b) by the conventional ("classical") methods of analysis, for, besides his interest in developing his skills in rock analysis, he felt their employment would meet two objectives connected with the geochemical studies:

1. The analyses and the descriptive petrographic data, sent to the participants in the cooperative study on fluoride analysis, would possibly aid them in choosing suitable procedures for the determination of that element.

2. Further studies on the geochemistry of fluoride would depend greatly on accurate analyses of rocks and minerals not only for fluoride but for other elements as well. The writer's broad objective, accordingly, was to train himself to do silicate rock analyses accurately by the conventional procedures and to use the rocks so analyzed as standards not only for training himself in the microanalysis of rocks and minerals but also for developing reliable rapid methods of analysis.

The completion of these two objectives will for example admit for study the relation, if any, between fluoride abundance and distribution to the grade of metamorphism for rocks of the same chemical composition (a suite which can be rather quickly obtained by screening specimens by rapid methods), and systematic compositional variation of certain hydroxyl-fluoride minerals with grade of metamorphism (a suite of minerals separated from rocks can be analyzed by micromethods, especially for Mg/Fe and OH/F ratios, as in biotites).

Silicate rock analysis, however, proved a more formidable task than expected, in great measure because some of the existing procedures gave unacceptable results in the writer's hands. Nevertheless, the writer did effect some progress, some modifications, and some findings on blanks, all of which, based mainly on analyses of synthetic solutions, he reports herein. He wishes to record also his great indebtedness to R.A. Chalmers for advising him to train himself on synthetic solutions, for, as Chalmers has pointed out, it is the only technique by which one knows accurately the amount present of each of several constituents added as pure compounds and so consequently knows what his errors are on recovering each of them.

The procedures are in the main those of Hillebrand, Lundell, Bright, and Hoffman (12); they are described in Appendix III, and the discussion of results obtained by their use is presented in the paragraphs to follow. The writer points out that he has taken verbatim from their book (12) such procedures or parts of them that he has employed successfully, not because he wants to arrogate to himself their findings, but solely for the reason that a description with continuity is less confusing than that which might arise if the reader were obliged to switch back and forth from the writer's own work to page references to theirs. However, references to their work are not cited, mainly because any beginner should read carefully not just the paragraphs giving the procedures but also the sections and chapters on general laboratory technique, errors in analysis, general considerations on each element, etc. In effect, most of the book should be consulted (12), and it is not unwise to examine other standard works in the field.

Modifications Adopted.- Tests on synthetic solutions indicated that the following modifications in the conventional procedures gave in the writer's hands superior results:

1. On the basis of Chalmer's findings (oral communica-

tion) the determination of the silicon dioxide present with the other mixed oxides is effected by direct volatilization with hydrofluoric and sulfuric acids rather than by dehydrating it with sulfuric acid after bringing all the mixed oxides into solution.

2. The determination of the total iron as ferric oxide is done on aliquots rather than on the entire solution. The titration error is somewhat greater for aliquots than that for the entire solution, but it is minimized by running two aliquots through the procedure. Use of aliquots permits reserving some sample solution for the determination of titanium dioxide.

3. The determination of titanium dioxide is done on an aliquot of the same sample solution used for the determination of the total iron. The procedure is that of Yoe and Armstrong (25); in the writer's experience it is more reliable than the peroxidized titanium method.

4. The determination of the mixed oxides is done by the usual double precipitation with ammonium hydroxide plus another double precipitation in the filtrates, evaporated to low bulk in platinum. A little aluminum was found sometimes to escape precipitation in the usual procedure. The recovery of aluminum in filtrates was not, however, done for the tests on synthetic solutions.

5. The determination of the calcium oxide and the magnesium oxide was carried out in more dilute solutions than Hillebrand, Lundell, Bright, and Hoffman prescribe, but their use has meant coarser, better-formed precipitates with consequent manifestly improved properties.

6. The determination of the strontium oxide is done by precipitating the nitrate in 80 percent nitric acid solution as described by Willard and Goodspeed (24). Filtrations have been effected by Emich's filterstick.

7. The determination of the calcium orthophosphate, barium orthophosphate, and, sometimes, strontium orthophosphate is done by precipitating these elements as their sulfates in 90 percent methyl alcohol. The procedure is that of Caley and Elving (2), who have used it for the separation of magnesium from calcium. Filtrations have also been effected by Emich's filterstick.

The adoption of the last two procedures above has been founded on tests on synthetic solutions. The writer has tried the alcohol-ether extraction method of Fresenius (3) as described by Hillebrand, Lundell, Bright, and Hoffman (4) and the nitric acid extraction method of Rawson (17) as described by Hillebrand, Lundell, Bright, and Hoffman (5) for correcting the impure calcium oxide precipitate for strontium oxide with high results on synthetic solutions of the elements. With Rawson's method there were plus errors of up to 9 milligrams on a single extraction. Gentle warming for prolonged periods, as for example 40°C overnight for Rawson's method (17), has still given high results. The writer has also tried on synthetic solutions the 75 percent by volume ethyl alcohol extraction method (6) and the 90 parts ethyl alcohol-10 parts methyl alcohol-1 part sulfuric acid extraction method (6) for correcting the impure magnesium pyrophosphate precipitate for calcium orthophosphate and barium orthophosphate with high results for the impurities. Here again prolonged standing and heating did not obviate the plus errors. These procedures are best suited to platinum-felted crucibles; filter paper, which was suggested as an alternate media (4, 6), was used for all these methods. It was established, however, that plus errors were due, not wholly to incomplete washing of papers, but largely to incomplete extraction of the major element. The errors, then, appeared to arise from slow attainment of equilibrium. It was felt methods providing for a preliminary solution of all elements followed by a precipitation of the elements present as impurities would give more satisfactory results. For this reason the writer chose Willard and Goodspeed's method (24) of precipitating strontium nitrate in 80 percent nitric acid as the procedure for correcting the impure calcium oxide for that element, and Caley and Elving's method (2) of precipitating calcium sulfate (and barium and strontium sulfates) in 90 percent methyl alcohol for correcting the magnesium pyrophosphate for these elements. The sharpness of the separations of the major elements from the minor ones, the speed and simplicity of operations, the efficiency of washing the precipitates, and the ease with which precipitations can be repeated were greatly enhanced by employing the filterstick for the filtrations. There is much to commend the use of the filterstick for operations of this sort.

Tests on Synthetic Solutions, Part I.- Tests of the methods for determining silicon dioxide, mixed oxides, total iron as ferric oxide, and titanium dioxide have been carried out on synthetic solutions. Stock solutions of the elements were prepared as follows:

1. aluminum oxide, 13.60 milligrams per 10.0 milliliters: Spec Pure aluminum rod was cleaned with hydrochloric acid, dried, weighed, and then dissolved in hydrochloric acid.

2. ferric oxide, 9.905 milligrams per 10.0 milliliters: A.R. ferric chloride was precipitated once with ammonium hydroxide, filtered, and dissolved in hydrochloric acid. The solution was standardized as follows: aliquots were treated with nitric acid by boiling and then keeping them hot for a period of time, made 1 normal in hydrochloric acid, reduced by silver, and titrated with ceric sulfate as described.

3. titanium dioxide, 2.69 milligrams per 10.0 milliliters: a titanium sulfate solution, prepared from potassium titanium oxalate salt, was made by precipitating the cupferrate in dilute hydrochloric acid (1 + 9). The cupferrate was filtered by suction, washed, and ignited in a silica crucible. Portions of this product were put in a platinum crucible and ignited to constant weight. The oxide was then dissolved by boiling it in a sulfuric acid-ammonium sulfate mixture (16). Some of this solution was withdrawn and the hydroxide precipitated in the cold twice with ammonium hydroxide. The second precipitate was washed until the test for sulfate on 5 milliliters of filtrate was negative. This precipitate was dissolved in hydrochloric acid. The solution was standardized by the colorimetric procedure using the titanium sulfate solution as the standard.

4. zirconium dioxide, 0.12 milligrams per 10.0 milli-

liters: Spec Pure zirconium oxychloride was weighed and dissolved in hydrochloric acid.

5. phosphorus pentoxide, 0.60 milligrams per 10.0 milliliters: A.R. diammonium phosphate was weighed and dissolved in hydrochloric acid. The solution was kept in a polythene bottle.

Each of the above stock solutions was made up 0.1 normal in hydrochloric acid. Any pipets used were "A" quality; the same pipets used for preparing and standardizing the stock solutions were also employed, whenever possible, for making up the synthetic solutions.

A batch of Laboratory Reagent silica was treated as follows: The silica was sieved on silk bolting cloth and the fraction that wholly passed 60 mesh per inch but not 110 mesh per inch was collected in a platinum dish and boiled with 50 milliliters of dilute hydrochloric acid (1 + 1) for 15 to 30 minutes, kept hot for 15 minutes more, and the liquid decanted. Another 50 milliliters of dilute acid was added, boiling and decantation repeated, and the acid-washed silica filtered by suction on Whatman 42 paper. The cake was washed thoroughly with hot water, put in a platinum dish, filter paper removed, and the cake dried for several hours at 135°C. Portions of this silica were placed in a platinum crucible, ignited to constant weight, and sodium carbonate added in an amount used for fusing a rock of its type. The fusion and the bringing of the melt into solution were conducted as described in Appendix III. The solution was transferred to a beaker, carefully acidified, and the appropriate volumes of stock solutions were pipetted in. Thence the treatment was the same as for rocks (cf. Appendix III). The results are summarized in Tables I through IV.

<u>Tests on Synthetic Solutions, Part II</u>.- Tests of the methods for determining calcium oxide, strontium oxide, magnesium oxide, and manganese oxide have also been carried out on synthetic solutions. Stock solutions of these elements were prepared as follows:

1. calcium oxide, 9.975 milligrams per 5.00 milliliters: A.R. calcium carbonate was ignited in platinum at 450°C to constant weight and dissolved in hydrochloric acid.

2. strontium oxide, 0.10 milligrams per 2.00 milliliters: Laboratory Reagent strontium nitrate was weighed to constant weight at 135°C in borosilicate glass and dissolved in hydrochloric acid.

3. magnesium oxide, 10.33 milligrams per 5.00 milliliters: Spec Pure magnesium rod was cleaned with hydrochloric acid, dried, weighed, and dissolved in hydrochloric acid.

4. barium oxide, 0.10 milligrams per 2.00 milliliters: A.R. barium chloride dihydrate was weighed and dissolved in hydrochloric acid.

5. manganese oxide, 0.10 milligrams per 2.00 milliliters: Laboratory Reagent manganese chloride quadrihydrate was weighed and dissolved in hydrochloric acid.

Each stock solution was made up 0.1 normal in hydrochloric acid. 25.0 milliliters of each of the calcium and magnesium oxide stock solutions were taken to check the concentration by a single precipitation of each by the methods described. Aliquots of the manganese solution were taken for a check on the concentration by the colorimetric procedure, using an A.R. manganese sulfate solution as the color standard.

The appropriate volumes of each stock solution were pipetted into a beaker. Also added was the amount of sodium carbonate, previously dissolved in the equivalent amount of hydrochloric acid, that would be used for fusing a rock of its type, plus ammonium salts (added as equivalent amounts of hydrochloric acid and ammonia) in nearly the same amounts that would be present after a double precipitation of the mixed oxides. These synthetic solutions were then carried through the methods given in Appendix III; the results are summarized in Tables V through VIII.

The compositions of the synthetic solutions were based on actual analyses, selected for completeness of analysis and range of composition, taken from Turner and Verhoogen (20).

The Determination of Blanks.- The results in Tables I through VIII are corrected for blank determinations, which the writer found were difficult to determine. If the reagents alone were carried through the methods, the blanks tended to be either low as for the calcium oxide determination or even nil as for the magnesium oxide determination. That the blanks were known to be low was established in the tests on the synthetic solutions, for both the calcium oxide and magnesium oxide results were high by a rather constant amount for each oxide. For example, the calcium oxide brought down as oxalate and ignited was almost always 0.5 milligrams higher than the weight of it taken. There was also some calcium present as orthophosphate in with the magnesium pyrophosphate, and its amount was about 1.4 ±0.3 milligrams (calculated as the orthophosphate). Similarly, after deducting the weights of barium orthophosphate, strontium orthophosphate (if present), and manganese pyrophosphate found, there was still left a small weight, 1.2 ±0.2 milligrams, calculated as the difference in weights of pure magnesium pyrophosphate found and pure magnesium pyrophosphate taken. These discrepancies were not attributable to improper technique, such as precipitation and ignition, for single determinations on aliquots of the pure magnesium and calcium stock solutions gave results that agreed to within 1 to 2 parts per thousand of the calculated weights.

The data in Table IX illustrate both the consistency of these discrepancies and the importance of making corrections in the pyrophosphate precipitate for a reliable magnesium oxide determination.

That no calcium oxide and magnesium oxide were found in blanks on the reagents alone when the magnesium was precipitated might have been due to the fact that their concentrations were in the "region of uncertain reaction." Richter (18), experimenting on the precipitation of dilute solutions of magnesium with sodium ammonium phosphate, found that with only 24 out of 40 trials did a magnesium ammonium phosphate precipitate form when he added 40 milliliters of 0.005 percent sodium ammonium phosphate to 40 milliliters of a 0.005 percent magnesium solution. As the writer's magnesium-containing blank solutions were of lower concentration than those of Richter's, it is possible such blanks were in the "region of uncertain reaction." On the other hand, the writer expected precipitations in ice cold solution and use of a precipitant of a far higher concentration than that of Richter would remove this "region of uncertain reaction." Whatever the explanation of the problem is, the writer felt all uncertainties about blanks can be eliminated in actual analyses by adding a small known amount of a pure compound of the element to the reagents just before the blank for that element is to be determined.

Accordingly, about 10 milligrams each of aluminum oxide, calcium oxide, and magnesium oxide were added prior to the precipitation of the element in question. The difference between the weight of the element found and that taken was accepted as the blank. In order to determine the blank on the silicon dioxide amounts of iron and aluminum, added in amounts equal to that present in the synthetic olivine gabbro and granodiorite, respectively, were put in with the reagents to act as collectors of the silicon dioxide (7). The determinations of the blanks have, of course, been carried out in exactly the same manner as the determinations of the corresponding oxides.

Table X presents some typical figures for blanks determined on the "main portion" in the manner given in the paragraph above. The amounts of reagents vary, depending on the rock type analyzed (they are generally higher the more basic the rock); this variation has been kept in mind in running off these blanks. However, no consistent relationship between the amount of reagent and the blank for a given oxide could be found; consequently, all blanks are averages that are deducted irrespective of the rock type analyzed. Bearing in mind that the author uses tank ammonia (which is imperative for a low silicon dioxide blank in particular), distilled water which is then passed through a mixed base ion-exchange resin, and A.R. grade chemicals, the reader can make his own conclusions regarding the necessity of running off blanks.

<u>Sources</u> <u>of</u> <u>the</u> <u>Blanks</u>.- The writer cannot satisfy himself as to the source of the high calcium oxide blank, and the explanation of the values for the other oxides in Table X can be founded only on indirect evidence. With regard to the silica blank it has been pointed out to the writer by R.A. Chalmers (oral communication) that insoluble silica will not be removed by passing water through an ion-exchange column. Is it possible that any calcium present as the carbonate and (or) sulfate will also pass through the column? Some time before the writer made these analyses, he noticed that a 4 percent ammonium oxalate solution left

standing for a week or so developed a fine white precipitate (calcium oxalate?). This observation, the low pH (about 5) of once-distilled water, and the fact that the water supply was from a mine shaft (due to the drought in the summer of 1959) made the writer decide to treat distilled water with an ion-exchange resin. But the above considerations indicate that it would be better to run a second distillation of water from an all-Pyrex outfit. The reagents employed may contribute part of the blank for silica and calcium oxide; it is not unreasonable that reagents are responsible for most of the blank values for the other oxides in Table X. It is a mistake to accept the manufacturer's "Maximum Limits of Impurities" at face value (23); Chalmers (oral communication) has apprised the writer of his finding that A.R. potassium bisulfate contains by far more iron than that reported by the manufacturers. Impurities in the stock solutions employed for the tests on synthetic solutions cannot have been even minor sources of blanks, for, as mentioned in a preceding paragraph, the difference between the weight of oxide found and that taken is, allowing for experimental error, independent of the amount of each oxide taken for analysis.

Impurities in the Silicon Dioxide.- In addition to the usual reagent blanks there were for the tests on synthetic solutions two more corrections owing to the impurities in the silicon dioxide used. A sample of this was ignited in the usual manner and the silica volatilized. The residue for 582.5 milligrams of impure ignited silica amounted to

4.3 milligrams. This residue was dissolved by adding a little sulfuric and hydrofluoric acids and bringing down to copious fumes of the former. Dilute ammonium hydroxide (1 + 5) was added until methyl red just changed to a distinct yellow. The hydroxides were filtered off and ignited in the same crucible. This residue weighed 1.6 milligrams. It was dissolved by fuming again with sulfuric and hydrofluoric acids and the ferrous-o-phenanthroline complex developed by which method 0.3 milligrams of ferric oxide was found. A qualitative flame test on the filtrate from the mixed oxide precipitation indicated sodium was present in considerable amount; one or two drops of 8-hydroxyquinoline added to the filtrate made ammoniacal gave no visible precipitate. Therefore, the remaining residue, 4.3 milligrams minus 1.6 milligrams, was calculated as sodium sulfate, and its weight, as sodium oxide, was deducted from the weight of impure ignited silicon dioxide. Deductions of the weights of mixed oxides, ferric oxide, and sodium oxide, based on this single purity check, were made proportionately for the weights of impure ignited silicon dioxide taken for the synthetic solutions. The first two deductions were also applied to the weights of mixed oxides found.

Separation of Manganese from the Mixed Oxides.- The writer has satisfied himself that the separation of the manganese oxide from the mixed oxides for the synthetic solutions is sharp; the precipitation of the latter was done in the presence of 1.0 milligram of manganese oxide added to each solution. The separation of manganese from the calcium oxalate precipitate is not so sharp. As a rule of thumb, the writer reckons about 10 to 20 percent of the total manganese oxide comes down with the calcium. As a precaution the filtrate from the precipitation of the strontium nitrate is examined for manganese by the standard colorimetric procedure (see Appendix III).

Summary of Findings.- The data summarized in Tables I through VIII have shown that the silicon dioxide, mixed oxides, total iron as ferric oxide, magnesium oxide, calcium oxide, titanium dioxide, manganese oxide, and strontium oxide can be determined with acceptable precision and accuracy on a single portion of the rock powder.

The work on synthetic solutions did show, however, two possibly significant trends, on the basis of which two changes in the procedures were adopted:

1. The aluminum oxide found tended to be somewhat low. Following the findings of Chalmers (oral communication) and Washington (22) that some of the aluminum escapes precipitation, the author has adopted in the main the latter's procedure for recovering it. Since his work on synthetic solutions, the writer has indeed found a little aluminum (less than 1 milligram to sometimes around 5 milligrams) often enough in the evaporated filtrates to warrant employing Washington's procedure as a precaution.

2. The barium corrections to the magnesium pyrophosphate precipitate were found to be low. The method used to separate the calcium sulfate from the barium sulfate

in these tests was precipitation of the latter as nitrate in 80 percent nitric acid; the method has now been revised as given in the procedure. As the determination of calcium and barium orthophosphates serves only as corrections for the determination of the magnesium oxide, it matters little to the accuracy of the magnesium oxide determination if even up to 0.1 percent barium oxide in a rock is wholly reckoned as calcium orthophosphate and deducted as such from the impure magnesium pyrophosphate. However, the barium, reckoned as calcium, will give high results for that element. Yet it is of interest to note that the calcium oxide results in Tables VII and VIII are not apparently so affected. Possibly the barium forms a stable complex with citrate so that it is not precipitated as the orthophosphate.

The work also illustrates the importance of determining blanks, on which there must be further investigation to ascertain the source(s) of impurities. In addition, more work may show that some blanks are more complex in composition than indicated in Table X. The figures therein are uncorrected for the ash in filter paper. The writer has found that the weight of the residue of one or two ashed and ignited filter papers is usually negligible for the hardened papers he always uses. But here again the behavior of a residue may be different when a precipitate is present from its behavior when a paper alone is ashed and ignited. The blank for magnesium may well include a little silica also, for the magnesium ammonium phosphate precipitate can coprecipitate silica. The writer concludes that determination of blanks by the method given (addition of a small, known amount of a pure compound) has the feature that conditions are more closely approximate to those extant in actual analyses than those obtained in runs on the reagents alone.

Use of the Methods.- With experience and modifications gained from the analysis of the synthetic solutions the writer intended to effect complete analyses of the ten rocks used as fluoride interlaboratory standards (see Chapter I -3, section b). Below is the work done to date.

Petrographic Data.- A list of the rocks giving type, from where obtained, and by whom is given in Table XI. From a single thin section for each rock mineral identification and point count data were obtained by Dr. E.J. Cobbing and Dr. C.H. Emeleus. This information is summarized in Tables XII through XX.

Table XI

Data on Ten Rock Types

Used as Fluoride Interlaboratory Standards

1. Shap Porphyritic Quartz-Monzonite
   Wasdale Head Quarry, Shap, Westmorland, England
   Code Number: E/S 1
   Collected by: R.P. Hollingworth

2. Penryn Granite
   Quarry by road on route 394, between Edgcumbe and Rame, Cornwall, England

Code Number: E/P 1

Collected by: R.P. Hollingworth

3. Nepheline Syenite

About 0.5 miles northwest of Grønnedal, Southwest Greenland

Code Number: G/G 1

Collected by: C.H. Emeleus

4. Porphyritic Tonalite

Roadside outcrop, about 2.2 miles west of Strontian, Inverness-shire, Scotland

Code Number: S/T 1

Collected by: R.P. Hollingworth

5. Whin Sill Diabase

Crossthwaite Quarry, Holwick, Yorkshire, England

Code Number: E/M 1

Collected by: N.H. Harbord

6. "Great Eucrite" of Center III

Roadside exposure in shallow valley, about 1 mile southeast of Achnaha, Ardnamurchan, Inverness-shire, Scotland

Code Number: S/A 1

Collected by: C.H. Emeleus

7. Migmatite

Old quarry by road from Pont de Menat to Menat, about 0.25 miles from Pont de Menat, Puy de Dome Department, France

Code Number: F/MC 17

Collected by: R.P. Hollingworth

8. Garnet-Biotite-Staurolite-Sillimanite Schist

   Exposure 0.5 miles due east of Doon House, Streamstown Bay, Clifden district, County Galway, Ireland

   Code Number: I/C 1

   Collected by: E.J. Cobbing

9. Biotite-Muscovite-Quartz-Plagioclase-Orthoclase-Andalusite Hornfels

   Barnahallia district, 30 yards south of Omey Island granite contact, along coast, County Galway, Ireland

   Code Number: I/C 2

   Collected by: E.J. Cobbing

10. Marine Shale (Carboniferous)

    Core sample from bore hole number 130/1, Settlingstones Mine, Hexam, Northumberland, England

    Code Number: E/H 1

    Collected by: K.C. Dunham

Table XII

Descriptive Petrographic Data

Shap Granite, E/S 1

Granitic rock with large crystals of perthitic alkali feldspar; quartz; plagioclase very much altered and sericitized. Biotite, accessory sphene, ore, and very rare orthite.

Alkali feldspar	40.2%	Biotite	9.9%
Quartz	32.8%	Sphene	1.4%
Plagioclase	14.5%	Ore	1.2%

Table XIII

Descriptive Petrographic Data

Penryn Granite, E/P 1

Granitic rock with quartz somewhat granulated and strained; perthitic alkali feldspar and plagioclase with sericitic alteration. Flakes of red-brown, intensely pleochroic mica, colorless muscovite, and red-brown, pleochroic tourmaline.

Quartz	30.2%	Muscovite	11.0%
Alkali Feldspar	30.7%	Biotite	5.4%
Plagioclase	20.6%	Tourmaline	2.1%

Table XIV

Descriptive Petrographic Data

Nepheline Syenite, G/G 1

Perthitic alkali feldspar	47.2%
Aegirine-augite	15.2%
Fresh nepheline	15.1%
Nepheline altered to micaceous product	9.2%
Cancrinite, interstitial to nepheline, perhaps replacing it as well	8.5%
Biotite and ore in fine-grain areas, interstitial to feldspar, nepheline, and aegirine-augite	4.8%

Under high power there appears to be some finely disseminated fluorite interstitial to the feldspar, nepheline, and aegirine-augite.

Table XV

Descriptive Petrographic Data

Tonalite, S/T 1

Dioritic rock with large crystals of plagioclase (oscillatory zoned and twinned), quartz, small amount of alkali feldspar, biotite, green amphibole, and accessory amounts of sphene, apatite, and zircon.

Plagioclase	45.9%	Biotite	6.5%
Quartz	18.7%	Amphibole	13.5%
Alkali Feldspar	14.5%	Accessories	0.9%

The potash feldspar was estimated without staining.

Table XVI

Descriptive Petrographic Data

Diabase, E/M 1

Dolerite, with small phenocrysts of orthopyroxene altering to green amphibole and sometimes rimmed by colorless grains of clinopyroxene. Discrete crystals of pale lilac clinopyroxene, laths of plagioclase feldspar, occasional small patches of brown biotite, and interstitial areas of quartz. Alkali feldspar (?) micropegmatite. Fairly numerous poikilitic plates of ore, accessory amounts of apatite in long, slender needles.

Orthopyroxene and amphibole rims	5.8%
Clinopyroxene	26.9%
Plagioclase plus sericitic alteration	37.5%
Ore	7.8%
Micropegmatite	9.5%
Sericitic alteration, mainly plagioclase	13.0%

Table XVII

Descriptive Petrographic Data

Eucrite, S/A 1

Plagioclase	83.7%
Olivine	7.8%
Altered olivine	3.4%
Pyroxene[a]	4.8%
Ore (not from olivine)	0.3%

a: A small proportion of the pyroxene is orthopyroxene; the greater amount is a diopsidic clinopyroxene.

Table XVIII

Descriptive Petrographic Data

Migmatite, F/MC 17

Marked granoblastic texture. Minerals present include quartz showing sutured margins between grains and strain extinction. Perthitic alkali feldspar, plagioclase with myrmekite sometimes developed between the two feldspars, flakes of brown biotite, and a small amount of muscovite.

Quartz	34.1%
Plagioclase + Alkali Feldspar	59.4%
Biotite	5.4%
Muscovite	1.1%

The volume percentage of plagioclase seems equal to that of the alkali feldspar; the thin section was not stained to check this.

Table XIX

Descriptive Petrographic Data

Schist, I/C 1

Quartz	22.1%	Sillimanite	9.7%
Plagioclase	14.1%	Garnet	10.4%
Biotite	39.4%	Staurolite	4.3%

Table XX

Descriptive Petrographic Data

Hornfels, I/C 2

No point count determination has been run on I/C 2. However, from a specimen taken from the same rock formation and close to I/C 2, the following minerals have been identified optically:

Quartz
Plagioclase
Orthoclase
Muscovite
Biotite
Andalusite

The rock is classified as a semi-pelite (about 55 percent silica).

The modes in the above tables are volume percentages.

No thin section was prepared for the marine shale; Dr. G.A.L. Johnson considers that carbon as carbon and illite are probably abundant, and that free quartz is certainly appreciable.

<u>Some</u> <u>Partial</u> <u>Analyses</u>.- The writer had time only to run duplicate analyses of the quartz monzonite and the nepheline syenite, the results being given in Tables XXI and XXII. The writer is quite aware that the very favorable precision is in part at least due to the fact the duplicates were run concurrently; he did this in order to keep a check on his techniques.

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Table I

The Analysis of a Synthetic Olivine Gabbro

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
SiO_2	47.92	493.7	494.0
R_xO_y	31.14	312.5	311.3
Al_2O_3	18.87	189.0	189.2[a]
Fe_2O_3	10.79	107.9	107.1
TiO_2	1.40	14.8	14.2
ZrO_2	0.01	0.1	---
P_2O_5	0.07	0.7	---

(20) Data from original analysis, op. cit., page 230, Table XXIII, analysis 1. The ZrO_2 value is added to the original analysis.

a: Calculated assuming accurate values found for ZrO_2 and P_2O_5.

Table II

The Analysis of a Synthetic Hypersthene Andesite

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
SiO_2	60.09	609.9	607.8
R_xO_y	24.51	244.4	243.7
Al_2O_3	17.85	178.2	177.4[a]
Fe_2O_3	5.86	58.4	58.4
TiO_2	0.54	5.1	5.2
ZrO_2	0.03	0.3	---
P_2O_5	0.23	2.4	---

(20) Data from original analysis, op. cit., page 221, Table XXI, analysis 5. The ZrO_2 value is added to the original analysis.

a: Calculated assuming accurate values found for ZrO_2 and P_2O_5.

Table III

The Analysis of a Synthetic Tonalite

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
SiO_2	62.2	578.9	580.2
R_xO_y	23.8	238.9	238.6
Al_2O_3	16.6	165.9	165.5[a]
Fe_2O_3	6.4	64.4	64.4
TiO_2	0.7	7.3	7.4
ZrO_2	0.03	0.3	---
P_2O_5	0.09	1.0	---

(20) Data from original analysis, *op. cit.*, page 272, Table XXVII, analysis 1. The ZrO_2 value is added to the original analysis.

a: Calculated assuming accurate values found for ZrO_2 and P_2O_5.

Table IV

The Analysis of a Synthetic Granodiorite

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
SiO_2	73.4	712.7	712.0
R_xO_y	17.1	170.3	170.2
Al_2O_3	14.1	141.4	141.1[a]
Fe_2O_3	2.6	25.8	25.8
TiO_2	0.2	2.2	2.4
ZrO_2	0.05	0.5	---
P_2O_5	0.04	0.4	---

(20) Data from original analysis, <u>op</u>. <u>cit</u>., page 272, Table XXVII, analysis 2. The ZrO_2 and P_2O_5 values are added to the original analysis.

a: Calculated assuming accurate values found for ZrO_2 and P_2O_5.

Table V

The Analysis of a Synthetic Olivine Gabbro

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
CaO	10.46	103.7	103.4
SrO	0.20	2.0	1.9
MgO	7.82	78.5	78.6
MnO	0.11	1.1	1.1
BaO	0.02	0.2	0.1

(20) Data from original analysis, *op. cit.*, page 230, Table XXIII, analysis 1.

Table VI

The Analysis of a Synthetic Hypersthene Andesite

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
CaO	6.28	63.8	64.1
SrO	0.05	0.5	0.5
MgO	3.50	35.1	35.0
MnO	0.01	0.1	0.1
BaO	0.05	0.5	0.4

(20) Data from original analysis, op. cit., page 221, Table XXI, analysis 5. The MnO value is added to the original analysis.

Table VII

The Analysis of a Synthetic Tonalite

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
CaO	5.7	57.9	57.9
SrO	0.02	0.2	0.3
MgO	2.7	26.9	27.0
MnO	0.06	0.6	0.6
BaO	0.05	0.5	0.0

(20) Data from original analysis, *op. cit.*, page 272, Table XXVII, analysis 1. The SrO value is added to the original analysis.

Table VIII

The Analysis of a Synthetic Granodiorite

	% Oxide (20)	Wt. oxide taken, mg.	Wt. oxide found, mg.
CaO	2.1	21.9	21.6
SrO	0.01	0.1	0.1
MgO	0.4	4.1	4.1
MnO	0.02	0.2	0.1
BaO	0.05	0.5	0.0

(20) Data from original analysis, *op. cit.*, page 272, Table XXVII, analysis 2. The SrO value is added to the original analysis.

Table IX

Corrections Made for the Determination of Magnesium Oxide in Synthetic Rock Solutions

	I	II	III	IV
1. impure $Mg_2P_2O_7$ taken	220.1	97.8	76.2	12.4
2. impure $Mg_2P_2O_7$ found	222.7	100.3	78.5	13.6
3. $Ca_3(PO_4)_2$ found	1.2	1.7	1.7	1.0
4. $Ba_3(PO_4)_2$ found	0.2	0.5	0.0	0.0
5. $Mn_2P_2O_7$ found	2.2	0.2	1.2	0.2
6. $Sr_3(PO_4)_2$ found	0.9	---	---	---
7. pure $Mg_2P_2O_7$ taken	216.7	96.9	74.3	11.3
8. pure $Mg_2P_2O_7$ found[a]	218.2	97.9	75.6	12.4
9. difference[b]	1.5	1.0	1.3	1.1

I, II, III, IV: Olivine Gabbro, Hypersthene Andesite, Tonalite, and Granodiorite, respectively.

a: 2 - (3 + 4 + 5 + 6).

b: 8 - 7.

Table X

Blanks on Oxides Determined in the Main Portion

Oxide	Avg. mg. found	Avg. deviation
SiO_2	1.7	±0.3
Al_2O_3	0.6[a]	±0.2
Fe_2O_3	0.4[b]	0.0
MgO	0.4	±0.1
CaO	1.4	±0.3
TiO_2	0.0	0.0
MnO	0.0	0.0
SrO	0.0	0.0

a: Milligrams deducted from the weight of mixed oxides found.

b: Calculated from the volume of titrant, which volume is the sum of reagent impurities and indicator blank.

Table XXI

Analysis of the Quartz Monzonite

E/S 1

	% Oxide	
Oxide	Result 1	Result 2
SiO_2	70.10	70.05
R_xO_y	17.39	17.41
Fe_2O_3[a]	2.46	2.43
MgO	1.15	1.16
CaO	1.93	1.91
TiO_2	0.55	0.54
MnO	0.04	0.05
SrO	0.02	0.03

a: Total iron as ferric oxide.

Table XXII

Analysis of the Nepheline Syenite

G/G 1

Oxide	% Oxide Result 1	Result 2
SiO_2	52.88	52.88
R_xO_y	27.92	27.93
Fe_2O_3[a]	9.74	9.73
MgO	0.50	0.50
CaO	3.84	3.84
TiO_2	0.08	0.08
MnO	0.21	0.23
SrO	0.00	0.00

a: Total iron as ferric oxide.

Appendix I

Private Communications Cited in Bibliographies

Letter A.- H.N. Wilson to R.P. Hollingworth, 24 February 1958.

I am much obliged to you for sending me a reprint of your paper. I have read this with great interest, particularly your remarks on the new indicator, SPADNS, and your method of precipitating iron, alumina and silica, as I have previously believed that such a precipitate would always entrap some fluoride.

Letter B.- H.N. Wilson to R.P. Hollingworth, 10 November 1958.

Actually we now know, as a result of some other work, that it is very difficult, if not impossible, to determine fluoride in rocks etc. containing relatively large amounts of alumina by any modification of Willard and Winter's method, and we intend to try one of the modifications of the very old method of separating the silica and alumina by ammonia and zinc nitrate, or even Schaffgotsch's old method with mercuric oxide.

Letter C.- N.H. Furman to R.P. Hollingworth, 5 April 1960.

In response to your inquiry about the triphenyltin reagent for fluoride, I have looked over Dr. Allen's dissertation and find that a drawback to this method is the fact phosphate and silicate are also precipitated by the reagent. As far as I am aware it is necessary to make a good separation of fluoride from almost everything else in order to finish the determination with this reagent.

J.C. Warf and more recent workers at Oak Ridge have had a good deal of success in the so-called pyrohydrolitic method for separating fluoride from various solid substances by heating the substances with a tungstate or other suitable salt and with steam and a little air or oxygen running through. If you have to go to these lengths to separate the fluoride it might be just as well to finish the determination photometrically or by titration. The necessity of working in 70 percent alcoholic medium also militates against using this reagent if the solution contains appreciable quantities of sulfates.

To sum it up, this method should give excellent precision and accuracy if you are able to accomplish the necessary degree of prior separations.

Letter D.- H.N. Wilson to R.P. Hollingworth, 8 March 1960.

Your idea of making a sulphanilate buffer is ingenious, and we shall certainly try it. Your remark about the possible effect of pyrites on the pyrolitic method is also valuable. Actually the samples we are most often concerned with do not contain more than mere traces of pyrites (we have shown that sulphate added as calcium sulphate is without effect), but significant amounts of pyrites might lead to high results; it would depend on how the fluorine was finally determined. The Scott Sanchis colorimetric result, for example, is virtually unaffected by sulphate. The great advantages of the pyrolitic method, i.e. speed and freedom from interference by silica in any form, and alumina, would make it worth while to look into the effect of sulphate on the final determination very carefully. I can not see any other constituent of ordinary rocks that would interfere -- though that is a rather dangerous remark.

Appendix II

Determination of Fluoride in Two Rocks by a Modified Method D

This modified procedure was carried out to ascertain whether fluoride was entrapped in the precipitation of silica, alumina, and iron and adsorbed on borosilicate glass during the evaporation. The modification is as follows: Pour onto the precipitates left on the filter funnel 50 milliliters of cold water. Then add two milliliters of 1 to 1 sulfuric acid, and stir until dissolved, complete solution taking place in 10 to 15 minutes at most. Filter the solution by suction into the original beaker, and wash the funnel with some cold water. Set this beaker on the steam bath and pour in an excess of hot 5 percent sodium hydroxide solution slowly and with vigorous stirring. Adjust the pH, digest, and filter as before, catching all filtrates in a platinum dish. Evaporate these, distill, and titrate aliquots as for the original procedure. Carry a blank on all reagents through the procedure. For two high iron content rocks, the following results were obtained (Table I).

Table I

Code Number	D	Modified D
S/T 1	0.067	0.068
E/M 1	0.045	0.049

The modified method is simply an expedient one, simple to carry out. There are two objections to it: (1) The acid conditions might result in loss of some fluoride, and (2) the second precipitation gives a very gelatinous precipitate that does not improve much on digestion. But the work does suggest that fluoride is not quantitatively isolated from silica, alumina, and ferric oxide by a single precipitation, and that since E/M 1 has the greater iron content, that element is mainly responsible for low fluoride recoveries. On the other hand, the difference for E/M 1 only just exceeds the 95 percent confidence limit for method D. Recoveries, moreover, would seem from the above work to be 90 percent or better for method D.

Chapter II -1

Abstract

In Part II of this work the details are given of procedure in sampling, collecting, and laboratory determination for fluoride in 350 metamorphic rocks. Brief notes explain the geology of the areas from which the specimens were obtained. The significance of the fluoride content of the rocks with respect to the major mineral constituents, major oxide constituents, and the grade of metamorphism is examined. It is concluded that the fluoride in the rocks examined is in the main dependent on the original sedimentary type.

Chapter II -2

Field Sampling for the Geochemical Problem

General Considerations:- The Scottish Highland metamorphic terranes were selected as suitable field areas from which to collect samples, for there mineral zoning, reflecting changing pressure and temperature conditions, have long been recognized (13), and the petrography of the metamorphic rock types, whose variety is in any case considerable (slates, grits, schistose grits, semi-pelites, amphibolites, calc-silicates, and hornfelses) has been dealt with by a number of workers, especially Harker (9). Thus the role of composition, pressure, and temperature in governing fluoride abundance and distribution could be studied and the data for rocks which are common to almost any metamorphic terrane would be useful to other workers. Soon after the writer began his work, Mr. E.J. Cobbing commenced work on a petrological and structural study of an area composed mostly of metasedimentary rocks in the County Galway district of Ireland (5), and collaboration with him was started, rather late unfortunately, for reasons given in the Introduction. The suites studied do indeed cover the common mineral assemblages found in para-metamorphic rocks that have developed in the greenschist facies and the staurolite-quartz and sillimanite-almandine subfacies of the almandine-amphibolite facies (7) and in certain hornfels facies (5). There is also a suite of injection gneisses. Many members have undergone retrograde metamorphism. Thus the Table of Results, Chapter II -5, refers to a wide variety of metamorphic rock types which leads to problems which are discussed in subsequent chapters.

There are, however, some varieties not included in the suites: To expand the coverage the writer not only planned to analyze samples collected from the Massif Central, France, but also initiated with Prof. M. Roques a collaboration on his suites of the Massif Central series; however, insufficient progress has been made with this work to include the results in the present account.

<u>The Areas Sampled</u>:- Samples were collected from the following areas in Scotland:

1. the coastal strip from north of Stonehaven to Findon Ness (map 1).

2. the Pitlochry area, mainly in the River Garry (map 2).

3. the Loch Sunart area, the traverse being entirely along the north shore of the Loch (map 3).

4. the Loch Lomond area, samples taken entirely along the west side of the Loch, most near the shore (map 4).

In addition, samples from the Clifden district, County Galway, Ireland, were kindly supplied to the writer by Cobbing, who also analyzed certain of them for the major constituents (5).

<u>Technique of Sampling</u>:- To minimize bias in sampling the writer took the following action:

1. read the pertinent literature on each of the areas. This literature is cited in Chapter II -3, but he has read little more than that given.

2. sampled whenever possible from specific localities cited

by other workers. This locality sampling was used especially in Loch Lomond, thanks to Cunningham-Craig's work (6).

3. sampled usually in a series of traverses either when only general localities were given or when he wished to be certain of getting rocks of a particular type or when exposure was good for long distances. The writer adopted this method often in the Stonehaven-Findon Ness and Pitlochry areas for the reasons given. For example, it was especially difficult to be certain of obtaining staurolite schists, for it was usually found to be difficult to identify this mineral in hand specimen; the mineral is often strongly altered to a sericitic aggregate. These traverses usually involved taking a specimen from every formation that appeared even slightly different to the writer's eye, yet often these differences turned out to be very real on thin section examination.

Possible Criticisms of the Sampling:- The writer can only give a reasonable guess that the samples truly represent the areal distribution of all the rock types in these Scottish areas. He did suspect that arenaceous rocks and Green Beds were too well represented, for schists weather more readily, so it is more difficult to get fresh material, and Green Beds are appealing to the eye. Yet a number of Scottish workers have remarked on the preponderance of arenaceous members in the S/S, S/P, S/T, and S/L areas and the common occurrence of Green Beds in the S/P area (1, 4, 6, 10, 11, 12). The traverses were of short distance relative to the areas, so some rock types may have been omitted and others over-represented. Such short traverses for the S/S area meant the writer missed the sillimanite zone (map 1), which lies in Dalradian rocks of different lithology from those sampled. The albite gneisses of Cunningham-Craig (6) between Inveruglas and the north end of Loch Lomond are also not well represented.

No recent revision of the geological mapping has been published on these areas and the writer had insufficient time for such work though this might have improved the field control in rock sampling, as Grout has shown and discussed so well (8). Obtaining fresh samples took much time and labor alone.

Some Defences of the Sampling:- The rather good exposures in these areas, the number of samples representing each area, the variety of rocks in the writer's suites, and their mineral associations that are also reported by others (2, 4, 6, 9, 10), in relation to the extensive areas over which the major lithologic divisions of the Dalradian and Moine outcrop lead the writer to think his suites represent to a close approximation most of the rocks in these areas and their areal distribution. For the I/C series there can be little doubt that the samples have been collected with excellent field control.

Preparation of the Samples for Analysis:- The samples, all fresh, were in dimension anything from about 2 cubic inches to somewhat less than 3 X 4 X 1 inches in size, the increase reflecting the heterogeneity of the rock. About

50 to 60 grams of chips were taken from these specimens and this whole amount crushed and powdered in a manner described in Appendix III. The writer ran chemical analyses for most of the major constituents in 30 samples, using portions of the same powders. From about 80 percent of the rock specimens thin sections were prepared and the minerals and their relative abundance determined from examination of these sections. The writer also made brief petrographic descriptions which are not included in this work, although he used such data for some of the classifications. The writer intends to run point count determinations for these thin sections before publishing this work. On the combination of thin section and hand specimen identifications, the writer made classifications of the rocks into eight major classes, which are described in Chapter II -4.

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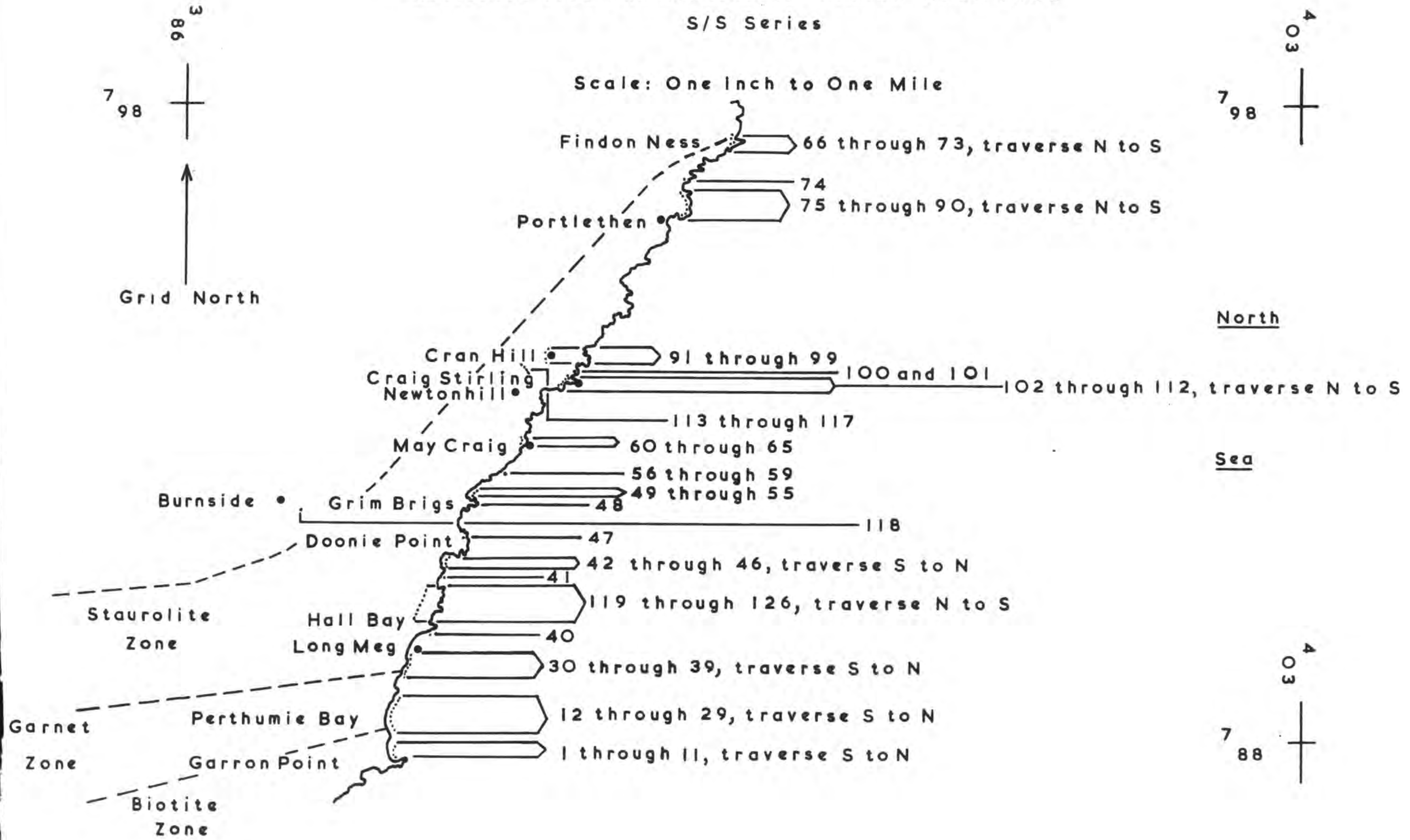
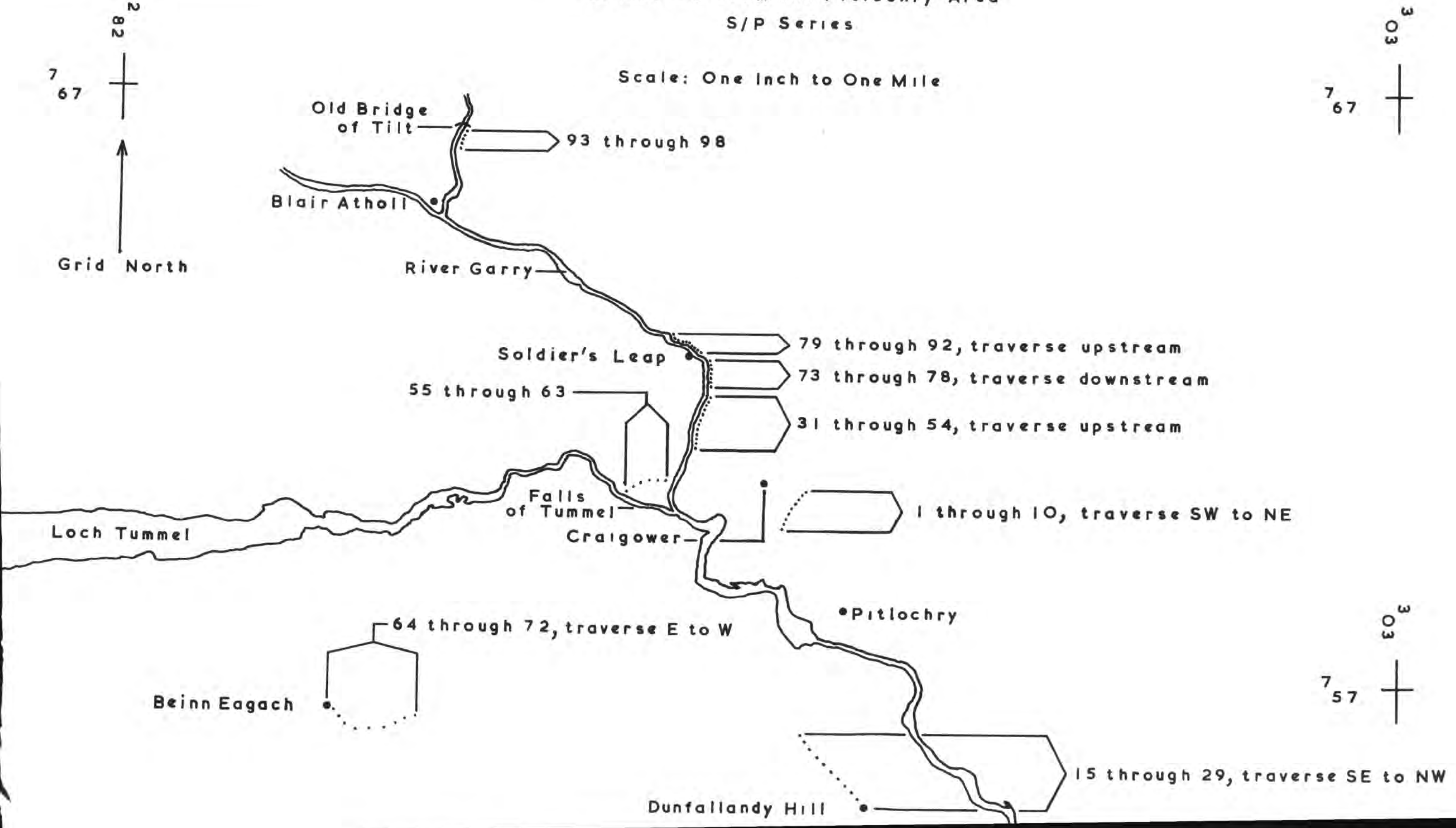
The Localities for the 121 Samples
Collected from the Stonehaven–Findon Ness Area
S/S Series

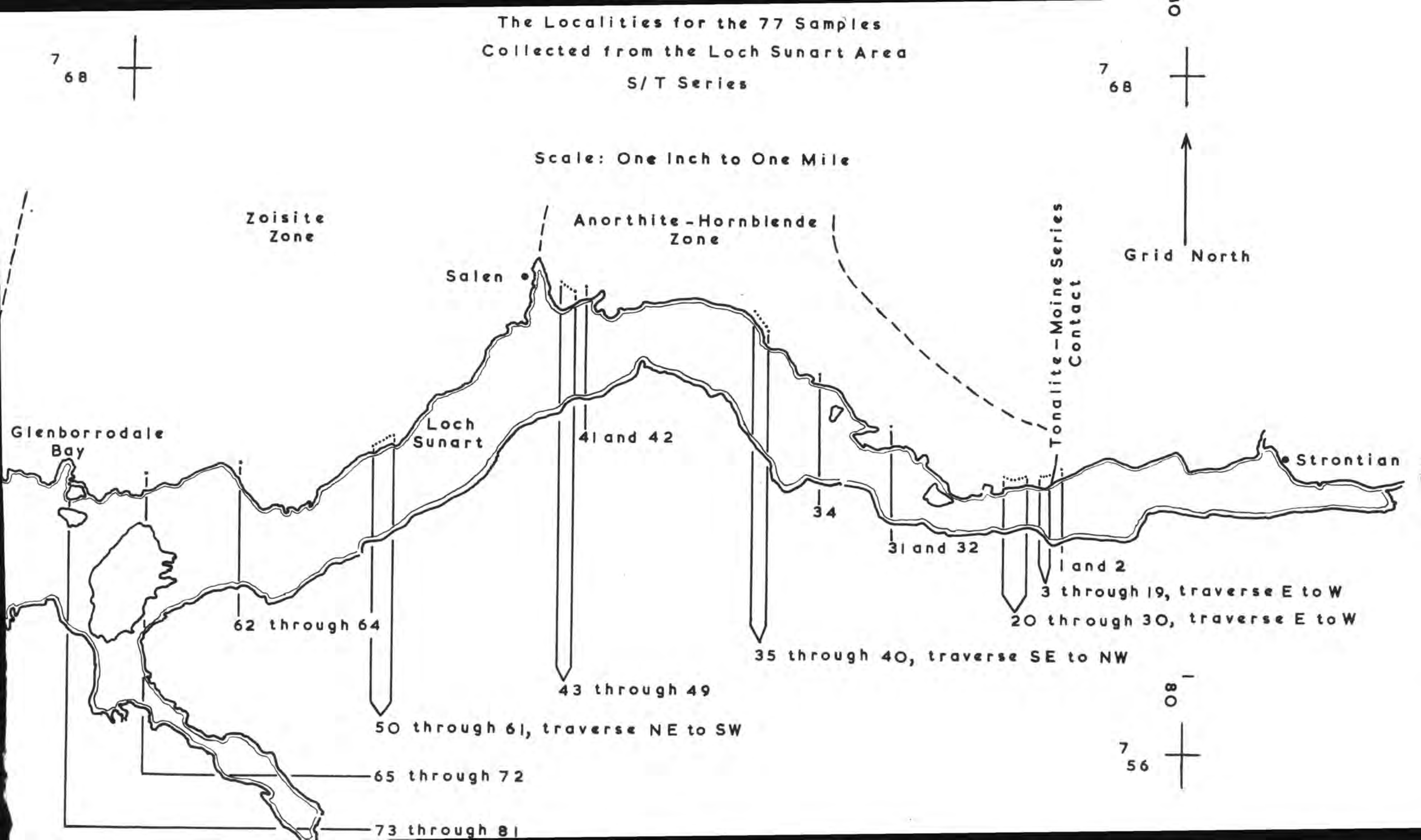


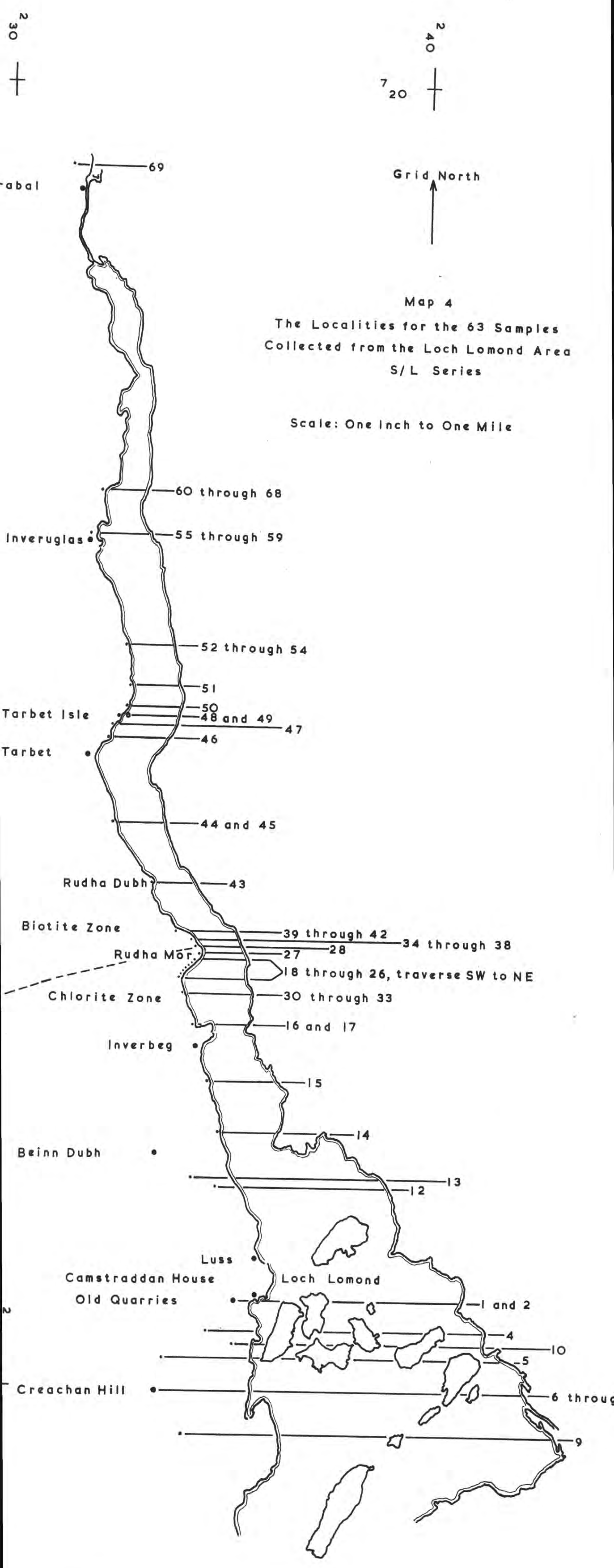
The Localities for the 72 Samples
Collected from the Pitlochry Area
S/P Series

Scale: One Inch to One Mile



The Localities for the 77 Samples
Collected from the Loch Sunart Area
S/T Series





Map 4

The Localities for the 63 Samples Collected from the Loch Lomond Area S/L Series

Scale: One Inch to One Mile

Chapter II -3

A Resume of the Pertinent Geological Data

Introductory Remarks:- The geology of the Scottish Highlands and the Clifden district of Ireland, from which areas most of these samples were collected, has a three-fold bearing on the geochemical problem:

1. the origin of the metamorphic rocks which compose the geology of the five areas from which samples have been collected and analyzed. The areas are given in Chapter II -2.

2. the types of metamorphic rocks outcropping in these areas.

3. the possible interrelationships between the mineralogy of a given rock type, the temperature, pressure, or both, to which this type has been subjected, and the structure of the area in question.

The writer reviews below the literature pertinent to the above factors.

The Origin of the Metamorphic Rocks:- The rocks outcropping in the Stonehaven to Findon Ness coastal strip, Pitlochry, and Loch Lomond areas are considered to be sedimentary in origin (21). Barrow provided an analysis of a grey slate, the high alumina (20 percent) being proof of this origin (2). Current-bedding, used to advantage by Vogt (25) and Bailey (2) to determine the order of deposition of the Dalradian series, is of course further proof of sedimentary origin, as are other sedimentary features preserved in the Dalradian (21). The presence of staurolite is also considered as evidence that the host rock is sedimentary (23).

Read and MacGregor (21) relate the metamorphic rock type of the Moine series to its sedimentary equivalent; e.g., siliceous granulites, muscovite-biotite gneiss (pelitic gneiss), semi-pelites, and zoisite granulites are metamorphosed sandstones, shales, sediments intermediate between these two, and marls, respectively. These authors considered the Dalradian series of the northeastern, eastern, and southwestern parts of the Grampians as "mostly sedimentary origin." The pebbles of quartz, in many of the writer's S/S, S/P, and S/L series, and the intercalations of grit with pelite are accepted as criteria of sedimentary origin.

The writer has analyzed 30 rocks from the S/S series for the major constituents; the data show many of the rocks are comparable chemically to either greywackes, shales, silty shales, or possibly protoquartzites, as is discussed in Chapter II -7.

Similarly, on the basis of comparability of chemical composition of certain metasediments with sedimentary rock types, Cobbing (8) has demonstrated that, allowing for differences in water content for these two types, the semi-pelites in the Clifden district are equivalent to shales in which the clay mineral fraction was high in proportion to the silt fraction. In addition, a feldspathic siliceous granulite (8) was similar chemically to a silty clay from the Mississippi delta, and a siliceous granulite to, more reasonably, a sedimentary protoquartzite.

Phillips considers the Green Bed group sedimentary in origin (19), as evidenced by clastic features. A massive amphibolite from the Clifden district analyzed by the writer for fluoride, is considered to be igneous; the bulk chemical composition indicates it might have been derived from a dolomitic marl, but there are significant relict igneous textures present (8).

The Moine series is represented by the Loch Sunart suite, the origin of which is considered by Phemister (18). On the basis of chemical analyses the following equivalences have been worked out:

1. siliceous granulite = sandstone, more or less feldspathic
2. pelitic schist = shale
3. staurolite garnet mica schist = shale of a more magnesian type
4. zoisite hornblende granulite = siliceous marl

Further proof of sedimentary origin comes from preserved sedimentary structures in the Moine (18, 22).

Source of the Sediment:- On the environment and source areas for the Dalradian and Moine series there is little published work. Elles and Tilley seem to assume the Dalradian and Moine series of the Central and South West Highlands were deposited in a geosyncline (10). The presence of graded bedding, repeated without intercalations of current beds, is in Bailey's view evidence "that the depth of the water has been too great to allow of any but very gentle bottom currents." Current-bedded sandstones, however, "belong either to the air or to shallow water" (2). Bailey concludes that graded sandstone beds are "often the records of seaquakes (movements communicated to sea water during disturbances of the bottom)", the coastal edge being the supplier of this sand and mud mixture. Bailey's view is close to what is considered by Pettijohn (17) and others as the cause of these graded beds, a common feature of greywackes: turbidity flows generated by seaquakes or other means typical of unstable tectonic environments, commonly obtained in the geosynclinal cycle (17). Pettijohn (17) thinks they are the "earmark of sedimentation ... especially in eugeosynclinal belts." However, Kay (12) thinks there is some danger in associating a rock type with any kind of geosyncline: "A class of geosynclines may be characterized by having some sorts of sediments in larger proportion than in another class, but changing conditions through time result in most kinds of sediments being present to some degree in all sorts of geosynclines", but nevertheless, "It is axiomatic that some classes of geosynclines have preponderance of particular types of sediments, as the sediments are an inherent factor in their definition." Kay has considered the eugeosynclinal class as a type in which the sinking exceeded deposition of detritus so that sediment remained poorly sorted and the finest material accumulated in deeper water, thereby effecting a greater prevalence of greywacke and argillite compared to slow-sinking environments where winnowing of finer sizes would be more effective. Poor sorting also required in Kay's view rapid erosion of the supplying land, the rock of which would be largely volcanic (andesitic) if one accepts Kay's hypothesis that island arcs are along the eugeosynclinal belts, which thus received volcanic detritus of greywacke and argillite type. Eugeosynclines also have volcanic rock associations; e.g., pillow lava flows and spilites associated with radiolarian cherts (12). In the Loch Awe area there are such pillow lava-spilite rocks contemporaneous with the Dalradian (21), but there is no certain evidence that the Dalradian east of Pitlochry has any such igneous rocks (21).

From the fact that meta-greywackes and meta-shales are common members of the analyzed S/S series (cf. Chapter II -7), that pillow lavas and spilites are contemporaneous with the Dalradian in Loch Awe, and from the considerations of Kay (12), Bailey (2), and Vogt (25), the writer considers the sediments are certainly orthogeosynclinal and perhaps eugeosynclinal, if one accepts Kay's complex system of classification. In other words, rocks of the Dalradian have been deposited in an unstable tectonic environment, to wit, a geosyncline, the rate of subsidence of the geosyncline exceeding that of deposition. Erosion was rapid, predominantly mechanical or physical rather than chemical. The source lands could have been igneous, possibly andesitic rather than granitic in character, but much source material could also have been older sediment (12).

For the Moine series around Loch Sunart to Loch Nevis Richey and Kennedy have reported many preserved sedimentary structures (22); current-bedding, cross-bedding, ripple marking, and lamination in schists led these authors to conclude that the Moine series was deposited in conditions like those for the Torridonian; e.g., shallow water with current action strong and recession of water common. But Phemister considered the Moine to be an estuarine or lagoonal instead of a flood-plain facies, owing to the rarity of conglomerate and true arkose (18). Kennedy considers the Moine a sedimentary differentiate of the Torridonian (13); if so, the Moine developed in the Caledonian geosyncline, and the source lands, of unspecified nature, were to the northwest of that geosyncline (13). Kennedy states, moreover, that the Moine series consists mostly of arenaceous sediments (feldspathic sandstones and arkoses).

On the basis of the silt to clay ratio of semi-pelites whose potash content dominates that of soda, and the two different rock associations in the Aughris Peninsula and Ballymaconry Peninsula, Cobbing (8) concluded that the semi-pelite dominant facies (his "striped amphibolite facies") developed by slow sedimentation under quiet, stable conditions, such as are obtained in a shelf sea, the bottom being below wave depth. The second facies (his "Connemara marble-quartzite facies") developed, according to Cobbing, in a shallow shelf sea, the intermixed semi-pelites being analogous, in their relation to the feldspathic and siliceous granulites, to deltaic deposits of siltstone and clays. Cobbing thinks both facies can be explained by postulating a shelf sea or trough being filled in as shallow water and deltaic conditions develop. The absence of true greywackes in the Clifden district suggests conditions of rapid erosion, deep burial, and high relief were not extant. Although there is no direct evidence, Cobbing states there is a "strong possibility" that the Clifden metamorphic rocks are Dalradian in age (8).

The Types of Metamorphic Rocks in the Areas Sampled:- In the writer's opinion there is little use in citing petrographic or field descriptions of rock formations outcropping in these areas, although some have done this (5, 6, 7, 19), for the two reasons that the writer has not necessarily taken samples from the type localities and has prepared his own identifications of the rocks on the basis of inspection of the specimens and thin sections. What is important to citer here is a brief review of the formations recognized in each area and their (possible) correlations with others elsewhere. He takes correlations worked out since or in the light of Vogt's application of the graded bedding principle (25) and the hypothesis that Highland structure is explained by recumbent folding and sliding (3, 4, 16).

For the Pitlochry area Anderson (1) has identified two main types of metasediments: psammitic and pelitic, the former being siliceous greywackes or schistose grits, the latter varying from slates to sillimanite schists, depending on the grade of metamorphism. He accepts the correlation of the psammitic rocks with the Ben Ledi Grits of Perthshire. On the basis of his interpretation of the structure of the area and field evidence the Pelitic Group rocks north of Findon Ness are part of the Pitlochry Schists, and the Pelitic Group rocks intercalated with the Ben Ledi Grits near Perthumie Bay and south, where they appear as slates and sericite schists, of the same age as those north of Findon Ness, are correlated possibly with the Aberfoyle slates. Further, the Aberfoyle slates are correlated with the Pitlochry schists (1).

The history of thinking on Grampian Highland stratigraphy is reviewed by Read and MacGregor (21). The standard Perthshire succession now agreed upon is, with the youngest bed at the top (21):

Leny and Ben Ledi Grits	+
Green Beds	+
Pitlochry Schists and Aberfoyle Slates	+
Loch Tay Limestone	
Ben Lui Garnetiferous Mica-schists	+
Ben Lawers Calcareous Schists	+?
Ben Eagach Black Schists	+
Central Highland (or Perthshire) Quartzite	+
Blair Atholl Series	+

Those starred have been sampled by the writer in the Pitlochry area; he is not certain whether he has typical members of the Ben Lawers Schists. For the Loch Lomond area the formations are (9), as one proceeds from the Highland Boundary Fault northwards:

Leny Grit	+
Aberfoyle Slates	+
Beinn Ledi Group	+

The accepted correlations for these three groups are evident from the standard Perthshire succession. But Gregory reported in 1928 different correlations (11).

A salient reason why the writer has not taken descriptions of these formations lies in the following paragraph of the Regional Guide (21):

> "(The stratigraphical units) are in many cases groups of strata composed of inter-stratified and interfolded metamorphic rocks of various types, among which the rock named is considered to be dominant at the type locality. The same name may be applied in another district to strata differing in metamorphic grade and to some extent in sedimentary facies. Herein lies a major difficulty of Highland geology. Further trouble has been caused by one or more transferences of the same outcrop to a differently named stratigraphical unit, group, or series. Groups and series are usually markedly heterogeneous."

Interrelationships of Structure, Mineralogy, and Pressure and Temperature of Metamorphism:- In addition to the controversies on stratigraphy there are further disagreements about tectonics and their time-relation to the metamorphism. Nevertheless all workers are agreed about the mineral zoning in the Highlands, pioneered by Barrow in 1893 (5) and extended by him in 1912 (6). Barrow thought the zoning to be related to the Older Granite intrusions. But in 1925 Tilley modified Barrow's mineral zones: He substituted chlorite zone for Barrow's clastic mica and digested clastic mica zones, the other zones being the same. Tilley's map (24) and Barrow's extended map (6) barely reach the Pitlochry area (south of Pitlochry), so the writer did not draw any zones for that area (map 2). Although most of the Pitlochry area sampled is probably in the garnet zone (24), Phillips has traced changes in the mineralogy of the Green Beds as the metamorphic grade increases northeastward (19). From Barrow's extended map (6) the writer has put in the mineral zones for the Stonehaven-Findon Ness area (map 1).

Cunningham-Craig observed mineral zones in the Loch Lomond area (9), the zoning reflecting, as one proceeds up from the Leny Grit Group, increasing dynamic metamorphism as one enters the Beinn-Ledi Group, then "normal thermometamorphism", and finally a hydrothermal metamorphism in the albite-gneisses, this metamorphism favoring the development of albite, together with chlorite. Cunningham-Craig's interpretation has been criticized by Tilley (24), who considered the albite gneisses to be simply a peculiar sediment. For the Loch Lomond area the writer has taken Tilley's zones (map 4).

Zoning in the Strontian area has been described by Kennedy (14), who used minerals in calc-silicate granulites as indices of zoning, since pelitic rocks in the Moine are not common and since the garnet zone covers a broad temperature range. These zones are given in map 3. Kennedy equated the biotite-calcite-zoisite zone and the higher temperature zoisite zone with the garnet zone that is revealed by pelitic rocks, and the anorthite-hornblende zone with the kyanite zone. The increase in grade is definitely equated with high temperatures brought into being by the development of an injection complex in the rocks, the anorthite-hornblende (kyanite) and anorthite-pyroxene (sillimanite) zones being very nearly delimited by the injection belt (14). There is no field evidence of thermal metamorphism at the Strontian granite-Moine series contact (15).

Cobbing has also observed regional mineral zoning in the semi-pelites of the Clifden district (8): The zones run as bands east to west and the grade of metamorphism increases from north to south as evidenced by the following mineral changes:

1. in the northern area staurolite appears alone.
2. at an east-west boundary sillimanite enters and they appear together in a region south of this line.
3. farther south from 2. staurolite exits and sillimanite appears alone. The east-west line of this exit is supposed to be somewhere in Streamstown Bay (see his map 2, opposite pg. 10).

Garnet is present in all these zones, the regional metamorphism thus considered to run from garnet grade in the north to sillimanite grade in the south (8). In addition to the regional metamorphism Cobbing has described thermal metamorphism about the Omey Island granite (8). He observes two aureoles, marked especially by changes in the mineralogy and fabric of two types of semi-pelite:

1. inner zone of entry of andalusite. Garnet and staurolite are absent in the orthoclase-bearing semi-pelite and a true hornfels develops with andalusite becoming the only macroscopically important mineral present.
2. outer zone of entry of biotite porphyroblasts, which develop as one nears the inner zone into a spotted schist. Garnet becomes less common and staurolite disappears as one approaches the inner zone.

Anderson (1) observed the following relations of structure to mineral zoning in the Stonehaven-Findon Ness area:

1. the Ben Ledi Grits are essentially as a syncline nestled by a Pelitic Group, which outcrops between the Highland Boundary Fault and the Grits, reappears north of Findon Ness, and sometimes thrusts intercalations up through the Grit Group.
2. it is these appearances of the Pelitic Group throughout the section that make possible the tracing of the mineral zoning.
3. the sequence is inverted northwards from the Highland Boundary Fault. This inversion means the higher grade metamorphic rocks appear higher in the section, a relation that also applies to the Perthshire succession, where it was first considered seriously by Tilley, who also found the mineral zones

were displaced by lateral faults, the Loch Tay fault being one (24).

Thus depth of burial correlates with grade of metamorphism, and the inversion accounts for the higher grades being superposed on higher formations (24). But Read disagrees (20).

Further relations of structure to mineral zoning are:

1. in general the mineral zones run parallel to the strike of the major rock types. In the area just northwest of Stonehaven the biotite-garnet-staurolite zones run entirely in the quartzite and schistose grit lithologic divisions of the Dalradian (see Plate II and figure 5 of the Regional Guide (21)). There has been no complete study of the structure of the Moine series (18, 22), although the major rock types have been mapped (18). They run in general parallel to the zones given by Kennedy for the area north of Loch Sunart (14). In the Clifden district the line of exit of staurolite is parallel to the strike, but the line of entry of sillimanite traverses it (8).
2. the mineral zones probably cut across slide and recumbent fold structures in Scotland (24). Whether the mineral zones traverse the major structures in the Clifden district is unknown.

The relation of the time of the metamorphism to the folding in the Dalradian has not been resolved (21). Whatever the actual age of the metamorphism of the Moine it is reckoned that it is associated with intense compressional forces. Most of the evidence suggests that the injection-gneisses were formed while this pressure was at its maximum, or, more likely, on the wane (18). In the Clifden district the metamorphism developed on the first, east-west folding in the area (8).

<u>Summary</u>:- The above resume is summarized as follows:

1. Fabric (textural) and chemical evidence amply demonstrate the sedimentogenic character of most of the Scottish and Irish suites. The origin of the Green Beds is also sedimentary.

2. Fabric, chemical, and rock association data support hypotheses that the Dalradian, Moine, and Irish suites each re-

flect different sedimentary environments.

3. Mineral zoning has been confirmed by several workers.

4. Some of the Dalradian groups (or series) in one area correlate with those elsewhere: Pelite Group-Pitlochry Schists-Aberfoyle Slates, for example. But the term series or group includes a considerable variety of rock types, of which one is dominant and characteristic.

5. The writer's Dalradian suites outcrop in inverted sequences. Thus metamorphic zones of greater intensity appear higher in the stratigraphical sequence. Higher grade rocks are believed to be associated with greater depth of burial in a geosyncline or trough.

6. The relation of mineral zoning to the tectonics and structure of the Dalradian is not completely known. It would appear to have developed before the lateral faulting and recumbent folding and sliding.

7. The metamorphism of the Moine was effected by intense compressive forces. Injection phenomena may have controlled or influenced the grade (temperature) of metamorphism and took place probably as the compressive forces began to relax.

8. Regional metamorphism in the Clifden district was concomitant with a folding, but probably not with the final folding. Thermal metamorphism was superposed on metasediments on intrusion of a granitic body in the same district.

9. Mineral zones run generally parallel to the strike of the rock series or types for all areas, the only exception being in Connemara.

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Chapter II -4

The System of Metamorphic Rock Classification Adopted

<u>Reasons for Adoption of a New Classification System</u>:- The 350 rocks analyzed for fluoride have been classified in order to bring to light, if possible, any relationships which may exist between fluoride abundance and the rock type, its genesis, and constituent minerals. Systems of classification used by a number of workers, including Scottish geologists, are unacceptable in the writer's view, for they are ambiguous, confusing, and are not valid for the writer's suites. The reasons are discussed below.

<u>Ambiguity of Present Terminology</u>:- The term "grit" can apply to any of the following:

1. psammitic metamorphic rocks in Scotland.
2. coarse, rough, or even pebbly sandstones (Millstone Grit.
3. both coarse and fine sandstones as in the Yorkshire Pennines.
4. greywacke sandstones as in the Welsh Lower Palaeozoics.

The term "granulite" to the French geologist is a two-mica granite, but to American metamorphic petrologists it is an even-grained metamorphic rock, without platy or elongate minerals, although it may have a foliation due to lenses of quartz and (or) feldspar (6). Some think the fabric of a granulite reflects genesis: "Products of regional metamorphism of the highest grade" (6).

The geologists' semanitic tangle, like Topsy, "just grew", as is evident from these definitions or uses of the word "gneiss":

1. "... a megascopically crystalline rock with a secondary crude foliation, developed in bands which are commonly different from those on either side, and nearly always with a mineral composition corresponding to some granitoid igneous rock. In most gneisses feldspar is prominent, and it is customary to let abundant megascopic feldspar distinguish gneisses from schists" (2).

2. "Coarse-grained, irregularly banded rocks, in which the schistosity is rather poorly defined because of the preponderance of quartz and feldspar over micaceous minerals. Products of regional metamorphism, especially of higher grades" (6).

3. "The most highly metamorphosed rocks, quartz-bearing or not, take on often, though by no means universally, a decidedly coarse texture. The principal constituent minerals ... tend to relatively large dimensions... While the general type of structure remains the same, the term 'hornfels' is not appropriate to these coarse-grained rocks, and they are generally designated by the name (itself vague and unsatisfactory) of 'gneiss'. Very characteristic is a more or less pronounced banded structure, evident inthe field or under the microscope. This has been determined by original differences of composition, but accentuated by a certain amount of segregation, rendered possible by the enlarged amplitude of diffusion at the highest temperatures of metamorphism." "... owing to slight original differences between successive seams, exaggerated by a process of segregation, there arises a pronounced gneissic banding" (1).

4. "With progressing regional metamorphism, the participating rocks often grown more coarse grained and appear more gneiss-like" (5).

5. "... such lithologic architecture (-Thin layers of marble, quartzite, or black shale remnants in granitic or quartz-dioritic gneiss masses of great areal extent-) is hard to explain unless the inclosing gneiss or gneissic granite represents the recrystallized or metasomatosed strata among which the still well-preserved sedimentary layers once were precipitated. In some cases the gneisses may represent a rather thoroughly altered and reactiviated substratum, upon which the sediments were once deposited. One may well ask: Where are the thick layers of graywacke, the shales, the thick sandstone beds, etc., which we know necessarily once occupied the geosynclinal column ... ? In an attempt to answer this question, it becomes rather evident that much of the pre-Cambrian, Caledonian, Hercynian, and Alpine gneisses have originated through replacement and recrystallization of such geosynclinal columns of sediments and lavas. Another major portion of the gneisses of different age are most likely just reactivated and thoroughly altered old basements" (4).

Thus a descriptive definition (albeit with a mineralogical restriction) has had attached to it varying genetic significances, the last one above implying gneiss development fits in a greater genetic schema for regionally metamorphosed rocks. Clearly these genetic connotations render terms more and more ambiguous and thus less useful to other workers.

Need for a Practical System:- A usable system had to meet two requirements:

1. It must be simple and applicable to all rocks, so that they could be classified into as few groups as possible. For example, the Scottish suites are largely arenaceous, which group covers in the Scottish terminology grit, schistose grit, albite gneiss, and some lime-rich types.
2. It must be understood by other workers, a requirement met by defining all terms used and by subordinating genetic terminology as much as possible.

Definitions of Terms:- A system that commends itself is one based on chemical (mineralogical) parameters. On the assumption, considered valid by workers in these areas (cf. Chapter II -3), that these rocks are in the main sedimentogenic, a suitable classification for examining fluoride geochemistry could be based essentially on the ratio of psammitic-arkosic (quartz and feldspar) to femic-aluminous-(calcic) elements; e.g., chlorite, garnet, staurolite, sillimanite, hornblende, pyrite, magnetite, sericite, and epidote. Muscovite would probably have an ambiguous position, for it could either occur in sediment as such or as an aluminous clay or develop through retrograde metamorphism (alteration of feldspar, for example). Conversely, some muscovite could be made over to feldspar in high metamorphic grades. By thin section examination the writer decided to count it with the femic-aluminous-calcic group when:

1. muscovite and sericite appeared interstitial to quartz and feldspar in low-grade rocks and when the latter mineral appeared fresh (incipient alteration was, however, allowed).
2. it appeared in similar habit as biotite.
3. evidence of reaction with feldspar was not observed. No such reaction was seen in any of the Scottish rocks; however, feldspar probably developed from muscovite in the I/C series and it would be difficult to estimate or even tell how much feldspar represented an aluminous clay element and (or) original muscovite.

Some minerals such as apatite, sphene, zircon, and tourmaline were ignored if they were of only accessory amount (about less than 1 to 2 volume percent), as was nearly always the case, even in the injection gneisses.

The Classification Adopted:- The eight major classes are defined as follows:

1. Quartzite:- Quartz makes up more than 90 volume percent of the rock in absence of feldspar; if feldspar is present, it makes up 5 to 10 percent and their sum is around 90 volume percent. Quartz grains are always anhedral (xenoblastic), forming a granoblastic matrix, which can be jig-saw puzzle, even- or uneven-equidimensional in aspect. Any femic-aluminous minerals, commonly garnet, biotite, and muscovite, can be disseminated, with or without preferred orientation, or in folia. An analysis of a quartzite is given in Table IV of Chapter II -7.

2. Psammitic Semi-Pelite:- Rocks in which quartz (and feldspar) are dominant; the sum of the volume percentages of the aluminous and femic minerals does not exceed that of quartz (and feldspar). No distinction is made with respect to the relative amounts of quartz and feldspar. Quartz grains are usually anhedral, granoblastic, but blastoporphyritic fabric is common. A jig-saw puzzle aspect is typical in the injection gneisses. Mortar structure best developed in S/L members. Quartz mosaic serves as matrix for femic-aluminous minerals whose variety of kind and habit is too great to typify this class. Chemical analyses for some are given in Tables I and V of Chapter II -7.

3. Semi-Pelite:- Rocks in which one aluminous or femic mineral is nearly equal in volume percent to that of quartz plus feldspar, and the sum of volumes of aluminous-femic minerals

significantly exceeds (by 10 volume percent or more, but less than about 20 percent) that of quartz plus feldspar. Quartz and feldspar mosaic are of same characters as for psammitic semi-pelites, except blastoporphyritic fabric is not as common.

4. Pelite:- Rocks in which one aluminous or femic mineral exceeds that of quartz plus feldspar, and in which all aluminous and femic minerals comprise 60 volume percent or more of the rocks, so that their habit characterizes them. Muscovite, biotite, and chlorite are common minerals in this class, usually subhedral, coarse, forming good schistosity. Garnet and staurolite also typical.

5. Amphibolite:- Rocks in which an amphibole in an appreciable amount is present, so that it typifies the rock, notably in fabric. Their unusual mineralogy and chemical composition justifies their isolation into a separate class; the term "calc-magnesian rock" may apply to them (3).

6. Calc-Silicate:- Rocks in which calcium minerals or calcium mineral associations dominate or make up one-third of the rock volume. Calcite, tremolite, diopside, lime-garnet, serpentine, phlogopite, and quartz in combination characterize this class. They are "impure marbles."

7. Marble:- Likened to quartzite in that calcite makes up by far the most abundant mineral. The matrix is typically even-equidimensional, although elongation-preferred orientation is sometimes discernible.

8. Migmatite:- The definition given by Williams, Turner, and Gilbert is accepted (6).

Subclasses:- Certain subclasses were also applied. The definitions given by Harker (1) and Williams, Turner, and Gilbert (6) for blastoporphyritic, porphyritic, banded, and granulitic textures, gneiss, injection gneiss, hornfels, schist, and criteria of retrograde and progressive metamorphism are taken. Since the term "gneiss" now has genetic connotations, the writer has adopted the term "false gneiss" for rocks having alternations of light and dark mineral that are most likely due to original differences in composition. Examples of this subclass are rocks whose light-dark layers represent relict banding and ones whose mortar structure produce apparent segregation lenses. Also, the writer has taken the term "disseminated" to denote rocks having a preferred orientation of one mineral which is not abundant enough to produce a schistose appearance. The "pepper and salt" rocks of the Moine are type examples.

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Chapter II -5

Table of Results for Fluoride in 350 Metamorphic Rocks

Summary of Other Work:- From the considerations discussed by the writer in the introduction to Chapter I -3, section b, fluoride values obtained only in connection with a specific study of that element can be considered at all reliable, and hence the writer will confine himself only to such papers. Barth and Bruun (2), Seraphim (16), Kokubu (12), Koritnig (13), Shepherd (17), and Commucci and Mazzi (5) analyzed fluoride in a variety of igneous rocks and discussed its geochemistry. Jahns (10) has analyzed pegmatitic material for fluoride.

Work on sedimentary rocks has been published by Seraphim (16), Koritnig (13), Michael and Blume (14), Jeffries (11), Kokubu (12), and Barth and Bruun (2). Oceanic sediments have been analyzed by Shepherd (17), Koritnig (13), and Seraphim (16).

Fluoride in soils was first investigated by Robinson and Edgington (15). Michael and Blume (14) and Jahn-Deesbach (9) have published further work, some of which has corroborated the pioneer investigations of Robinson and Edgington.

However, apart from Koritnig's work on greisens (13), only Seraphim (16), Barth and Bruun (2), Kokubu (12), and Engel and Engel (7) have obtained data on metamorphic rocks.

Seraphim (16) studied the change in abundance of fluoride across three granitic contacts.

Correns has reviewed halogen geochemistry (6). Other reviews are published by Koritnig (13), Kokubu (12), Barth (1), Borchert (3), and Gmelin (8), the last providing an extensive list of fluoride-containing minerals.

Key to Table of Results:- The writer has grouped the 350 metamorphic rocks analyzed for fluoride into eight classes and twelve subclasses, all defined in Chapter II -4. Not all rocks were subclassed; only those specimens which showed distinctly the characters as defined were put in the appropriate sublcass. For example, a good number of specimens showed, by means of thin section examination, at least incipient retrograde metamorphism or alteration; these were excluded from the retrograde and progressive metamorphism subclasses. Only such distinct mineral reactions as chlorite reacting to form garnet or sillimanite developing from muscovite or biotite were taken as evidence of progressive metamorphism. A few rocks showed both types of metamorphism, so they were subclassed in both categories.

For each class the rocks are listed in order of increasing fluoride content, and the constituent minerals identified are listed in estimated decreasing order of volume percent, with some exceptions governed by the definitions relative to the class: The sum of the quartz and feldspar fixed the class of the rock, so these two minerals are usually given first if their sum does determine the class. If two minerals are considered about equal in volume percent in the rock, this is signified by an equal sign between them. For 20 of the Clifden district rocks and one Massif Central specimen, volume percent values have been obtained by Cobbing (4) and Dr. C.H. Emeleus; these figures, rounded off to a maximum precision of about 1 part in 50, are set in front of the corresponding mineral.

To minimize ancillary data, the writer had adopted the following key:

1. Two code numbers are given:

   Table Serial Number in parenthesis: (000)

   Sample Code Number prefixed with following letter codes:

S/S	Stonehaven-Findon Ness series.
S/P	Pitlochry series.
S/T	Loch Sunart series.
S/L	Loch Lomond series.
I/C	Clifden district series.
F/MC	Massif Central (France) series.

2. A + sign in front of the mineralogy denotes a thin section was prepared and examined.
3. ACC: denotes accessory minerals identified.
4. SC: denotes a subclass, which can be one or more of the following:

   GRA: granulite texture.

   FGN: false gneiss.

   BLAS: blastoporphyritic texture.

   DISS: a mineral disseminated in quartz and feldspar matrix, but showing a preferred orientation.

BAN: very coarse light and dark mineral banding in quartzite.

POR: porphyritic texture.

SCH: schist.

GN: gneiss.

IGN: injection gneiss.

HORN: hornfels.

RM: rock with evidence of retrograde metamorphism.

PM: rock with evidence of progressive metamorphism.

Two Examples:-

(257) 0.058 + Feldspar-Quartz-Biotite-Muscovite-Sericite-
S/T 13 Pyrite
ACC: Magnetite
SC: GRA, IGN

(298) 0.078 + 25 Plagioclase-16 Quartz-26 Biotite-
I/C H16 13 Muscovite-9 Staurolite-4 Chlorite-
4 Garnet-1 Sericite-1 Sillimanite
ACC: 0.8 Tourmaline, 0.2 Opaque
SC: GN, RM

The numbers (257) and S/T 13 in the left hand column are the table serial number and code number, respectively. Proceeding to the right, in the next column, is the percent fluoride, based on a single analysis. 54 samples were analyzed in duplicate to determine the precision of the method (cf. Chapter I -3, section a), but to retain comparability in the geochemical studies, only the first value for these 54 samples is given and used. To the right of the fluoride value the + sign signifies that a thin section was examined. Beneath the list of minerals accessories (ACC) and subclasses (SC), if any, are given. The second example above illustrates the use of volume percent data: The thin section contains 25 volume percent plagioclase, etc.

Quartzite Class

Code No.	% F	Minerals Present in Order of Abundance
(001) I/C 35	0.001	+ 84 Quartz-11 Orthoclase-5 Muscovite
(002) S/T 43	0.005	+ Quartz-Feldspar-Muscovite-Biotite
(003) I/C 67	0.005	Quartz-Feldspar
(004) S/P 61	0.005	+ Quartz-Microcline-Chlorite-Garnet SC: GRA
(005) S/S 6	0.006	Quartz-Feldspar
(006) I/C 10	0.007	+ 77 Quartz-13 Orthoclase-5 Biotite-4 Muscovite-1 Plagioclase
(007) S/P 59	0.007	+ Quartz-Albite-Microcline
(008) S/P 72	0.009	+ Quartz-Muscovite-Graphite ACC: Zircon
(009) S/P 50	0.015	+ Quartz-Muscovite-Biotite-Feldspar-Chlorite
(010) S/P 71	0.016	Quartz-Graphite ACC: Muscovite

Code No.	% F	Minerals Present in Order of Abundance
(011) S/P 25	0.017	Quartz-Muscovite-Biotite
(012) S/P 92	0.018	+ Quartz-Biotite-Muscovite-Garnet-Sphene ACC: Pyrite, Apatite SC: GRA
(013) S/P 63	0.023	Quartz-Biotite-Garnet SC: BAN
(014) S/P 58	0.037	Quartz-Biotite-Garnet-Chlorite SC: BAN
		Psammitic Semi-Pelite Class
(015) S/S 7	0.006	Quartz-Chlorite-Feldspar-Sericite
(016) S/T 54	0.006	+ Quartz-Feldspar-Biotite-Epidote-Muscovite ACC: Magnetite
(017) S/T 4	0.007	+ Quartz-Feldspar-Sericite (Muscovite)-Biotite-Chlorite ACC: Limonite SC: GRA
(018) S/S 4	0.007	Quartz-Chlorite
(019) S/T 52	0.007	+ Quartz-Feldspar-Biotite-Epidote SC: FGN

Code No.	% F	Minerals Present in Order of Abundance
(020) S/T 50	0.008	Quartz-Biotite-Feldspar-Muscovite-Epidote-Sphene=Ilmenite SC: FGN, PM
(021) I/C 240	0.008	+ 69 Quartz-15 Orthoclase-13 Muscovite-2 Plagioclase-1 Biotite SC: PM
(022) S/T 58	0.009	+ Quartz-Feldspar-Biotite-Muscovite-Epidote-Sphene SC: FGN, PM
(023) S/T 34	0.010	Quartz-Feldspar-Biotite-Muscovite SC: IGN
(024) S/T 60	0.011	+ Quartz-Feldspar-Biotite-Epidote-Muscovite ACC: Ilmenite, Sphene SC: FGN, PM
(025) S/T 37	0.011	+ Quartz-Feldspar-Biotite-Sericite-Sphene
(026) S/S 12	0.011	+ Quartz-Biotite-Muscovite (Sericite) ACC: Zircon, Apatite, Magnetite SC: FGN
(027) S/S 22	0.011	Quartz-Muscovite (Sericite)-Chlorite
(028) S/S 28	0.011	Quartz-Muscovite (Sericite)

Code No.	% F	Minerals Present in Order of Abundance
(029) S/L 46	0.012	+ Quartz-Muscovite-Chlorite-Feldspar-Biotite-Magnetite SC: FGN, RM
(030) S/T 36	0.012	+ Quartz-Feldspar-Biotite-Sericite-Sphene=Ilmenite-Apatite SC: GN
(031) S/P 2	0.012	+ Quartz-Chlorite-Biotite-Plagioclase SC: RM
(032) S/T 53	0.013	+ Quartz-Feldspar-Biotite-Epidote-Muscovite-Sericite SC: GN, RM
(033) S/L 27	0.013	Quartz-Muscovite-Chlorite-Biotite-Plagioclase SC: BLAS, PM
(034) S/S 59	0.013	Quartz-Muscovite-Biotite
(035) S/T 38	0.014	+ Quartz-Feldspar-Biotite-Sphene-Ilmenite-Sericite ACC: Chlorite, Apatite SC: FGN, RM
(036) S/S 75	0.014	+ Quartz-Biotite-Plagioclase ACC: Sericite, Muscovite SC: FGN, RM
(037) S/L 6	0.015	+ Quartz-Sericite-Chlorite-Albite-Pyrite-Limonite-Calcite SC: BLAS, RM

Code No.	% F	Minerals Present in Order of Abundance
(038) S/S 84	0.015	+ Plagioclase-Quartz-Biotite-Chlorite-Muscovite ACC: Apatite, Magnetite, Zircon
(039) S/L 34	0.016	+ Quartz-Oligoclase-Muscovite-Chlorite-Graphite-Tourmaline ACC: Calcite, Sphene SC: BLAS
(040) S/L 49	0.016	+ Quartz-Muscovite-Chlorite-Plagioclase-Magnetite SC: SCH
(041) S/T 51	0.016	+ Quartz-Feldspar-Biotite-Epidote SC: DISS, PM
(042) S/S 114	0.016	Quartz-Biotite-Muscovite-Garnet
(043) S/S 15	0.016	Quartz-Sericite-Limonite
(044) S/L 44	0.017	+ Quartz-Biotite-Muscovite-Calcite-Plagioclase-Graphite-Magnetite SC: SCH, RM
(045) S/T 62	0.017	+ Quartz-Feldspar-Biotite-Epidote-Muscovite-Sericite-Limonite SC: DISS, RM

Code No.	% F	Minerals Present in Order of Abundance
(046) S/S 13	0.017	Quartz-Sericite-Chlorite
(047) S/S 55	0.017	+ Quartz-Biotite ACC: Apatite SC: FGN, PM
(048) S/S 97	0.017	+ Quartz-Biotite-Pyrite-Plagioclase-Garnet-Muscovite-Zircon ACC: Apatite, Pyrite or Magnetite SC: FGN
(049) S/T 6	0.018	+ Quartz-Feldspar-Biotite-Sericite ACC: Chlorite, Sphene SC: IGN
(050) S/T 61	0.018	+ Quartz-Biotite-Feldspar-Epidote-Muscovite-Sphene ACC: Sphene, Chlorite SC: DISS, RM
(051) S/T 59	0.018	+ Quartz-Muscovite-Feldspar-Epidote-Sphene-Biotite SC: FGN
(052) S/L 60	0.018	+ Quartz-Chlorite-Calcite-Muscovite-Garnet-Magnetite SC: GN
(053) S/L 52	0.018	+ Quartz-Muscovite-Biotite-Chlorite-Magnetite SC: GN

Code No.	% F	Minerals Present in Order of Abundance
(054) S/T 29	0.018	+ Quartz-Feldspar-Biotite-Magnetite ACC: Sphene, Apatite, Chlorite SC: IGN
(055) S/S 74	0.019	+ Quartz-Biotite-Plagioclase ACC: Garnet, Chlorite, Muscovite, Apatite SC: FGN, RM
(056) S/L 45	0.020	Quartz-Biotite-Muscovite-Chlorite
(057) S/T 63	0.020	+ Quartz-Epidote-Biotite-Feldspar-Muscovite-Sphene-Limonite-Garnet SC: FGN
(058) S/T 28	0.020	+ Feldspar-Quartz-Biotite SC: FGN, RM
(059) S/T 47	0.020	+ Quartz-Feldspar-Biotite-Garnet SC: FGN, PM
(060) S/T 67	0.020	+ Quartz-Muscovite-Feldspar-Biotite-Sphene SC: FGN, PM
(061) S/S 5	0.020	Quartz-Chlorite?
(062) S/L 15	0.020	+ Quartz-Chlorite-Muscovite-Albite-Calcite ACC: Pyrite, Sphene SC: FGN

Code No.	% F	Minerals Present in Order of Abundance
(063) S/T 21	0.020	+ Quartz-Feldspar-Biotite-Muscovite ACC: Sphene, Magnetite, Sericite SC: IGN
(064) S/T 30	0.020	+ Quartz-Feldspar-Biotite ACC: Sericite SC: IGN
(065) S/P 33	0.020	Quartz-Muscovite-Biotite-Garnet SC: POR, PM
(066) S/S 52	0.021	Quartz-Biotite
(067) S/L 7	0.022	+ Quartz-Sericite-Chlorite-Albite-Limonite ACC: Muscovite, Pyrite SC: BLAS
(068) S/L 19	0.022	+ Quartz-Muscovite-Biotite-Calcite ACC: Sphene, Limonite, Oligoclase SC: BLAS, FGN
(069) S/T 7	0.022	+ Quartz-Feldspar-Biotite-Sericite ACC: Magnetite SC: GN
(070) S/L 61	0.022	+ Quartz-Calcite-Muscovite-Chlorite-Garnet-Epidote-Magnetite SC: GN
(071) S/L 18	0.022	+ Quartz-Muscovite-Biotite-Albite ACC: Epidote, Zircon SC: BLAS, SCH

Code No.	% F	Minerals Present in Order of Abundance
(072)	0.022	Quartz-Muscovite-Chlorite-Biotite
S/L 48		SC: BLAS, FGN
(073)	0.023	Quartz-Biotite-Muscovite-Garnet
S/P 17		SC: DISS, PM
(074)	0.023	Quartz-Muscovite-Chlorite
S/P 60		SC: RM
(075)	0.023	Quartz-Biotite-Muscovite
S/P 75		ACC: Chlorite
		SC: RM
(076)	0.023	Quartz-Biotite
S/S 71		SC: SCH
(077)	0.023	+ Quartz-Sericite-Hematite-Biotite
S/S 40		SC: BLAS, FGN, RM
(078)	0.023	+ Quartz-Sericite-Chlorite-Limonite
S/S 14		ACC: Calcite
		SC: BLAS, RM
(079)	0.024	Quartz-Sericite-Chlorite
S/L 9		SC: BLAS, FGN
(080)	0.024	+ Quartz-Biotite-Muscovite-Garnet-Calcite-Albite
S/P 62		ACC: Sphene, Apatite, Zircon
		SC: DISS

Code No.	% F	Minerals Present in Order of Abundance
(081)	0.024	Quartz-Biotite
S/S 54		
(082)	0.024	+ Quartz-Biotite-Garnet
S/S 51		SC: FGN, PM
(083)	0.024	+ Quartz-Muscovite-Biotite-Plagioclase-Chlorite
S/L 42		ACC: Limonite
		SC: BLAS, SCH
(084)	0.024	Quartz-Sericite-Biotite
S/S 16		SC: FGN
(085)	0.025	Quartz-Biotite
S/S 78		SC: FGN
(086)	0.025	+ Quartz-Biotite-Feldspar-Epidote-Garnet-Sphene
S/T 66		SC: FGN
(087)	0.025	Quartz-Muscovite-Biotite
S/S 43		
(088)	0.025	Quartz-Sericite-Chlorite
S/S 31		ACC: Calcite
		SC: RM
(089)	0.026	+ Quartz-Chlorite-Calcite-Muscovite
S/L 33		ACC: Limonite
		SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(090) S/L 40	0.026	Quartz-Chlorite-Muscovite-Biotite SC: BLAS, FGN
(091) S/L 50	0.026	+ Quartz-Muscovite-Plagioclase-Biotite-Magnetite-Chlorite ACC: Zircon SC: FGN, RM
(092) S/L 28	0.026	+ Quartz-Muscovite-Chlorite-Graphite-Oligoclase ACC: Limonite SC: FGN
(093) S/P 15	0.026	+ Quartz-Biotite-Muscovite-Plagioclase-Sphene-Garnet ACC: Apatite SC: DISS, PM
(094) S/P 84	0.026	+ Quartz-Biotite-Garnet ACC: Apatite, Feldspar, Zircon, Chlorite SC: DISS, POR, PM
(095) S/S 107	0.026	Quartz-Biotite
(096) S/S 86	0.026	Quartz-Biotite-Plagioclase SC: FGN
(097) S/T 68	0.026	+ Quartz-Feldspar-Biotite-Muscovite-Sphene-Epidote-Sericite ACC: Garnet SC: FGN

Code No.	% F	Minerals Present in Order of Abundance
(098) S/S 69	0.026	Quartz-Biotite SC: SCH
(099) S/S 66	0.026	Quartz-Biotite
(100) S/T 5	0.027	+ Quartz-Feldspar-Biotite-Sericite-Chlorite ACC: Hematite
(101) S/P 74	0.027	+ Quartz-Feldspar-Muscovite-Biotite-Chlorite-Garnet ACC: Pyrite, Apatite SC: GRA
(102) S/P 77	0.027	Quartz-Biotite-Muscovite
(103) S/S 72	0.027	Quartz-Biotite-Garnet SC: FGN
(104) S/L 47	0.027	+ Quartz-Chlorite-Muscovite-Feldspar-Magnetite ACC: Hematite, Pyrite, Epidote SC: BLAS, SCH
(105) S/S 111	0.027	Quartz-Muscovite-Biotite
(106) S/S 70	0.027	+ Quartz-Biotite-Garnet-Chlorite ACC: Pyrite, Limonite, Apatite, Plagioclase, Sericite SC: GN, RM

Code No.	% F	Minerals Present in Order of Abundance
(107) S/S 8	0.027	Quartz-Sericite-Chlorite SC: BLAS
(108) S/L 10	0.028	+ Quartz-Muscovite-Biotite-Epidote-Albite-Calcite SC: FGN
(109) S/P 45	0.028	Quartz-Biotite-Muscovite-Chlorite-Garnet SC: POR, DISS
(110) S/S 122	0.028	Quartz-Biotite
(111) S/S 105	0.028	+ Quartz-Biotite-Feldspar-Garnet ACC: Sericite, Apatite SC: FGN
(112) S/L 51	0.028	+ Quartz-Muscovite-Biotite-Plagioclase-Epidote-Magnetite-Calcite ACC: Sericite, Sphene, Zircon SC: FGN, RM
(113) S/S 46	0.029	+ Quartz-Biotite-Garnet-Pyrite ACC: Chlorite, Apatite, Zircon SC: FGN, PM
(114) S/S 119	0.029	+ Quartz-Muscovite-Biotite ACC: Plagioclase, Sericite, Limonite SC: FGN
(115) S/T 8	0.029	+ Quartz-Feldspar-Biotite-Sericite SC: IGN

Code No.	% F	Minerals Present in Order of Abundance
(116) S/P 23	0.029	+ Quartz-Muscovite-Biotite-Garnet-Plagioclase ACC: Apatite, Epidote SC: DISS, POR
(117) S/P 8	0.029	Quartz-Biotite SC: DISS
(118) S/S 93	0.029	Quartz-Biotite-Garnet-Plagioclase-Muscovite ACC: Apatite, Chlorite SC: GN
(119) S/S 64	0.029	Quartz-Biotite
(120) S/L 14	0.030	Quartz-Sericite-Chlorite SC: BLAS, FGN
(121) S/P 22	0.030	+ Quartz-Biotite-Garnet-Feldspar-Muscovite ACC: Apatite, Sericite SC: FGN, POR, PM
(122) S/S 60	0.030	Quartz-Biotite-Garnet
(123) S/T 9	0.030	+ Quartz-Feldspar-Biotite-Muscovite- Sericite-Magnetite SC: IGN
(124) S/S 32	0.030	Quartz-Biotite-Muscovite
(125) S/S 21	0.030	Quartz-Biotite SC: BLAS

Code No.	% F	Minerals Present in Order of Abundance
(126) S/S 9	0.030	Quartz-Sericite-Chlorite
(127) S/L 64	0.031	Quartz-Chlorite-Muscovite SC: FGN
(128) S/P 31	0.031	+ Quartz-Biotite-Muscovite-Garnet ACC: Apatite, Sphene, Albite, Chlorite SC: DISS, POR, PM
(129) S/P 66	0.031	+ Quartz-Biotite-Muscovite ACC: Apatite, Pyrite, Albite, Chlorite
(130) S/S 57	0.031	+ Quartz-Biotite ACC: Apatite SC: FGN, PM
(131) S/P 90	0.032	Quartz-Biotite-Muscovite-Garnet-Chlorite SC: DISS, POR, RM
(132) S/T 35	0.032	+ Quartz-Feldspar-Biotite-Sphene ACC: Apatite SC: DISS, PM
(133) S/T 25	0.032	+ Quartz-Feldspar-Muscovite-Biotite-Pyrite ACC: Graphite? SC: IGN
(134) S/S 42	0.032	Quartz-Muscovite-Biotite-Garnet SC: FGN
(135) S/S 25	0.032	Quartz-Sericite ACC: Limonite, Tourmaline, Calcite

Code No.	% F	Minerals Present in Order of Abundance
(136) S/S 61	0.033	+ Quartz-Muscovite-Plagioclase-Biotite-Sericite ACC: Chlorite, Apatite SC: GRA, PM
(137) S/S 91	0.033	+ Quartz-Biotite-Feldspar-Garnet-Hornblende-Epidote-Muscovite ACC: Apatite SC: FGN
(138) S/L 69	0.033	+ Quartz-Sericite-Chlorite-Plagioclase-Magnetite SC: HORN
(139) S/S 58	0.033	Quartz-Biotite-Muscovite
(140) S/L 37	0.034	Quartz-Muscovite-Chlorite-Graphite ACC: Tourmaline SC: SCH
(141) S/S 95	0.034	Quartz-Biotite-Muscovite-Garnet
(142) S/S 19	0.034	Quartz-Sericite-Chlorite SC: BLAS
(143) S/S 79	0.034	Quartz-Biotite-Muscovite SC: BLAS
(144) S/L 25	0.035	+ Quartz-Muscovite-Plagioclase-Biotite-Calcite-Epidote-Chlorite ACC: Sphene SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(145) S/P 80	0.035	+ Quartz-Biotite-Muscovite-Garnet ACC: Pyrite, Apatite, Sphene SC: DISS, POR, PM
(146) S/P 32	0.035	+ Quartz-Muscovite-Biotite-Garnet-Chlorite ACC: Albite, Apatite, Sphene SC: DISS, POR, PM and RM
(147) S/P 87	0.035	Quartz-Biotite-Muscovite-Garnet-Chlorite SC: POR, DISS, PM and RM
(148) S/S 17	0.035	+ Quartz-Sericite-Chlorite-Plagioclase SC: BLAS, POR, PM
(149) S/S 11	0.035	Quartz-Sericite-Chlorite SC: BLAS
(150) S/S 48	0.035	+ Quartz-Biotite-Muscovite ACC: Apatite, Cordierite, Chlorite, Feldspar SC: GN, PM
(151) S/S 20	0.036	Quartz-Sericite-Chlorite SC: BLAS
(152) S/T 40	0.037	+ Quartz-Feldspar-Biotite ACC: Garnet, Apatite SC: IGN
(153) S/T 74	0.037	+ Quartz-Feldspar-Biotite-Calcite-Garnet-Sphene SC: DISS, PM

Code No.	% F	Minerals Present in Order of Abundance
(154) S/P 39	0.037	+ Quartz-Biotite-Muscovite-Garnet-Chlorite SC: DISS, POR, RM
(155) S/S 83	0.037	+ Quartz-Biotite-Plagioclase-Muscovite ACC: Apatite, Pyrite, Magnetite SC: DISS, PM
(156) S/S 87	0.037	+ Quartz-Biotite-Plagioclase-Muscovite ACC: Apatite SC: FGN, PM
(157) S/L 8	0.038	+ Quartz-Sericite-Chlorite-Albite ACC: Pyrite SC: BLAS, FGN
(158) S/S 116	0.038	+ Quartz-Plagioclase-Biotite-Staurolite-Sericite-Garnet ACC: Magnetite SC: BLAS, FGN, RM
(159) S/L 21	0.038	+ Quartz-Muscovite-Chlorite-Biotite-Sphene SC: BLAS, SCH, PM
(160) S/S 98	0.038	Quartz-Biotite-Muscovite SC: FGN
(161) S/S 88	0.038	+ Quartz-Biotite-Muscovite-Plagioclase ACC: Apatite, Zircon SC: FGN
(162) S/S 63	0.038	Quartz-Muscovite-Biotite

Code No.	% F	Minerals Present in Order of Abundance
(163) S/L 22	0.039	Quartz-Muscovite-Biotite-Chlorite SC: FGN
(164) S/P 54	0.039	+ Quartz-Biotite-Muscovite-Garnet-Chlorite ACC: Apatite SC: DISS, POR, PM
(165) S/S 118	0.039	Quartz-Biotite-Muscovite
(166) S/P 29	0.040	Quartz-Biotite-Muscovite SC: DISS
(167) S/S 24	0.040	+ Quartz-Sericite ACC: Limonite, Apatite SC: BLAS
(168) S/L 24	0.040	+ Quartz-Muscovite-Biotite-Graphite-Plagioclase-Chlorite ACC: Sphene, Calcite SC: BLAS, SCH
(169) S/P 68	0.040	+ Quartz-Biotite-Muscovite SC: FGN, PM
(170) S/S 26	0.040	+ Quartz-Sericite-Chlorite-Garnet ACC: Limonite SC: POR, PM
(171) S/T 10	0.041	+ Quartz-Feldspar-Biotite-Muscovite-Sericite ACC: Sphene, Chlorite, Magnetite SC: GRA, RM

Code No.	% F	Minerals Present in Order of Abundance
(172) S/T 20	0.041	+ Quartz-Feldspar-Biotite-Garnet ACC: Magnetite, Sphene, Sericite SC: IGN
(173) S/S 121	0.041	Quartz-Biotite-Muscovite
(174) S/S 18	0.041	Quartz-Sericite-Chlorite ACC: Feldspar, Magnetite SC: BLAS
(175) S/S 10	0.042	+ Quartz-Sericite-Chlorite ACC: Magnetite, Feldspar SC: BLAS, RM
(176) S/P 26	0.043	+ Quartz-Muscovite-Biotite-Garnet-Chlorite ACC: Tourmaline, Epidote? SC: DISS, POR, PM
(177) S/P 73	0.043	+ Quartz-Biotite-Chlorite-Garnet-Muscovite ACC: Apatite SC: FGN, POR, RM
(178) S/S 112	0.043	Quartz-Biotite
(179) S/L 13	0.044	Quartz-Sericite-Chlorite ACC: Albite? SC: BLAS

Code No.	% F	Minerals Present in Order of Abundance
(180) S/P 48	0.044	+ Quartz-Plagioclase-Biotite-Muscovite-Garnet-Chlorite ACC: Apatite, Sericite SC: DISS, POR, RM
(181) S/S 53	0.044	Quartz-Biotite-Garnet SC: DISS
(182) S/P 44	0.045	Quartz-Biotite-Muscovite-Garnet-Chlorite SC: DISS, POR, RM
(183) S/P 42	0.048	+ Quartz-Biotite-Muscovite-Garnet-Chlorite ACC: Apatite, Sphene SC: DISS, POR, RM
(184) S/P 37	0.048	Quartz-Biotite-Muscovite-Garnet
(185) S/S 96	0.049	+ Quartz-Biotite-Muscovite-Garnet-Plagioclase ACC: Apatite, Magnetite, Chlorite SC: FGN, PM
(186) I/C 170	0.050	+ 37 Quartz-33 Plagioclase-29 Biotite-1 Garnet ACC: Opaque, 0.5 volume percent SC: GRA
(187) S/T 22	0.050	+ Quartz-Muscovite-Biotite-Feldspar-Chlorite ACC: Limonite, Pyrite SC: SCH, RM
(188) S/S 126	0.050	Quartz-Biotite-Muscovite

Code No.	% F	Minerals Present in Order of Abundance
(189) S/L 26	0.051	+ Quartz-Muscovite-Chlorite-Biotite-Oligoclase ACC: Sphene, Calcite SC: BLAS, SCH, RM
(190) S/L 17	0.051	Quartz-Muscovite-Chlorite
(191) S/P 19	0.051	+ Quartz-Biotite-Muscovite-Garnet-Plagioclase ACC: Limonite, Apatite, Epidote SC: DISS, POR, PM
(192) S/S 27	0.051	Quartz-Muscovite-Biotite
(193) S/S 101	0.052	Quartz-Muscovite-Biotite
(194) S/S 80	0.052	Quartz-Biotite-Muscovite SC: FGN
(195) S/T 69	0.054	+ Quartz-Biotite-Muscovite-Feldspar-Garnet-Apatite-Sphene SC: POR, PM
(196) S/S 85	0.054	Quartz-Biotite-Feldspar-Garnet
(197) S/S 82	0.054	+ Quartz-Biotite-Feldspar-Muscovite ACC: Magnetite, Sphene, Sericite, Garnet SC: FGN

Code No.	% F	Minerals Present in Order of Abundance
(198) S/S 33	0.054	+ Quartz-Muscovite-Biotite-Chlorite ACC: Apatite, Limonite SC: FGN, RM
(199) S/L 16	0.055	+ Quartz-Muscovite-Chlorite-Limonite ACC: Sphene SC: BLAS
(200) S/L 4	0.055	Quartz-Chlorite-Pyrite
(201) S/S 56	0.055	+ Quartz-Biotite-Garnet-Staurolite-Sericite-Muscovite ACC: Apatite, Magnetite SC: FGN, RM
(202) S/T 14	0.056	+ Feldspar-Quartz-Biotite-Muscovite-Sericite ACC: Pyrite SC: IGN (GRA)
(203) S/S 45	0.057	+ Quartz-Biotite-Feldspar-Muscovite-Garnet-Calcite ACC: Limonite, Pyrite, Sericite SC: POR, GRA, RM
(204) S/L 12	0.058	+ Quartz-Sericite-Chlorite-Albite ACC: Sphene SC: BLAS, SCH

Code No.	% F	Minerals Present in Order of Abundance
(205) S/L 43	0.061	+ Quartz-Muscovite-Chlorite-Calcite ACC: Magnetite SC: SCH
(206) S/S 73	0.063	+ Quartz-Biotite-Plagioclase ACC: Apatite, Chlorite, Zircon SC: POR, FGN
(207) S/S 102	0.063	Quartz-Biotite
(208) S/S 44	0.064	+ Quartz-Biotite-Muscovite-Chlorite-Calcite-Pyrite-Garnet ACC: Hematite, Sericite SC: POR, FGN, RM
(209) S/P 83	0.066	+ Quartz-Biotite-Muscovite-Garnet-Chlorite ACC: Pyrite, Apatite SC: DISS, POR, RM and PM
(210) S/L 30	0.070	+ Quartz-Muscovite-Graphite-Calcite-Chlorite SC: SCH
(211) S/S 110	0.079	Quartz-Muscovite-Biotite-Garnet
(212) S/S 92	0.086	Quartz-Hornblende=Biotite-Feldspar-Garnet
(213) S/S 123	0.087	Quartz-Biotite-Garnet

Semi-Pelite Class

Code No.	% F	Minerals Present in Order of Abundance
(214) S/L 59	0.017	+ Quartz-Plagioclase-Chlorite-Muscovite-Garnet-Magnetite SC: GN, RM
(215) S/L 57	0.020	+ Quartz-Muscovite-Plagioclase-Chlorite-Garnet-Biotite-Calcite-Magnetite-Epidote SC: GN, RM
(216) S/L 66	0.025	+ Quartz-Muscovite-Biotite-Plagioclase-Chlorite-Magnetite-Calcite SC: GN
(217) S/T 48	0.034	+ Feldspar-Quartz=Garnet=Biotite-Magnetite-Sericite ACC: Apatite SC: POR, GN
(218) S/L 65	0.035	+ Quartz-Muscovite-Chlorite-Feldspar-Epidote-Garnet-Magnetite-Calcite SC: GN
(219) S/L 63	0.036	+ Quartz-Garnet-Chlorite-Feldspar-Muscovite-Magnetite SC: GN, PM
(220) S/L 39	0.039	+ Quartz-Muscovite-Chlorite-Oligoclase-Biotite ACC: Sphene, Graphite? SC: BLAS, SCH

Code No.	% F	Minerals Present in Order of Abundance
(221) S/L 41	0.039	+ Quartz-Muscovite-Chlorite-Sphene-Plagioclase-Biotite-Graphite ACC: Calcite SC: SCH, PM
(222) S/T 15	0.040	+ Feldspar-Quartz-Muscovite-Biotite-Sericite ACC: Apatite SC: IGN
(223) S/L 56	0.041	+ Quartz-Chlorite-Feldspar-Biotite-Muscovite-Magnetite, Calcite-Sphene ACC: Apatite SC: GN
(224) S/L 55	0.042	+ Quartz-Feldspar-Chlorite-Muscovite-Magnetite SC: GN
(225) S/T 73	0.044	+ Quartz-Feldspar-Muscovite-Biotite-Garnet-Magnetite-Apatite-Calcite SC: POR, SCH
(226) S/T 64	0.044	+ Quartz-Biotite-Feldspar-Muscovite-Epidote ACC: Sphene, Apatite SC: SCH
(227) S/T 26	0.044	+ Quartz-Biotite-Feldspar-Sillimanite-Garnet ACC: Sphene SC: IGN, PM
(228) S/L 67	0.044	+ Quartz-Chlorite-Plagioclase-Muscovite-Magnetite-Garnet SC: SCH, PM

Code No.	% F	Minerals Present in Order of Abundance
(229) S/L 58	0.046	+ Quartz-Chlorite-Garnet-Plagioclase-Muscovite-Magnetite-Epidote-Calcite SC: GN, HM
(230) S/S 15a	0.047	+ Quartz-Sericite-Chlorite-Pyrite ACC: Limonite, Tourmaline SC: BLAS, SCH
(231) S/T 57	0.048	+ Quartz-Muscovite-Feldspar-Biotite-Epidote ACC: Sericite SC: SCH
(232) S/S 115	0.049	Quartz-Biotite-Muscovite-Garnet
(233) S/S 23	0.049	Quartz-Sericite-Chlorite
(234) S/T 42	0.049	+ Feldspar-Biotite-Quartz-Muscovite-Sericite ACC: Garnet SC: GN(IGN), PM
(235) S/T 65	0.049	+ Quartz-Muscovite-Biotite-Feldspar-Garnet-Epidote-Sphene SC: POR, SCH, PM
(236) S/L 1	0.049	Slate or Phyllite
(237) S/S 90	0.050	Quartz-Muscovite-Biotite-Garnet SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(238) S/S 29	0.050	+ Quartz-Chlorite-Sericite-Chloritoid-Staurolite ACC: Opaque Mineral, Apatite, Tourmaline SC: POR, SCH, RM
(239) S/P 95	0.050	+ Quartz-Muscovite-Biotite-Graphite-Pyrite-Chlorite-Garnet SC: POR, SCH, RM
(240) S/S 76	0.051	Quartz-Biotite
(241) I/C 222	0.052	+ 21 Quartz-19 Plagioclase-26 Biotite-16 Muscovite-14 Staurolite ACC: Opaque, 3 volume percent; Garnet, 0.2 SC: POR, GN, PM
(242) S/S 81	0.054	+ Quartz-Biotite-Plagioclase-Muscovite ACC: Sericite SC: GN, PM
(243) S/S 36	0.054	+ Quartz-Muscovite-Biotite-Chlorite-Magnetite ACC: Apatite SC: POR, SCH, PM
(244) S/S 30	0.054	+ Quartz-Biotite-Sericite-Staurolite-Chlorite SC: BLAS, POR, SCH, RM
(245) S/T 70	0.054	+ Quartz-Muscovite-Biotite-Feldspar-Garnet-Sphene ACC: Epidote, Pyrite SC: GN, PM

Code No.	% F	Minerals Present in Order of Abundance
(246) S/T 41	0.054	+ Feldspar-Quartz-Biotite-Garnet-Muscovite-Sericite ACC: Apatite SC: GN(IGN)
(247) S/L 68	0.055	+ Quartz-Muscovite-Garnet-Chlorite-Plagioclase-Calcite-Magnetite SC: GN
(248) S/L 2	0.055	Slate or Phyllite
(249) S/T 55	0.056	+ Quartz-Feldspar-Biotite-Muscovite ACC: Apatite SC: SCH
(250) S/S 34	0.057	+ Quartz-Sericite-Chlorite-Pyrite ACC: Apatite, Tourmaline SC: SCH, RM
(251) I/C 2	0.057	Plagioclase-Quartz-Biotite=Muscovite-Andalusite-Cordierite SC: HORN
(252) F/MC 21	0.057	+ Quartz-Feldspar-Biotite-Sillimanite-Muscovite ACC: Garnet, Kaolin SC: GN, PM
(253) S/S 108	0.058	Quartz-Muscovite-Biotite-Garnet SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(254) S/S 65	0.058	+ Quartz-Biotite-Muscovite-Plagioclase-Sericite ACC: Apatite SC: FGN
(255) S/S 62	0.058	Quartz-Biotite-Muscovite-Garnet
(256) S/S 94	0.058	+ Quartz-Muscovite-Biotite-Garnet-Plagioclase-Sericite-Staurolite ACC: Magnetite, Apatite SC: POR, FGN, RM
(257) S/T 13	0.058	+ Feldspar-Quartz-Biotite-Muscovite-Sericite-Pyrite ACC: Magnetite SC: GRA, IGN
(258) I/C 38	0.058	+ 39 Plagioclase-31 Quartz-18 Biotite-8 Orthoclase-4 Muscovite ACC: Opaque, 0.4 volume percent, Epidote SC: GN, PM
(259) S/P 76	0.059	+ Quartz-Biotite-Muscovite-Garnet-Chlorite ACC: Apatite, Zircon SC: POR, FGN, RM
(260) S/T 45	0.059	+ Feldspar-Quartz-Muscovite-Garnet-Biotite-Magnetite-Sericite ACC: Pyrite, Apatite SC: POR, GN, PM

Code No.	% F	Minerals Present in Order of Abundance
(261) I/C 37	0.059	+ 35 Plagioclase-33 Quartz-25 Biotite-7 Muscovite SC: DISS
(262) S/S 49	0.062	+ Quartz-Biotite-Muscovite-Calcite-Feldspar-Garnet-Staurolite-Sericite ACC: Pyrite, Limonite, Apatite SC: POR, FGN, RM and PM
(263) S/L 5	0.062	Slate or Phyllite
(264) S/T 49	0.063	+ Quartz-Feldspar-Muscovite-Garnet-Biotite-Magnetite-Sericite SC: POR, SCH
(265) S/T 32	0.063	+ Quartz-Feldspar-Biotite-Muscovite-Sericite SC: IGN
(266) S/T 77	0.063	+ Quartz-Biotite-Muscovite-Feldspar-Garnet-Sphene-Apatite-Calcite ACC: Ilmenite SC: POR, FGN, PM
(267) S/T 11	0.063	+ Feldspar-Quartz-Biotite-Muscovite-Sericite-Pyrite ACC: Zircon SC: GRA, IGN

Code No.	% F	Minerals Present in Order of Abundance
(268) S/T 44	0.064	+ Feldspar-Biotite-Quartz-Pyrite-Garnet ACC: Apatite, Chlorite, Sericite SC: IGN
(269) S/T 23	0.064	+ Feldspar-Biotite-Quartz ACC: Sphene, Apatite SC: FGN, PM
(270) S/L 54	0.064	+ Quartz-Muscovite-Chlorite-Calcite-Magnetite-Epidote-Feldspar SC: SCH
(271) I/C 91A	0.064	+ 39 Quartz-33 Plagioclase-15 Biotite-5 Muscovite-8 Sphene + Epidote ACC: Calcite, Chlorite SC: GN, RM
(272) S/T 16	0.066	+ Feldspar-Quartz-Biotite-Muscovite-Garnet-Sericite SC: IGN, PM
(273) S/P 52	0.066	Quartz-Muscovite-Biotite-Garnet-Chlorite SC: SCH, RM
(274) S/S 38	0.067	Quartz-Biotite
(275) S/T 76	0.067	+ Feldspar-Quartz-Muscovite-Biotite-Garnet-Magnetite-Chlorite SC: POR, SCH, RM

Code No.	% F	Minerals Present in Order of Abundance
(276) S/T 39	0.067	+ Feldspar-Biotite-Quartz ACC: Sericite, Apatite, Sphene
(277) S/L 36	0.067	+ Quartz-Muscovite-Chlorite-Graphite SC: SCH
(278) S/T 79	0.067	+ Quartz-Feldspar-Muscovite-Biotite-Garnet-Chlorite-Magnetite-Apatite-Calcite-Sericite SC: SCH, RM
(279) S/S 109	0.068	Quartz-Biotite-Garnet
(280) S/T 72	0.068	+ Quartz-Feldspar-Garnet-Muscovite-Biotite-Chlorite ACC: Magnetite, Sericite SC: POR, SCH, PM
(281) S/T 75	0.068	+ Quartz-Muscovite-Feldspar-Biotite-Magnetite ACC: Apatite SC: POR, SCH
(282) S/T 78	0.068	+ Quartz-Muscovite-Feldspar-Biotite-Garnet-Chlorite-Magnetite ACC: Apatite SC: POR, SCH
(283) S/T 19	0.068	+ Quartz-Feldspar-Biotite-Garnet-Sericite ACC: Apatite, Muscovite, Sillimanite? SC: IGN, PM

Code No.	% F	Minerals Present in Order of Abundance
(284) S/T 31	0.069	+ Quartz-Feldspar-Biotite-Muscovite-Sericite-Apatite SC: IGN
(285) S/T 71	0.069	+ Feldspar-Quartz-Biotite-Garnet-Muscovite-Magnetite ACC: Apatite, Chlorite SC: POR, SCH
(286) S/T 18	0.069	+ Feldspar-Biotite-Quartz-Muscovite-Sericite ACC: Garnet, Hydrobiotite SC: IGN, RM
(287) I/C 179	0.069	+ 31 Plagioclase-26 Biotite-21 Muscovite-16 Quartz-4 Cordierite-2 Garnet SC: HORN
(288) I/C 1A	0.070	+ 22 Quartz-14 Plagioclase-39 Biotite-10 Garnet-10 Sillimanite-4 Staurolite SC: GN, PM
(289) S/P 96	0.073	+ Quartz-Muscovite-Biotite-Graphite-Pyrite-Chlorite SC: SCH, RM
(290) S/S 113	0.074	+ Quartz-Biotite-Muscovite-Staurolite ACC: Apatite, Chlorite, Sericite, Opaque SC: POR, SCH, RM
(291) S/S 99	0.075	Quartz-Biotite-Muscovite-Garnet SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(292) S/S 120	0.075	Quartz-Biotite-Muscovite
(293) S/T 81	0.075	+ Quartz-Feldspar-Biotite-Muscovite-Garnet-Magnetite-Chlorite-Apatite SC: POR, SCH, RM
(294) S/T 80	0.076	+ Quartz-Feldspar-Muscovite-Biotite-Chlorite-Garnet-Magnetite-Calcite-Apatite SC: POR, SCH, RM
(295) S/S 39	0.076	Quartz-Biotite
(296) S/L 38	0.077	+ Quartz-Muscovite-Chlorite-Graphite SC: SCH
(297) I/C S_3	0.077	+ 28 Quartz-20 Plagioclase-20 Biotite-14 Sillimanite-12 Garnet-3 Muscovite-2 Staurolite ACC: Opaque, 1 volume percent SC: GN, PM
(298) I/C H16	0.078	+ 25 Plagioclase-16 Quartz-26 Biotite-13 Muscovite-9 Staurolite-4 Chlorite-4 Garnet-1 Sericite-1 Sillimanite ACC: 0.8 Tourmaline, 0.2 Opaque SC: GN, RM

Code No.	% F	Minerals Present in Order of Abundance
(299) S/T 17	0.079	+ Feldspar-Biotite-Quartz-Muscovite-Garnet-Sericite-Pyrite ACC: Chlorite SC: GRA, IGN
(300) S/S 89	0.079	Quartz-Biotite-Garnet SC: POR, SCH
(301) S/L 53	0.081	+ Quartz-Muscovite-Chlorite-Magnetite ACC: Plagioclase, Tourmaline SC: SCH
(302) S/P 70	0.081	+ Quartz-Muscovite-Graphite SC: SCH
(303) I/C 89	0.082	+ 33 Quartz-23 Biotite-12 Plagioclase-16 Sillimanite-15 Muscovite-2 Garnet SC: GN, PM
(304) I/C 154	0.086	+ 29 Plagioclase-12 Quartz-24 Muscovite-23 Biotite-5 Garnet-4 Cordierite-2 Andalusite ACC: 0.7 Opaque SC: HORN
(305) I/C 26	0.088	+ 21 Quartz-18 Plagioclase-30 Sillimanite + Sericite-19 Biotite-12 Muscovite ACC: 0.4 Opaque, Garnet SC: GN, RM

Code No.	% F	Minerals Present in Order of Abundance
(306) S/T 27	0.090	+ Quartz-Feldspar-Biotite-Muscovite-Sillimanite-Magnetite-Sericite-Garnet SC: GN, PM
(307) S/L 31	0.091	+ Quartz-Muscovite-Graphite-Chlorite ACC: Biotite? SC: SCH
(308) S/S 35	0.093	+ Quartz-Biotite-Muscovite + Sericite-Garnet ACC: Limonite, Pyrite, Apatite SC: POR, SCH, PM
(309) S/S 117	0.093	Quartz-Biotite-Muscovite-Garnet
(310) S/T 46	0.095	+ Quartz-Muscovite-Feldspar-Garnet-Magnetite-Chlorite-Sericite ACC: Pyrite, Apatite SC: POR, SCH
		Pelite Class
(311) S/S 100	0.045	+ Quartz-Biotite-Garnet-Plagioclase ACC: Pyrite, Sericite, Chlorite, Apatite SC: POR, DISS, PM
(312) S/S 50	0.070	+ Quartz-Muscovite-Biotite-Garnet-Staurolite-Sericite-Calcite ACC: Limonite, Tourmaline, Chlorite SC: POR, SCH, RM

Code No.	% F	Minerals Present in Order of Abundance
(313) S/S 104	0.072	Muscovite-Biotite-Quartz-Garnet SC: SCH
(314) S/S 41	0.081	+ Quartz=Biotite-Muscovite-Chlorite-Garnet-Sericite-Staurolite ACC: Pyrite, Apatite SC: SCH, RM
(315) S/S 47	0.086	Biotite-Quartz-Muscovite-Garnet
(316) S/L 35	0.087	+ Muscovite-Quartz-Chlorite-Graphite-Tourmaline SC: SCH
(317) S/S 124	0.087	+ Muscovite-Biotite-Quartz-Garnet SC: POR, SCH
(318) S/S 103	0.088	+ Muscovite-Biotite-Calcite-Quartz-Garnet ACC: Pyrite, Limonite SC: SCH
(319) I/C 11	0.092	+ 34 Muscovite-22 Biotite-22 Quartz-12 Plagioclase-9 Sillimanite + Sericite ACC: 2 Opaque, Chlorite SC: GN, RM
(320) S/S 77	0.102	Muscovite-Quartz-Biotite SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(321) I/C 169	0.105	+ 31 Muscovite-25 Plagioclase-21 Biotite-15 Quartz-6 Orthoclase ACC: 1 Opaque SC: GN
(322) S/S 106	0.151	+ Muscovite-Biotite-Quartz-Garnet-Pyrite ACC: Apatite SC: SCH
(323) S/L 32	0.155	+ Muscovite-Quartz-Graphite SC: SCH

Amphibolite Class

Code No.	% F	Minerals Present in Order of Abundance
(324) S/P 82	0.017	Hornblende-Quartz-Garnet-Biotite SC: POR, SCH, PM
(325) S/P 49	0.019	+ Hornblende-Quartz-Epidote-Biotite-Plagioclase-Calcite ACC: Sphene SC: SCH, PM
(326) S/P 6	0.020	Hornblende-Quartz-Epidote-Biotite
(327) S/P 51	0.022	+ Hornblende-Quartz-Epidote-Garnet-Plagioclase ACC: Sphene SC: POR, SCH, PM
(328) S/P 3	0.024	+ Hornblende-Epidote-Quartz SC: SCH

Code No.	% F	Minerals Present in Order of Abundance
(329) S/P 89	0.033	+ Hornblende-Quartz-Sphene-Garnet-Biotite ACC: Epidote, Apatite SC: POR, SCH, PM
(330) S/P 40	0.034	+ Hornblende-Quartz-Calcite-Epidote-Biotite ACC: Feldspar SC: SCH
(331) S/P 1	0.035	Hornblende-Quartz-Plagioclase-Pyrite SC: SCH
(332) S/P 36	0.035	+ Hornblende-Quartz-Calcite-Plagioclase-Garnet-Biotite ACC: Epidote SC: SCH
(333) S/P 57	0.036	+ Hornblende-Quartz-Garnet-Chlorite-Calcite-Muscovite ACC: Epidote?, Apatite? SC: POR, SCH
(334) S/P 4	0.036	Hornblende-Quartz-Garnet-Epidote SC: SCH
(335) S/P 91	0.037	+ Hornblende-Quartz-Sphene-Biotite-Garnet SC: POR, SCH
(336) S/P 81	0.041	+ Biotite-Quartz-Garnet-Hornblende-Pyrite ACC: Apatite SC: POR, SCH, RM?

Code No.	% F	Minerals Present in Order of Abundance
(337) S/P 35	0.043	+ Quartz-Hornblende-Biotite-Garnet-Muscovite-Sericite-Plagioclase-Chlorite-Calcite ACC: Apatite SC: POR, SCH, RM
(338) S/P 28	0.046	+ Quartz-Hornblende-Epidote SC: SCH
(339) S/P 16	0.047	+ Quartz-Hornblende-Garnet-Biotite-Plagioclase ACC: Apatite, Sericite SC: POR, FGN, PM
(340) S/P 46	0.052	+ Hornblende-Quartz-Garnet-Feldspar-Pyrite ACC: Apatite, Chlorite SC: SCH, RM?
(341) I/C 51	0.055	+ 54 Hornblende-40 Plagioclase-6 Sphene SC: SCH
(342) S/P 86	0.062	+ Hornblende-Quartz-Garnet-Magnetite ACC: Apatite, Epidote SC: POR, SCH, PM

Calc-Silicate Class

Code No.	% F	Minerals Present in Order of Abundance
(343) I/C 24	0.034	+ 70 Calcite-21 Serpentine-9 Phlogopite ACC: Chlorite, Sulfide SC: RM

Code No.	% F	Minerals Present in Order of Abundance
(344) S/P 94	0.065	+ Quartz-Calcite-Muscovite-Graphite-Biotite-Pyrite-Chlorite SC: SCH
(345) I/C 1	0.081	+ 45 Calcite-26 Orthoclase + Plagioclase-12 Diopside-7 Tremolite-6 Biotite-4 Quartz ACC: Sphene SC: HORN?
(346) S/P 55	0.101	+ Quartz-Epidote-Muscovite-Biotite-Calcite-Chlorite ACC: Apatite SC: SCH
(347) I/C 3	0.155	Calcite-Feldspar-Diopside-Tremolite-Biotite-Quartz

Marble Class

Code No.	% F	Minerals Present in Order of Abundance
(348) S/P 93	0.009	+ Calcite-Graphite-Quartz
(349) I/C 8	0.015	+ 91 Calcite-4 Quartz-6 Sulfide

Migmatite Class

Code No.	% F	Minerals Present in Order of Abundance
(350) F/MC 17	0.088	+ 59 Plagioclase + Alkali Feldspar-34 Quartz-6 Biotite-1 Muscovite

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Chapter II -6

Possible Relations between Fluoride and the Constituent Minerals of Some Metamorphic Rocks

The writer has not yet made fluoride determinations on metamorphic minerals. But it is possible to make some tentative conclusions based on the relative abundance of the constituent minerals of these rocks, Although more volume percent data must be made available, the writer believes on the basis of the calculations below that volume percent data alone are of little value in bringing to light fluoride distribution in metamorphic minerals.

General Relationships:- It is clear from the frequency distribution of fluoride in the quartzite, psammitic semi-pelite, semi-pelite, and pelite classes (cf. Chapter II -8) and from the definitions of these classes (cf. Chapter II -4) that the fluoride content increases as the sum of the volume percents of aluminous and femic minerals increases relative to the quartz plus feldspar. Although the overlap in fluoride abundances for the psammitic semi-pelite and semi-pelite classes may be in part due to errors in estimation of the relative abundances of the constituent minerals, this overlap is a suggestion that the fluoride content of rocks is not linearly related to either one or the sum of aluminous and femic minerals present.

Taking the simple case in which rocks of the semi-pelite class having quartz plus feldspar as the two most abundant minerals and comparing their fluoride contents with rocks having quartz (or feldspar) plus biotite and quartz (or feldspar) and muscovite as the two most abundant elements, it is evident that the range and average fluoride for each of these subclasses are not significantly different:

	Avg. % F	Range
Quartz-Feldspar	0.061	0.017-0.090
Quartz (or Feldspar)-Muscovite	0.058	0.020-0.095
Quartz (or Feldspar)-Biotite	0.066	0.044-0.093

The range of samples in each class is 26 to 30. The average semi-pelite contains 0.060 percent fluoride (cf. Chapter II -8).

Similarly, no clear correlations between the abundance of hydroxyl minerals and the fluoride content of amphibolites are discernible.

Quantitative Considerations:- Point count determinations have been made for 20 rocks, as mentioned elsewhere. Using the volume percent data and assuming 1) that fluoride is entirely present replacing the hydroxyl ion and 2) that for these calculations volume percents are approximately equal to the weight percents (3), and ignoring accessory amounts of hydroxyl-bearing minerals, it is possible to make some calculations giving magnitudes of fluoride in certain minerals.

Discounting analytical errors and considering the fluoride content of the muscovite in rock serial number (001) equal to that in serial number (006), the biotite must contain 0.12 percent fluoride to account for all of that element in (006). Proceeding in an analogous manner, the biotite in rock serial number (186) contains 0.17 percent fluoride; if the biotite in (021) has the same amount, the muscovite must have 0.05 percent fluoride.

In six granites Seraphim has found that the mean fluoride content of the biotites, 1.45 percent, is about 9 times that of the muscovites, 0.17 percent (4). Butler found that this same ratio in a Cornish adamellite is nearly 5 to 1 (1). The migmatite, serial number (350), whose feldspar contents are probably equal and whose mineral abundances are similar to those in granites (3), might have like ratios for fluoride in the biotite and muscovite. Assuming the percent fluoride ratio is 4 to 1 and 10 to 1, the fluoride contents are 1.4 and 0.4 and 1.4 and 0.14 percent, respectively, for biotite to muscovite.

Although with limitations, the above calculations show how great the fluoride range in biotite might be, a range evidenced by other work (1, 2, 4).

Examination of the volume percent data supports the considerations mentioned in the section on general relationships; that is, the positive correlation of fluoride content to the sum of femic and aluminous minerals appears only as a trend going from the quartzite through the pelite classes.

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Chapter II -7

The Relations between the Fluoride Content, Major Constituents of 30 Metamorphic Rocks, and the Grade of Metamorphism

Introduction:- Soon after the writer developed his fluoride method (cf. Chapter I -3, section a), he decided to analyze a suite of rocks for the major constituents, for a chemical characterization would be invaluable in relating fluoride abundance to the mineralogy and grade of metamorphism. Such data would also help to ascertain whether the rocks are sedimentogenic. The writer chose the rapid methods of Shapiro and Brannock (10), but he found in tests on synthetic solutions and standard rock and mineral samples that two of their procedures were not reliable and two others had to be modified because the necessary equipment was not in Durham. Consequently, he had to spend some time making modifications, which are described by Cobbing (1). In tests of the modified procedures on G-1 and W-1, carried out as a check prior to doing the 30 samples, all of the S/S series, the writer obtained results that agreed favorably with the accepted values (10).

The summation is not usually near 100 percent; as the silica content of these 30 rocks decreases, so does the summation. One or two rocks sum only to about 87 percent. The total water, not determined, may account for about 2 percent and the writer's finding that the alumina method gave low results may account for 2 to 3 percent alumina for the pelitic types. But to account for the 5 to 8 percent remaining is difficult. The coprecipitation of magnesium with the mixed oxide group and that of magnesium by calcium tungstate may be sources of error. On the other hand, the acceptable values obtained for G-1 and W-1 are not reconcilable to such errors.

The results reported are averages of duplicate determinations for all constituents except for the alumina, for which oxide the higher result was taken. The precision for each oxide is at least as good as that reported by Mercey for rapid methods (5).

Predicted Relations between Fluoride and Major Constituents in Sedimentary Rocks:- Since there is much evidence to suggest the Dalradian series are sedimentogenic, it is worth investigating briefly the relations between sedimentary rock type and the fluoride abundance. Of first order consideration is a calculation based on the total amount of igneous rock weathered in geologic time, reckoned by Goldschmidt (6) to be 160 kilograms of rock per square centimeter of earth's surface. Using his figure, 278 kilograms of sea water per square centimeter of earth's surface, about 800 p.p.m. of fluoride in the average igneous rock (2), and 1.4 p.p.m. in sea water, it can be calculated that less than 0.2 percent of the fluoride in the weathered rock remains in sea water; that is, over 99 percent of the fluoride derived from this material finds its way into the sediments. Second, the tabulations given by Correns (2) show fluoride is more abundant in the pelitic than in the psammitic members, a relation not surprising in view of the high values for fluoride in certain clays (2, 9). Moreover, some of the hydroxyl minerals, found definitely to contain fluoride; e.g., kaolinite, sericite, chlorite, illite, montmorillonite, and muscovite, are capable of exchanging hydroxyl for fluoride in laboratory conditions (3, 4, 7, 8). Thus, from the chemical compositions of fluoride-containing minerals common in sedimentary rocks, the fluoride might well be positively correlated with the alumina, ferric oxide, magnesium oxide, and potash contents of the rock. The resistate fraction would have the effect of diluting the fluoride concentration.

The reasonableness of the positive correlations is evident from the fact that fluoride forms stable complexes and insoluble compounds with elements classed as hydrolyzates (6). The writer has reviewed work on the stability constants of AlF_x^{3-x} and FeF_x^{3-x} in Chapter I -2; possibly, since aluminum, ferric hydroxide, and titanium dioxide hydrate colloids can be positively charged (6), the negative fluoride ion may be adsorbed on them, although the writer knows of no work showing adsorption is appreciable for elements forming a stable complex with the colloid-forming element. However, adsorption is strongest for elements that form an insoluble compound with the colloid-forming element (6); the positively charged zirconium dioxide hydrate and thorium dioxide hydrate colloids may thus have a significant role in concentrating fluoride in hydrolyzate sediments.

Correlations Found:- For the thirty analyzed rocks the regression of fluoride on eight major oxides and the correlation coefficients were obtained by programming on the Ferranti "Pegasus" Computer. These data are given in figures 1 through 8, and show the correlations are very significant between fluoride and the silica, alumina, total iron as ferric oxide, magnesium oxide, potash, and titanium dioxide contents. Moreover, the position of the Y -intercept relative to the origin for each of these oxides can be simply explained on the assumption these samples are sedimentogenic.

Fluoride Abundance and the Grade of Metamorphism:- Four sets of analyses (cf. Tables I and II) consist of rocks having similar bulk chemical compositions:

Set 1. Two rocks in the semi-pelite class, S/S 35 and S/S 89, having 0.079 to 0.093 percent fluoride.

Set 2. Two semi-pelite plus one psammitic semi-pelite members, S/S 30 and S/S 34 plus S/S 33, respectively, having 0.052-0.054 percent fluoride.

Set 3. Four psammitic semi-pelite members, S/S 10, S/S 58, S/S 83, and S/S 73, the first three having 0.033 to 0.042 and the last 0.063 percent fluoride.

Set 4. Three psammitic semi-pelite members, S/S 43, S/S 60, and S/S 78, having 0.025 to 0.030 percent fluoride.

From the mineralogy (cf. Chapter II -5) and the localities for the members of each set (map 1) there is no convincing evidence that fluoride is mobilized with increasing grade of metamorphism. But there is no clear evidence that fluoride is unaffected by grade either. For set 1 there is some suggestion that the mineral assemblage of S/S 89 represents a higher metamorphic grade, so some of the fluoride may have been mobilized to account for its lower value. On the other hand, S/S 10 is quite different mineralogically from S/S 83, one occurs in the garnet zone, the other in the staurolite zone, and yet the fluoride values are not significantly different. The high fluoride value for S/S 73 compared to that in S/S 10 runs opposite to the trend discussed for the two samples in set 1. The mineralogies for the samples in sets 2 and 4 are not very different.

Comparisons of S/S series rocks with Cobbing's analyzed samples (cf. Tables V through VII) cannot be made safely, for his psammitic semi-pelite members have potash dominant over soda and semi-pelite ones have much higher alumina and potash contents (1). Comparison's within Cobbing's semi-pelites are not possible, for the few analyses show appreciable variations in some oxides. Cobbing (1) found from analyses of hornfelsed semi-pelites that no metasomatism took place. That there are no significant differences in the average and range of fluoride values corroborates this observation.

<u>Fluoride Contents of Meta-Sediments Compared with Those of Sediments</u>:- Nineteen samples of the analyzed S/S rocks are doubtless greywackes (cf. Tables I and II, also Chapter II -8). The average fluoride content of 17 greywackes, tabulated by Correns (2), is 40 p.p.m., which is low compared to the average fluoride, 0.029 percent, for the 19 meta-greywackes. The range of fluoride is 0.006 to 0.055 percent. A

fluoride value based on a composite of the 11 analyzed semipelites and pelites of the S/S and I/C series (the hornfelses were excluded), 0.075 percent, is close to a composite of values for clays tabulated by Correns (2). Seraphim (9) reported an average fluoride of 750 p.p.m. for 9 shales.

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Table I

Analyses of Psammitic Semi-Pelites

Code No. Ser. No.	S/S 7 (015)	S/S 12 (026)	S/S 97 (048)	S/S 51 (082)	S/S 54 (081)
<u>Oxide</u>					
SiO_2	82.7	83.5	81.7	76.3	81.2
Al_2O_3	6.7	8.5	9.6	12.0	10.2
$Fe_2O_3^a$	1.6	2.4	3.0	3.3	2.6
MgO	1.0	0.4	0.3	0.9	0.6
CaO	2.6	0.6	2.0	1.9	1.3
Na_2O	2.6	2.6	2.5	3.2	2.5
K_2O	0.5	0.6	0.6	1.4	1.3
TiO_2	0.08	0.37	0.66	0.39	0.35
MnO	0.05	0.02	0.04	0.03	0.03
P_2O_5	0.01	0.02	0.02	0.01	0.01
F	0.006	0.011	0.017	0.024	0.024
Total	97.9	99.0	100.5	99.5	100.2

a: Total iron as ferric oxide

Table I

Analyses of Psammitic Semi-Pelites

Code No.	S/S 78	S/S 43	S/S 46	S/S 21	S/S 60
Ser. No.	(085)	(087)	(113)	(125)	(122)
<u>Oxide</u>					
SiO_2	74.7	73.5	75.8	72.4	75.0
Al_2O_3	11.7	14.2	12.3	12.6	12.8
Fe_2O_3[a]	3.9	4.0	3.9	5.1	3.2
MgO	1.2	0.6	0.9	0.9	0.6
CaO	1.4	1.0	2.2	0.9	2.0
Na_2O	3.1	2.6	1.5	0.2	2.4
K_2O	2.0	2.3	1.3	2.4	1.6
TiO_2	0.52	0.59	0.43	0.61	0.68
MnO	0.03	0.04	0.01	0.05	0.04
P_2O_5	0.00	0.05	0.02	0.06	0.00
F	0.025	0.025	0.029	0.030	0.030
Total	98.6	98.9	98.4	95.1	99.3

a: Total iron as ferric oxide.

Table I

Analyses of Psammitic Semi-Pelites

Code No.	S/S 25	S/S 42	S/S 58	S/S 91	S/S 48
Ser. No.	(135)	(134)	(139)	(137)	(150)
<u>Oxide</u>					
SiO_2	66.0	74.0	67.5	77.4	72.0
Al_2O_3	14.7	14.2	14.8	11.8	13.8
Fe_2O_3[a]	6.3	3.2	4.5	2.7	4.5
MgO	1.0	0.9	1.5	0.5	1.1
CaO	0.9	1.6	1.4	3.2	2.5
Na_2O	0.6	2.9	3.1	2.3	3.8
K_2O	2.0	2.3	3.2	0.9	1.4
TiO_2	0.65	0.39	0.61	0.45	0.65
MnO	0.15	0.03	0.02	0.06	0.02
P_2O_5	0.09	0.00	0.03	0.12	0.03
F	0.032	0.032	0.033	0.033	0.035
Total	92.5	99.6	96.7	99.5	99.9

a: Total iron as ferric oxide.

Table I

Analyses of Psammitic Semi-Pelites

Code No. Ser. No.	S/S 83 (155)	S/S 10 (175)	S/S 53 (181)	S/S 33 (198)	S/S 82 (197)
<u>Oxide</u>					
SiO_2	67.0	67.3	69.1	62.4	80.0
Al_2O_3	14.7	14.8	14.1	15.0	9.5
Fe_2O_3[a]	5.5	6.0	4.8	6.0	1.7
MgO	1.5	3.0	1.3	2.1	0.7
CaO	2.3	1.0	2.7	1.9	1.8
Na_2O	4.0	3.9	3.0	1.1	2.4
K_2O	2.8	2.8	1.8	1.5	1.3
TiO_2	0.93	0.77	1.01	0.88	0.42
MnO	0.06	0.06	0.08	0.09	0.03
P_2O_5	0.13	0.14	0.11	0.13	0.00
F	0.037	0.042	0.044	0.054	0.054
Total	98.9	99.8	98.0	91.2	97.9

a: Total iron as ferric oxide.

Table I

Analyses of Psammitic Semi-Pelites

Code No. Ser. No.	S/S 56 (201)	S/S 45 (203)	S/S 73 (206)	S/S 44 (208)
Oxide				
SiO_2	64.2	70.9	67.9	64.4
Al_2O_3	15.2	13.1	14.4	15.2
Fe_2O_3 [a]	6.6	6.0	5.6	7.7
MgO	1.7	1.9	1.7	2.6
CaO	2.7	1.8	2.4	1.5
Na_2O	3.3	1.9	3.3	1.5
K_2O	2.2	2.3	2.3	4.1
TiO_2	0.74	0.57	0.76	0.78
MnO	0.13	0.05	0.07	0.10
P_2O_5	0.13	0.08	0.05	0.09
F	0.055	0.057	0.063	0.064
Total	96.9	98.7	98.6	98.1

a: Total iron as ferric oxide.

Table II

Analyses of Semi-Pelites

Code No. Ser. No.	S/S 30 (244)	S/S 34 (250)	S/S 49 (262)	S/S 89 (300)	S/S 35 (308)
Oxide					
SiO_2	63.4	63.2	57.3	52.5	52.6
Al_2O_3	14.9	14.4	15.3	16.4	16.3
$Fe_2O_3{}^a$	8.2	9.6	8.5	8.9	9.7
MgO	2.4	2.2	2.3	2.9	3.1
CaO	0.5	1.7	1.8	1.1	2.0
Na_2O	0.9	2.0	1.6	1.6	3.4
K_2O	2.6	3.9	4.3	5.1	4.6
TiO_2	0.71	0.91	0.78	1.16	1.27
MnO	0.05	0.07	0.10	0.11	0.12
P_2O_5	0.08	0.22	0.14	0.09	0.19
F	0.054	0.057	0.062	0.079	0.093
Total	93.8	98.2	92.2	90.0	93.4

a: Total iron as ferric oxide.

Table III

Analysis of a Pelite

Code No. Ser. No.	S/S 41 (314)
Oxide	
SiO_2	46.2
Al_2O_3	17.0
Fe_2O_3[a]	10.4
MgO	3.7
CaO	1.1
Na_2O	2.5
K_2O	5.9
TiO_2	1.01
MnO	0.14
P_2O_5	0.14
F	0.081
Total	88.1

a: Total iron as ferric oxide.

Table IV

Analysis of a Quartzite

Code No. Ser. No.	I/C 35 (001)
Oxide	
SiO_2	93.0
Al_2O_3	2.3
Fe_2O_3[a]	0.5
MgO	0.5
CaO	0.5
Na_2O	0.1
K_2O	3.4
TiO_2	0.0
MnO	0.0
P_2O_5	0.0
F	0.001
Total	100.3

[a]: Total iron as ferric oxide.

Table V

Analyses of Psammitic Semi-Pelites

Code No. Ser. No.	I/C 240 (021)	I/C 170 (186)
Oxide		
SiO_2	81.7	69.0
Al_2O_3	7.6	14.3
Fe_2O_3[a]	1.2	4.5
MgO	1.4	2.0
CaO	2.7	1.7
Na_2O	1.0	2.7
K_2O	4.0	3.6
TiO_2	0.0	0.6
MnO	0.0	0.18
P_2O_5	0.19	0.16
F	0.008	0.050
Total	99.8	98.8

a: Total iron as ferric oxide.

Table VI

Analyses of Semi-Pelites

Code No.	I/C 222	I/C 179	I/C S3	I/C H16	I/C 89	I/C 154
Ser. No.	(241)	(287)	(297)	(298)	(303)	(304)
Oxide						
SiO_2	56.4	55.1	52.4	53.0	56.1	54.0
Al_2O_3	19.8	18.4	19.0	19.2	18.7	19.0
Fe_2O_3[a]	11.5	8.0	11.1	11.1	7.4	8.0
MgO	2.2	2.4	3.2	1.8	2.0	1.6
CaO	2.8	4.4	4.5	3.4	3.7	5.0
Na_2O	1.9	2.2	1.4	2.2	2.4	2.7
K_2O	4.2	7.2	4.8	5.9	6.2	5.3
TiO_2	0.16	0.72	0.20	0.17	0.69	0.68
MnO	0.10	0.08	0.29	0.18	0.18	0.04
P_2O_5	0.02	0.17	0.26	0.35	0.30	0.20
F	0.052	0.069	0.077	0.078	0.082	0.086
Total	99.1	98.7	97.2	97.2	97.8	96.6

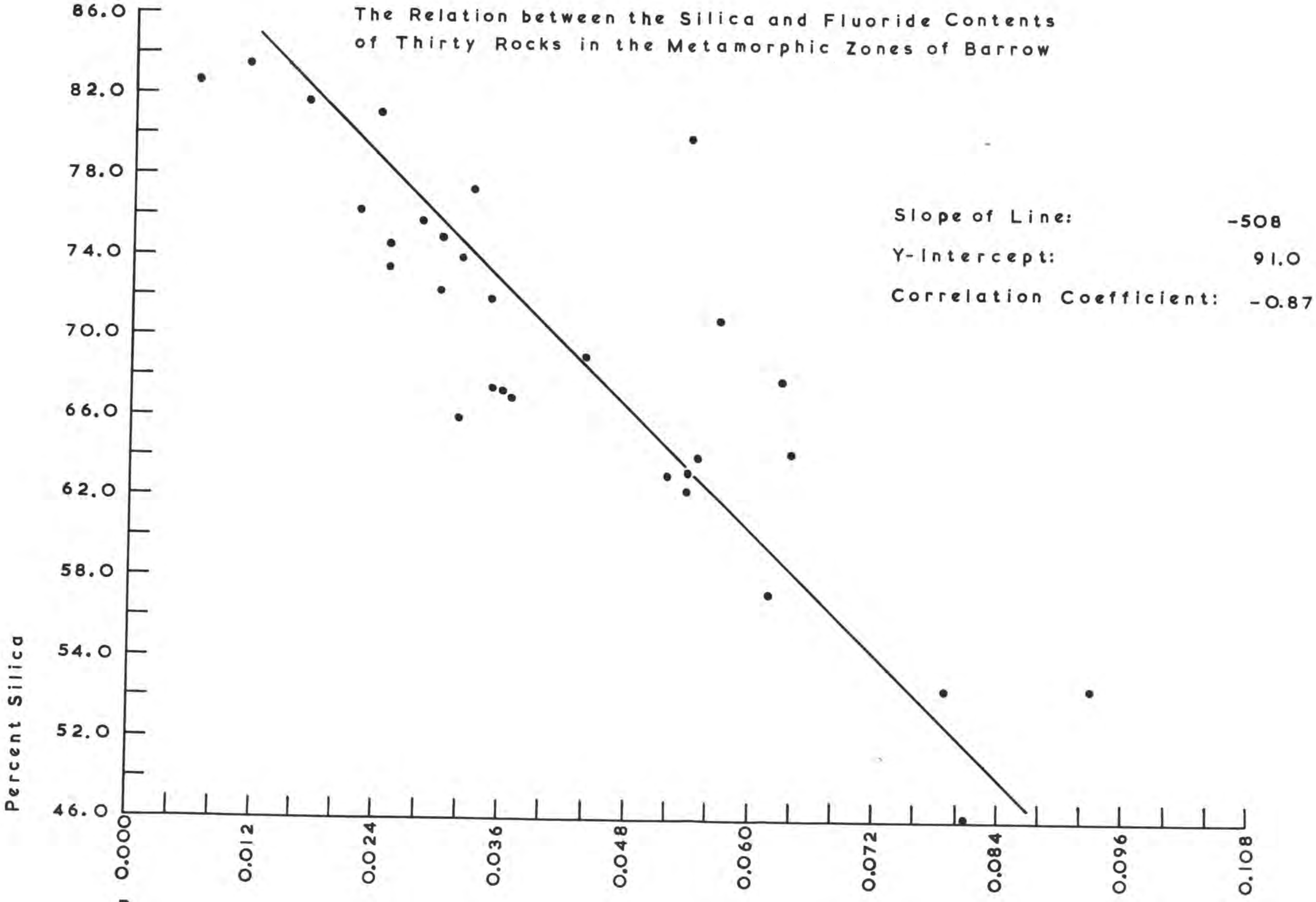
a: Total iron as ferric oxide.

Table VII

Analysis of a Pelite and an Amphibolite

Code No. Ser. No.	I/C 169 (321)	I/C 51 (341)
Oxide		
SiO_2	54.3	46.6
Al_2O_3	18.1	14.6
Fe_2O_3 [a]	6.93	10.0
MgO	6.6	7.1
CaO	1.7	15.5
Na_2O	1.9	2.2
K_2O	7.7	2.7
TiO_2	0.80	1.90
MnO	0.14	0.12
P_2O_5	0.24	0.45
F	0.105	0.055
Total	98.5	101.2

a: Total iron as ferric oxide.



The Relation between the Silica and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow

Slope of Line: -508

Y-Intercept: 91.0

Correlation Coefficient: -0.87

FIGURE 2

The Relation between the Alumina and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow

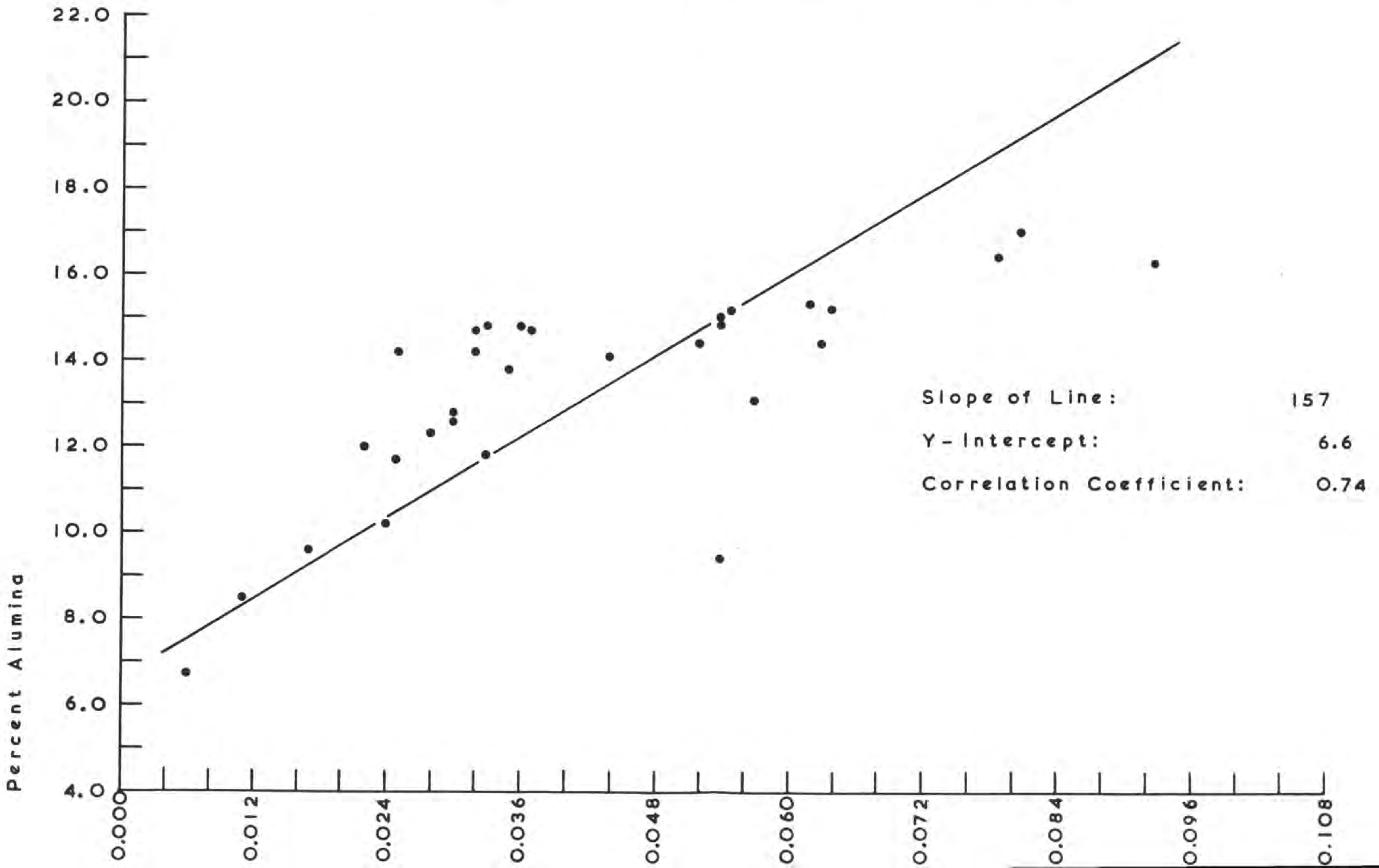
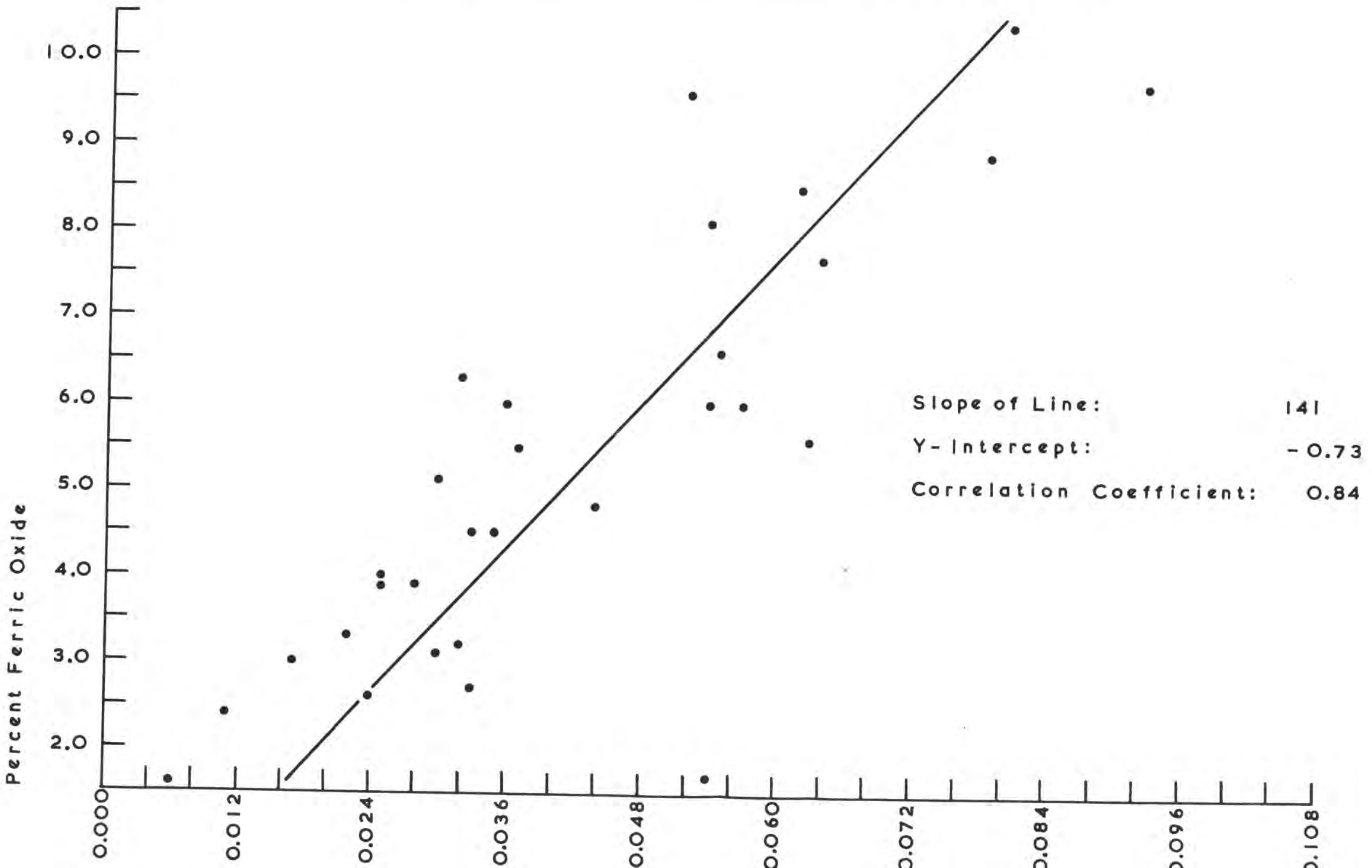
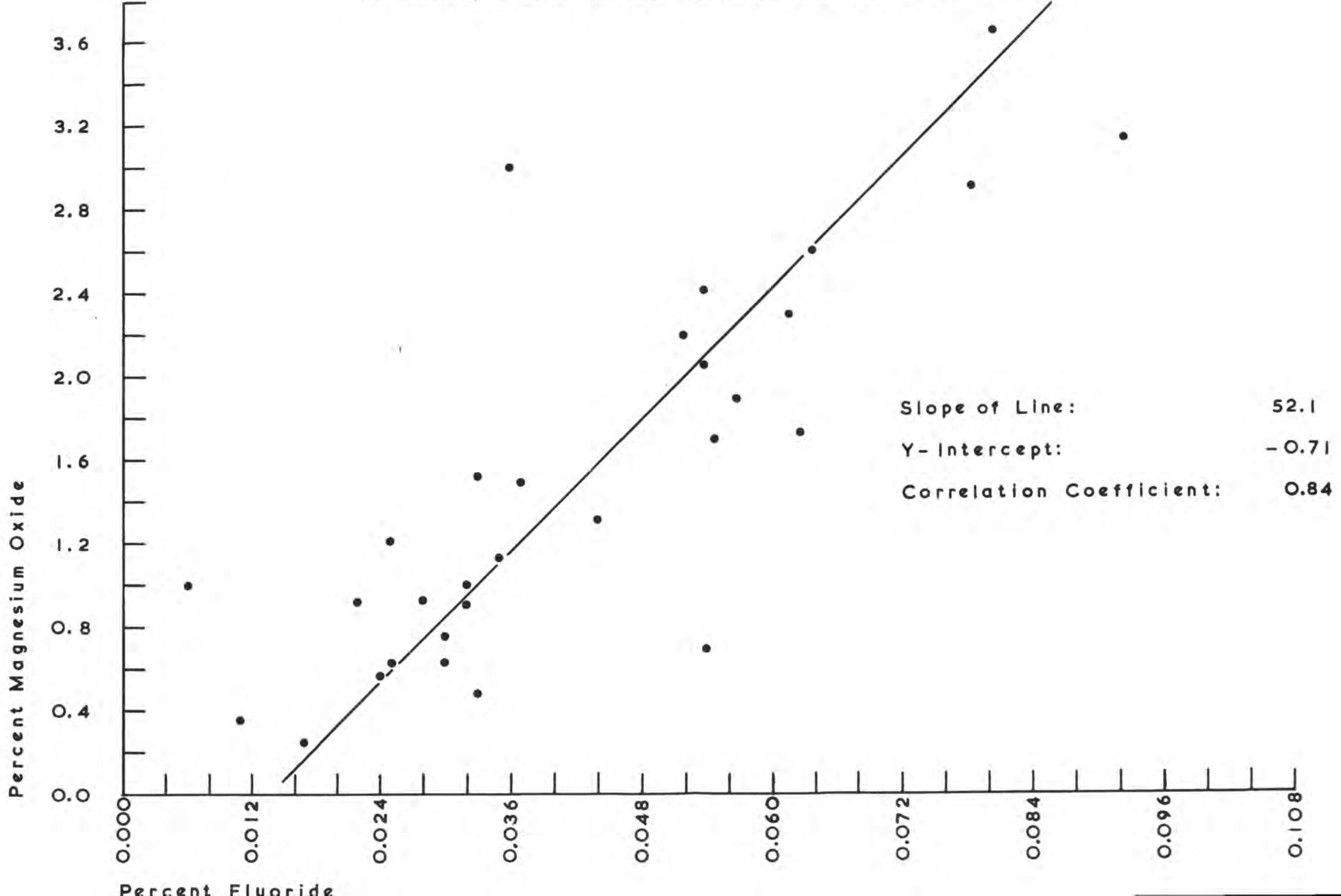


FIGURE 3

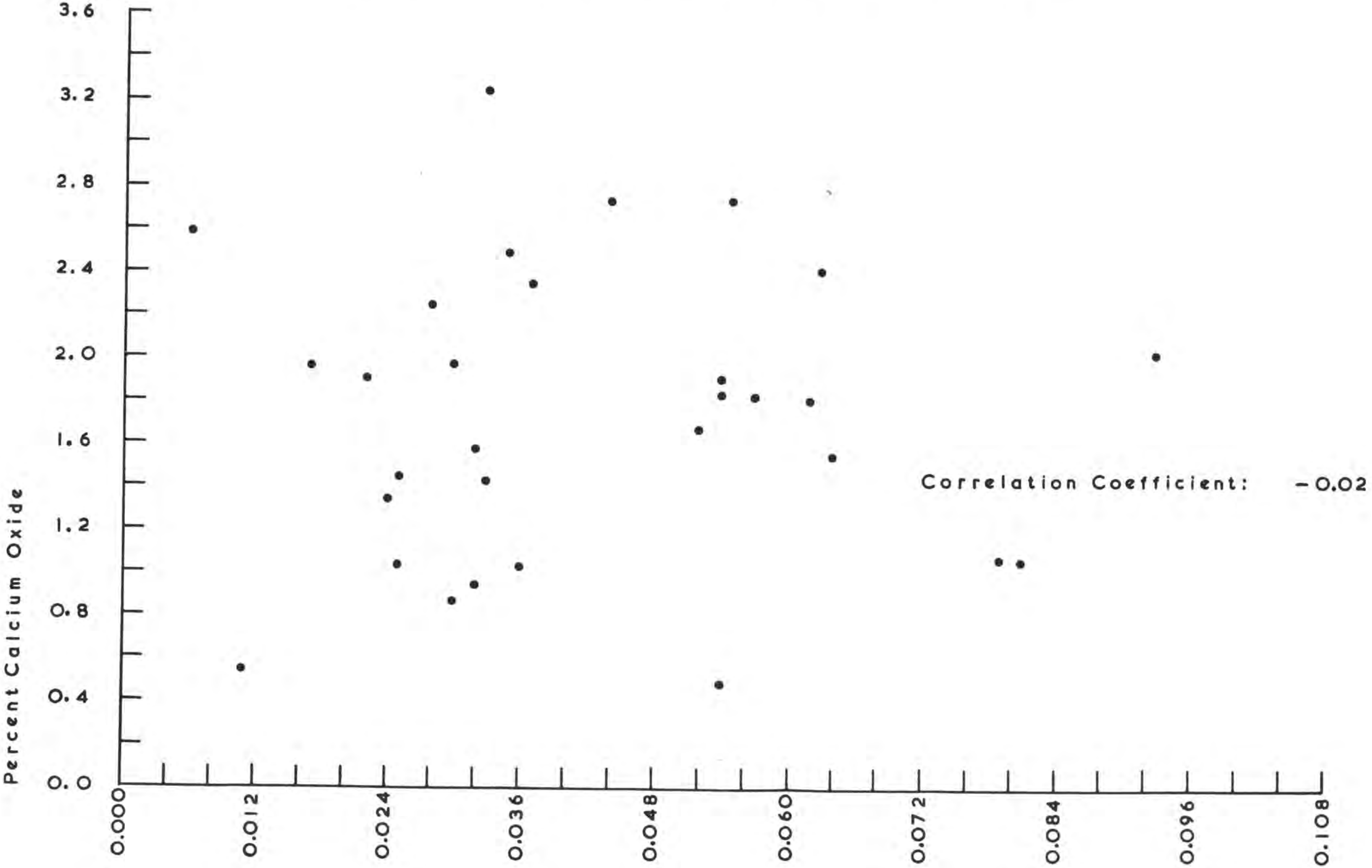
The Relation between the Total Iron as Ferric Oxide and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow



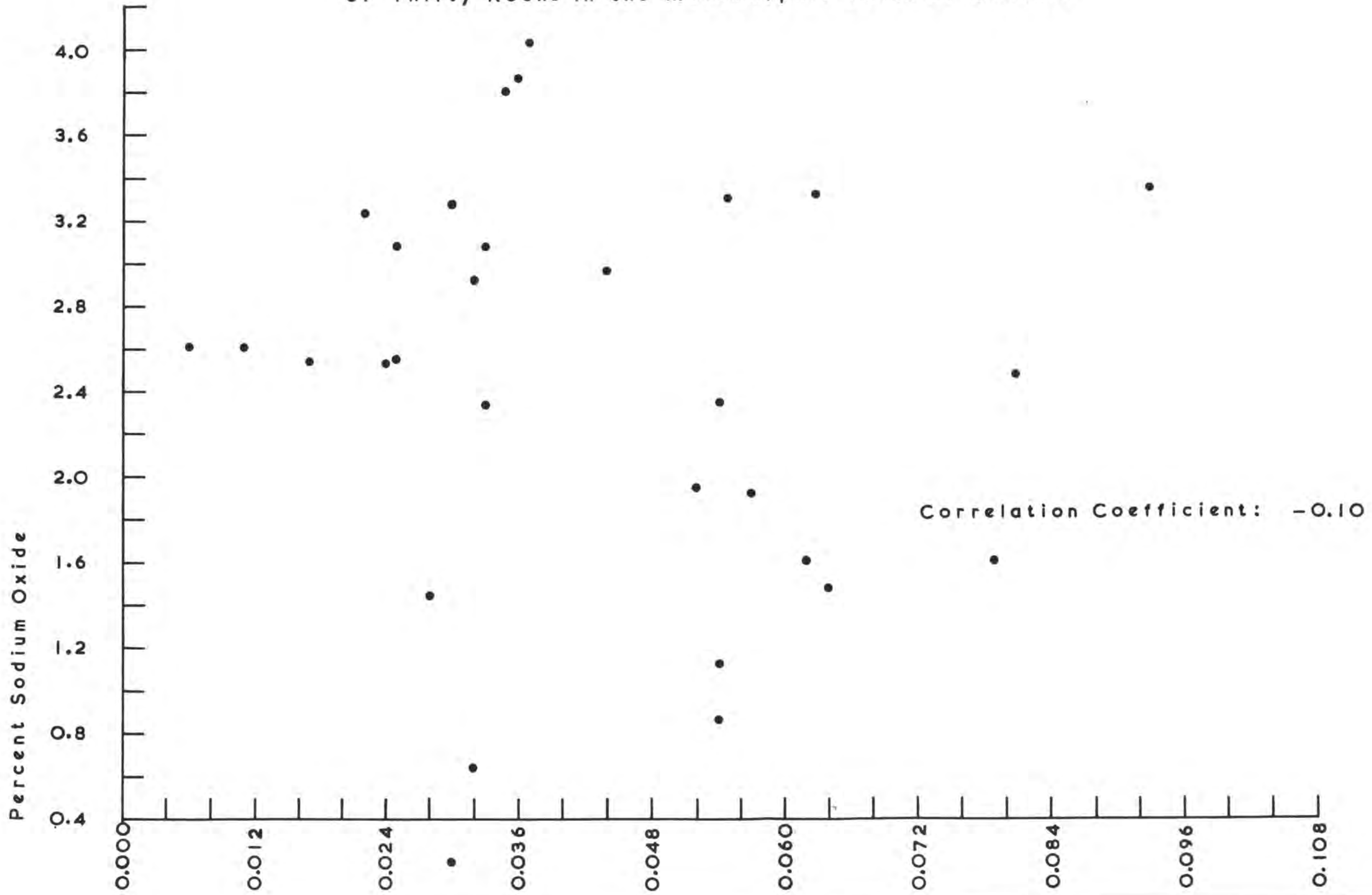
The Relation between the Magnesium Oxide and Fluoride Contents
of Thirty Rocks in the Metamorphic Zones of Barrow



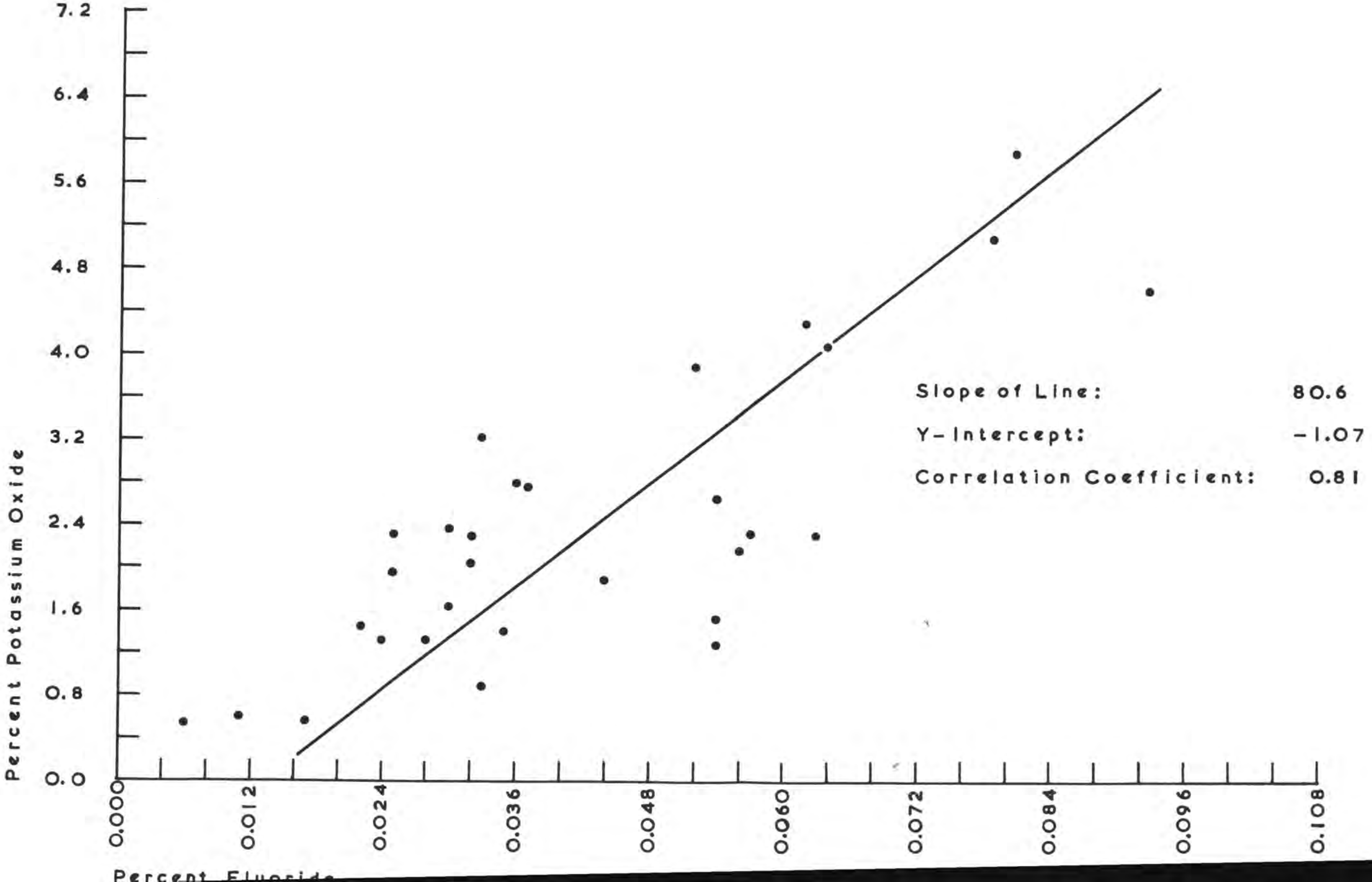
The Relation between the Calcium Oxide and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow



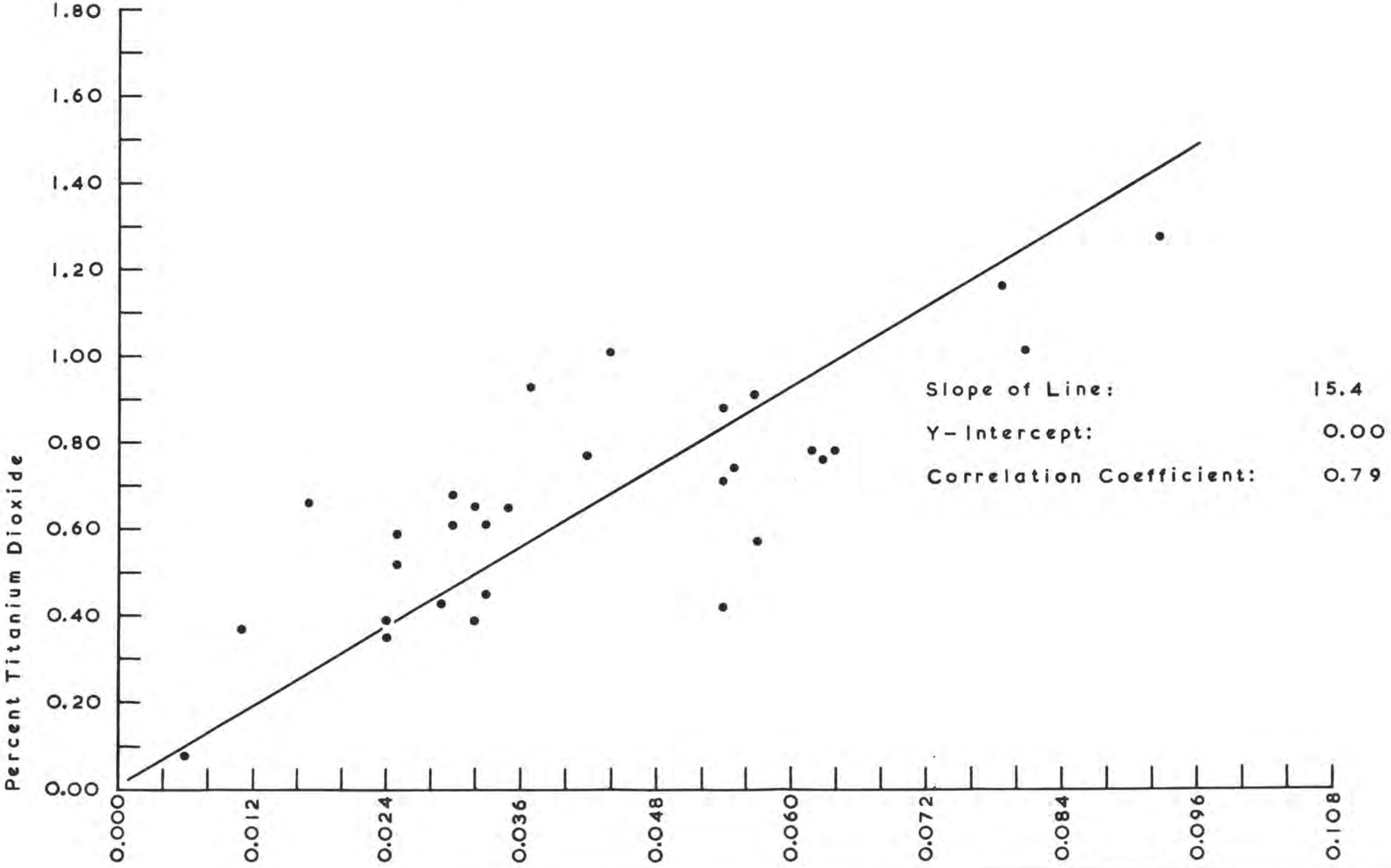
The Relation between the Sodium Oxide and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow



The Relation between the Potassium Oxide and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow



The Relation between the Titanium Dioxide and Fluoride Contents of Thirty Rocks in the Metamorphic Zones of Barrow



Chapter II -8

Data on the Geochemistry of Fluoride in the Eight Major Classes of Para-Metamorphic Rocks and in the Five Metamorphic Terranes

The Eight Classes of Metamorphic Rocks:- The principal reason the writer classified the 350 rocks was that he wished to ascertain whether fluoride leaves or enters certain metamorphic rock systems as for example injection gneisses and hornfelses. Since other work had shown that the fluoride concentration in metasediments is most reasonably explained as a function of original sedimentary character (cf. Chapter II -7), it was necessary to minimize this variable in examining whether pressure, temperature, and allochemical processes affected fluoride concentration. The writer felt the system of classification adopted, based essentially on the ratio of femic and aluminous minerals to quartz and feldspar, although possessing some drawbacks, would serve to account for the bulk chemical composition function.

A chemical characterization of the writer's metamorphic rock classes is based on the analyzed S/S and I/C series samples (cf. Tables I through VII). A comparison of analyses for the former series and sedimentary rock analyses and criteria given by Pettijohn (2) shows that:

1. psammitic semi-pelite members include meta-greywackes, as is evident from the soda to potash ratios for S/S 7, 10, 12, 42, 43, 46, 48, 51, 53, 54, 56, 60, 73, 78, 82, 83, 91, and 97. S/S 58 is considered to be a meta-greywacke also. S/S 33 and 45 could be meta-subgreywackes or micaceous sandstones, and

S/S 21 and 25 could be meta-feldspathic sandstones. The composition of S/S 44 resembles the composite of 12 phyllites from central Norway (3).

2. semi-pelite members show similarities with shales (2, page 344, columns D and E).

3. the one member of the pelite class, S/S 41, is also equivalent to a shale, but having a higher clay fraction.

Cobbing (1) was able to show that some I/C members of the semi-pelite class are chemically equivalent to winter varves (2, page 345) and potash-rich shales (2, page 370). One psammitic semi-pelite is similar chemically to a silty clay from the Mississippi delta (2, page 344) and the other psammitic semi-pelite to a protoquartzite.

Tables of Results by Classes:- Listed below are the data on fluoride abundance for the eight major classes of metamorphic rocks.

Table I

Fluoride Abundance in the Quartzite Class

	Avg. % F	No. of Samples
Average Quartzite	0.012	14
I/C series members	0.004	3
S/S series members	0.006	1
S/P series members	0.016	9
S/T series members	0.005	1

Table II

Fluoride Abundance in the Psammitic Semi-Pelite Class

Average Psammitic Semi-Pelite	0.031	199
I/C series members	0.029	2
S/S series members	0.034	86
S/P series members	0.034	32
S/L series members	0.031	41
S/T series members	0.023	38

Table III

Fluoride Abundance in the Semi-Pelite Class

	Avg. % F	No. of Samples
Average Semi-Pelite	0.060	97
I/C series members	0.070	12
S/S series members	0.063	24
S/P series members	0.066	5
S/L series members	0.049	20
S/T series members	0.062	35
F/MC series members	0.057	1

Table IV

Fluoride Abundance in the Pelite Class

Average Pelite	0.094	13
I/C series members	0.099	2
S/S series members	0.087	9
S/L series members	0.121	2

Table V

Fluoride Abundance in the Amphibolite Class

	Avg. % F	No. of Samples
Average Amphibolite	0.037	19
I/C series members	0.055	1
S/P series members	0.036	18

Table VI

Fluoride Abundance in the Calc-Silicate Class

Average Calc-Silicate	0.087	5
I/C series members	0.090	3
S/P series members	0.083	2

Table VII

Fluoride Abundance in the Marble Class

Average Marble	0.012	2
I/C series member	0.015	1
S/P series member	0.009	1

Table VIII

Fluoride Abundance in the Migmatite Class

	% F	No. of Samples
F/MC series member	0.088	1

Tables of Results by Subclasses:- Below the data on the subclasses of the Psammitic Semi-Pelite and Semi-Pelite classes are tabulated. For the other classes there is not sufficient subclass data to warrant summarizing in this form.

Table IX

Fluoride Abundance in Textural and Genetic Subclasses of the Psammitic Semi-Pelites

Subclass	Avg. % F	No. of Samples
GRA	0.039	7
FGN	0.029	54
BLAS	0.032	30
SCH	0.036	17
POR	0.042	23
DISS	0.035	27
GN	0.023	8
IGN	0.028	11
HORN	0.033	1
PM	0.030	35
RM	0.034	35

Table X

Fluoride Abundance in Textural and Genetic Subclasses of the Semi-Pelites

Subclass	Avg. % F	No. of Samples
GRA	0.067	3
FGN	0.061	6
BLAS	0.047	3
SCH	0.064	38
POR	0.063	25
DISS	0.059	1
GN	0.054	23
IGN	0.061	13
HORN	0.071	3
PM	0.061	24
RM	0.060	21

Table XI

The Regional Distribution of Fluoride for Five Metamorphic Terranes

Area	Avg. % F	No. of Samples
I/C	0.060	24
S/S	0.044	120
S/P	0.036	67
S/L	0.040	63
S/T	0.041	74

Average Percent Fluoride in 348 Rocks: 0.042.

Range of Fluoride by Regions, Percent: 0.036 to 0.060.

The Frequency Distribution of Fluoride in Metamorphic Rocks:- Using the single analyses of fluoride in Chapter II -5, the frequency distribution was plotted at a 0.001 percent fluoride interval. See Figure 9. Omitted from this figure and subsequent computations are serial numbers (252), (350), (322), and (321). From the data in Figure 9 histograms at two different class intervals were prepared (Figures 10 and 11) for the 345 samples. The 0.004 class interval histogram, which interval just exceeds the 95 percent confidence limit for the method, shows a distinct positive skewness. This type of skewness has been recognized by other geochemists, the arguments on which need not be reviewed here. By calculating the relative frequency for each class interval and the range of relative frequencies expected at infinite sampling for the 95 percent confidence limit, it can be shown that the gaps at the 0.028-0.031, 0.044-0.047, and 0.060-0.063 class intervals are not significant (cf. Figure 11).

The Frequency Distribution of Fluoride in Certain Classes of Metamorphic Rocks:- There was sufficient data to make histograms for the psammitic semi-pelite and semi-pelite classes; these are given in figures 12 and 13, the class interval being again 0.004 percent fluoride. The relative frequencies were again calculated for each histogram. For figure 12 it was found from this calculation that although each class interval at 0.056-0.059 and above could at infinite sampling be nil, as a subclass of 12 members it was a significant group. Furthermore, the test for skewness shows clearly that the psammitic semi-pelite class is positively skewed. But the same test applied to the semi-pelite class shows the test results are compatible with the assumption the distribution is normal. It must be remembered that a normal distribution cannot be proved; one can state only that the distribution is "not skewed. Actually, the test for skewness for the semi-pelite group indicated an insignificant negative skewness.

Significance of the Frequency Distributions:- The system of rock classification adopted here is phenomenological. It is suggested that geologic processes consist of macro-phenomenological and micro-phenomenological parameters, which can be separated by classifications of the sort proposed. Such distinctions might enable workers to discern the effect of variables acting on the two classes of parameters.

Bibliography

1. Cobbing, E.J., "The Metamorphic Petrology and Structure of the District North West of Clifden, County Galway", Ph.D. thesis, University of Durham, 1959.

2. Pettijohn, F.J., "Sedimentary Rocks", 2nd ed., pp. 283-380, Harper and Brothers, New York, 1957.

3. Rankama, K., Sahama, Th.G., "Geochemistry", pp. 189-247, pg. 222, University of Chicago Press, Chicago, 1950.

Chapter II -9

Summary and Conclusions, Part II

1. Correlations of the fluoride present in a rock to the volume percents of individual minerals are apparent only as a broad trend developing from the quartzite class through the pelite class. But the correlation of the fluoride content either to one or to the sum of femic and aluminous minerals present are not distinct among members of either the psammitic semi-pelite or the semi-pelite classes.

2. Calculations suggest that biotite can accomodate a considerable range of fluoride content. The fluoride content of this mineral may be in part a function of the grade of metamorphism.

3. Analyses of 30 rocks from the Barrovian metamorphic zones show that correlations between their fluoride content and the silica, alumina, total iron as ferric oxide, magnesium oxide, potash, and titanium dioxide contents are significant. The correlations are those predicted for rocks of sedimentary origin, and their persistence suggests that regional metamorphism does not obscure the relation of fluoride to the oxides mentioned.

4. Corroboration of the sedimentary origin of the 30 analyzed rocks is found in their similarity chemically to certain analyzed sediments.

5. Examination of the abundance of fluoride for chemically similar rocks having different mineralogy and (or) occurring in different Barrovian zones indicates there are no certain relations to these parameters.

6. The average abundance of fluoride in 19 meta-greywackes and 4 meta-shales fits in the range of fluoride for greywackes and shales, respectively.

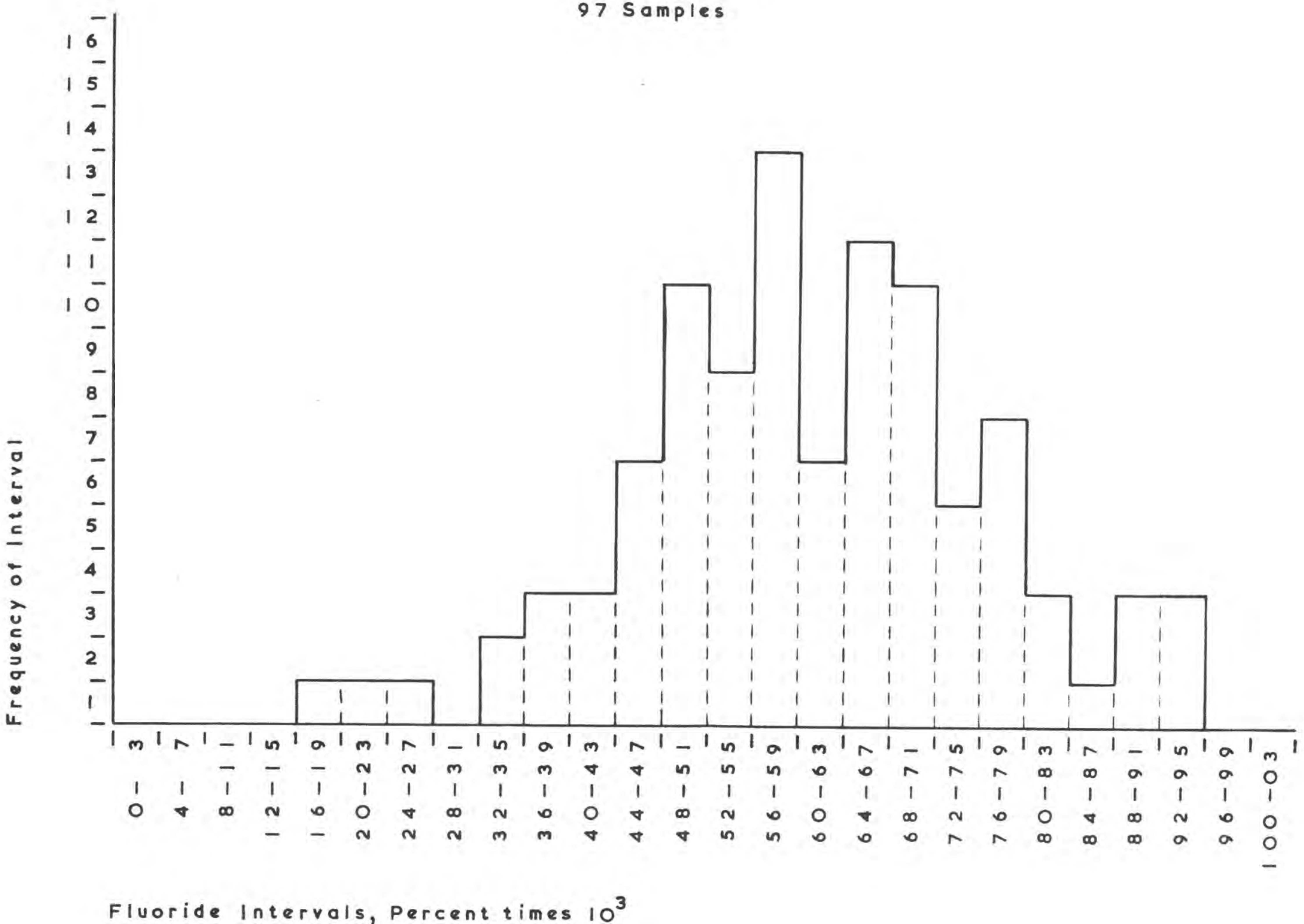
7. There is no regional variation of fluoride content for a given class of rock. But the higher average fluoride for the I/C series is significant when compared to the average fluoride for 345 metamorphic rocks. However, the difference is explainable by what is considered to be a different sedimentary environment compared with that for a number of the Scottish samples.

8. For a given class the fluoride content is not significantly different for various textural and genetic subclasses. Fluoride apparently does not take part in allochemical processes considered to be extant for some injection gneisses.

9. Although further work must be done with chemically analyzed rocks, the weight of evidence suggests fluoride content of these metamorphic rokcs is mainly a function of the original sedimentary rock type. That is, the abundance of fluoride is not affected by regional, injection, and thermal metamorphism in these areas.

The Frequency Distribution of Fluoride in the Semi–Pelite Class

97 Samples



Some Aspects of the Geochemistry of Fluorine in Metamorphic Rocks

Appendix III

A Thesis Submitted in Partial Fulfillment

of the Requirements for the Degree

of Doctor of Philosophy

Submitted in December 1960

by

Richard Peck Hollingworth

of Hatfield College in the University of Durham

CONTENTS

Appendix III

Detailed Procedures for Silicate Rock Analysis

Introduction:- The procedures are in the main those of Hillebrand, Lundell, Bright, and Hoffman. However, the writer has not given references to their work for each oxide; reasons for the omission are given in Chapter I -4. Such references given here are by page for Hillebrand, Lundell, Bright, and Hoffman's work and by name of author for others. The pages and names are listed in the Bibliography of Chapter I -4.

Preparation of Sample for Analysis:- See Hillebrand, Lundell, Bright, and Hoffman, pages 809 to 814 for the preparation of the sample. The writer uses a mortar consisting of a block and cylinder and a pestle essentially of Ellis' design. All parts are of specially chilled and surface-hardened steel. Crushing is effected by striking the pestle with a one-pound hammer, and is repeated on portions of the rock powder until the whole passes 60 meshes per inch silk bolting cloth and until more than three-quarters of it pass 110 meshes per inch. The fraction not passing is then ground in an agate mortar and pestle until it also passes 110 mesh per inch silk bolting cloth. The sieving is done gently in a sieve made of Perspex. Chips to be crushed in the percussion mortar and pestle are made by breaking the rock up on a steel plate with a light hammer, both of which are also made of hardened steel.

In tests on clear quartz crystals carried through chipping, crushing, and grinding operations, the writer has found the iron introduced is around 50 p.p.m. Sandell has found up to 300 p.p.m. iron in similar tests.

Fusion of the Sample:- Weigh to the nearest 0.1 milligram a 1.0 gram sample into a 35 milliliter capacity platinum crucible.[a+] For acid rocks add about 3 grams of micro analytical reagent grade sodium carbonate and mix thoroughly with a thin, clean, and dry glass rod, taking care, after mixing, to remove adhering particles from the rod with small portions of the flux.[b] Then sprinkle a layer of the flux on top of the sample so that the total weight of flux is 4 grams. For basic rocks mix the sample with about 5 grams of flux, and add another gram as a layer on the top. Set the crucible in a hole in an asbestos board; the hole should expose only the lower quarter of the crucible to the flame, and the board should be tilted so the flame gases may excape to one side of it.

Heat over a low flame, the crucible bottom showing but the faintest red for the first 15 to 30 minutes. Increase the heat gradually over the next one-half hour to one hour until the bottom of the crucible is red-orange. By gradually increasing the flame intensity once every 15-20 minutes or so, bring the entire exposed part of the crucible to a red-orange color. Continue to increase the heat slowly so as to avoid violet action, finally bringing the temperature to about 1000°C (crucible is orange at this temperature). Hold at this temperature for 15 to 60 minutes, and then bring to the

+ See footnotes, page 31.

full heat of the Meker. When it is judged that there is no or little further effervescence, transfer the crucible to a silica traingle, and bring the temperature upto 1200°C (full heat of the Meker^{c}). Fuse at this temperature for about 15 minutes, remove flame, and let crucible cool briefly. Cautiously remove the cover, and if the melt appears quiescent, return the Meker flame and fuse for another 15 minutes at 1200°C with the crucible cover removed, such treatment giving no further effervescence. The flames should not envelop the crucible; tilting the burner is usually necessary. If all operations have been carefully done, the melt should be confined to the lower quarter of the crucible, upper walls and lid should have but little splattered material, and the melt itself will appear "in the case of highly siliceous materials as a viscous liquid, occasionally almost clear, though generally more or less turbid. With less siliceous matter, the fusion is less pronounced, though this does not necessarily imply incomplete decomposition." Return the cover to the crucible, remove the flame, and allow the crucible and contents to cool thoroughly. Then heat the crucible quickly to about 300 to 400°C, and immediately plunge it for two-thirds of its depth into cold, distilled water, keeping the cover on for all operations. Allow to cool well, and then repeat the quick heating and plunging into water two times more. For the second and third heating heat quickly until the walls of the crucible just above the level of the cake begin to turn red, then plunge it into the water. The melt, appearing as a well-formed "pill", should now have a crack separating it from the crucible wall. By means of a rubbercushioned spatula, tap the crucible with its cover on until the "pill" is completely separated. The tapping must be so effected that the crucible is not at all deformed. Carefully invert the crucible in a 10 centimeter diameter platinum dish, and allow the fragments to slide into the dish. The removal of the "pill" is generally better from palladium-gold crucibles than from platinum ones; however, of greatest importance is that the crucibles be well blocked before the fusion is made.

<u>Determination of the Silicon Dioxide</u>:- To the platinum dish which should be covered with a borosilicate glass cover glass add about 100 to 150 milliliters of water just off the boil, and stir and agitate the melt fragments from time to time until the cake is well disentegrated. Compounds of iron form a sintered material; the analyst must be certain this material is well leached and is made fine. As the solution effervesces considerably on acidification, transfer it with washing of the platinum dish with water to an 800 milliliter capacity borosilicate glass beaker. Cover the beaker and add gradually under the lid in some excess dilute hydrochloric acid (1 + 1). Bring the solution to the boil; if the leaching of the cake has been carried out properly, fine material quickly dissolves, and the solution is nearly clear. Add one or two milliliters of ethyl alcohol to reduce manganate, chromate, and vanadate that might be present. If not reduced, these compounds will yield chlorine which will attack the platinum. The solution of the cake in the dish should require no more than one-half hour, and further

treatment in the beaker should not exceed 20 minutes.

Transfer the contents of the vessel to the platinum dish in which the solution of the cake was made, rinsing the beaker with one or two portions of hot water. Small amounts of silica adhering to the beaker are of no moment if the beaker is reserved and a second dehydration is to be made. Place the platinum dish on the steam bath and evaporate the contents to no more than apparent dryness, a state attained when the ferric salts are straw-yellow, but never reddish. Cover the dish, remove from the steam bath, let cool, and add in one smooth stroke under the cover 10 milliliters of hydrochloric acid, and then, after one or two minutes, 100 milliliters of hot water. Allow to stand on the bath for 5 to 10 minutes, and stir the solution occasionally. Filter by decantation at first. The silica should not be too coarse; if the solution of the cake in the platinum dish was thorough, there is in the writer's experience no need to crush it finer on filtering. If much iron is present, it may be advisable at this stage to add hydrochloric acid of half strength and heat. Then with the aid of the wash liquid, hot, dilute hydrochloric acid (5 + 95), bring the silica upon the filter. A film commonly remains on the dish; this and the dish should be washed, but the film need not be removed if a second dehydration is made.[d] Wash the main lot of silica with the hot, dilute acid until the color of the paper of the filter indicates removal of most of the iron. Then wash the dish and paper with hot water until the test for chloride is negative.

For acid rocks use at least twelve 10 milliliter portions of hot water before making the test; for basic rocks use somewhat greater amounts. Collect the filtrate and washings in the beaker used for the solution of the cake.

Boil the filtrate, transfer portions of it to the same platinum dish, and evaporate as before. Do not omit rinsing the beaker two to three times with hot water. When the contents of the dish are dry, cover, remove from the steam bath, and heat it in an oven for one hour at 110°C. Cool contents thoroughly, and add under the lid 10 milliliters of hydrochloric acid, and, one or two minutes later, 50 to 75 milliliters of hot water. Heat on the steam bath for 5 to 10 minutes, stirring occasionally. Filter immediately on a new and smaller paper, and wash with hot, dilute hydrochloric acid (1 + 99) and finally with hot water until the test for chloride is negative. Reserve the filtrate and washings in which there is still a small amount of silica. A film of silica usually adheres to the platinum dish; with a half circle of Whatman 41 filter paper, well soaked in water, swab the dish by pushing the paper about with a glass rod and then transfer it into a 35 milliliter capacity platinum crucible. Rinse the dish with one or two portions of hot water. Place the combined papers containing the silica in the platinum crucible, moisten them with a few drops of dilute sulfuric acid (1 + 4), and place in an oven at 105°C. Allow to dry overnight. Char the paper and oxidize carbon slowly, for otherwise carbides are likely to form. Turning of the crucible should be done carefully and as few times as possible, for light particles of silica might otherwise escape. The safest procedure is to remove the flame, let the crucible cool somewhat, cover it, and then turn it not more than through 90°. Oxidation of carbon is best done at dull red heat. When carbon has been fully removed, cover the crucible, set it upright in a silica triangle, and heat at 1200°C for 30 minutes. To avoid flames enveloping the crucible, use a tilted arrangement as for the fusion. Cool over a good desiccant, weigh while still covered, and repeat the ignition for 10 minute periods until constant weight is obtained. A tightly fitting crucible lid is imperative to avoid loss of silica by drafts; for the same reason when repeat ignitions are run, it is wise to heat the crucible slowly up to the desired temperature.

Correct for impurities in the ignited silica as follows: Moisten the silica with water added under the cover by means of a fine-tipped polythene pipet, then add a few milliliters of hydrofluoric acid in the same manner, and then two to five drops of dilute sulfuric acid (1 + 1), higher amounts of this acid being required according as the basicity of the rock increases. Place the crucible on a sand bath so that the bottom of it is at around 140°C. Swirl the contents occasionally. After copious fumes of sulfuric acid have come off for a minute or so, remove from the sand bath, and continue the fuming treatment with a low flame. The fuming should be done slowly; fumes of the acid should never billow swiftly out of the crucible. In fact, the fumes should be scarcely seen. After the exposed part of the crucible has been brought up to bright orange through gradual increase of flame intensity, increase the heat cautiously if there is no further fuming, and ignite the crucible for no more than 5 minutes at no more than 1000°C. Cool and weigh as before. The loss in weight represents nearly all the silica in the rock. Fuming off of the sulfuric acid must be done carefully, for otherwise phosphorus present is likely to be volatilized (page 694).

Determination of the Mixed Oxides:- To the residue in the crucible used for the silica determination add a small amount of the micro analytical reagent grade sodium carbonate, and fuse to bring the residue into solution. It is best to do this in such a manner that the flux is constantly swirled around bottom and lower walls of the crucible. When fusion is complete, cool, and add 2 to 4 milliliters of dilute hydrochloric acid (1 + 1) under the crucible cover. If careful heating over a low flame does not bring the residue into solution, it can almost always be dissolved by setting on a sand bath and allowing to remain there for some time, replenishing the water if necessary. Finally transfer this solution with rinsing to the beaker containing the filtrate and washings obtained from the second dehydration of the silica.

Boil the solution for about 5 minutes to ensure expulsion of any carbon dioxide. To the boiling hot solution, containing not more than 0.1 gram of aluminum plus iron per 200 milliliters, and having at least 5 grams of ammonium chloride per 200 milliliters of solution (to meet this requirement, add the equivalent amounts of acid and ammonia rather than the salt), carefully add dilute ammonium hydroxide (1 + 1) drop by drop until the precipitate begins to form well. Then add a few drops of methyl red solution (0.2 percent in alcohol). Continue the addition of ammonium hydroxide as before. When the solution just changes to a distinct yellow, boil it for 1 to 2 minutes, and place it either on the steam bath or a cool surface. Within a few seconds the precipitate settles enough so that a thin layer of clear mother liquor develops in which it is easy to check the indicator color. If it is orange or red, add with vigorous stirring more precipitant. Then filter at once. The recognition of the indicator color change and other operations take practice. The time the beaker with its precipitate stands in order to check the indicator color must be kept to a minimum; with practice in recognizing the color change this step is usually not necessary. Then filter continuously on a double thickness of Whatman 541 filter paper, the inner paper being of somewhat smaller diameter than the outer one. Wash the precipitate once or twice with a hot, neutral 2 percent ammonium chloride solution.[f] Reserve the filtrate and washings.

Dissolve the precipitate in warm, dilute hydrochloric acid (1 + 3), washing down the filter paper until most of the iron color disappears, then washing it with hot water. Reserve the paper as it retains some aluminum and titanium. Reprecipitate the mixed oxide group as before, giving attention to the volume of solution and ammonium salt content. When precipitation is complete, add a little macerated filter paper, boil, and filter as before. Wash the precipitate with the hot, dilute ammonium chloride solution once or twice, not forgetting also the beaker. Then wash with a hot, neutral 2 percent ammonium nitrate solution until the test for chloride on 10 to 20 drops of filtrate gives but a moderate turbidity. For granitic rocks this test need not be done until over six portions of wash liquid have been passed through the precipitate; for basic rocks the portions, about 20 milliliters each, required are not much higher. To enhance the efficacy of each washing direct a fine jet of wash liquid forcibly against the precipitate in the paper in order to agitate it well; this technique also hastens filtration time considerably. Now remove precipitate adhering to the beaker and stirring rod as follows: Place a half circle of Whatman 41 paper, moistened with the wash liquid, near the lip of the beaker. Ball the paper up and remove precipitate on the stirring rod by pressing the latter against the paper. Rinse the rod, collecting the wash liquid in the beaker. With the rod push the filter paper around the walls and bottom so as to swab the beaker thoroughly. Some pressure on the paper by means of the rod may be necessary. Remove wash liquid in the paper by pressing the wad in the beaker with the rod, and then with the aid of the rod push the paper into a 35 milliliter capacity platinum crucible that has been ignited to constant weight under the conditions of ignition employed for the mixed oxides. Rinse out the beaker once or twice again, allowing the liquid to come onto the precipitate.

Allow the precipitate to drain well, wrap the moist precipitate in its filter paper, place in the 35 milliliter platinum crucible together with the paper reserved from the first precipitation (as there is time during the second precipitation and as the mixed oxide precipitate is bulky, it is wise to dry, char, and destroy carbon of the first paper before adding the second one), dry in an oven at 105°C overnight, char, and destroy carbon.

Very occasionally some aluminum escapes precipitation or being caught by the filter paper, so carry out the following precautionary measure for all analyses: Evaporate all the filtrates from the double precipitation of the mixed oxides in a platinum dish, keeping the solution in the dish neutral, until the volume is around 50 to 100 milliliters. Add 2 milliliters of hydrochloric acid, stir for 2 to 3 minutes, and then add slowly with vigorous stirring dilute ammonium hydroxide (1 + 1) until the indicator just changes to yellow. Stir in a very little filter paper pulp, and filter immediately. Wash the precipitate twice with a hot, neutral 2 percent ammonium chloride solution. It is best to use a double thickness of Whatman 541 filter paper, smaller than that used for the double precipitation of the mixed oxides.

Now dissolve the aluminum, if any, with 8 milliliters of hot, dilute hydrochloric acid (1 + 3), then with some hot water, and finally with two or three portions of a hot, neutral 2 percent ammonium chloride solution, catching these liquids in the platinum dish. Return the dish and its contents, which sould not exceed 50 milliliters, to the steam bath, add a drop of indicator (0.2 percent methyl red in alcohol), and precipitate as before. Filter immediately on the same filter paper, and wash the dish and precipitate four or five times with the ammonium chloride solution. Swab out the dish and stirring rod with a small wad of filter paper, combine the papers in the crucible with the mixed oxides, dry, and then char and destroy carbon.

Ignite the mixed oxides at 1200°C for 10 minutes. Cool in a desiccator, weigh, and repeat the ignition for 5 minute periods until constant weight is obtained. As the precipitate contains reducible oxides, ignition must be so conducted as to ensure access of air to the interior of the crucible. A Meker tilted so its flame strikes the bottom and side of the crucible whose cover is open to the side opposite the flame is a suitable arrangement; the flame should not envelop the open side. As with the silica precipitate, great care must be taken to avoid loss of particles of precipitate.

Determination of Residual Silicon Dioxide:- To the mixed oxides add a few drops of water and then two to five drops of dilute sufluric acid (1 + 1) followed by 1 or 2 milliliters of hydrofluoric acid. Heat carefully on a sand bath, swirling the contents occasionally. By sinking the crucible to one-third or more of its depth in the sand and by increasing the temperature of the sand bath fume off as much sulfuric acid as possible on the bath. Transfer the crucible to a silica triangle, and fume with a very low flame. The fuming should be so gentle that the fumes are scarcely seen. In fact it should be so gradual that only the odor of sulfur trioxide is detectable above the crucible, which should be left open. Increase the intensity of heating by lowering crucible and triangle gradually over the steady flame until the crucible bottom becomes orange. Increase the heat until the walls become orange colored as well, and keep at this temperature for about 15 minutes, so long as fuming is not violent. When the odor of sulfur trioxide is no longer detected, bring the temperature up to the full heat of the Meker, taking care there are no more sulfur trioxide fumes evolved. Finally ignite at 1200°C for a 5 minute period, cool, and weigh as before. Repeat the ignitions for brief periods (3 minutes or so) at 1200°C to obtain constant weight. The loss in weight represents the residual silicon dioxide not recovered in the acid dehydrations. The lower weight less the weight of the empty crucible is the weight of mixed oxides. These must be brought into clear solution and the total iron as ferric oxide and the titanium dioxide determined.

Fusion of the Mixed Oxides:- Place about 7 to 8 grams of potassium bisulfate in a clean, dry platinum dish and fuse it without its splattering until copious fumes of sulfur trioxide evolve. Let the mass cool well; it usually separates from the dish without any further treatment. Transfer the pyrosulfate fragments to the crucible containing the mixed oxides; place this crucible in a holed asbestos board, the arrangement being the same as for the first stage in the carbonate fusion. Commence fusing the pyrosulfate with a low flame and with the crucible covered; bring the mixed oxides into solution at as low a temperature as will keep the contents molten until the whole has been dissolved. Usually no more than 2 to 3 hours are needed for complete fusion of rocks, the crucible is never more than dull red and then only for the last 15 minutes or so, and the amount of platinum brought into solution by the pyrosulfate rarely exceeds 2 milligrams. Completeness of fusion is easily ascertained in the case of potassium pyrosulfate, even when the liquid is dark red and opaque, by removing the crucible from the flame to a good light that shines down into the crucible and allowing the vessel to cool. At one point during the cooling, the liquid becomes transparent and so permits the bottom of the crucible to be seen. It is the alumina that requires the long period of fusion; ferric oxide comes into solution relatively rapidly. Use of a freshly converted pyrosulfate and of holed asbestos boards renders almost nil splattering, collection of pendant drops on the crucible lid, and wall "creep" of the melt. Properly carried out, the fusion is at all times quiet and the cake is nearly wholly confined to the bottom of the crucible.

When fusion is complete, cool the mass, and wipe the exterior of the crucible clean. Place it in a 600 milliliter borosilicate glass beaker, and add under the cover 5 milliliters of hydrochloric acid and about 30 milliliters of water. Bring the cake into solution by heating on the steam bath, and afterwards remove the crucible from the beaker, washing it thoroughly with hot water. Add 15 milliliters more of hydrochloric acid. Remove pyrosulfate from the crucible lid by swirling it in the hot solution for a few moments, gripping it with tongs. If a small residue remains, bring the solution to the boil, and, if necessary, boil for 30 minutes or more. Borosilicate glass tubing, made into Markownikoff boiling tubes, are invaluable for prolonged boilings of this sort, for boiling proceeds quietly and with little supervision. If a residue persists, it had better be filtered off on a small double thickness of Whatman 540 paper, washed thoroughly with hot water, paper placed in a silica crucible, charred, carbon destroyed, and the residue fused with a little potassium bisulfate. Add this melt to the main solution after dissolving it up in a little dilute hydrochloric acid (1 + 9). Now transfer the solution from the 600 milliliter beaker to a 200 milliliter volumetric flask, make nearly to volume, cool to 20°C, and make to the mark.[g]

Determination of Total Iron as Ferric Oxide:- To a silver reductor prepared according to Walden, Hammet, and Edmonds add about 50 milliliters of a 0.005 molar solution of ferrous ammonium sulfate in 1 normal hydrochloric acid.[h] Then flush the reductor with 150 milliliters of 1 normal hydrochloric acid saturated with carbon dioxide, adding the acid in portions at a time. Repeat until a blank on the acid and indicator, determined with 0.01 normal ceric sulfate, is constant; the blank should be less than 0.1 milliliter of titrant. With a 25 milliliter pipet[i] withdraw 75 milliliters of the sample solution in the 200 milliliter volumetric flask, and pass it through the reductor at a rate of 30 milliliters per minute, collecting the solution in a one liter capacity Erlenmeyer flask that contains 225 milliliters of 10 molar sulfuric acid.[j] Wash the reductor column with 150 milliliters of 1 normal hydrochloric acid saturated with carbon dioxide, rinsing the column with small amounts of the acid and allowing each portion to run through before adding the next one. As a precautionary measure while collecting the solution, allow carbon dioxide to issue below the liquid surface, the bubbling also serving to mix slowly the sulfuric acid solution with the hydrochloric acid-ferrous iron one. Then to the solution add one drop of 0.025 molar o-phenanthroline-ferrous complex and titrate as quickly as possible to the disappearance of the indicator color.[k] Flush the reductor once again with the ferrous ammonium sulfate and hydrochloric acid solutions. Withdraw another 75 milliliter aliquot of the sample solution and reduce and titrate as before. Take the average volume of titrant to calculate the total iron as ferric oxide.

Determination of the Titanium Dioxide:- Withdraw from the 200 milliliter volumetric flask a 5 to 10 milliliter aliquot, depending on the amount of titanium expected, and place in a 100 milliliter volumetric flask. Add about 30 milliliters of water and then dilute ammonium hydroxide (1 + 1) until the hydroxides of iron and aluminum form. Then add 10 milliliters of a 4 percent tiron solution (4 grams of disodium-1,2-dihydroxybenzene-3,5-disulfonate in 100 milliliters of water) followed by 10 milliliters of a buffer solution prepared by mixing equal volumes of molar ammonium acetate and molar acetic acid. Reduce the iron of the sample by adding dropwise a dilute solution of sodium dithionite until the color of the ferric-tiron complex disappears. Then add a few drops in excess, make the solution to the mark, mix carefully to avoid reoxidation of the iron, and determine the optical density of the sample solution at 430 millimicrons, using a blank of all reagents as the reference standard. Prepare standards with a standard titanium sulfate solution to which should be added potassium bisulfate equivalent to the amount employed in the pyrosulfate fusion and ferric chloride approximately equal to that present in the rock prior to developing the tiron color.[1]

<u>Determination of the Calcium Oxide</u>:- Slightly acidify the combined filtrates from the mixed oxide determination and evaporate so that the concentration of calcium oxide, after addition of its precipitant, will be around 0.5 to 0.7 milligrams per milliliter. In the writer's opinion the determination of calcium oxide, magnesium oxide, and the impurities which these precipitates almost always contain make this part of the analysis scheme the most exacting in silicate analysis.

Add two drops of methyl red indicator solution and add dilute ammonium hydroxide (1 + 1) until the indicator is just yellow. Then heat the solution to boiling, transfer it to the steam bath, and add slowly (1 drop per 5 seconds) while stirring vigorously sufficient of a hot 4 percent solution of ammonium oxalate to precipitate all of the calcium plus, added also slowly, about a 100 percent excess. Then pour in enough of the oxalate solution to provide an excess of 1 gram per 100 milliliters of final solution. Then partially immerse the covered beaker in boiling water for about 4 minutes,[m] let stand on the steam bath for one-half hour, allow to cool at room temperature, and filter on a Whatman 540 paper at the end of one hour. Wash the paper and precipitate with five 10 milliliter portions of a cold, neutral 0.1 percent solution of ammonium oxalate, washing the precipitate by decantation. Reserve the filtrate and washings.

Dissolve the precipitate in 50 milliliters of warm, dilute hydrochloric acid (1 + 4), washing the filter paper also with several portions of warm water. Discard the filter paper.[n] Dilute the solution so that the concentration of calcium oxide will be about 0.5 to 0.7 milligrams per milliliter at final conditions. Add 1 gram of ammonium oxalate per 100 milliliter of solution, heat to boiling, transfer to the steam bath, and add slowly (1 drop per 5 to 7 seconds) dilute ammonium hydroxide (1 + 1). When the precipitate begins to form well, add two drops of the methyl red indicator solution, and continue the slow addition of ammonium hydroxide until the indicator just changes to yellow. Digest as in the first precipitation. With 10 milliliter portions of wash liquid wash the precipitate once by decantation, and then, with the next two to three portions, transfer it quantitatively onto the paper. Clean the stirring rod and swab out the walls of the beaker with a half circle of Whatman 41 paper in a manner described for the mixed oxides. Now rinse the beaker with another portion of wash liquid, let the walls drain well, and inspect them in a suitable light for any precipitate not removed. Then wash the precipitate once or twice more so as to concentrate it in the very bottom of the paper.

Wrap the moist precipitate in the filter paper, place in a 25 milliliter capacity platinum crucible that has been ignited to constant weight under the same conditions as for the ignition of the calcium oxide. Dry in an oven at 105°C. Carefully char the paper, and then increase the flame so as to destroy carbon; the crucible bottom need not be more than dull red for this. When the carbon is removed in this manner, the precipitate is never more than a dull grey. Carefully set the crucible upright, cover it, and heat it at about 1200°C for about 7 or 8 minutes (for large amounts of the oxide use 10 minutes). Throughout the heating it is well to protect the oxide from contamination by oxides of sulfur from burning gases or by volatile matter given off in muffles or burners that are in general use. The writer employs a tilted arrangement as for the ignition of the mixed oxides. Immediately after removing the Meker, lift the cover for a moment to permit escape of entrapped carbon dioxide, place the covered crucible in a desiccator containing some 98 percent sulfuric acid in a little dish, and weigh as soon as cool.[p] The first ignition and weighing is a preliminary one and should be followed by a short ignition (2 to 3 minutes) and a second weighing in which the weights are already placed on the pan and only the rider is quickly adjusted. Often, particularly with large amounts of oxide, a third brief ignition is called for; the writer's policy is to make repeated brief ignitions until constant weight is obtained. Inspect the precipitate; it should be pure white. A yellow, brown, or green coloration is due to some compound of manganese. Following the above procedure, particularly with respect to the methyl red color change, the writer has never had but a trace (less than 0.1 milligrams) of manganese oxide contaminant. Reserve the precipitate for the determination of the strontium oxide, which in the usual case is quantitatively precipitated with the calcium oxide.

Determination of the Magnesium Oxide:- Acidify the combined filtrates from the calcium oxide determination with 4 milliliters of hydrochloric acid and evaporate the solution until the salts just begin to crystallize out, salt formation commencing usually when the volume of solution is about 100 to 150 milliliters. Rinse the glass hooks and cover glass. Add under the cover approximately 3 grams of nitric acid for every gram of ammonium chloride; an excess does no harm. Warm gently and let stand at room temperature until vigorous evolution of gas ceases, and then evaporate the contents to dryness. Evolution of gas must not be violent; the reaction may be controlled by immersing the beaker in cold water. Cool the salts thoroughly, and then add under the cover a small amount of water to moisten them.[q] Then rinse cover, glass hooks, and walls of the beaker. Add 1 milliliter of hydrochloric acid and 0.5 grams citric acid and bring to the boil. If the salts do not dissolve, add 1 milliliter more of hydrochloric acid. A small white residue is probably largely silica derived from the glassware; this residue is dealt with after the first precipitation of the magnesium ammonium phosphate. Transfer the solution to a 400 milliliter capacity borosilicate glass beaker, washing the large vessel with several portions of hot water.

Add to the solution in the 400 milliliter beaker as a freshly prepared solution sufficient diammonium phosphate to precipitate all of the magnesium and to provide 2 grams in addition for every 100 milliliter of solution. The final volumes of solution should be 75 to 200 milliliters for 1 to 100 milligrams of magnesium oxide. Chill the solution in an ice bath, and with vigorous stirring add slowly (one drop per 5 to 10 seconds) dilute ammonium hydroxide (1 + 3) until the precipitate begins to form. With ice cold solutions commencement of precipitation is readily seen, for the precipitate appears sometimes as a flash of white crystals that dissolve with stirring or, more often, as a faint white turbidity. At this stage slow the rate of addition of precipitant to about one drop per 15 seconds, and continue at this rate until the solution is distinctly ammoniacal. At this point add 10 milliliters of concentrated ammonium hydroxide for each 100 milliliters of solution, and set the solution aside with the stirring rod left in the solution. Cover the beaker with cellophane secured with a rubber band, and let the contents stand overnight. Filter through Whatman 540 paper. Wash the beaker, precipitate, and paper with four 10 milliliter portions of cool, dilute ammonium hydroxide (5 + 95) containing 50 grams of diammonium phosphate per liter, transferring as much of the precipitate as possible onto the paper with the aid of the wash liquid.

Now dissolve the precipitate by passing 50 milliliters of hot, dilute hydrochloric acid (1 + 19) through the paper, catching the solution in the beaker in which the precipitation was made. Wash the filter paper with a few portions of hot water also. Take care to dissolve all precipitate, giving attention to walls and lip of the beaker and the stirring rod. Place the filter paper in a platinum crucible, char and destroy carbon, and treat the residue with a few drops of perchloric acid and as many of hydrofluoric acid. Heat gradually with a low flame until nearly all the perchloric acid is expelled; dissolve any residue remaining with a little hot water, and transfer this solution to the main filtrate. If the large beaker in which the wet attack of the ammonium salts was carried out is thought to have adhering residue, it can be swabbed out with a wad of paper, and this combined with the filter paper for treatment of residue.

Add 0.1 to 0.3 grams diammonium phosphate depending on the amount of magnesium present, and adjust the volume of the solution to between 50 and 200 milliliters for 1 to 100 milligrams of magnesium oxide. Chill in an ice bath, and add shlowly dilute ammonium hydroxide (1 + 2) until the precipitate just begins to form. Precipitate by adding slowly (one drop per 10 to 15 seconds) and with vigorous stirring a more dilute ammonium hydroxide (1 + 5), continuing the slow addition until the solution is distinctly ammoniacal. Then add 5 milliliters of ammonium hydroxide per 100 milliliters of solution, cover the beaker as before, and digest for at least 4 hours. Filter through paper and wash by decantation with four 10 milliliter portions of cool, dilute ammonium hydroxide (5 + 95).

Redissolve and reprecipitate as for the second precipitation. Filter after letting the precipitate digest for at least 4 hours. Transfer as much of the precipitate as possible with two to three 10 milliliter portions of wash liquid. With a half circle of Whatman 41 paper wipe off adhering precipitate on rod and beaker walls in a manner described for the calcium oxide determination. The magnesium ammonium phosphate precipitate adheres well to glass surfaces, so it is an advantage to have a wad of filter paper well soaked in wash liquid for swabbing. Transfer the wad to a 35 milliliter capacity platinum crucible which has been ignited to constant weight under the conditions of ignition of the magnesium precipitate. Rinse the beaker with another portion or two of the wash liquid, let the walls drain well, and inspect them in a suitable light for any precipitate not removed. Then wash the paper once or twice more, using proper technique to concentrate the precipitate in the very bottom of the paper.

Wrap the moist precipitate in the filter paper, place in the platinum crucible, and dry in an oven at 105°C. Char the paper very slowly, and burn off the carbon over a flame that never heats the bottom of the crucible to more than the faintest red seen in a well-darkened room. Rotate the crucible every half hour or so, taking care there is no loss of particles. After about 3 to 6 hours all carbon but that adhering to the precipitate will be removed. Then increase the flame so that the crucible bottom is as faint a red as seen in a normally lit room. Maintain these conditions as long as the blackness or greyness of the precipitate diminishes. If there is no further whitening, increase the flame over an hour or more until the crucible bottom is a bright red (around 700°C). Maintain these conditions for the low temperature removal of carbon until the precipitate is a faint grey. Finally heat for 30 minutes at 1000 to 1100°C with the cover partly off as in the ignition of the mixed oxides. Cool in a desiccator, weigh as magnesium pyrophosphate, and repeat the heating for 20 minute periods until the weight remains constant. Then heat for about 5 minutes at 1200°C, and take this weight as the final weight of the crucible and precipitate. Reserve the precipitate for the determination of impurities, which can often be calcium, strontium, barium, and manganese (and iron, aluminum, and zinc if citric acid is not employed for their separation).

Determination of the Strontium Oxide:- To the calcium oxide precipitate in the platinum crucible add under the cover 2 or 3 milliliters of water and sufficient 2 molar nitric acid to provide an excess. Warm gently to dissolve all of the precipitate and transfer it with a minimum of washings to a 25 milliliter capacity borosilicate glass Erlenmeyer flask. Evaporate the contents of the flask to dryness on a sand bath, the surface temperature of which does not exceed 150°C. If any manganese has come down with the calcium, it will be readily seen in the nitrate solution as brown flecks or a brown coloration; the test is very sensitive. Allow the dry nitrates to cool, and then precipitate the strontium nitrate as follows: Add sufficient water so that final conditions will provide 2 milliliters of 80 percent nitric acid solution per 5 milligrams of calcium oxide present plus an excess of about 10 milliliters of acid solution per 100 milligrams of oxide. Then by means of 100 percent nitric acid or fuming nitric acid (greater than 95 percent nitric acid), added dropwise to the flask immersed in tap water, precipitate the strontium nitrate. Cover the flask and allow to stand in a cool place (about 15°C) for 2 to 4 hours. Then with a micro filter-stick, porosity 4, filter by suction the mother liquor, and wash the precipitate with three 1 milliliter portions of 80 percent nitric acid. Collect the mother liquor in a 50 milliliter Erlenmeyer flask; the manganese in it may be determined if its amount is thought to be significant.

As a single precipitation does not usually give a sharp separation of the calcium from the strontium, reprecipitate the strontium nitrate after drying the salts at 135°C for one hour. Precipitate in half the volumes of water and acid used for the first precipitation. Of course, the filterstick must be removed prior to drying the salts and reprecipitating the strontium nitrate; the filterstick should also be dried, preferably in a horizontal position. After precipitating let stand again in a cool place for 2 to 4 hours. Return the filterstick to the flask and filter and wash as before. Sometimes, especially if the amount of calcium oxide is high (more than 100 milligrams), a third precipitation may be necessary. If so, reprecipitate as for the second precipitation, although, if possible, use smaller volumes of water and nitric acid. Dry the strontium nitrate in the flask together with its filterstick for 2 hours at 135°C, cool the flask in a desiccator, and weigh. The weighing should be done quickly; if time is taken in adjusting weights, the flask and its contents had best be dried briefly, cooled, and weighed again with the weights already on the balance pan.

Then with portions of hot water containing two or three drops of nitric acid per 100 milliliter dissolve the strontium nitrate, removing the solution by suction with the filterstick. Dry, cool, and weigh the flask and filterstick under exactly the same conditions as before, and take the loss in weight as the amount of strontium nitrate.^{r} Small amounts of strontium nitrate are probably slow to precipitate in nitric acid; therefore, as small volumes as possible of the precipitating medium should be used and also the longer periods of digestion. Often after filtering some of the precipitate adheres to the bottom of the filter stick; it had better be dislodged by a fine stream of the wash liquid, collecting the liquid and precipitate in the Erlenmeyer flask, before carrying out the next operation. The analyst must assure himself that his acid solutions are of the specified concentration and that his manipulations of filterstick and flask are correct, for which he should consult Benedetti-Pichler. Small amounts of strontium oxide (0.1 to 0.2 milligrams) are scarcely seen in the precipitating medium; consequently, it is imperative to carry out all operations before concluding strontium oxide is not present in the rock.

Determination of Calcium Oxide and Barium Oxide in the Magnesium Pyrophosphate:- Moisten the magnesium pyrophosphate precipitate with a little water and then add 1 milliliter of dilute sulfuric acid (1 + 1) plus 5 milliliters of nitric acid. Allow to stand overnight. Place on a sand bath so that the nitric acid is expelled quietly. As fumes of sulfuric acid begin to come off, heat the bottom of the crucible up to 180°C or more and allow as much of the acid to fume off under these conditions. Cool the crucible, add a little water, and dissolve as much of the precipitate as possible with gentle heating. Transfer the solution and any residue to a 50 milliliter Erlenmeyer flask. Rinse the crucible with a little warm water. The Erlenmeyer flask together with its filterstick should previously be weighed to constant weight after igniting them at 450°C. Again evaporate the contents of the flask, which should now not have its filterstick, to dryness in an oven at 105°C. Cool, add 3.0 milliliters of water, 0.5 milliliters of dilute sulfuric acid (1 + 3), and heat gently to dissolve as much of the salts as will come into solution with 2 to 3 minutes heating at nearly 100°C. Cool, then add dropwise with swirling of contents 31.5 milliliters of methyl alcohol (a technical grade redistilled is acceptable), cover the flask, and let stand at room temperature overnight.[a] Return the filterstick to the flask and filter by suction, washing the precipitate with a water-acid-methyl alcohol solution prepared in the ratios given. Collect the mother liquor and wash liquid in a 250 milliliter beaker, reserving it for the manganese determination.

A single precipitation of the calcium and barium sulfates tends to give high results. Therefore, add one drop of sulfuric acid to the flask after expelling methyl alcohol in it by drying it at 80°C. Set the flask without its filterstick in an oven at 200°C and bring the temperature up quickly to around 300°C. Heat until no more fumes of sulfuric acid come off. The treatment ensures the elements present are wholly converted to sulfates. Cool, add 1.5 milliliters of water, 0.25 milliliters of dilute sulfuric acid (1 + 3), and heat gently as specified for the first precipitation. Then add dropwise 15.8 milliliters of methyl alcohol and allow to stand for 4 hours. Return the filterstick to the flask, filter by suction, and wash as before, reserving the filtrates for the manganese determination. First dry the precipitates at 105°C, and then for 1 hour at 450°C. Cool in a desiccator for one hour and weigh quickly. The weight of residue is the sum of calcium, barium, and, sometimes, strontium sulfates. If the ratio of calcium oxide to strontium oxide is 100 to 1 or more, the latter is nearly quantitatively (97 percent) precipitated with the former in the oxalate precipitate. If from the calcium oxide and strontium oxide determinations, the ratio appears to be 80 to 1 or less, strontium will be brought down with the magnesium, and in alcoholic solution it will appear with the calcium and barium.

To determine the calcium (and strontium) sulfates, proceed as follows: Wash the sulfates with three 5 milliliter portions of warm water containing 1 drop of sulfuric acid per liter. Filter by suction with the filterstick (the filtrate need not be reserved unless strontium is to be looked for), ignite at 450°C for one hour, cool, and weigh as before. The loss in weight represents the amount of calcium sulfate (and strontium sulfate) contaminant(s). To correct for strontium sulfate the filtrate above must be reserved; the strontium can be precipitated by 80 percent nitric acid as described. Its separation from calcium sulfate is not as efficient as when both are present as nitrates, but double precipitations for the small amounts of each usually present are adequate. To correct the magnesium pyrophosphate precipitate for the calcium, barium, and strontium impurities, calculate the weight of each as the orthophosphate (page 640).

Determination of the Manganese Oxide:- Evaporate the combined alcoholic filtrates from the calcium and barium sulfate precipitation at 80°C, and then add 5 milliliters of sulfuric acid plus 2 to 3 milliliters of nitric acid. Boil for a few minutes and then heat on a sand bath until fumes of sulfuric acid appear. Add 0.5 milliliters of perchloric acid and repeat the fuming. Cool, add 10 milliliters of nitric acid, and adjust the volume to around 40 to 50 milliliters. Add at least twice as much potassium periodate as is theoretically required (1 gram potassium periodate per 0.1 gram manganese), cover the beaker, boil for one minute, keep hot for 10 to 15 minutes, cool, and dilute to 100 milliliters. Measure the solution spectrophotometrically at 525 millimicrons, using reagents alone as the reference solution. Compare with standards of known manganese content similarly treated.^{t} When ready for test, the solution should not contain more than 1 milligram of manganese per 50 milliliters. Calculate the manganese oxide found as manganese pyrophosphate, and correct the magnesium pyrophosphate precipitate accordingly.

Footnotes

a: Palladium-gold crucibles can also be used; the separation of the melt is a little better from them.

b: The glass rod must be smooth; cleanliness, especially freedom from grease, can be insured by washing it with soapy water, drying, and holding in the flame briefly. The writer has found the following a useful technique for removing adhering particles: Place a little of the flux in a 4-centimeter Whatman 541 filter paper, twirl the rod in the flux while the paper is held as a trough between the fingers. Then sprinkle the flux on the top of the flux-sample mixture in the crucible. Repeat two times more.

c: The efficiency of the burner had better be checked from time to time by placing in a crucible some orthoclase powder, which should readily melt when the Meker is on full power.

d: The amount of the film is usually kept to a minimum by cleaning the platinum dish just prior to use either with dilute hydrochloric acid (1 + 2) or with potassium bisulfate.

e: Boiling expels air in the solution which otherwise will come out as the solution is heated and evaporated. As bubbles rise to the surface, they break and by splattering liquid cause loss of a little of it.

f: The A.R. ammonium chloride and A.R. ammonium nitrate give a distinct acid reaction when added to specially purified water whose pH is 7.5. To ensure the wash liquids are neutral, the writer adds a drop of the methyl red indicator and adjusts the acidity with dilute ammonium hydroxide (1 + 1).

g: Heats of dilution of strong acid solutions are appreciable; therefore, to be certain volumes of solution are made up at 20°C, the analyst must take necessary precautions

h: The ferrous iron solution passed through the reductor ensures removal of peroxide that might be present in the column.

i: The pipet must be calibrated relative to the flask, for which consult Pierce and Haenisch or some other standard work.

j: Titrations of iron with ceric sulfate in the presence of o-phenanthroline-ferrous complex done in 5 molar sulfuric acid are without effect of chromium, vanadium, and titanium. See Walden, Hammet, and Edmonds.

k: Platinum, derived from the pyrosulfate fusion in particular, is present in the iron-containing solution as PtII after reduction. It is not oxidized by ceric sulfate appreciably provided the titration is done quickly, particularly near the equivalence point. The writer is inclined to think the oxidation of PtII is somewhat slower in 5 molar sulfuric acid solutions than in 1 normal hydrochloric acid ones.

l: Synthetic bases of aluminum, iron, and potassium sulfate closely approximating the composition of those solutions obtained in rock analyses can be prepared with the saving of much labor by employing simply the potassium pyrosulfate-fused aluminum and iron oxides used in determining the blank on the silicon dioxide. Aluminum and iron used as collectors for the silica can be added in such amount to give rocks of basic and acidic composition. Synthetic bases for the titanium determination for intermediate rocks can of course be prepared by mixing portions of the basic and acidic rock synthetic bases. In fact, however, the writer has found the usual range of aluminum, iron, and potassium sulfates encountered in rock analyses affect not at all the optical density of the titanium-tiron complex. Nevertheless, the writer uses these bases for the preparation of standard titanium solutions in order to keep working conditions for knowns and unknowns at all times equal.

m: The neutral solutions are prone to "bumping" when boiled.

n: The analyst must assure himself that no calcium is left on the filter paper. To check this, ash the paper in platinum.

o: It is wise to let the crucible cool well, to cover it, and then to set it upright. The calcium oxide is light, so particles may fly out as with silicon dioxide if precautions are not taken.

p: Fifteen minutes is sufficient cooling time for most precipitates ignited in platinum. See Pierce and Haenisch for the technique of cooling crucibles in a desiccator.

q: The water should be added under the cover, for its addition often causes dustlike particles to fly up.

r: The 80 percent nitric acid has a solvent action on either the filterstick glass or the borosilicate glass or both, so the strontium nitrate cannot be weighed directly.

s: Caley and Elving have found that as the magnesium to calcium ratio increases, the former tends to retard the precipitation of the latter. If the ratio is at or around 100 to 1, 24 hours standing is required for complete precipitation of calcium as sulfate. If the ratio is in doubt, the writer adds a known amount of calcium oxide as the chloride; 1.00 milligrams pipetted in is usually sufficient.

t: A suitable standard is prepared by igniting to constant weight in platinum at 450 to 500°C some manganese sulfate quadrihydrate. The salt is dissolved and made to a definite volume which is rendered 0.1 normal in sulfuric acid.

FIGURE 12

The Frequency Distribution of Fluoride in the Psammitic Semi-Pelite Class

199 Samples

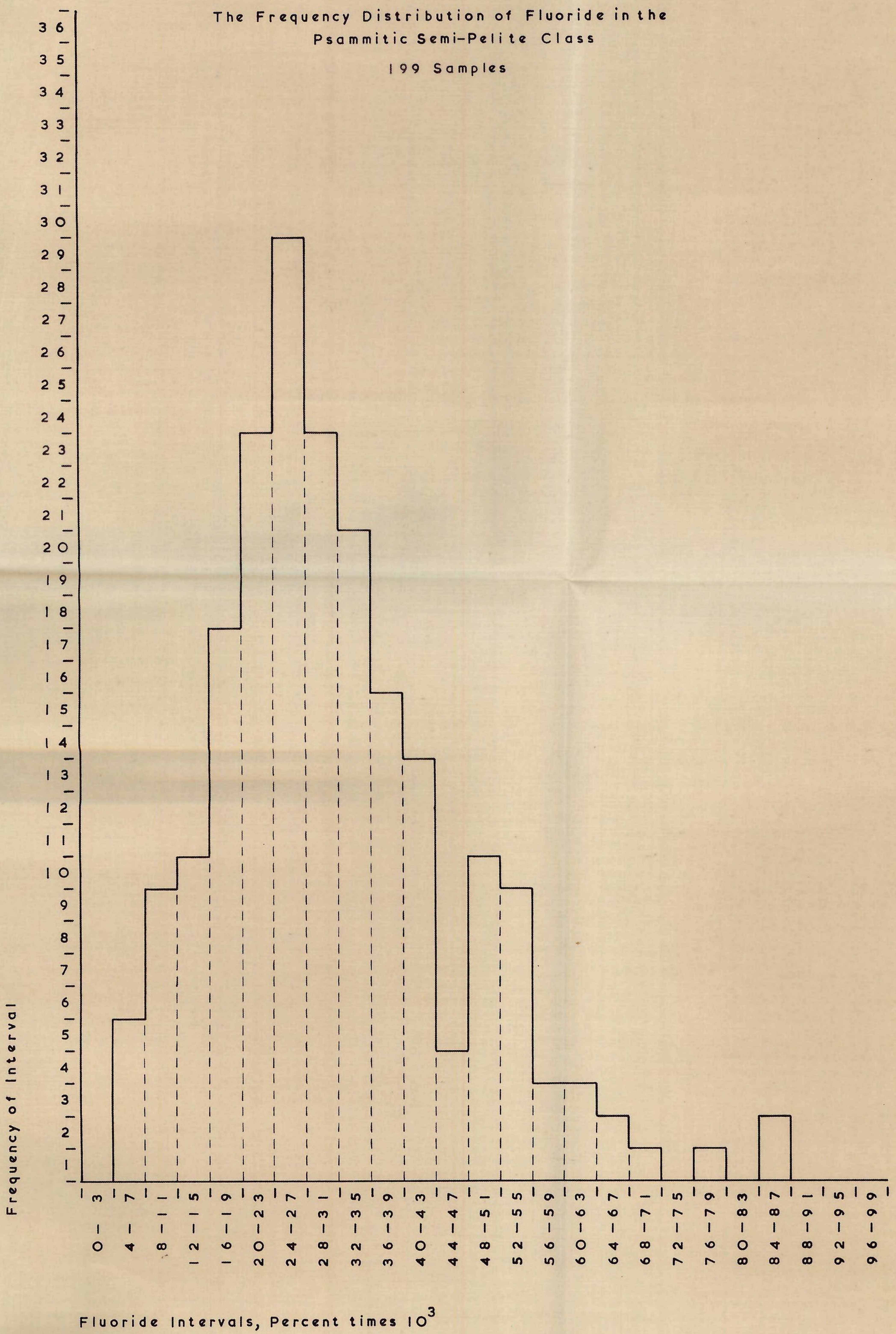


FIGURE 11

The Frequency Distribution of Fluoride in 345 Metamorphic Rocks

A Histogram at a 0.004 Percent Fluoride Interval

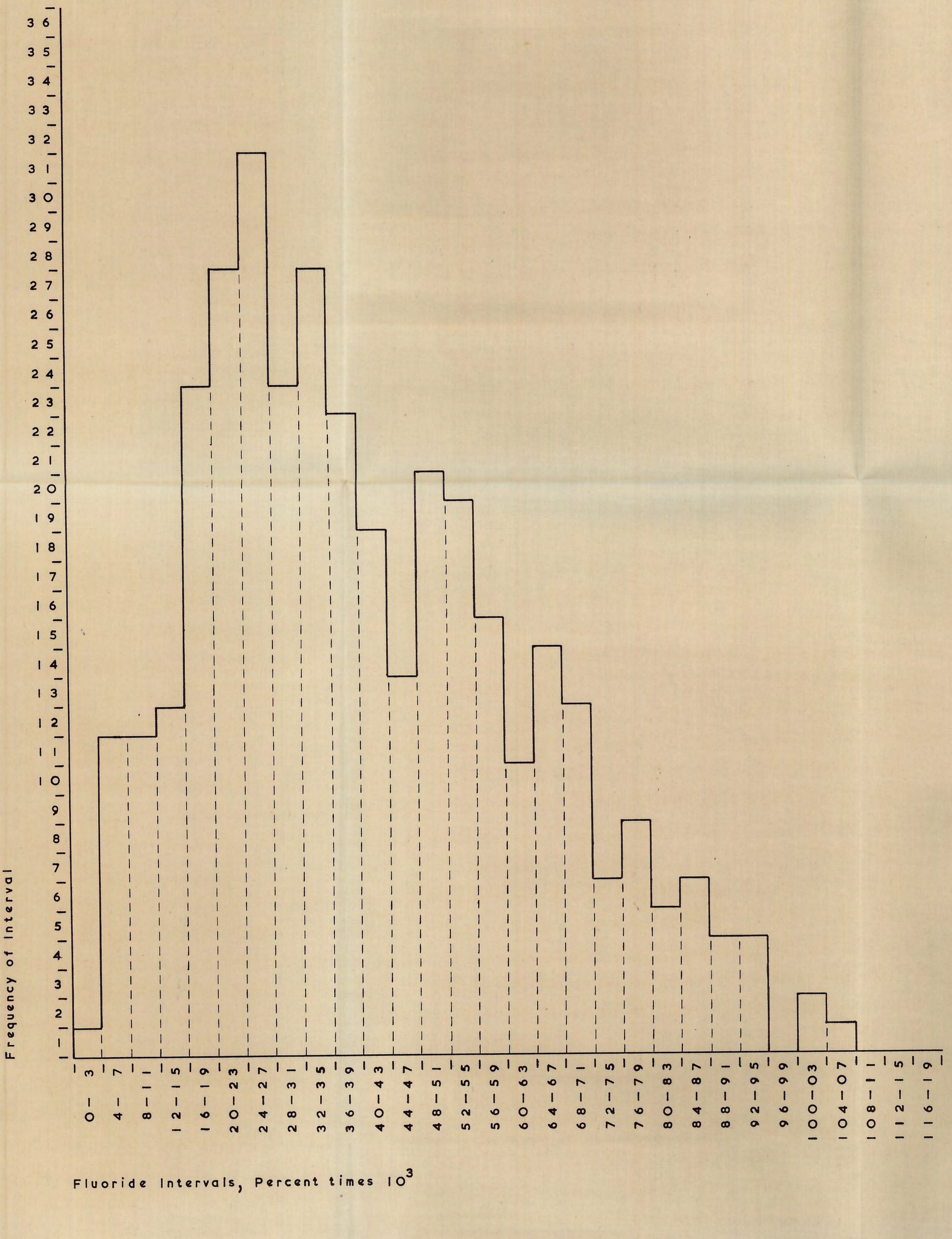


FIGURE 10

The Frequency Distribution of Fluoride in 345 Metamorphic Rocks

A Histogram at a 0.003 Percent Fluoride Interval

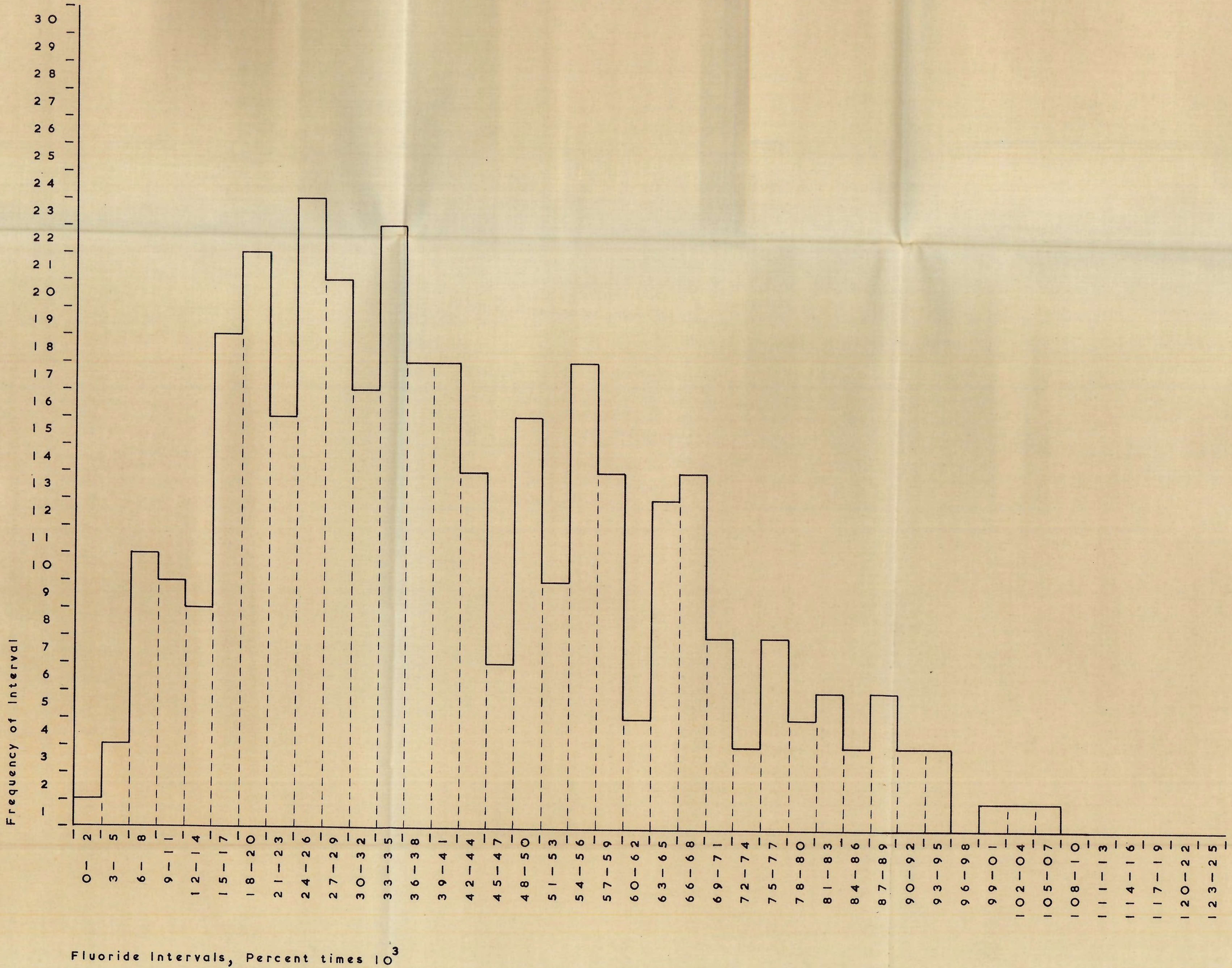


FIGURE 9

The Frequency Distribution of Fluoride
in Metamorphic Rocks from the Stonehaven, Pitlochry, Loch Sunart, Loch Lomond, and Clifden Areas

345 Samples