THE

GEOCHEMISTRY

0 F

APATITE

THE GEOCHEMISTRY

OF APATITE

By

EDGAR FRAMK CRUFT, B.Sc. (Hons)

A thesis

Submitted to the Faculty of Graduate Studies in Partial Fulfilment of the Requirements for the Degree Doctor of Philosophy

> McMaster University September, 1962

DOCTOR OF PHILOSOPHY (1962) (Geochemistry)

McMASTER UNIVERSITY Hamilton, Ontario

TITLE: The Geochemistry of Apatite.

AUTHOR: Edgar Frank Cruft, B.Sc Hons. (Durham University). SUPERVISOR: Professor Dennis M. Shaw.

NUMBER OF PAGES: xii, 215

SCOPE AND CONTENTS: A detailed review is presented of previous work in the apatite mineral series. A precise d.c. arc spectrographic method was developed for the analysis of minor and trace elements in apatite, and 46 apatite samples from igneous pegmatitic and metamorphic environments analysed. The data were analysed statistically using an electronic computer. Apatite from all environments is enriched relative to the lithosphere in Ge, La, Y, and Sr, and apatite from many granite pegmatites is a lso enriched in Mn. The incorporation of trace elements is discussed from the point of view of lattice position and structural and environmental control. A mechanism is proposed to account for the high Y/Ce + La ratio in apatite from granite pegmatites. The variation of trace elements within a single large crystal of apatite was examined by analysing 102 core samples taken from a section within the crystal. The inhomogeneity of trace element content is discussed in the light of crystal growth, habit modification and geochemical significance.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to Prof. D. M. Shaw, my Research Director, for valuable assistance and direction in this investigation and for providing many of the apatite samples.

The assistance of Drs. J. H. Crockett, T. N. Irvine and G. W. King, other members of the Research Committee, is gratefully acknowledged.

Faculty members and fellow students who assisted in many ways are thanked here, particularly Dr. G. V. Middleton, for the use of his r-matrix computer program, and Messrs. A. M. Kudo and G. B. Skippen, who contoured an element distribution diagram for comparison purposes and put forward valuable viewpoints. Miss Michele Stewart kindly assisted by colouring many diagrams.

During the period of this study the writer was partly supported by a Cominco Fellowship, a National Research Council Studentship, and a teaching assistantship from McMaster University. These awards are gratefully acknowledged, together with research grants from the Geological Survey of Canada and the National Research Council.

I am indebted to the donors of the apatite samples, who include Drs. V. B. Meen and J. A. Mandarino for the Royal Ontario Museum, H. D. Wright, J. H. Reesor, H. H. Schmitt, A. B. Carpenter and D. P. Gold.

Finally, a large share of the thanks is given to my wife, Ivonne, who typed this thesis and provided great moral encouragement.

ABSTRACT

A detailed review of the mineralogy, chemistry and occurrence of apatite has been made.

A precise d.c. arc method was devised for the quantitative analysis of trace and minor elements in spatite. Samples were arced in a 80:20 argon-oxygen atmosphere, using the Stallwood jet, and analyses calculated from spectral line transmission values using a Bendix G-15 computer.

46 apatite samples from igneous, pegmatitic and metamorphic environments were analysed in triplicate. Correlation coefficients, using arithmetic and logarithmic data, were computed for all possible element combinations in the samples as a whole, and for the samples grouped according to environment.

Apatite from igneous and metamorphic environments is enriched relative to the lithosphere in Ce, Y, La, and Sr; apatite from many granite pegmatites is also enriched in Mn; and apatite separated from igneous intrusives is enriched in Zr. The bulk of the Zr, and much of the Fe and Mg content, is, however, probably present within inclusions, but can also occur as "trapped ions" within the structure if present at high concentrations in the environment. These elements appear to be substituting for Ca in the structure, but the P position is far less amenable to impurity incorporation, and only Si^{4+} , and probably C^{4+} , can normally be incorporated in this position in appreciable amounts.

iv

As⁵⁺ and V^{5+} do not substitute to any degree for P^{5+} , and this is partly due to environmental and partly to structural control. The latter appears to be the main factor preventing V^{5+} incorporation, however.

At concentrations less than about 1%, charge balancing in the structure by coupled cation replacements does not appear to be important for any of the elements analysed. This is in accord with the stability of defect apatite structures.

The ratio of Y to Ce + La is higher, and total Ce + La + Y content lower, in pegmatite apatites than in apatite from regional metamorphic and plutonic environments. This is interpreted as the result of selective incorporation of the Ce-earths in K-felspars and monazite during the crystallisation of granites and pegmatites, and enrichment of the Yearths in residual solutions.

Apatite from igneous intrusives tends to have higher Sr (greater than 1000 ppm) than apatite from granitic pegnatites, the highest Sr content occurring in apatite from ultrabasic and alkalic rocks. Ea is also enriched in apatite from alkalic complexes and carbonatites.

A new sampling technique permitted 102 small core samples (of 3.4 mms. diameter) to be taken from points on a basal section of a large apatite crystal, and analysed in triplicate. Variance analysis of the results, using the computer, showed the content of Si, Al, Fe, Mn, Ce, Y to be markedly inhomogeneous in the crystal. Some indications of trace element zoning are present, particularly for Ce.

Some of the Fe, Al, and Si content of the crystal can be correlated with biotite inclusions. Correlation coefficients between pairs of

elements show a greater number of correlations between elements in this crystal than for the apatites from varied environments, although, surprisingly, correlations between Ce, Y, and La are weak or absent. This is probably due to small local fluctuations obliterating the large scale coherence of these elements in the restricted environment in which this crystal grew.

The effect of impurity element incorporation on crystal growth is discussed in general, and the analytical results examined in this light. The incorporation of up to 1.0% Ce as an impurity might affect the crystal habit by inhibiting the development of faces. A mechanism of crystal growth is suggested to account for the element distribution and habit modification in the crystal.

v1

TABLE OF CONTENTS

		Page
I.	INTRODUCTION	1
II.	ANALYTICAL METHODS	4 4 9 10
III.	SAMPLE PREPARATION	16
IV.	STATISTICAL METHODS	19
۷.	MINERALOGY Introduction and nomenclature Morphological crystallography Optical properties Colour Fluorescence Gem apatites	23 23 28 29 30 31 32
VI.	SYNTHETIC STUDIES	34
VII.	STRUCTURE	41
VIII.	THE CARBONATE-APATITE PROBLEM	50
IX.	ENVIRONMENT AND OCCURRENCE	54 54 63 64 69 79
х.	TRACE ELEMENT GEOCHEMISTRY OF APATITE Rare earths	85 93 101 104 106 108

,

Page

X.	TRACE ELEMENT GEOCHEMISTRY OF APATITE	Cont.
	Zirconium	110
	Nickel and Copper	111
	Vanadium and Arsonic	113
		115
	Notes on some other elements	128
	Conclusions	131
XI.	TRACE ELEMENT VARIATIONS NITHIN A SINGLE APATITE CRYSTAL .	13/
	Purposes of the study	13/
	Natural environment of the apatite crystal	147
	Method of study	149
XII.	DISCUSSION OF RESULTS	153
	Conclusions	161
XIII.	APPENDICES	186
	1. Apatite sample localities	186-187
	2. Analyses of apatite sample localities	183-189
	3. Physical parameters of apatite samples	190-192
	4. Analyses of samples from the single apatite crystal	193-195
	5. Inclusions in samples from the single apatite crystal	196-198
XIV.	BIBLIOGRAPHY	199

LIST OF TABLES

	Page
I.	Spectrograph parameters for apatite analysis 14
II.	Spectral lines used
III.	The apatite group of minerals
IV.	Varieties of apatite, $A_5(XO_4)_3$. Zq
V.	Cell parameters for some natural and synthetic apatites 48
VI.	Statistical data of P in igneous rocks
VII.	Analyses of magnatic apatites
VIII.	Analyses of Mn and Sr rich pegmatite apatites
IX.	Analyses of apatites from the Grenville of Ontario & Quebec 74-75
х.	Analyses of sulfate-apatites
XI.	Trace element analyses of apatites, compiled from various published sources
XII.	Correlation coefficients for 46 apatites with data in units of k
XIII.	Correlation coefficients for 46 apatites with data in units of log ₁₀ k
XIV.	Correlation coefficients for 25 metamorphic apatites with data in units of k
XV.	Correlation coefficients for 25 metamorphic apatites with data in units of log ₁₀ k • • • • • • • • • • • • • • • • • • •
XVI.	Correlation coefficients for 21 igneous apatites with data in units of k 120
XVII.	Correlation coefficients for 21 igneous apatites with data in units of log ₁₀ k

Page

į

XVIII.	Means and ranges of analyses for 46 apatites
XIX.	Means and ranges of analyses for 25 metamorphic apatites . 123
XX.	Means and ranges of analyses for 21 igneous apatites 124
XXI.	Distribution of rare earths in minerals from the Kirovograd granite
XXII.	Content of U, in ppm, in apatite
XXIII.	Distribution of U, in ppm, in minerals from the Susamyr batholith
XXIV.	Major element analysis of the single epatite crystal 135
XXV.	Statistical parameters for analyses of single apatite crystal
XXVI.	Analysis of variance tables for single apatite crystal analyses
XXVII.	Correlation coefficients for 102 samples from the single apatite crystal
XXVIII.	Values of $\sum_{i=1}^{1=7} \frac{k_i}{\bar{x}}$ for samples from the single apatite crystal 167

LIST OF FIGURES

Page

. .

⊥ •	phosphate mixture
2.	Plate calibration curves, showing the effect of using only Fe lines for calibration
3.	Vertical symmetry elements in fluorapatite
4.	Network of Ca, O, and P chains in fluorapatite 45
5.	Atomic structure of fluorapatite
6.	Variation in lattice parameters with substitution of Cl for F in apatite
7.	Content of F and Cl in several apatites from igneous rocks, plotted as a function of SiO ₂ content of the rock
8.	Fe content of apatite samples as a function of staining on fractures
9.	Example of good correlation, between Ce and La 91
10.	Example of no correlation, between Ng and Al 92
11.	Lanthanide assemblages in apatite and other minerals 95
12.	Triangular diagram of Ce:Y:La ratios in apatite 97
13.	Plot of Y/Y+Ce+La against total Y+Ce+La in apatite 98
14.	Plot of Sr against La in apatite from igneous intrusives and pegmatites
15.	Plot of Ce against Si in apatite from igneous intrusives and pegmatites
16.	Content of U in apatite as a function of U in total rock for igneous rocks of the Boulder Batholith

ki

Page

17.	Effect of SDBS and TDMAC on the specific growth rate of various faces of adipic acid	141
18.	The effect of growth velocity on the development of crystal faces	14,5
19.	Key to core sample locations in the single apatite crystal	168
20+30	Contoured diagrams of element distributions and inclusions in the single apatite crystal	169-179
31-33	Contours of Ce values in the single apatite crystal by three independent operators, JHC, AMK and GS	180-182

LIST OF PLATES

I.	Cut section of the single apatite crystal normal to the c-axis, prior to mounting and sampling	183
II.	15-day autoradiograph of the single apatite crystal	184
III.	Single apatite crystal, showing mounting and drill assembly during core sample	185

INTRODUCTION

I

Apatite is the most abundant phosphate mineral in the earth's crust, occurring in a very wide range of environments. The published literature on the composition, synthesis, structure and occurrence of apatite is widely dispersed, and it was decided to review and bring together much of this information in one volume.

Quantitative spectrographic analyses of the minor and trace element contents of apatite are relatively meagre, and special techniques are required because of the high P content and spectral line coincidences from rare earth elements.

A thorough knowledge of the chemistry of mineral groups is required as the framework on which a better understanding of the chemistry of rock-forming processes can be built. Apatite, by virtue of its ubiquitous, although minor, occurrence in a wide variety of rocks, is an interesting mineral to investigate. In addition, being a phosphate, it may be expected to have an inherently different geochemical role, with respect to trace element incorporation, from the rock forming silicates. This aspect has received little attention in the past.

The minor and trace element content can be examined in the light of conditions of formation far more readily than for minerals of restricted occurrence. The abundances of the major cations (Ca and P) in apatite appear to be fairly constant, in contrast to many silicates

of Ca, Fe and Mg, also of widespread occurrence. This enables the trace element composition to be correlated with structural and environmental factors with greater control than for those minerals where the additional factor of large scale major element variation is involved.

A precise spectrographic technique was required, therefore, to make analyses of apatite samples from a wide range of igneous, pegmatitic and metamorphic environments. Comparison of the trace element composition with environment could then be made.

As a study in mineral chemistry, it should be possible to determine the degree of stability of the Ca and P sites to trace elements in diadochic substitution. Ca^{2+} and P^{5+} are markedly different in radii, charge, and environment in apatite, and differences in the ability of the two sites to accommodate other elements should become apparent from an investigation of this kind.

Apatite has long been known to be a mineral in which coupled cation substitutions can occur. It would be valuable to determine if coupled substitutions are necessary when impurity elements are present at low concentrations, as this would require additional conditions for a trace element to be incorporated in the structure, i.e., that another element must also be incorporated to balance charges in the crystal.

There is no available data on how trace elements can vary within a single crystal, and variations in the abundance of certain elements in the growth medium might be reflected in the composition of the crystal. This could provide information on the nature of the growth process, as well as the composition of solutions in the growth medium.

If the trace element composition of a single crystal were not homogeneous this could have repercussions on geochemical interpretations made from single mineral fragments, unless adequate sampling precautions were taken.

Fairly recent work in experimental crystal chemistry has firmly established the role of impurity elements in affecting the growth of crystals and modifying their shape. This is discussed in some detail in a later section, as much of the work has probably not been brought to the attention of most geologists. If this occurs in natural environments it might be possible to obtain information from an examination of crystals, in the field, on the growth process and consequent geological history. Crystal habit is often a readily visible feature in the field, requiring no complex equipment for its observation, but unfortunately has been shown little more than passing interest by most geologists.

It was naturally not expected to obtain positive answers to all these questions from this study, but if some features could be pointed out which might begin to answer a few of them, the laborious sampling and analytical work would be considered worthwhile.

ANALYTICAL METHODS

II

The apatite samples were analysed by a D.C. arc spectrographic method, using a controlled atmosphere. The behaviour of phosphates in the arc differs from silicates and it was necessary to examine existing techniques, mainly developed for the analysis of silicates, to see if they could be extended to phosphate samples, and to try out new methods.

It subsequently turned out that a modification of the Pd-graphite method (Shaw, 1960a; Ahrens, 1961), using an $A-O_2$ atmosphere, gave the best results. Many of the methods tried gave information which is applicable to silicate analysis, and will be discussed in some detail here.

Choice of method

Minor elements in a phosphate rich sample may show a marked selective volatilisation in the arc, characterised by a double period of emission. Selective volatilisation curves for several elements in a phosphate matrix are given in Figure 1. These curves were made by racking the photographic plate holder up at 10 second intervals while arcing, in air, and using the Stallwood jet, a 1:1 mixture of graphite and calcium orthophosphate containing In, Ti, Mn and Fe oxides at concentrations less than 0.5%. The drop in intensity over the middle portion of the burn is readily visible to the operator while arcing.

FIGURE 1

Order of volatilisation of several elements in a graphite-phosphate mixture, at concentrations less than 0.5%.



.

 $\lambda_{i} =$

Experiments were made using Li_2CO_3 and KOL as a flum to depress the initial emission peak and hence smooth the burn, but these proved generally unsatisfactory and resulted in a decrease in consitivity.

Using the Stallwood air jet smooths the emission somewhat, presumably by cooling the lower electrode. Aroing in a controlled minture of A and O_2 gives a very smooth burn. A constant ratio of O_2 to A must be maintained during the burn, however. Harly experiments used separate tanks of A and O_2 regulated through flow meters at the tank nossles. It required extreme care to maintain a constant gas mixture under these conditions, and the problem was never satisfactorily solved until tanks containing A and O_2 already mixed to specifications were obtained from the supplier (Canadian Liquid Air Company Ltd.).

An A-O₂ atmosphere reduces or eliminates cyanogen spectra, pormitting the use of spectral lines which would otherwise be masked. Several experiments were made to test the use of other gases. OO_2 has been used in some laboratories to occlude N₂ from the arc (C*Neil and Suhr, 1960). Preliminary experiments with OO_2 applied to this phosphate study, however, should no appreciable reduction of cyanogen, and the technique was not pursued further.

Some time was devoted to developing a technique enabling the sample to be aread in an atmosphere of pure O_2 (Weber, 1961). In an O_2 atmosphere the time for complete sample combustion is about ene-tenth that in air. Loss of material from the electrode cavity is rapid, owing to the explosive nature of the burn and the rapid combustion of the orater wall. Arcing a 1:1 minture of L_2O_3 :phosphate sample was even

FIGURE 2

Plate calibration curves, showing the effect of using only Fe lines to calibrate the line of another element in the same spectral region.



.1

more violent, probably due to the rapid evolution of CO₂. Using a 1:1 mixture of graphite:sample it was found possible to largely eliminate splattering of the material, if care was taken not to use a high initial current.

The major disadvantage of the pure O_2 technique is a marked decrease in sensitivity for most elements. Experimentation failed to overcome this difficulty. Ni could not be detected below 100 ppm using pure O_2 and a 1:1 graphite:sample mixture, whereas in an atmosphere of 80% A and 20% O_2 the sensitivity of Ni is 3 to 4 ppm. Similar results were obtained for other elements.

It is believed that arcing in pure 0_2 results in a marked increase in arc temperature, due to the rapid combustion of C and its introduction into the arc. C has the relatively high ionisation potential of 11.3 volts, and as its concentration in the arc increases so does the temperature of the arc. The degree of ionisation of an element in the arc is a function of its ionisation potential and the arc temperature. For any element, the degree of ionisation increases with the arc temperature, according to Saha's equation (Ahrens, 1961):

$$\frac{\log k^2}{1-k^2} = \frac{-5050V_i}{T} + 2.5 \log T - 6.5$$

where:

T = absolute temperature, ${}^{\circ}K$. k = fraction of the atoms ionised V = ionisation potential of the element

For most elements in the D.C. arc the most sensitive lines are the atom

lines, and it is therefore desirable to keep ionization down to a minimum. The use of the pure oxygen atmosphere appears to have the opposite effect in promoting ionization by increasing the arc temperature. The most consitive lines for all but a few elements are therefore decreased in intensity, although the ion lines may compensate by becoming more sensitive.

Experiments were then made to determine the best proportions of A and O_2 , and it was decided that the use of a controlled atmosphere of 80% A and 20% O_2 was the most desirable. Using a higher concentration of A appears to increase sensitivity, but would require inconveniently long burning times of the order of several minutes.

The instrument parameters of the spectrograph, and arcing conditions are summarised in Table I.

Choice of internal standard and apactral lines

Semi-quantitative analyses of several apatites were made by comparison with Spex Industries Inc. G-standards to determine initially the minor elements present and their general abundance. Master plates of each element found were prepared to check for line coincidences.

Line coincidences are a severe problem in the analysis of apatite, as the minerals contain concentrations of rare earths. Most rare earth spectra are exceedingly complex, and lines from these elements, particularly Ce, may coincide with other elements. While the standard wavelength tables are valuable as a general guide, the order of intensities can vary widely in different matrices under variable arcing conditions.

Palladium was found to be generally valuable as an internal standard, and gives reproducible results with elements as different from it in properties and ionisation potential as Ba. Other elements tested as internal standards (Sn, In, Ag, Lu) were rejected because of line coincidence problems or because they required too low a concentration to be accurately weighed. A concentration of 0.08% PdCl₂ in graphite, mixed 1:1 with the apatite sample, enables the Pd lines at 3258.8Å and 3894.2Å to be measured at a satisfactory intensity.

Table II lists the spectral lines used with their concentration ranges.

A series of artificial standards was prepared, containing known weights of the various elements that were found to be present in the apatites. An artificial phosphate matrix was prepared by precipitating calcium orthophosphate from spec-pure calcium carbonate and reagent grade orthophosphoric acid. The standards were also mixed 1:1 with graphite containing 0.08% PdCl₂ and four replicates were arced at each concentration. Working curves relating the log concentration of each element to the mean ratio of the log intensities of the element line and the standard line (ΔY) were constructed. It was judged not necessary to calculate a linear regression equation as a straight line could be fitted by eye to pass through the means of the replicate analyses. Photometry

Spectral line intensities were measured on an ARL photodensitometer. Clear plate readings were made before each measurement and the transmission value was adjusted to 100%. The background intensity on

any step was measured adjacent to the line being recorded.

Programmes were written to enable a Hendix G-15 digital computer to compute the analysis result from the densitometer transmission value and punch it on IBM data processing cards.

Using 5 transmission readings, A, taken on a series of exposures, the mean calibration factor, f, relating the Seidel function¹, S, to the log intensity² of the emitted light for a given spectral line was computed. The Seidel function has a linear relation to the log intensity, which facilitates computation of log intensity values, i.e. $S = S_0 + f \log_{10} I$.

Log intensity is arbitrarily assigned a value of zero when the Seidel function is zero so that the calibration curve passes through the origin of the coordinates ($S_0 = 0$) and the equation is then simply, $S = f \propto \log_{10} I$.

The response of the photographic plate to light was determined initially using the two-step iron are method. It was suspected that this method of plate calibration contributes too great an error, so a separate calibration factor was then determined for each spectral line.

It was found that the calibration factor determined for a spectral line (other than iron) was different from the calibration factor determined from an iron are spectrum in a wavelength region spanning that spectral line (Fig. 2). The reason for this is not known. It may be that the distributions of elements in the are are appreciably different, enough to affect the intensity of light along the slit, and also that the two-step iron are calibration is usually carried out with

> ¹Seidel Function, S, = $\log_{10}(\frac{100}{4} - 1)$ ²T = log intensity, I.

a high iron concentration in the arc. It is concluded that this procedure can introduce an error, and that it is better to calibrate the plate for each spectral line measured, with the elements in the range of concentrations encountered in the samples.

When the calibration factors are known it is possible to compute the logarithms of the ratios of the intensities of the analysis line, I_{g} , to the internal standard line, I_{g} , for any known concentration, k. This log ratio is called \triangle Y. Pairs of values of k and \triangle Y will then define the working curve, whose equation may be included in a computer programme, so that it becomes possible to convert transmission readings to concentration of the element in the unknown sample in pure.

The sequence of operations is as follows:

Each \triangle Y calculation requires that four transmission readings be obtained on the same step (when a background correction is applied).

 $A_{ab} = \%$ transmission of the background near the analysis line, $A_{a+ab} = \%$ transmission of the analysis line (includes background), $A_{a+ab} = \%$ transmission of background near the standard line, $A_{a+ab} = \%$ transmission of the standard line (includes background). $A_{a+ab} = \%$ transmission of the standard line (includes background). Each transmission reading is converted to the Seidel function, S,

by the relation:

$$S = \log_{10} \left(\frac{100}{A} - 1 \right)$$

- - -

and to the log intensity by:

 $\log_{10}I = \frac{S}{f}$, where f is the calibration factor. The log intensity is then converted to intensity, and the background intensity is subtracted from the line intensity³ to give:

³ It is possible to obtain directly the relation $log(I_{a+ab}-I_{ab})$ if Gaussian logarithms are used.

I, intensity of the analysis line corrected for background, and

Is, intensity of the standard line corrected for background. Whence:

AY = log101 = log101 =

I is a linear function of the log concentration, logk, and the value of k can be computed if the coefficients of the working curve, m and c, are known.

 $\log_{10} k = a \Delta Y + c$

Values of k were punched on ISM data processing cards to provide easy handling and storage of data.

The values of the calibration factor may vary with the emulsion and must be checked periodically, but values of m and c are constant. Values of the working curve constants for the analysis lines used are given in Table II. Spectrograph parameters for apatite analysis

Spectrograph: Jerrall-Ach 21 foot grating instrument, Wadsworth mount, with a first order dispersion of 54/mm.

Condensing optics: A cylindrical lens, horisontal axis, of focal length 25 cms. at the elit; a cylindrical lens, vertical axis, of focal length 6.7 cms. placed 16.1 cms. from the slit, and a 5 cm. disphragm placed 27.5 cms. from the slit. The are to slit distance is 72.5 cms.

Are gep: 4 me.

Slit width: 30 µ

Intensity control: 7 stop sector at the alit, log intensity ratio of 0.2, and one wire mosh screen.

Slit length: 10 mm.

Electrodes: National Carbon Co. "Special" grade 1/8" graphite rod as cathode. United Carbon Products ultrapurity preformed 1/8" graphite electrode as anode, with a 1/16" x 3/8" crater.

- Enuleions and range: Hastman Kodek SAI plate, 2400-3700A. Hastman Kodek III-F plate, 3700-5000A.
- Freessing: 3 mins 15 sees. development in Kodek D19 developer at 20 C, 10 sees. stop bath, 15 mins. acid fix and 40 mins. washing.

Voltage: 225 volts open circuit.

Exposure: To completion, approximately 110-120 secs.

Gurrent: 7 amps.

Jet: Stallwood jet, with a mixture of 80% argon, 20% oxygen at a flow of 18 soft. Silice glass housing enclosing the electrodes.

Photometry: ARL photodensitometer, background corrections applied.

Sample composition: Apatite sample mixed 1:1 with Spec-pure graphite containing 0.08% FdCl_p as internal standard.

TABLE II

Spectral Lines Used

Lir	10	Internal	Concentration	Prostetor	Working curve	
	St.	andard Line	Range	Freeiston	m, slope factor	c, intercept
Si 298	37.65 Po	d 3258.78	500pp=-4%	4.75*	0.9353	3.8921
A1 308	32.16	ft	10-2000pm	5.4%	1.3764	2.3560
Mg 279	90.79	12	500-8000ppm	6.6%	0.4898	3.4133
NI 344	46.26	15	5-1000ppm	-++	1.0132	2.1271
Cu 327	73.96	19	0.5-120ppm	12.83	0,9572	0.9823
Fe 302	20.64	18	5-4000ppm	5.90	1.4740	2.14.61
Fe 302	25.84	22	0.04%-1.00%	13.0%	0.7452	3.1903
Zr 343	38.23	18	1-1000ppm	-**	1.3166	1.7559
X 341	48.81	19	600ppn-2.5%	5.0%	0.7888	3.6021
Y 320	03.32	28	50-2000ppm	5.45%	1.2401	2.5911
Ce 320	01.71	£9	60ppm-2.0%	6.1%*	1.2730	3.3802
V 43'	79.24 P	d 3894.20	8-1500ppa	10.25	1.1864	2.1847
Sr 460	07.33	11	5-1000pm	7.1%	1,3680	1.6532
Sr 483	11.88	11	0.15%-4.0%	10.0%	1.0228	3.9217
La 43	33.73	10	10-3500ppm	7.1%*	1.0584	2.5051
Mn 40	34•49	21	5-1000ppm	6.05	1.0403	1.8048
Ba 45	54.04	11	1-200pm	9.9%	1.0566	1.0864
lin 40	55-54 P	d 3258.78	0.1%-2.0%		1.0897	3.4843

"Calculated from triplicate analyses of single crystal. All others calculated from triplicate analyses of general series of apatite samples.

Wavelongths taken from Harrison (1939).

*In units of log ppa.

##Insufficient data to calculate precision for these lines.

III

SAMPLE PREPARATION

Prior to analysis some physical parameters were determined for each specimen. The characters were ranked by coding, and are listed below with the corresponding code number.

i) Fracture

Each specimen was exemined under a binocular microscope at 35x magnification, and the degree of fracturing in the sample was recorded using the following code.

1 - Perfect, unfractured.

- 2 Slightly fractured.
- 3 Moderately fractured.
- 4 Extensively fractured.
- 5 Highly fractured and broken.

ii) Cleavage

The (0001) basal cleavage is the most conspicuous in apatite,

and this was estimated as for fracture.

- 1 Visible cleavage absent.
- 2 Poor cleavage.
- 3 Modorate cleavage.
- 4 Distinct cleavage.
- 5 Very marked cleavage.

iii) Luotre

Lustre was classified as adamantine, vitreous, sub-resincus or dull, according to the generally accepted definitions of these terms.

iv) Staining

Staining on fractures, crystal surfaces and cleavage planes was classified as below, and the type of staining noted.

No visible staining.
 Very light staining.
 Moderate staining.
 Marked staining.
 Specimen very highly stained.

v) <u>Transparency</u>

Transparency of crystal fragments approximately 1mm. x 1mm. was determined as below.

- 1 Transparent.
 2 Semi-transparent.
 3 Translucent.
 4 Dull, partially translucent.
- 5 Opaque.

This coding system was introduced for convenience in dealing with a large number of specimens, and to enable statistical correlations to be carried out. It is emphasized that the determination of the parameters is qualitative, by the very nature of the features measured. The coding system was applied to obtain as regular a change in the individual features as possible in going from one class to the next.

The <u>colour</u> of each apatite specimen was measured with reference to the rock-colour chart published by the National Research Council, Washington, D.C. in 1948. This chart uses the Munsell Colour identification system, with the colour names based on the ISCC-NES system.¹

Inter-Society Colour Council - National Bureau of Standards.

Each colour is given a symbol which represents the hue, degree of lightness and chroma. The colours are divided into ten major hues, and each hue has 10 divisions. Five would mark the centre of any hue, and ten the boundary between one hue and the next. The degree of lightness grades continuously from 1 to 10, lightness increasing with the number. The chroma refers to the degree of saturation of the colour, with greyish hues having low numbers and vivid colours having high numbers, the range in most rocks and minerals varying from 2 to 6. A colour classified as 5G7/4 would therefore refer to a pure green hue, with a lightness of 7, and a chroma of 4. This would be a light green. The mineral sample is compared with a series of coloured strips in the rock chart, and the correct symbol recorded.

The mineral sample was then ground in an agate mortar, and a known volume of the 150-200 mesh fraction was immersed in oil of refractive index 1.634. Inclusions were identified as far as possible, and counted.

The remainder of the sample was further ground, and mixed 1:1 with graphite containing 0.08% PdCl₂. The mixing was done in analytical grade acetone. This reduces the time of mixing and ensures a more homogenous product. Blank samples were run at intervals to check that there was no contamination introduced in the mixing process.

Approximately 16 mg. of the mixture was loaded into a high density, high purity graphite electrode of 1/8" diameter, with a preformed crater, 1/16" by 3/8".

STATISTICAL METHODS

IV

A single classification of variable analysis of variance was performed on the triplicate analyses from the single crystal, in order to:

- i) determine the precision of the analytical technique,
- ii) determine the variance about the means of the individual samples,
- and iii) separate the variances about means and within groups, so that a F-test could be applied to determine whether the means were significantly different.

For the spectrographic method the absolute dispersion of the analytical data about the mean, for a series of replicates, is a function of the mean. This is illustrated as follows:

If the method is used to analyse samples containing 100 ppm Sr and the results show a standard deviation of 10 ppm, it is found that the standard deviation at a concentration of 1000 ppm Sr is not 10 ppm but 100 ppm. The absolute dispersion varies, although the relative dispersion does not. This arises because the working curve is linear in units of $\log_{10}k$, where k = ppm. The coefficient of variation (standard deviation/mean) is, however, the same in each case.

Transforming the analytical results into units of log₁₀k, the absolute dispersion (in these units) and the variance become homogeneous. It is logical, therefore, to calculate analytical precision, and to perform all statistical computations requiring a homogeneity of variance,

in units of log10k. The theory is outlined in the following paragraphs.

Let $x_{ij} = \log k_{ij}$, for the jth replicate on the ith sample, with n_i replicate analyses. The variance for sample i, S_i^2 , is:

$$S_{i}^{2} = \frac{1}{n_{i}-1} \sum_{j}^{n_{i}} (x_{ij} - \bar{x}_{j})^{2}$$

where $\bar{x}_{i} = \frac{1}{n_{i}} \sum_{j}^{n_{i}} x_{ij}$

For p samples (i = 1,2,3...p), the pooled variance,
$$S_p^2$$
, is:

$$S_p^2 = \frac{(n_1-1)S_1^2 + (n_2-1)S_2^2 + \dots + (n_p-1)S_p^2}{(n_1-1) + (n_2-1) + \dots + (n_p-1)}$$

$$= \frac{\sum_{i=1}^{p} (n_i-1)S_i^2}{\sum_{i=1}^{p} n_i-p}$$

In the present case, $n_1 = n_2 = \dots n_i = 3 = n$, and

$$s_{p}^{2} = \frac{\sum_{i=1}^{p} (n-1)s_{i}^{2}}{pn-p} = \frac{\sum_{i=1}^{p} s_{i}^{2}}{p}$$

 S_p^2 is an estimate of G^2 , the within groups population variance. The analytical precision is estimated by the standard error, S, of the mean (for p samples analysed in triplicate) where:

$$s^2 = \frac{s_p^2}{n} = \frac{s_p^2}{3}$$

An approximation, C, to the arithmetic coefficient of variation may be obtained from S^2 as follows:

Let log U (upper limit) = $\bar{x} + S$ and log L (lower limit) = $\bar{x} - S$, and C(%) = 100 x $\frac{U-L}{2\bar{k}}$, where \bar{x} is the grand mean in log₁₀ units and \bar{k} = antilog \bar{x} . Values of C(%) are given in Table II. The variation about means of the individual samples is obtained in a similar way, when the data are expressed in units of $log_{10}k$, by

$$s_{M}^{2} - s_{p}^{2} = n\epsilon_{m}^{2}$$

 $\mathfrak{S}_{\mathbb{M}}^{2}$ is the mean square about means (categories) obtained from the analysis of variance, and $\mathcal{C}_{\mathbb{m}}^{2}$ is the population between means variance.

Therefore
$$S_m = \sqrt{\frac{S_m^2 - S_p^2}{n}}$$

C(%) is obtained using the upper and lower limits, similar to the calculation of precision.

To test whether there is a significant difference between sample means, i.e., if $G = \frac{2}{m}$ is significantly different from zero, the ratio $F = \frac{S_M^2}{S_p^2}$ obeys the F-distribution with (p-1) and p(n-1) degrees of freedom. F values for the requisite degrees of freedom and the chosen level of significance are tabulated in Dixon & Massey (Table A7c, 1957).

Using a computer program, prepared by Dr. G. V. Middleton for a Bendix G-15 computer, the correlation coefficient matrix was obtained for all possible pairs of elements in a series of samples. To determine whether any population correlation coefficient, ρ_{ij} (estimated by the matrix element r_{ij}) was significantly different from zero at the chosen level of significance (i.e., to test the hypothesis that $\rho = 0$), a value of r was calculated from $r = \frac{t}{\sqrt{t^2 + N-2}}$, which has a t distribution with N-2 degrees of freedom, and compared with the r_{ij} value obtained from the matrix.

It should be noted here that all statistical computations were performed with the computer carrying 12 figures in the calculations, and
analyzes and statistical results have been rounded in the relevant Tables. More figures have been retained than the analysis methods probably justify, in order not to compromise any future recalculations.

.

MINERALOGY

V

Introduction and nomenclature

The apatite group of minerals includes complex phosphates, arsonates and vanadates that crystallise in the dipyramidal class of the hexagonal crystal system (space group $C6_{3/m}$).

The name apatite was first applied by Werner in 1788 to a mineral that was identified as being similar in composition to calcined bone by Proust and by Klaproth in the same year. The mineral was already known as a separate species, but had been often confused with olivine, fluorite, anothyst and other minerals; hence Werner's choice of the name apatite from the Greek $\propto \pi \propto \tau \propto \tau \propto \tau$ meaning to deceive.

Dana's System divides the group into three series on the basis of the cations occupying the A and X positions in the general formula $A_5(XO_4)_3.2_q$ (Palache, Berman and Frondel, 1951). (See Table III).

It is immediately apparent that this is not a rigorous classification as there are five species that cannot be included in any of the series.

The individual members of the apatite series may be further classified into distinct mineral species from the nature of the anion group in the Z position, i.e. <u>fluorapatite</u>, <u>chlorapatite</u>, etc. These minerals exhibit such a wide and continuous range of compositions between the F-, Cl- and OH- end members that compound names are often

TABLE III

The apatite group of minerals (after Palache, Berman and Frondel, 1951)

Apatite Series	<u>a:0</u>
Fluorapatite, $Ca_5(PO_L)_3F$	1:0.7346
Chlorapatite, Ca5(PO,)3Cl	1:0.70
Hydroxylapatite, Ca ₅ (PO ₁) ₃ (OH)	1:0.737
Carbonate-apatite, Ca ₁₀ (PO ₄) ₆ .(CO ₃).(H ₂ O)	-
Pyromorphite Series	
Pyromorphite, Pb ₅ (PO ₁) ₃ Cl	1:0.7632
Mimetite, Pb ₅ (As0,) ₃ Cl	1:0.7224
Vanadinite, Pb ₅ (VO ₄) ₃ Cl	1:0.7122
Svabite Series	
Svabite, $Ca_5(AsO_1)_3(F,OH)$	1:0.7109
Hedyphane, $(Ca, Pb)_5 (AsO_4)_3 CL$	1:0.7052
Dehrnite, $(Ca, Na, K)_5(PO_1)_3(OH)$	1:0.737
Lewistonite, $(Ca, K, Na)_5 (PO_{1})_3 (OH)$	1:0.737
Fermorite, (Ca,Sr) ₅ (PO, AGO,) ₃ (F,OH)	1:0.7292
Wilkeito, $Ca_5(PO_1, SO_1, SiO_1)_3(Cl, F, OH)$	1:0.73
Ellestadite, $Ca_5(PO_4, SiO_4, SO_4)_3(C1, F, OH)$	1:0.725

TABLE IV

Veriet	tics of Ag	atito,	. A. (20)	1)3·20
Kene	R EL	X		heference
Abukumalito ²	Y	34	F,OH	Hata (1938), Machatschki (1939),
Britholite ²	Na,Ce	31	F, CH	Hagels & Machatschki (1953). Hachatschki (1939), Hachatschki (1939), (1900)
Corapatito	Co		FoO	Fereman (1926a and 1926b), Palacha, Berman & Frondel (1951).
Cuproapatite Dahllite	Cu	62	OH	Palacho, Berman & Frondel (1951). Falacho, Berman & Frondel (1951),
Carbapatito Podolito Quercyito	eyng With	nynou dahll) Lito	Brassour & Ballemogne (1949), Geiger (1950), McConnoll (1952).
Collophanita (part)			2. 1. A.D.	
Dehrnite Erikite ²	He, S	C7 S1	633	Larsen (1942) Boeggild (1903), Gerasinovsky (1937).
Fernorite	Sr	1.3	9	Prior & Smith (1910)
Prancolite Euphyrchroite		67	oh?e	Villiers (1942), Hutton & Scelyo (1942), Geiger (1950),
Grodnolite Nauruite Stoffelite	sync with	franc	olite	McConnell (1952), Altschuler, Cieney & Barlow (1953).
Hautefeuillite (apstit	e?) Ng		R_0+	Michel (1893)
kurskite	Ka	6?	P,0H	Chirvinsky (1919), McConnell (1938a).
Levistonito	K, Na		CH	Larson & Shannon (1930), McConnell (1938a) Larson (1942).
Manganapatite	En		Ŷ	Walkar & Parsons (1924), Schairer (1926), Otto (1935), Queneel (1937), Brasseur & Dallemagne (1949), Kratochvil (1952).
Hangualditz	Mn		F,OH	de Jesus (1933), Suensel (1937), Eason (1941), Mason (1942).
Merrillite (apatite?)	1a		0?	Wherry (1917)
Cateolite		07	OH?	Thewlis, Clock & Murray (1939), de Jong (1926).
Pyroclasite			F,OH	Mitchell, Paust & Hendricks (1943)
Pyroguanite	-		F,OH	Mitchell, Faust & Hendricks (1943)
Saamite	Sr,TR		F,0?	Volkova & Melentiav (1939)
Soda-dehrnite	Na(K)	62	\$223	Larsen & Shannon (1930)

TABLE IV (Continued)

Name	A	X	<u>Z</u>	Reference
Talc-apatite Voelckerite			C1 0	Palache, Berman & Frondel (1951). Simpson (1929), Trömel (1932), Rogers (1912), Bredig, Franck & Füldner (1933).
Wilkieite		Si,S		Eakle & Rogers (1914), McConnell (1937), McConnell (1938a).

A Major cation in A position other than Ca.

X Major cation in X position other than P.

Z Anion in Z position.

¹References are, in most cases, of main publications on the variety in question, and do not comprise a complete bibliography of occurrences.

²Not an apatite as defined in text, since rare earths are in excess of Ca and Si is in excess of P.

³TR refers to rare earth elements (terres rares).

used, such as <u>hydroxyfluorapatite</u> (with OH and F in the Z position) and <u>chlorfluorapatite</u>. Palache, Berman and Frondel (1951) and Hey (1955) list these as "varieties" of the species.

Partial substitutions of other elements for Ca in the structure (particularly Sr, Mn, Ce and Y) have led to the use of further varietal names such as <u>manganapatite</u> and <u>cerapatite</u>.

To add to the confusion in the terminology, there are in existence many names for apatites of peculiar composition or from different environments. These have arisen partly from a poor conception of the chemical limits of the term apatite as a species name, and partly from the naming of fine grained phosphate minerals that have later been shown to be chemically and structurally members of the apatite series.

Noting the broad variation in chemical composition of members of the apatite group, Fisher (1958) writes (p.185):

> With the composition of apatites viewed in this broad way, it seems that the mineralogist will defeat himself if he insists on giving a non-chemical name to each of these potential apatites. His subdivisions would not only have to be arbitrary, they would approach infinity.

Fisher suggests that the non-chemical names for members of the pyromorphite series be retained, as their high lead content and geological occurrence separate them from other members of the group.

A working definition of the term apatite as a mineral species for the purposes of this study is as follows:

"Apatite crystallises in the dipyramidal class of the hoxagonal crystal system, with symmetry 6/m. The general chemical formula is $A_5(XO_4)_3 \cdot Z_q$, where

a) Ca is the dominant cation in the A position, and

b) P is the dominant cation in the X position."

It is realised that there are drawbacks to this classification, since Si and S can substitute for P in the X position, and thereby give rise to what may be a continuous isomorphous series between apatite and the end member of the series, ellestadite (McConnell, 1937). The arbitrary definition of apatite above would cut through this series. Similar considerations would apply to the substitution of Si for P, and rare earths for Ca leading to the minerals britholite, crikite and abukumalite (see Table IV). In practice these considerations are not important, as complete solid solutions between apatite and these rare earth-, Si- and S- rich minerals are not common in nature.

Most common apatites are fluorine rich, and it is therefore not necessary to use the prefix <u>fluor</u>, when referring to a fluorine apatite. <u>Chlor</u> and <u>hydroxy</u> as prefixes should be retained for use when Cl or OH is dominant in the Z position.

Most of the non-chemical synonyme for apatite as defined above are listed in Table IV.

Morphological crystallography

As noted previously, apatite crystallises in the dipyramidal class of the hexagonal crystal system, of point group symmetry 6/m. The axial ratios are published in Palache, Berman and Frondel (1951) and Winchell (1951).

In igneous and metamorphic rocks the crystal habit is commonly long prismatic, although shorter prisms and tabular crystals may be developed in voin and pegmatite apatites. A first order pyramid or a basal

plane is the usual termination, and some crystals may show faces of the hexagonal dipyramid. A (0001) indistinct basal cleavage is normally developed, and (1010) in traces.

Etch figures conform to the 6/m symmetry. Lovell (1958) suggested that etch pits on the (0001) plane are formed at edge dislocations along low angle boundaries. These pits were apparently symmetrical with the hexagonal crystal edges.

Optical properties

Apatite is normally colourless in transmitted light, and is uniaxial negative. Some varieties show a weak pleochroism (see p. $_{30}$), and others are anomalously biaxial with a 2V up to 20°.

The refractive indices vary with composition, and Winchell (1951) lists the following:

Uno romano e	ω	ε
Fluorapatite	1.634	1.629
Chlorapatite (syn.)	1.667	1.664
Hydroxylapatite (syn.)	1.651	1.644
Carbonate-apatite	1.629	1.624

The replacement of F by Cl or OH increases the refractive index, while the incorporation of C in the lattice decreases it.

Curves relating the change in optical properties with composition are published in Winchell (1951), but he points out that the numerous substitutions that can occur in the spatito lattice make accurate correlations as yet impossible.

Optical absorption bards in the infra-red have been used by analysts working on organic material, i.e. teeth and bone, to distinguish between fluorapatite and hydroxylapatite (Fischer and Ring, 1957).

The optical absorption in the ultra-violet has been used to study heavy metal impurities in synthetic apatites. Johnson (1961a) showed that synthetic apatite has an intrinsic absorption due to the lattice beginning at 1500Å, with peaks at 1320Å and 1180Å. Added Mn and Sb give rise to absorption bands in the region 1600Å to 3000Å. Mn in higher valence states than Mn⁺⁺ gives rise to an absorption extending into the visible region.

Colour

Natural apatites exhibit a wide range of colours, from colourless to white, and various shades of green, blue and red. The correlation of colour with composition is poorly known, although varieties rich in Mn have long been recognised to be a dark blue-green colour.

Hoffmann (1938) showed that di- and trivalent Fe together in the crystal will produce a green colour in apatites, while Mn imparts a green-blue colour. Reddish hues could not be produced artificially by the addition of Mn. Colour changes could also be produced by fusing apatites with rare earths, i.e. the addition of Ce gives a yellow-green. Hoffmann found that marked colour changes resulted on exposing the mineral to heat, x-rays or even ultra-violet radiation.

Wherry (1917) suggested, probably on insufficient evidence, that the violet colour of apatite is due to necdynium impurity.

The existence of pleochroic apatites has already been noted. Winchell (1951) reports a weak dichroism in Mn bearing apatite, from Z rich green to X blue-green. Dichroic colour centres in synthetic apatites were quantitatively examined by Johnson (1961b). When colourless

synthetic crystals of fluorapatite were exposed to an x-ray beam, a bluegreen colour was visible when the electric vector of the transmitted radiation was parallel to the optic c-axis. Ultra-violet irradiation produced a similar, but weaker effect. After irradiation some of the green colour was bleached at room temperature, although the crystals became a stable bluish green, without further colour change. Irradiated chlorapatites were pink during and after irradiation due to absorption in a different wave length region.

Johnson concludes that the absorbing centre is uniaxial and is oriented parallel to the mineral c-axis. The change in absorption energy with the change in the halogen, and its orientation, define the colour centres as being in the F^- positions. He believes the possibilities are either 0⁻ substituting for F⁻, an F centre or a V centre. If Mn, Cr or Sb impurities are incorporated in the crystal the absorption pattern is different, suggesting that the dichroic colour centres with absorption perpendicular to the c-axis are not produced by impurities.

Fluorescence

Some specimens of apatite fluoresce under ultra-violet radiation at room temperature. Iwase (1935) noted that apatite crystals from metalliferous veins fluoresced strongly over a broad band width, while prismatic apatite from basic rocks gave weak narrow bands. Ulrich (1933) found that the apatites from pegnatites and tin veins emitted a strong yellow- to pink-brown radiation, but other specimens a dark violet. Kohler and Haberlandt (1934), during their research on the fluorescence of various mineral species, noted that apatite had a weak yellow or

violet fluorescence or none at all.

It is not surprising that there is such a wide variation in the type and intensity of the fluorescent radiation from apatite minerals. Many of the versatile impurity activators that can function at low concentrations are present in widely different concentrations in various apatites, i.e., Mn, Fe, Cu, V and Pb. The incorporation of any of these elements in excess (greater than approximately 0.1%) can markedly reduce or modify the intensity of the emitted radiation. In addition, apatite commonly is rich in the rare earth elements, which can act as efficient impurity activators over a wide range of concentrations.

Synthetic apatites activated with Mn or Sb are in general use as fluorescent lamp phosphors. Mn-activated synthetic apatites produce a yellow fluorescence, and Sb-activated crystals fluoresce in the blue. The addition of Mn and Sb together results in a white emission, although the fluorescent efficiency is somewhat reduced.

Wick (1937) demonstrated that apatites exhibit triboluminescence, analogous to the well known triboluminescence of fluorite.

Gem apatites

Finely coloured and transparent apatites from some localities are of gem quality, although the mineral is too soft to be widely used as a gemstone.

Some localities of gen quality apatites are Ehrenfriedersdorf and Schlaggenwald in Germany; Auburn, Maine; from gravels in Ceylon;

¹Triboluminescence is luminescence produced by the mechanical disruption of crystals.

Mogok, Burma; Ajmer and Davada, India; Durango, Mexico, and St. Gothard, Switzerland. (Kraus & Lawson, 1947; Smith, 1952).

SYMTHETIC STUDIES

Up to the present there has not been any systematic attempt to synthesize apatite hydrothermally over the range of magnatic and metamorphic temperatures. Thermal synthesis of apatite has been extensively studied, however,

- i) to obtain structural data,
- ii) to determine the degree of isomorphous replacement of cations (Ca, Sr, Ea, Pb, Ni and Cr) in the apatite lattice,
- and iii) to determine the degree of anionic substitutions possible in the lattice (particularly with respect to OH, CO,, SO, and O) and the stability of these anion-substituted apatites.

Chlorapatites containing appreciable contents of Ce and Y were synthesized by Zambonini (1915). He made chlorapatite from the fusion of the chloride and phosphate of Ca at 1150° C, and added CePO₄ to the mixture. By this method he was apparently able to obtain apatites containing 1.6%, 8.0% and 12.0% CePO₄. Adding TPO₄, he obtained an apatite containing 6.8% TPO₄. From these results he concluded that there was a solid solution series between calcium apatites and rare earth apatites.

A review of the replacement of Ca^{2+} by trivalent rare earths in the apatite lattice, with replacements of P^{5+} by Si^{4+} and some Ca^{2+} by Na⁺, to preserve electrical neutrality, is given by Trömel & Eitel (1957).

VI

A synthetic mixed crystal series between $Ca_9(PO_4)_2$. $CaCl_2$ and $Ca_9(PO_4)_2$. NaCl was demonstrated by Borgstrom (1932), with part of the Ca in the lattice replaceable by Na, and with anionic defects in the Z position.

Brasseur & Dallemagne (1949) thermally synthesized chlor-, oxy-, and carbonate-apatites with Ba, Pb, Mg, Ni, Sr and Zn replacing part of the Ca in the A position. The compounds synthesized by them were:

> $Ca_9(PO_4)_6$.XCl₂ where X was Ba, Pb, Mg, or Ni, $Ca_9(PO_4)_6$.XO where X was Ba, Sr, Pb, or Ni, and $Ca_9(PO_4)_6$.XCO₃ where X was Ba, Sr, Pb, or Zn.

The replacement of Ca by other cations in the hydroxyapatites was demonstrated by Klement (1938, 1939a) and Klement & Dihn (1938a), who synthesized Sr-, Ba-, and Pb-hydroxyapatites at 900 - 1200°C in steam.

Coupled cation replacement in synthetic materials was shown by Klement (1939b), who prepared the compounds $Ca_6Na_4(PO_4)_2(SO_4)_4$. F_2 and $Ca_4Na_6(SO_4)_6$. F_2 with an SO_4^{2-} group replacing PO_4^{3-} , and Na⁺ replacing Ca²⁺ to preserve electrical neutrality. Franck, Bredig & Frank (1936) produced a mixed Na,Ca-apatite in their thermal study of the system $CaO-Na_2O-P_2O_5-CO_2$, but with $(CO_3)^{2-}$ apparently acting as the anionic group, instead of the $(SO_4)^{2-}$ as in Klement's product. These workers also synthesized a compound $Ca_8K_2(PO_4)_6$ in the ternary system $CaO-K_2O-P_2O_5$, which they found to have an apatite structure. Such a compound would be completely anion-defective in the Z-position, but doubt was cast on the validity of this compound by Klement & Dihn (1938b), who showed it to be a mixture of CaKPO₄ and $/\beta$ $-Ca_3(PO_4)_2$.

Pierruccini (1947) thermally synthesized a fluorapatite containing 1.8% Al_2O_3 , and suggested that the Al was replacing both Ca and P, such that $3Al^{3+} \longrightarrow 2Ca^{2+} + P^{5+}$. He also obtained apatites containing 0.05% Fe₂O₃, 0.1% PbO and 0.01% MoO₃.

Minguzzi (1941) synthesized a chrome-bearing chlorapatite using 0.75% Cr_2O_3 and 1.84% CrO_3 . Assuming the Cr is incorporated in the apatite lattice in these valence states, he suggested that Cr was replacing P, by $Cr^{3+} + 2Cr^{6+} \longrightarrow 3P^{5+}$.

Apatites containing Si and S are known in nature and Dihn \dot{a} Klement (1942) showed that Si and S could completely replace P in synthetic materials, with $\operatorname{SiO}_{4}^{4-} + \operatorname{SO}_{4}^{2-} \longrightarrow 2\operatorname{PO}_{4}^{3-}$; such a replacement can occur without a coupled change in the Ca²⁺ cation. If the amounts of Si and S replacing the P are such that the electrical charge is not balanced in the tetrahedral P position, a coupled replacement such as Na⁺ ----> Ca²⁺ is necessary.

Anion-defective apatites have been mentioned above, and Eitel (1958) notes that the apatite structure is so stable that it can support multiple defects of many kinds. Synthetic $Ca_{9.5}(P_3S_2Si)O_{24}F_2$ is an example of a cation-defective structure, while the compounds $Ca_{10.5}(P_5Si)O_{24}F_2$ and $Ca_{10.5}(P_3Si_2)O_{24}F_2$ are examples of apatites with a cation excess.

The production of fluor-, chlor- and oxy-apatites at temperatures below fusion¹, i.e., in the "solid state", was studied by Chaudron &

¹Trömel (1932) determined the melting point of fluorapatite as 1660°C, and of chlorapatite as 1580°C.

Wallaeys (1949). They synthesized these apatites from $CaO.P_2O_5$ mixed with the chloride, fluoride or oxide of Ca at temperatures of $800-900^{\circ}C$. They were further able to convert the synthetic chorapatite to fluorapatite by heating with CaF_2 at $300^{\circ}C$ (Wallaeys & Chaudron, 1950). Similarly, heating hydroxyapatite with CaF_2 or $CaCl_2$ yielded fluorapatite or chlorapatite respectively. Hontel & Chaudron (1951) formed fluorapatite from $Ca_3(PO_4)_2$ and CaF_2 at a temperature of 550°C.

A great amount of experimental work has been done on apatites that contain OH, C or CO_3 groups, or loosely bound H₂O in the structure. This work bears mainly on the composition and identification of the finely crystalline apatite minerals found in low temperature natural environments (i.e., sedimentary and biogenic). The problem of the carbonate apatites is well known, and will be dealt with briefly in a later section. Much of this work is both contradictory and inconclusive, and it would not lie within the scope of the present study to deal with it in great detail. Some of the more important papers dealing with the synthesis of these minerals are discussed below, however, in so far as they have a bearing on the isomorphism that can occur with anionic substitutions in the apatite lattice.

A review of experimental work up to 1938 in the systems $CaO-P_2O_5$ and $CaO-P_2O_5-H_2O$ is given by Eisenberger, Lehrman & Turner (1940). They point out the difficulties inherent in identifying mineral phases in the systems, the slow reaction rates of phosphates, the difficulty of attainment of equilibrium, and the possibilities of absorption effects. Their summary of much of the work in this field is as follows (idem, p.34):

There has been no fundamental investigation of the basic calcium phosphates which has given proper consideration to all the foregoing factors. This undoubtedly accounts for the fact that the comparatively large amount of work in this field is repetitious, disorganized and contradictory.

The system CaO-Po0, was studied by Bredig, Franck & Fuldner They found that it was not possible to synthesize a compound (1933).with the apatite structure in this system, agreeing with the earlier conclusions of Tromel (1932). The phases $Ca_{L}P_{2}O_{9}$ and $Ca_{3}(PO_{L})_{2}$ are the stable forms in the anhydrous system, but both of these compounds are apparently unstable in the presence of moisture, and will readily form hydroxyapatite. The possibility of a pure oxyapatite (voelckerite) with 0²⁻ in the anionic positions, crystallizing from a melt, is therefore probably to be eliminated. Bredig et al (1933) suggest, however, that it is possible to obtain 60-70% of the oxyapatite molecule in isomorphous mixture with fluor- or hydroxy-apatite. Their conclusions are based on the fact that if they mixed CaF, or H₂O with Ca, P₂O, in amounts less than that required stoichicmetrically for the formation of fluor- or hydroxyapatite, they produced on fusion what they believed to be a mixed hydroxy-oxyapatite or fluor-oxyapatite. Hany workers, however, notwithstanding the failure to produce oxyapatite in the completely anhydrous CaO-P205 system, claim to have synthesized it. Brasseur & Dallemagne (1949), as noted earlier, claim to have synthesized oxyapatite with various cations in the A position. It appears that either the identification of the synthetic products is in doubt in some of the cases, or that the systems have not been kept completely dry, and a mixed hydroxy-oxyapatite has been formed.

The compound hydroxyapatite, $Ca_{10}(PO_4)_6 \cdot (OH)_2$, forms readily at high temperatures in the CaO-P₂O₅-H₂O system. Tromel (1932) found it formed as high as 1100° C, and was stable up to 1400° C. A hydroxyapatite analysis will therefore fall short of 100% if the material is not ignited to 1400° C (which is usually the case), as some water will remain in the structure.

The formation of hydroxyapatite in the low temperature range is well documented. Schleede, Schmidt & Kindt (1932) produced hydroxyapatite by the hydrolysis of CaHPO₄, 4CaO.P₂O₅ or Ca₃(PO₄)₂ with hot water. Fouretier (1937) showed that mixing H_3PO_4 and lime water produces an amorphous precipitate which ages to hydroxyapatite. Eisenberger <u>et al</u> (1940) point out that various workers have found this method of producing hydroxyapatite leads to a compound with the CaO/P₂O₅ mole ratio in excess of that required to form Ca₁₀(PO₄)₆(OH)₂. They conclude that the apatite lattice is tolerant to large variations in the system CaO-P₂O₅-H₂O, and believe that hydroxyapatite does not exist in aqueous systems as a unique, stoichicmetric compound.

The possible existence of a hydrated apatite, having the formula $Ca_9(H_2O)_2(PO_4)_6$ was proposed by Hendricks, Hill, Jacob & Jefferson (1931). If this compound exists it might be valid to write the formula as $Ca_9(PO_4)_6 \cdot H_2(OH)_2$ allowing a structural comparison with hydroxyapatite $Ca_9(PO_4)_6 \cdot Ca(OH)_2$. Whether a precipitate from aqueous solution can have the composition of a hydrated apatite has been a matter of some controversy (Eisenberger et al, 1940; Brasseur, 1958). Brasseur (1958) believes that a series of solid solutions is formed between "hydrated" apatite and hydroxyapatite, but that the molecular formula of the compound is $Ca_4H(PO_4)_3$. The Z anionic position in the structure would not be occupied in a compound of this composition. As evidence that such an anion defective compound could have an apatite structure, Brasseur cites the synthesis of $Ca_8K_2(PO_4)_6$ in the ternary system $CaO-K_2O-P_2O_5$ by Franck, Bredig & Frank (1938). Whether this compound exists is, however, in doubt, as was noted earlier (p. 35).

The synthesis of apatites containing CO_3 in the structure has been a matter of long controversy. The problem of the carbonate apatites will be treated in a later section, although the recent work of Ames (1959, 1960) should be mentioned here. Using radioactive tracer techniques, Ames was able to show that calcite is replaced by apatite when in contact with dilute solutions (>0.09 ppm PO_4^{3-}) containing Na₃PO₄, at 15-25°C. The reaction rate is affected by temperature, PO_4^{3-} concentration, pH, HCO₃ concentration, and calcite grain size. According to Ames the idealized reaction leading to the formation of hydroxyapatite is as follows:

NaOH + $3Na_3P0_4$ + $5CaC0_3 \longrightarrow Ca_5(P0_4)_3$ OH + $5Na_2C0_3$ Up to $10\% C0_3^{2-}$ may be retained in the apatite lattice, however, with Na⁺ in the Ca²⁺ positions to maintain electrical neutrality. During the process of phosphate replacement Ames was able to show that cations other than Ca²⁺ were incorporated into the apatite lattice from the solution (i.e., $U0_2^{2+}$, Sr^{2+} and coupled Pm^{3+} - Na⁺, in the Ca²⁺ position).

VII STRUCTURE

The atomic structure of fluor-apatite was first determined by Naray-Szabo (1930), and Mehmel (1930, 1931), who, working independently, came to similar conclusions. It was redetermined by Ecevers & McIntyre (1945), using further X-ray data, and the structure of Naray-Szabo was shown to be essentially correct, with a small correction in the position of the P atoms. A further correction of the P position has been made by Hayashi (1960) using nuclear magnetic resonance analysis.

The space group of fluorapatite is hexagonal $C_{3/m}$. Vertical symmetry elements in the structure are reproduced in Fig. 3.

A chain of Ca-O atoms extends in the c-direction along the vertical 3-fold rotation axes at the corners of the hexagons. These Ca atoms are in nine fold co-ordination, each Ca being surrounded by 9 O atoms, with three O's almost in the same plane as the Ca. At alternate sites in the Ca-O chain these three O's are elevated slightly above the Ca-plane, and at the next site are beneath the plane. Only every second Ca site in the chain is identical therefore. The Ca-O chains are linked together by PO_4 groups to form a hexagonal network, and Fig. 4 shows the arrangement of two of these chains, linked by the P atoms.

A channel is left in the centre of the hexagonal network into which fit further Ca atoms and F. Six Ca atoms fit into "caves" in the wall of the channel, at two levels of 3 each, producing a 6-fold axis at the centre of the hexagonal network. In this position the Ca is in 7-fold

co-ordination with six O's and one F.

The F atoms lie on the vertical hexagonal axis, each F being bonded to 3 Ca's at its own level. Fig. 5 shows the complete structure looking down the c-axis.

The F ion (1.36%) and the OH ion (1.40%) have similar ionic radii, and OH may substitute for F in the structure, with a slight increase in the lattice parameters (Table V). Using synthetic hydroxyapatite the structure was determined by Perloff, Posner & Diorio (1958). The Ca_{II} atoms (those liming the wall of the channel) were found to be in 7-fold co-ordination with six O's and one OH analogous to the fluorapatite structure. The fit of the anionic group in the apatite structure is very critical in that only ions within a narrow size range can be accommodated, and this is responsible for the fact that fluorapatite is more stable than hydroxyapatite. Fossil bone, essentially a hydroxyapatite, will selectively take up fluoring from ground waters and become transformed to fluorapatite. This replacement has been proposed as a method of age dating, although it is generally unsatisfactory (see Goldschmidt, 1954).

The structure of other members of the apatite group was studied by Hendricks, Jefferson & Mosley (1932). They point out that although a complete solid solution series is known to exist between F and Cl in synthetic apatites, there is seldom more than one half of the F replaced by Cl in natural apatites. Goldschmidt (1954) is also doubtful if there is any considerable substitution between F and Cl in minerals. The radius of the Cl⁻ ion is 1.31^A, considerably larger than F⁻ or CH⁻. The

apparently complete solid solution between chlor- and fluor-apatite at the high temperatures of synthesis (800° C) has been demonstrated by Wallaeys and Chaudron (1950). Fig. 6 shows the regular change in the lattice parameters with composition in the series. From structural data, Hendricks <u>et al</u> believe it probable that there is a compound, $Ca_{10}(PO_4)_6$.CL.F with ordering of the Cl and F atoms, and bearing similar relations to chlor- and fluor-apatite as dolomite does to magnesite and calcite. The positions of Cl and F in the apatite structure are apparently not identical, as Cl is too large to fit in exactly the same site as F, but are separated by an amount equal to $\frac{1}{4}$ the length of the unit cell in the c-direction.

There is no evidence from synthesis studies, therefore, that chlorapatite and fluorapatite do not form a complete isomorphous series, but the data on natural apatites is poor, and often inaccurate. The quantitative determination of small quantities of halogens is notoriously difficult.

Some lattice parameters for synthetic and natural apatites are given in Table V.

These determinations of the unit cell parameters are in fairly close agreement, except for the chlorapatite⁸, determined by Hendricks <u>et al</u>. This is the value quoted (wrongly) in Palache, Berman & Frondel (1951). The analysis of this apatite shows 0.17%F, and 4.13%Cl, and possibly contains some other impurity. Omitting this specimen, the range of values encountered in the above Table is:

Vertical symmetry elements in fluorapatite (after Beevers & McIntyre, 1945).



Network of Ca, O, and P chains in fluorapatite (after Beevers & McIntyre, 1945). Black - Calcium Grey - Oxygen White - Phosphorus



Atomic structure of fluorapatite, viewed down the c-axis (after Beevers & McIntyre, 1945). Black - Calcium Grey - Oxygen White - Phosphorus Red - Fluorine



Variation in lattice parameters with substitution of Cl for F in apatite (after Wallaeys & Chaudron, 1950).



Call parameters	for some natu	ural and synthetic ap	atites
Material	<u>1,7pe</u>	<u>a A</u>	cÅ
l _{Fluorapatite}	syn.	9.369	6.884
² Fluorapatite	min.	9.377	6.884
Fluorapatite	min.	9.36	6.88
⁵ Fluorapatite	min.	9.36	6.85
⁶ Fluorapatite	min.	9.37	6.88
8 _{Fluorapatite}	min.	9.37	6.88
⁹ Fluorapatite	min.	9.386	6.878
10 _{Fluorapatite}	min.	9.364	6.879
¹ Chlorapatite	syn.	9.629	6.777
⁸ Chlorapatite	min.	9.52	6.85
10 Chlorapatite	min.	9.630	6.777
1 Hydroxyapatite	syn.	9.422	6.882
² Hydroxyapatite	syn.	9.420	6.885
³ Hydroxyapatite	tooth	9.43	6.88
4 _{Hydroxyapatite}	min.	9.420	6.935
7 _{Hydroxyapatite}	syn.	9.432	6.881
8 Hydroxyapatite	syn.	9.40	6.93
9 _{Hydroxyapatite}	nin.	9.413	6.875
10 Hydroxyapatite	m in .	9-419	6.887

•

2 Perdok (1952)
Thetalis (1940)
4 McConnell (1938 a)
[Hehnel (1930)
Naray-Szabo (1930)
Verloif, Posner & Diorio (1998)
Altschuler Gisney & Earlow (1952)
Brasseur (1954)
syn synthetic product.
min naturally occurring mineral.

Fluorapatite:	a	9.36(0) - 9.386, c $6.85(0) - 6.884$	
Chlorapatite:	a	9.629 - 9.630 ^A , c 6.777 ^A	
Hydroxyapatite:	a	$9.40(0) - 9.432^{\text{A}}$, c $6.875 - 6.935^{\text{A}}$	
a marked change	in	the a parameter with change of phion. Th	4

There is a marked change in the a parameter with change of anion. This increase in the a-dimension can be correlated with increase in anionic radius ($F^{-} = 1.36^{\circ}A$, $OH^{-} = 1.40^{\circ}A$, $CI^{-} = 1.81^{\circ}A$).

The replacement of F by OH in the lattice causes a slight increase in the c- dimension as might be expected, but it is reduced by the substitution of Cl (see also Fig. 6). This is apparently due to the slight difference in position of F and Cl in the apatite lattice, as noted earlier.

VIII

THE CARBONATE-APATITE PROBLEM

Phosphate minerals from low temperature sedimentary and biogenic environments have long been recognized to include members of the apatite series. These apatites vary with a fairly broad composition range, and may contain all or some of the following groups and elements: F, OH, H_2O , C, Na or K. Numerous species names have been proposed for many of these minerals, as was noted earlier (p. 27 & Table IV). Many of these names are falling into disfavour, but the mire ral name francolite is commonly used to refer to apatite from the low-temperature environment containing several per cent CO_2 , F and H_2O . The name dahllite is also often used to refer to a similar apatite with a F content less than 1% (McConnell, 1938b,1958a, 1958b).

The controversy that has occupied much space in the geological and chemical literature since the early 1930's has mainly been concerned with the significance of the CO_2 content of these minerals. Apart from the genesis of the mineral, the points at issue are:

i) is the CO₂ determined on analysis derived from the apatite mineral or from a finely admixed phase, i.e. calcite;

and

ii) if present in the apatite structure, does CO₂ occur as CO²in the anion position, as (CO₄)⁴⁻ replacing (FO₄)³⁻, or³ as C replacing Ca?

The answer to the first point seems to depend on what is being analysed. There is no doubt that calcite may be associated with apatites in general, and with those from sedimentary environments in particular.

If a clean mineral separation (a difficult task in itself) is not made of the fine grained apatite, there is every likelihood that a variable content of calcite will be incorporated in the final fraction. Geiger (1950), for example, took samples of several rock phosphates from Florida, Tunis and Morocco containing from 2.59-7.40% CO, and heated them to 1200°C. CO2 was evolved and the x-ray pattern after heating showed the presence of CaO. As the CaO could not have come from the breakdown of apatite at this temperature, one may logically conclude, therefore, that some of the CO2 was present as calcite in included grains in the original phosphate rock. McConnell (1952) discounts the possibility that inpure fractions of francolite may still contain calcite inclusions on a microscopic or molecular scale. Although there appears little doubt now that C is incorporated in the apatite lattice (Altschuler, Cisney & Barlow, 1953; Silverman, Fuyat & Weiser, 1952), the possibility of some CO₂ being present as calcite inclusions should be kept in mind in evaluating analyses.

Hendricks, Jefferson & Mosley (1932) concluded that a sample of bone, containing 3.09% CO₂, had a structure similar to fluorapatite, from a study of the X-ray diffraction pattern. Assuming that one molecule of water was present in the structure, they wrote the formula as $Ca_{10}(CO_3)(H_2O)(PO_4)_6$, and suggested that the CO_3^{2-} ion was located in the channels in the centre of the apatite hexagonal network, i.e., nearly occupying the F⁻ position. They noted at the time that this arrangement would lower the symmetry of the structure. Gruner & McConnell (1937) pointed out that if this substitution took place the content of F in the

carbonate-apatites should be reduced, but in fact the mineral francolite contains an appreciable content of both CO_2 and F (3.36% CO_2 and 4.11% F in their sample). The structural parameters and density are also not in accord with this substitution. These workers came to the conclusion that the bulk of the C in the structure is replacing P, with a small amount occupying Ca positions on the 3-fold axes at the corners of the hexagons. A statistical distribution of the atoms in the structure of francolite would therefore be, from Gruner & McConnell, corrected by Deans (1938):

10Ca	=	9.810Ca	+	0.077.ig	÷	0.1130
6P	=	5.322P	+	0.026	+	0.6520
240	=	22.8320	+	1.0000H	+	0.168F
2F	-	2.000F				

It is not proposed to deal here in further detail with the numerous publications on the structure of the carbonate-apatites, many of which are somewhat repetitive, but the more important publications are mentioned below.

Arguments proposing the substitution of C for P in apatites are given in Bornsmann-Starinkevitch & Belov (1940), and Ames (1959). A paper by McConnell (1952) discrediting both the substitution of CO_3 for F, and the existence of calcite as an admixed phase, suggests that, in the light of recent analyses, the structure of francolite can be represented by the substitution of CO_3 and of $(OH)_4$ for PO_4 , and also suggests that the Ca position can be occupied by neutral H_2O molecules. Earlier papers proposing the C for Ca substitution are McConnell (1938a, 1938b, 1939), Sandell, Hey & McConnell (1939), and Hutton & Seelye (1942)

Some other papers dealing with the mineralogy of sedimentary and biological carbonate-apatites and their bearing on the carbonate apatite

problem are McConnell & Gruner (1940), McConnell (1950, 1955, 1958a, 1958b), Thewlis (1940), and Thewlis, Glock & Murray (1939).
ENVIRONMENT AND OCCURRENCE

IX

Apatite is probably one of the most widely occurring minerals known, although it is seldom present in great abundance. It is the most abundant phosphate mineral in the earth's crust, and its formation and occurrence is probably governed more by the availability of P than any other factor. Most of the P in the lithosphere is fixed in apatite; Rankama & Sahama (1950) estimate that 95% or more of the P content of igneous rocks is fixed in apatite alone.1

Apatite forms and is stable over a surprisingly wide range of temperatures and pressures. It occurs in meteorites, igneous rocks, from very basic to acid, pegmatites, and high end low temperature orebearing veins associated with the end stages of igneous activity. It is found in high and low grade metamorphic rocks, and often in abundance in skarn deposits in calcite rocks. At the low temperature end of the scale it occurs as a resistate and authigenic mineral in sediments, as a chemical and organic precipitate in marine environments, often forming huge phosphate deposits, and as a principal component in biological materials such as teeth, bone and shells.

Apatite in magmatic rocks i)

Apatite is well known as an accessory mineral in igneous rocks. It is not restricted to rocks of any one composition or from any

It is interesting to note, however, that Goldschmidt (1954) estimates that only 1/5th of the fluorine in igneous rocks is fixed in the apatites.

particular environment, although it is more abundant in basic and in alkalic rocks. The content of apatite in the average igneous rock is given by Rankama & Sahama (1950) as 0.7% in the norm and 0.6% in the mode. Landergren (in Goldschmidt, 1954) collected P analyses of some frequently occurring igneous rocks, and these are included here in Table VI.

The arithmetic means show decreasing P content (and hence apatite?) from basic to silicic rocks, for both the plutonic and the volcanic series. Consideration of the medians and the modes, however, suggest a far more uniform distribution for the plutonic rocks. Landergren notes that this is due to the assymetric distribution of P in the rocks, since the vast majority of the analyses fall within his lowest class interval (0-870 ppm P). Kind (1939) demonstrated a similar decrease in P content with increasing silica, although there is a marked concentration of P in the very basic alkalic rocks (almost 2.0% P_2O_5), although peridotites are low in P.

In most igneous rocks apatite occurs as an accessory mineral and is generally considered to be fluor-apatite. Few reliable chemical analyses of igneous apatites are available, and it appears that most of the identifications of this variety were based on refractive index determinations, which can only be considered reasonably reliable if it be assumed that the composition of the apatite is close to a mixed fluorchlorapatite with no other lattice substitutions or defects. Kind (1939) analysed the apatite from seven igneous rocks of varying composition (see Table VII). Complete chemical analyses of magmatic apatites of satisfactory quality are rare in the literature. Many that are quoted

TABLE VI

Statistical data of P in igneous rocks

(after Landergren, in Goldschmidt, 1954)

Rocks	No. of Analyses	Arith. Mean	Median	Mode (all in ppm.)
Basalt	342	2440	2000	1300	
Andesite	220	1230	1130	650	
Rhyolite	83	550	580	220	
Gabbro	171	1700	1140	440	
Diorite	200	1440	1140	650	
Syenite	194	1330	1150	650	
Granite	340	870	800	650	

56

÷

are found to come from pogmatitic or hydrothermal veins associated with these rocks.

Theoretically the maximum amount of F in a fluor-apatite, according to the formula $\operatorname{Ca}_5(\operatorname{FO}_4)_3$ F is 3.77%, although there is the possibility that the structure can accommodate more than this if some of the F substitutes for O, as appears to be the case in the carbonate-fluorapatites. The analyses of the magnetic apatites above are deficient in $F + \operatorname{Cl} + \operatorname{OH}$, and several possibilities exist:

a) the voslckerite molecule is in solid solution with the fluor-apatite (i.e. 0^2 - is occupying the F positions),

or b) the structure is anion defective.

If (a) is the case, then either the P^{5+} will be replaced by a cation of similar size with a valency greater than 5, or the Ca²⁺ is replaced by a similar cation with a valency greater than 2. The substitution of trivalent rare-earths for Ca²⁺ could restore electrical neutrality, although there is no apparent correlation between content of TR³⁺ and total anions.

The total content of F in ignoous rocks is far more than can be accommodated in the small amount of apatite (Goldschnidt, 1954; Correns, 1956), and much of this excess F goes into the amphiboles and micas.

The contents of F and Cl in magmatic apatite were plotted by Kind (1939) as a function of the SiO_2 content of the total igneous rock, and his diagram is reproduced in Fig. 7. He showed an increase in F, and a corresponding decrease in Cl, with increasing acidity of the rock. The validity of these results was questioned by Corrons (1956) however,

FIGURE 7

Content of F and Cl in several apatites from igneous rocks, plotted as a function of SiO_2 content of the rock (after Kind, 1939).



A	Analyses of magnetic apatites (after Kind, 1939)									
	1	2	3	Ļ.	5	6	7			
CaO	53.46	48.39	42.55	53.55	50.85	51.64	54.19			
P_05	40.84	42.30	40.31	40.02	41.21	40.94	40.11			
AI 03	0.68	-	-	0.22	~	0.89	0.93			
FegOa	-	2.01	3.11	0.24	0.09	0.14,	0.14			
FeO	0.08	-	-	0.66	0.61	1.48	428			
hg0	0.10	2.09	7.54	1.42	2.57	1.06	1.38			
lin0	0.00	0.15	n.d.	0.03	0.10	0.18	0.05			
Sr0	2.00		-	-	-	-	-			
BaO	0.04	-		-	-	-	-			
TR203	0.77	3.13	4.21	1.49	2.64	-				
Na20	1.21	n.d.	n.d.	n.d.	n.d.	1.2/;	0.79			
K20	0.06	n.d.	n.d.	n.d.	n.d.	0.68	0.33			
H20 +	0.19	n.d.	n.d.	n.d.	n.d.	0.54	0.40			
H20 -	-	-	-	-	-	0.13	0.28			
CI	0.31	0.08	0.21	0.33	0.15	0.13	0.96			
F	1.10	1.35	2.52	2.56	1.98	1.83	1.72			
0 = F, Cl	0.53	0.59	1.11	1.15	0.87	0.80	0.94			
TOTAL	100.31	98.91	99.34	99.42	99•53	100.08	100.34			
Percentage of apatite in rock	49.0	0.42	0.49	2.14	0.28	1.90	1.50			

្រា	AR	TT	VTT
- A.	ND.	متعل	VII

¹Apatite rock, Kola Feninsula. ²Biotite-granite, Lausitz, Saxony, with 66.03% SiO₂. ³Monzonite, Ehrenberg, Thuringia, with 60.12% SiO₂. ⁴Sesexite, Kongstock, Czechoslovakia, with 50.50% SiO₂. ⁵Scdalite-syenite, Schwaden, Czechoslovakia, with 48.64% SiO₂. ⁶Ijolite, Iiwaara, Finland with 43.02% SiO₂. ⁷Olivine-nephelinite, Rossberg, Cdenwald, with 40.39% SiO₂.

TABLE VII (Continued)

The analyses were recalculated on the basis of P = 6000 gm.atoms x 10^4 , and the following formulae derived:

1.
$$C^{a}_{9,94}^{A1}_{0,14}^{Fe}_{0,01}^{Mg}_{0,03}^{Sr}_{0,20}^{TR}_{0,05}^{Na}_{0,41}^{K}_{0,01}^{(P0}_{4})_{6}^{OH}_{0,22}_{F_{0,60}^{C1}_{0,09}}$$

2. $C^{a}_{8,69}^{Fe}_{0,25}^{Mg}_{0,57}^{Mn}_{0,02}^{TR}_{0,20}^{(P0}_{4})_{6}^{C1}_{0,02}^{F}_{0,72}$
3. $C^{a}_{8,02}^{Fe}_{0,41}^{Mg}_{1,95}^{TR}_{0,29}^{(P0}_{4})_{6}^{C1}_{0,06}^{F}_{1,40}$
4. $C^{a}_{10,16}^{A1}_{0,05}^{Fe}_{0,13}^{Mg}_{0,37}^{Mn}_{0,01}^{TR}_{0,10}^{(P0}_{4})_{6}^{C1}_{0,10}^{F}_{1,43}$
5. $C^{a}_{9,38}^{Fe}_{0,13}^{Mg}_{0,66}^{Mn}_{0,01}^{TR}_{0,18}^{(P0}_{4})_{6}^{C1}_{0,04}^{F}_{1,08}$
6. $C^{a}_{9,57}^{A1}_{0,18}^{Fe}_{0,23}^{Mg}_{0,27}^{Mn}_{0,03}^{Na}_{0,42}^{K}_{0,15}^{(F0}_{4})_{6}^{OH}_{0,62}^{C1}_{0,04}^{F}_{1,02}$
7. $C^{a}_{10,24}^{A1}_{0,19}^{Fe}_{0,02}^{Mg}_{0,36}^{Na}_{0,27}^{K}_{0,07}^{(P0}_{4})_{6}^{OH}_{0,47}^{C1}_{0,29}^{F}_{0,96}$

on the basis that the figure for F in a granite apatite (3.5%F) had been determined by another worker, whereas the obtained figure of 1.35%F from the Lausitz granite had been rejected by Kind because of possible analytical error.

Of particular interest are igneous rocks where apatite is no longer an accessory, but becomes a major constituent. These occurrences are restricted to areas of alkalic, alkalic ultrabasic or certain carbonate rocks. As well as being enriched in P, F and CO₂, these rocks are noted for their high concentrations of some of the "rarer elements", i.e. rare earths, Sr, Ba, Nb, Ta?, Zr, and Ti. Such rocks are relatively uncommon, but in some regions occur in profusion, generally being circular or elliptical in outcrop. Syenites, nepheline syenites, ijolites and urtites are the principal rock types, and, in some areas, carbonatites.

In the Kola Peninsula of Russia the alkaline Khibina pluton is well known for the vast deposits of nepheline-apatite² rock developed in association with nepheline-symmite and urtite-ijolite. It has been estimated that 60-2000 million tons of apatite-nepheline rock are present, containing 60-80% apatite (Fersman, 1929; Antonov, 1934). This body of apatite rock occurs in a flat sheet, between overlying nepheline-symmite and urtite-ijolite, and is considered to have formed by the crystallisation of a residual magma from a P-rich alkalic ultra-

²Apatite refers to the fluorine-bearing variety in the discussion of these occurrences, unless otherwise stated.

basic. Sphene-apatite rocks from the N.W. Khibina have been similarly accredited to the independent intrusion of a P-rich magma (Svyatlovsky & Dieterikhs, 1939).

A pyroxenite containing 7-10% apatite and 3-12% magnetite is associated with an alkalic stock near Libby, Montana (Larsen & Pardee, 1929). The pyroxenite grades into a biotite-pyroxenite, with apatite and magnetite becoming less abundant as the biotite content increases. Apatite-pyroxenites have also been described from a composite alkalic stock at Iron Hill, Colorado (Larsen, 1942a). At Palabora in the Eastern Transvaal, large apatite deposits occur in a pyroxenite associated with syenite and limestone. There is every gradation from a diopsidicpyroxenite, containing accessory apatite, to a pure apatite rock (Shand, 1931; Du Toit, 1931).

The ubiquitous occurrence and petrology of apatite in the nephelinesyenites, urtite-ijolites and carbonatites of the alkalic rocks in S.E. Uganda has been described by Davies (1947, 1956).

A more detailed review of all the occurrences of apatite in these well known alkalic. and carbonatite complexes is not necessary here. The papers of Pecora (1956) and Rowe (1958) contain descriptions of these deposits and detailed bibliographies. Apart from the areas mentioned above, these workers note the occurrence of apatite in many other alkalic, alkalic ultrabasic and carbonatite complexes including the following: Jacupiranga, Brazil; Kaiserstuhl, Germany; Isoka, N. Rhodesia; the Fen district of Norway; Alno Island, Sweden; Chilwa, Nyasaland; Panda Hill, Tanganyika; Magnet Cove, Arkansas; Mountain Pass, California; Spitzkop,

S. Africa; Hemegos, Ontario; Oka, Queboc.

In many instances apatite from these areas may belong to more than one phase of mineralisation. Gutkova (1925) considers, for example, that apatite from the Khibina area of the Kola Peninsula may belong to the magnetic, epimagnetic and pneumatolytic phases.

ii) Apatite in meteorites

P and Cl are relatively abundant in meteorites, although much of the P is concentrated in the metal phase as phosphides of Fe and Ni, in keeping with the siderophile nature of the element. Apatite has been reported as a very minor accessory in stony meteorites, however, and is apparently always chlor-apatite (McLintock & Ennos, 1922; Lacroix, 1923). Shannon & Larsen (1925) found 4.87% Cl in apatite from the New Concord stony meteorite.

Goldschmidt (1954) gives values of 1050 ppm P, 1000-1500 ppm Cl and 3.3 ppm F as the average contents of these elements in meteorites. Although there are several other estimates of the Cl content in meteorites (Correns, 1956), and the data on F is meagre, it appears that the Cl/F ratio in meteorites is at least about 50 times that in the lithosphere. It is not surprising, therefore, that the apatites from meteorites are chlorapatites, in view of the apparent solid solution existing between Cl- and F- varieties at high temperatures.³

³It is interesting to note, however, that in the low temperature environment of the ocean, where the Cl/F ratio is probably about 600 times greater than in meteorites, Cl is not significantly incorporated in apatite.

iii) Apatite in permatites and hydrothermal veins

Apatite is a fairly common mineral in pegmatitic deposits, and is sometimes associated with rare phosphate minerals. A fluor-manganapatite containing 4.93% Mn from the phosphate pegmatites of the Oberpfalz and Bavarian Forest was described by Laubmann & Steinmetz (1920) and Mullbauer (1925). Mullbauer considered that apatite forms in the early magmatic phase and in a later hydrothermal phase. Kn rich apatites from pegmatites have also been described by Walker & Parsons (1924) from Nova Scotia; Schairer (1926) from Strickland Quarry, Portland. Maine (in a granite pagnatite associated with Li and other phosphate minerals); Landes (1929) in the granite pegmatites of S. Dakota; Quensel (1937) and Mason (1941a, 1941b) from the Li and P rich granite pegnatite at Varutrask, Sweden; Pehrman (1939) from a hornblende-gabbro pegmatite, Lennas, Finland; Mitchell & McGavock (1960) from the Morefield pegnatite, Virginia; Yakzhin (in Tatarinov, 1937) from the Kondakova pegnatites, U.S.S.R.; and Kratochvil (1952) from granite pegmatites at Meclov. Mario de Jesus (1933) described mangualdite (a Mn-apatite) containing 31.47% Mn from the granite pegmatites of Mangualde, Portugal.

The paragenesis of minerals in the granite pegnatites of central Maine was extensively studied by Landes (1925). He considered manganapatite (containing 8.67% Mn and 3.80% F) to form at the first, i.e., liquid, stage of pegnatitic crystallization, accompanied by microcline, quartz, biotite, tournaline, beryl, garnet and arsenopyrite. This was followed by three hydrothermal stages of gradually decreasing temperature. Minor apatite occurs in the first high temperature hydrothermal phase

A	nalyses o	of lin and	Sr rich	n pegnat:	ite apati	tes	
	1	2	3	4	5	6	7
CaO	50.60	47.33	50.31	52.00	46.23		46.30
P205	39.85	41.43	41.50	41.84	39.20	40.31	39.20
AI203	1.92	nil		0.15	3.13		0.38
Fe ₂ 0 ₃	2.53	0.55		0.35	0.32		0.27
FeO			0.26	nil	0.50		
MgO	0.16	nil	0.04	0.10	nil		0.25
MnO	3.12	8.67	5.32	4.31	8.84		0.02
SrO						1.23	11.60
BaO						0.03	0.06
Na20			nil	0.03	(0.10
K20			nil	0.07	0.56		0.02
1.120				0.01	nil		
H20+	0.93	0.06	0.25	0.17	0.21		0.14
H ₂ 0-			0.03	0.04	0.20		
CI				0.02	0.15		
F	1.84	3.80	3.41	1.43	1.20		2.57
Insol.			0.35	0.18			
Less O=F,Cl	0.77	1.60	1.56	0.60	0.57		1.08
TOTAL	100.18	100.24	99.91	100.10	100.59*		100.01***
1 2Wal 3Clar 3Que 4Que 5Yak 6Afa 7Lar	ker & Pa des (192 nsel (19 nsel (19 zhin, in nasev (1 sen, Fle	rsons (19 5) 37) 37) Tataring 948) tcher & (924) ov (1937 Cisney () 1952)			

^{\leq}Includes Si0₂ 0.25%, Ti0₂ 0.02%, B₂0₃ 0.35%. [#]Includes Si0₂ 0.14%, Ti0₂ 0.04%.

TABLE	VIII

TABLE VIII (Continued)

The analyses were recalculated on the basis $(P + Si) = 6000 \text{ gm.atoms} \times 10^4$, and the following formulae derived:

1.
$$C^{a}_{9.65}^{iin}_{0.47}^{iig}_{0.04}^{F_{0}}_{0.34}^{A1}_{0.38}^{(PO}_{4})_{6}^{(OH)}_{1.10}^{F_{1.04}}$$

2. $C^{a}_{8.42}^{Mn}_{1.26}^{F_{0}}_{0.07}^{(PO}_{4})_{6}^{(OH)}_{0.07}^{F_{2.06}}$
3. $C^{a}_{9.21}^{Mn}_{0.77}^{F_{0}}_{0.04}^{Mg}_{10.01}^{(PO}_{4})_{6}^{(OH)}_{0.28}^{F_{1.84}}$
4. $C^{a}_{9.44}^{Mn}_{0.62}^{Mg}_{0.03}^{F_{0}}_{0.05}^{A1}_{0.03}^{Na}_{0.01}^{Na}_{0.01}^{(PO}_{4})_{6}^{(OH)}_{0.19}^{F_{0.75}}$
*5. $C^{a}_{8.73}^{in}_{1.32}^{A1}_{0.65}^{F_{0}}_{0.12}^{(Na+K)}_{0.16}^{(P}_{5.85}^{Si}_{0.04}^{B}_{0.11}^{O}_{24}^{O}_{4}^{(OH)}_{0.25}_{C1}_{0.02}^{F_{0.67}}$
7. $C^{a}_{8.93}^{Sr}_{1.21}^{A1}_{0.08}^{F_{0}}_{0.04}^{Mg}_{0.07}^{Na}_{0.04}^{(P}_{5.98}^{Si}_{0.02}^{O}_{24}^{O}_{4}^{(OH)}_{0.17}^{F_{1.46}}$

$$(P + Si + B) = 6000 \text{ gm. atoms x } 10^4.$$

associated with clevelandite, and also is of vory minor occurrence at the last hydrothermal stage. These are similar conclusions to those of Laubmann & Steinmetz (1920) and Mullbauer (1925) noted earlier. The pegnatite at Varuträsk, Sweden, contains manganapatite (and manganvcelckerite?) as an early pegnatite mineral (Quensel, 1937) and also a manganhydroxy-apatite occurring as veinlets within secondary oxidation minerals (Mason, 1941b) The occurrence of mangan-apatite, containing 4.74% Mn at the primary pegnatite stage was noted by Pehrman (1939), in the Lemass gabbro pegnatites of Finland. An apatite containing less Mn (1.80% Mn) from a later hydrothermal stage of the same pegnatite is recorded, and apatite from a geode in the pegnatite contained only 0.28% Mn.

The occurrence of manganess-rich apatite in the primary stages of granite pegmatite crystallization is thus well substantiated. There is some evidence of a decrease in Mn content of apatite crystallizing in the later stages of pegmatite crystallization. Analyses of Mn-rich pegmatite apatites are presented in Table VIII.

The occurrance of pegmatite apatites rich in Sr has been noted by Afanasev (1948) who found up to 4.0% SrO in apatite from a pegmatite vein associated with the Caledonian intrusions of the Western Caucasus Mountains. Larsen, Fletcher & Cisney (1952) found 11.60% SrO in apatite from veins in a syenite dyke in Montana. The apatite separated from the syenite rock, on the other hand, contained no appreciable Sr. Volkova & Melentiev (1939) found up to 11.42% SrO in apatites from Khibina, and found an increase in rare-earth content with increasing Sr. Analyses of Sr-rich apatites are included in Table VIII.

Goldschmidt (1954) and Rankama & Sahama (1950) state that, in their experience, the apatite of basic igneous rocks and pegmatites is richer in rare earths than apatite in granite pegmatites and hydrothermal veins. Goldschmidt notes, however, that the apatites of nepheline syenites are usually richest in rare earth elements. There is little data available, however, on the rare earth content of pegmatite apatite, so this topic will be deferred to a later section, using the present results.

Apatite from other pegnatite and hydrothermal deposits has been described by Mieleitner (1921) from the Li-rich granite pegnatites of Fuchsbau, Germany; Reuning (1923) from P-rich granite pegnatite veins near Dinard, France; Janisch (1927) from granite pegnatites, associated with barite, in Zoutspansberg, S. Africa; Nowacek (1928) from gabbro pegnatites in eastern Bohemia; Gevers and Fromnurze (1930) from Snbearing granite pegnatites in Erongo, S.W. Africa; Dittler (1932) from a pyroxene-calcite-apatite vein in serpentine from Salzburg; Murdoch (1955, 1958) from the Li and P-rich granite pegnatites of Borborema, Brazil; Lindberg & Pecora (1955) from the Li- and P-rich Sapucaia granite pegnatite, Brazil; and Melon & Toussaint (1957) from the Liand P-rich granite pegnatites at Kivu, in the Congo.

The occurrence of apatite in high temperature Sn and W ore veins from Bolivia has been noted by Ahlfeld (1931), and by Lacroix (1933) from Sn-W veins in basalts in Indo-China.

In a paper seen in abstract only, Harada (1938) describes apatite crystals in vugs in a quartz-diorite, encrusted with zeolites and chlorite. The apatites have a white exterior zone, believed due to hydrothermal

alteration. The interior of the crystal contains 3.74% Cl, 1.15% F, and 0.06% H₂O, while the altered zone contains 1.42% Cl, 0.44% F and 0.10% H₂O.

The occurrence of apatite of "solfataric" origin has been described by Starraba (1942) coating haematite crystals on blocks of reddened scoria from Mt. Etna vulcanism.

iv) Apatite from metamorphic rocks

The interplay of magmatic, metamorphic and metasomatic processes gives rise to difficulties in classifying apatite from metamorphic rocks. Probably it would be best to consider such apatites merely as being in a metamorphic environment, recognizing that some were probably formed from pegmatitic and hydrothermal processes similar to those discussed in the previous section. Hogarth (1957), for example, describes apatite-bearing veins from Nisikatch Lake, Saskatchewan. Apatite occurs in well defined zones in the veins, associated with hyalophane, allanite, epidote, thorite, sphene and specularite. The country rock consists of PreCambrian gneisses and amphibolites, and Hogarth considers the veins to be "part intrusive and part hydrothermal", associated with the later stages of igneous activity. From the mineralogy and the environment of the veins it is apparent that igneous and metamorphic processes have both played a part in the evolution of the veins. Occurrences of this type will be treated in this section as apatite from a regional metamorphic environment. Similar considerations might apply to the phlogopite-apatite deposits of Quebec and elsewhere.

The contact metamorphism of phosphorite beds by granite in

Kazakhstan, U.S.S.R., has been described by Bezruzov (1939). A light coloured, fine grained apatite rock is developed within the thermal aureole. Lowell (1955) has described a similar occurrence in S.W. Montana, where Tertiary andesite sills and a quartz-monzonite stock have baked and indurated the Permian Phosphoria Formation. Assimilation of phosphate sediment by the intrusives is apparently absent, although "collophane" and francolite in the sediment adjacent to the igneous contacts have been recrystallized to a fine grained apatite rock, and some migration of P has occurred to form quartz-apatite veins.

The occurrence of apatite in metamorphosed limestones, either in a zone adjacent to igneous intrusion, i.e., contact metamorphic and metasomatic skarns, or in an area of regional metamorphic and igneous activity, has been frequently recorded. Pegmatoid segregations and intrusive veins may be extensively developed, and apatite may be of ubiquitous occurrence. Commonly associated with apatite in this environment are calcite, diopside, fluorite, alkali-felspar and scapolite. Apatite in skarn deposite of the Fennoscanian Shield was described by Laitakari (1921) and von Eckermann (1922). Laitakari described the occurrence, at Pargas, Finland, of apatite and other skarn minerals at limestone contact zones in regionally metamorphosed amphibolites, gneisces and granites. Von Eckermann noted the similarity of the apatite in limestone skarns at Mansjo Mt., Finland to those described from Pargas.

Apatite in the rocks of the Grenville Province of Canada was described in the classic memoir of Adams & Earlow (1910) on the geology of the Haliburton-Bancroft area, and earlier by Adams & Lawson (1888),

in association with scapolite. Dawson (1876) suggested that the apatite deposits in the Grenville were produced by the metamorphism of phosphate sediments. Subsequent descriptions of these areas mentioning apatite incidentally are too numerous to list here, particularly those of the Provincial Government Surveys of Ontario and Quebec. More recent papers by Hewitt (1957), Hewitt & James (1955) and Satterley (1943), amongst others, mention the occurrence of apatite in calcite-fluorite skarns, and in diopside-scapolite-phlogopite pyroxenites, often associated with radioactive minerals.

Canadian apatite-phlogopite deposits were described by Spence (1920), the apatite-phlogopite deposits of Quebec extensively by Landes (1938), and an occurrence in Ontario by Currie (1951). These deposits are associated with diopsidic pyroxenite, apparently intrusive into Grenville gneisses and limestones. Calcite, phlogopite and apatite occur in veins cutting the pyroxenites. Scapolite is a common associate of the deposits, best developed at the contact of the pyroxenite and a microcline pegmatite. Landes considered the deposits to be hydrothermal, derived from the deep-seated crystallization of a granitic magma rich in P. Currie (1951) considered the mica-apatite deposit in Lanark Co., Ontario, to be formed by the contact metamorphism and metasomatism of limestones by pegmatitic solutions.

Shaw (1960b) considers the formation of scapolite as "part of a more widespread plutonic metasomatic metamorphism, which also led to the development of anatectic syenite, granite, and migmatites, and concentrated particular elements into the widespread deposits of magnetite,

apatite, phlogopite, talc, corundum, lead, zinc, rare-earths, and radio active minerals". The interplay of the various processes of metasomatiam, metamorphism and magnatism in the formation of scapolite, and probably in the formation of the phlogopite and apatite is implicit in this statement of Shaw's. It is doubtful if it is reasonable to assign the formation of many apatite veins in the PreCambrian to any one process, without due regard for the others.

Similar deposits to those in Canada have been described by Smirnov (1925) from Slyudyanka, in the Transbaikal, U.S.S.R. Apatite, calcite, diopside and scapolite occur in phlogopite veins and pods within amphibolites, limestones and pegmatites. Smirnov considers the deposits to be metasomatic from residual granitic solutions. The occurrence of apatite associated with scapolite in gneisses is mentioned by Adams (1926) from Mogok, Burma. Lacroix (1940) considers the phlogopiteapatite deposits in pyroxenite from southern Madagascar to be very similar to those of eastern Canada.

Apatite, occurring in skarn type mineralization at the contact of a granite and limestone, is associated with epidote, diopside and calcite, at Center Strafford, New Hampshire, (Stewart, 1939). The occurrence of apatite and lepidomelane in calcite lenses in the nephelinesyenites of Faraday Twp., Ontario, was described by Walker and Parsons (1926). Another paper by Walker and Parsons (1925) on a calcite-apatite vein from Turner's Island, Renfrew, Ontario, considers the vein to be of high temperature igneous origin, since they believe that the calcite has inverted from a high temperature form.

Analyses of apatites from the deposits in the Grenville are reproduced in Table IX. Most of these are from a paper by Dadson (1933), who attempted, without success, to find a correlation between crystal habit of the apatite and its chemical composition.

Apatite containing appreciable contents of S and Si in the structure has been described from several environments. Brauns (1916) analysed apatite from the sanidinites of the Laacher See, Cermany. The apatite, containing 1.30% SO₃, occurs in fragments and blocks ejected from the Laacher See volcances and now enclosed in trachyte and tuffs. Scapolite, and minerals characteristic of the high temperature, low pressure, near surface, metamorphism of the sanidinite facies, i.e. sanidine, cordierite, spinel, corundum and hyperstheme, are associated with the apatite. SiO₂ was not recorded in Braun's analysis.

Eakle & Rogers (1914) were the first to discover appreciable amounts of S and Si in apatite. The analysed specimen came from the well known mineral locality at Crestmore, California, and contained 12.28% SO₃ and 9.62% SiO₂. The Crestmore occurrences are in Palaeozoic crystalline limestomes, intruded and metamorphosed by later quartz-monzonite porphyry intrusives. Diopside, wollastonite, scapolite, vesuvianite, garnet and a host of extremely rare mineral species occur in the limestome contact rocks, as the result of metasomatism by solutions emanating from the porphyry. Apatite occurs as an accessory in most of the igneous and sedimentary rocks of the area, although the S and Si rich variety (named wilkieite by Eakle & Rogers) is restricted to the limestones and contact rocks adjacent to the intrusives (Daly, 1935). McConnell (1937) found

Analyses	of apatites	iron th	e Grenville	of Ontari	o and Que	ebec.
	1	2	3	4	5	6
CaO	53.96	55.16	55.48	55 .3 8	55.25	55.10
P205	39.70	41.30	40.31	41.05	41.12	41.24
A1203	0.98	0.24	0.36	0.23	0.35	0.12
Fe203	1.28	0.63	0.58	0.51	0.36	
FeO		0.14				0.36
Mg0	0.10		0.26			0.23
MnO	0.01	0.12		0.04	0.01	0.12
Na20			0.18	0.16		
K ₂ Õ			0.22	0.12		
H ₂ 0	0.23	0.01	0.11	0.13	0.11	
Cl	0.11	0.09	0.30	0.48	0.88	
F	3.40	3.67	3.47	2.35	3.31	
c0 ₂	0.47	0.50	0.14	0.22	0.33	0.73
Insol.	1.16	0.28	0.42	0.35	0.27	0.22
Less O=F,Cl	1.45	1.56	1.52	1.09	1.58	1.54
TOTAL	99.95	100.58	100.31	99.93	100.41	100.23

TABLE IX

¹From Eganville, Renfrew Co., Ontario, with included haematite and calcite.

²From Faraday Twp., Hastings Co., Ontario, with possible calcite and unidentified inclusions.

From Battle Creek, Quebec, with quartz and haematite inclusions.

⁴From South Sherbrooke, Ontario, with haematite and unidentified inclusions.

⁵From Elmsley, Ontario, with calcite, mica? and unidentified inclusions.

⁶From Faraday Tup., Hastings Co., Ontario.

1-5 After Dadson (1933)

6. After Walker & Parsons (1926)

TABLE IX (Continued)

The analyses were recalculated on the basis (P + C) = 6000 gm.atoms $\times 10^4$, and the following formulae derived:

1.
$$C_{a}_{10.13}^{A1}_{0.20}^{Fe}_{0.17}^{Hg}_{0.03}^{(P}_{5.89}^{C}_{0.11}^{024}^{(OH)}_{24}^{(OH)}_{0.27}^{C1}_{0.03}^{F}_{1.89}^{F}_{1.89}$$

2.
$$Ca_{9.95}^{A1}0.05^{Fe}0.10^{Hn}0.02^{(P}5.88^{C}0.12^{O}24)^{(OH)}0.01^{C1}0.03^{F}1.95$$

$${}^{3} \cdot {}^{Ca}_{10.39} {}^{A1}_{0.08} {}^{Fe}_{0.08} {}^{Kg}_{0.07} {}^{Na}_{0.06} {}^{C0}_{0.05} {}^{(P}_{5.97} {}^{C}_{0.03} {}^{O}_{24} {}^{(OH)}_{0.13} {}^{C1}_{0.09} {}^{F}_{1.92} {}^{C1}_{0.09} {}^{F}_{0.09} {}^{F}_{0.0$$

4.
$$Ca_{10.16}^{A1}0.05^{Fe}0.07^{IIa}0.05^{K}0.03^{(P}5.95^{C}0.05^{O}24^{)(OII)}0.15^{C1}0.14^{F}1.27$$

5.
$$C_{a_{10.07}A1}O.07^{Fe}O.05^{(P}5.92^{C}O.08^{O}24)^{(OH)}O.13^{C1}O.26^{F}1.78}$$

an apatite containing 20.69% SO3, and 17.31% SiO2 from the same environment as the wilkieite at Crestmore, and named this mineral ellestadite. The P_2O_5 content was very low (3.06%) and McConnell believed this was very near to the end member of a complete solid solution series between apatite and ellestadite, with Si and S substituting for P in the apatite lattice. Wilkieite would fall in the middle of the series. 0.61% CO2 was found in the analysis of this mineral, and in the light of McConnell's views on the position of the C in the apatite structure at that time he assigned the formula Ca₆(F,Cl,O,OH)₂/(S,Si,P,C)O₄7₆(Ca,C)₄ to ellestadite, with C replacing some of the Ca atoms on the 3-fold axes. Regardless of the validity of this conclusion, the essential feature is a coupled replacement of Si^{4+} and $S^{6+} \longrightarrow 2P^{5+}$ in the lattice. Vasileva (1958) doubts that the CO2 content in the analyses of wilkieite and ellestadite represents more than admixed calcite, although he considers the coupled substitution mentioned above as proven, in view of the close similarity of the ionic radii, i.e., $S^{6+} = 0.39^{\circ}$ and $P^{5+} = 0.35^{\circ}$, and the balancing of charges in the crystal.

Sulphate-apatites have also been reported from the contact metamorphic deposits of the Shishin Mine in the Urals, U.S.S.R., by Borneman-Starinkevitch (1938), who agreed with the Si and S substitution for P, but considered the C for Ca substitution unlikely. Further analyses of S and Si bearing apatites are reported by Vasileva (1958) from the phlogopite-apatite deposits in the Aldan district, U.S.S.R. Analyses of these apatites are reproduced in Table $\frac{X}{2}$.

	Analyses of	Sulfate-	-apatites	(after Va	sileva, l	958a)	
	l	2	3	4	5	6	7
P205	20.85	3.06	39.66	32.91	40.36	40.54	38.63
SiO	9.62	17.31		3.77	0.47	0.40	abs.
SO3	12.28	20.69	1.30	3.74	0.53	0.36	2.58
c02	2.10	0.61	abs.	1.80	abs.	abs.	1.05
CaO	54.44	55.18	53.60	55.73	53.54	53.94	53.23
SrO				0.10		0.02	0.20
TR203				abs.	2.05	1.29	tr.
FegOz		0.22	1.10	abs.	abs.	abs.	abs.
A1_0_		0.13	1.10	abs.	abs.	abs.	abs.
MnO	0.77	0.01		abs.	abs.	0.02	tr.
MgO		0.47	0.14	abs.	abs.	0.18	abs.
К_0			2.70	abs.	abs.	abs.	abs.
Na 0			2.70	abs.	0.35	0.16	0.98
F		0.57	0.93	abs.	2.56	1.80	0.10
H ₂ 0	tr.	0.63	abs.	1.59	0.28	0.39	0.79
cĩ		1.64	0.42	0.62	0.81	2.10	3.50
Insol.	abs.	abs.	0.60	abs.	abs.	abs.	abs.
$-0 = F_{,0}C$	1	0.61	0.47	0.14	1.25	1.22	0.81
	100.06**	99.91	99.98	100.12	99.70	99.98	100.25
		10000					

ET A TO	T T3	22
TAB	Lake .	4
and the second se	_	_

"Recorded as "rare earths", presumed to be oxides.

"" It is amazing that this analysis, without determining F or Cl, and with only a trace of H₂O, sums to 100%. Vasileva considers the analysis as of doubtful value.

[#]F is recorded as absent in this analysis by Vasileva. In the original analysis of apatite from the Shishim Mine, Bornemann-Starinkevitch determined 0.78% F.

Wilkieite, Crestmore, Calif. after Eakle and Rogers. Ellestadite, Crestmore, Calif. after McConnell. Laacher See, Germany, after Brauns. Shishim Mine, Urals, U.S.S.R. Loglier, Aldan, U.S.S.R. Emeldzhak, Aldan, U.S.S.R. Madezhnoe, Aldan, U.S.S.R. Samples 4, 5, 6 & 7 analysed by Vasileva.

TABLE X (Continued)

Analysis 2, recalculated by McConnell (1937), led to the following statistical distribution of atoms.

Analyses 4 and 7 were recalculated to atomic proportions by Vasileva (1958a), who included Si and S in the P position, and Sr and Na in the Ca position. $CaCO_3$ was presumed to be present as calcite. Further recalculation on the basis (P + Si + S) = 6000 gm.atoms x 10^4 leads to the following formulae:

4.
$$^{Ca}_{9.98}$$
^{Sr} $_{0.01}$ ^{(P} $_{4.85}$ ^{Si} $_{0.66}$ ^S $_{0.49}$ ^O $_{24}$ ^(OH) $_{1.85}$ ^{C1} $_{0.18}$
7. $^{Ca}_{9.63}$ ^{Sr} $_{0.02}$ ^{Na} $_{0.33}$ ^{(P} $_{5.66}$ ^S $_{0.34}$ ^O $_{24}$ ^(OH) $_{0.91}$ ^F $_{0.05}$ ^{C1} $_{1.03}$

In view of the uncertainties regarding the assignment of elements to structural positions, these recalculations are presented as they stand.

v) Apatite in magmatic and metasomatic iron ores.

Iron ores associated with igneous and high temperature metamorphic activity are often rich in P, and may contain apatite as an accessory, or even an essential mineral.

Apatite-bearing magnatic iron ores are probably best known from the large deposits of fluorapatite and magnetite at Kiruna, Sweden (Geijer, 1931). The intrusive nature of the apatite-magnetite body was conclusively shown by Geijer, and Bateman (1951) considers the ore to be a late magnatic differentiate of Fe and P with a long purification process to free the ore of silicates, and subsequent injection into Precambrian porphyries.

An association of apatite with magnetite oro occurs in some of the iron ores of the Adirondacks. McKeown & Klemic (1956) analysed apatite from the magnetite deposits at Mineville, N.Y. with a surprisingly high content of rare-earth, ranging up to 32.4% total rare-earth oxides. The Mineville deposits occur within highly matamorphosed Precambrian sediments and interlayered igneous rocks.

Magnetite-apatite rocks, often associated with Nb deposits, have been described from areas of carbonatites and alkalic intrusions. These areas have been discussed previously (pp.61-3), and according to Pecora (1956), the occurrence of magnetite-apatite with carbonatites and felspathoidal alkalic rocks may be a distinct association compared to the "rare-earth minerals variety" of carbonatite, the latter being generally associated with more silicic alkalic rocks. The apatitemagnetite variety is considered by Pecora to be more videspread and

"includes such classic localities as Fen, Alno, Kaiserstuhl, Magnet Cove, and several African localities". He notes that apatite and magnetite are absent or rare in those deposits rich in bastnaesite (a rare-earth fluorcarbonate) and monazite. Rowe (1958) describes magnetite-apatite rock associated with an alkalic complex at Chapleau, Ontario and occurring as "lenticles, bands and patches in ijolite and malignite", with minor sodic pyroxene and pyrochlore in the rock. Ore reserves of the apatitemagnetite deposit are quoted as over 5 million tons containing 69.60% magnetite, 21.88% apatite and 0.173% Mb₂0₅ and several other ore zones exist in the area. Hodder (1958) suggests that the magnetite-apatite rock is intrusive into fractures and breccia zones.

Apatite in martite from Durango, Mexico, has been described by Foshag (1929). The martite-apatite, with minor goethite, occurs within latites, tuffs and rhyolites, and is probably a replacement deposit.

Skarn-type mineralization has already been discussed and it is only necessary to note here that extensive development of magnetite may occur within these skarns, sometimes associated with apatite. Sumin (1957), in a paper seen in abstract only, suggested there was a genetic connection between the apatite of skarn iron ores in the U.S.S.R. and magnatic rocks, from their minor element content.

vi) Apatite in low temperature sedimentary and biological environments

It is proposed to deal only in brief outline with the occurrence of apatite in low temperature environments, in view of the poor understanding of the mineralogy of the fine-grained, microcrystalline apatitelike minerals that occur in chemical and organic sediments. Careful

separation of these minerals and extensive mineralogical study, involving special techniques, will be required before it is possible to attempt a systematic study of the phosphate minerals in this environment. Such a project is outside the scope of this present one and should be bound in with a study of the geochemistry of phosphorites and chemical sediments in general. Mevertheless, a review of some of the more salient papers in the field will be given here.

Huge deposits of colitic sedimentary phosphate beds occur in the Permian Phosphoria Formation in the western United States, and the surveyed areas, mainly in Idaho, are estimated to contain 6,000 million tons of commercial rock phosphate (Bateman, 1950). Extensive deposits occur in the Eocene of Morroco, Algeria and Tunisia, and the Cretaceous of Egypt.

The petrography of the phosphorites⁴ has been summarized by McConnell (1950). The common variety of apatite occurring in these deposits is either francolite or dahllite, although some workers refer to the mineral as fluorapatite. The structure and composition of these minerals have been briefly discussed in the section on Carbonate Apatites (pp.50-53).

Both chemical and biochemical processes have been invoked to explain the genesis of the marine sedimentary phosphates. Experimental data on low temperature aqueous phosphate systems and mineralogical data

⁴As McConnell (1950) points out, the term "phosphorite" has been used to describe sedimentary accumulations of varieties of apatite. McConnell proposes that the term should be used to include all rock phosphates of Ca, irrespective of their mineralogy.

on the deposits are probably insufficient at present for the controversies of their origin to be satisfactorily resolved. Increasing research (i.e., mineralogical, geochemical and oceanographic) in this field can be noted in recent years, however.

The role of microganisms in concentrating P in sediments has been emphasized by Cayeux (1936). Dietz, Enery & Shepard (1942) studied nodular phosphates from the sea floor off Southern California, chiefly composed of collophane⁵ and francolite. They also reviewed the world distribution of phosphorites and theories of their origin. Their conclusion is that sea water deeper than a few hundred meters is saturated with $Ca_3(PO_h)_2$, and that slight changes in the physical-chemical environment cause direct precipitation of apatite. Krumbein & Garrels (1952) consider that a chemical precipitate of calcium phosphate might occur in a restricted basin with somewhat low pH (7.0-7.5). If soluble phosphate ion is supplied to the basin, "phosphorite" could be precipitated, whereas CaCO, would not, because of the pH. The replacement of CaCO, by phosphate solutions to form carbonate-apatite has been experimentally demonstrated by Ames (1959). McConnell (1958b) believes that the formation of phosphate deposits may not be simply a question of 'solubility of phosphate in the ocean' but may involve organic activity.

²Collophane has become a very misleading term. Originally it was used in application to phosphate material that appeared to be cryptocrystalline or amorphous under the microscope. Dietz <u>et al</u> (1942) use the term to refer to a microcrystalline equivalent of what appear to be apatite minerals, i.e., francolite. McConnell (1950, 1956a) suggests it be applied to microcrystalline material giving an apatite pattern by x-ray diffraction, but when uncertainty arises as to its precise chemical composition. It is necessary to determine in most publications in the field of rock phosphates in which sense the author uses the term. This is unfortunately often the case for many papers where the terms apatite, collophane, fluorapatite, francolite, etc. are used.

A few other salient papers in the field are those of Mansfield (1940) on the role of F in phosphorite deposition and the association with volcanism; Redfield (1958) on P in the ocean and its relation to the biochemical cycles; and Ronov & Korzina (1960) on P in sedimentary rocks. These papers, with those already discussed, furnish a good bibliography of phosphorites and P in the ocean.

Other rocks which may contain important reserves of phosphete are the "pebble beds" and residual accumulations. Land pebble beds in Florida are the biggest sources of phosphate in the United States, formed by the reworking of phosphatic limestones and the deposition of the erosion-resistant phosphatic pebbles in gravel beds. Residual accumulations, well developed in Tennessee, are outcrops residually enriched in phosphate, from the weathering of phosphatic limestones.

The phosphate deposits of some of the Pacific Islands are formed by leaching of phosphate solutions from bird guano, and the reaction of these solutions with underlying limestones to produce "insular phosphate rock". Frondel (1943) identified carbonate-hydroxy-fluorapatite from these deposits.

A small P_2O_5 content in most sediments may be related to apatite present as a resistate mineral. Some of the apatites from Eritish granites have characteristic inclusions (Groves & Mourant, 1929; Fleet & Smithson, 1928), and the latter workers attempted to determine the origin of detrital apatite found in the Cambrian quartzite and the Bunter, Keuper and Carboniferous sandstones of Eritain, from the inclusions. Apatite was shown to be a persistent and stable detrital mineral by

Pettijohn (1941).

The chief mineral component of teeth, bone and phosphatic shell is an apatite. Much controversy has resulted over the exact chemical nature and structure of this apatite, which is completely outside the scope of this study, but it appears that it is a hydroxy-apatite (Thewlis, Glock & Murray, 1939; Thewlis, 1940) or a carbonate-hydroxyapatite (McConnell, 1958a). Carbonate-apatite and hydroxyapatite have been reported from kidney and bladder urinary calculi (Frondel & Prien, 1942). The medical and dental literature on this subject is voluminous and controversial.

TRACE ELEMENT GEOCHEMISTRY OF APATITE

Quantitative spectrographic analyses of apatite are fairly meagre in the literature. Most of the analyses available are of apatites separated from igneous rocks, and are generally samiquantitative, being analysed by the existing techniques used for silicate minerals. Line coincidences from rare earth spectra make some analyses reporting a large number of elements at low concentrations suspect, unless the analysts have been fully aware of this effect, and taken proper experimental precautions.

Table XI lists some trace element analyses of apatite from various igneous rock series. In view of the diversity of methods used, it is not considered wise to correlate individual analytical results too closely with each other or with this study, but, for most elements, they will be valuable as a guide to orders of magnitude of element concentrations.

In this study a total of 46 apatite samples were analysed spectrographically, using the method discussed in a previous section. The samples were obtained through the generosity of several donors, and came from various environments and localities (see Appendix 1).

21 samples were classified as occurring in an igneous environment, either in intrusive rocks or from associated pegmatites. Two of these samples were associated with sulphide mineralisation and were included for correlation purposes with the apatite samples

x

TI	١B	LE	XI
_	_		

			Tr	acee	lemen	t ana	lyses	s of a	patit	.08. 0	ompil	ed fr	rom va	rious	publ	ished	sou	ces		
		l	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Ee														*						
Ga		**	3	*	*	*	**	*	*	*	-16-	*	*	**	*	*				
Cr		*	3	-35-	*	31-	-}}-	*	×	38	*	쑸	35	10	-35	*				
V		¥	*	*	**	35	10	10	10	35	*	*	*	90	60	60		80		÷
Mo		3F	*	*	*	*	36	¥	ᅷ	35	が	35	*		35	35		25		÷⊱
Li		*	÷.	*	1	35	*			*	*	3	*		-16	35				
Ni		*	36	¥	샦	·*	45	×	카는	36	*	*	31-	20	ž	**	20			*
T1														500						
Co		*	*	*	**	45	*	쓹	*	*	45	-15	샤	*	*	*				
Cu		*	*	200	200	30	10	10	10	10	*	35	*	100						
Sc		¥e.	30	10	*	-12	*	**	35	*	*	36	36	9	×	*		·····································		
Zr		10	30	20	50	51	lligh	High	High	1000	3000	High	High	100	10:	*		- <u>}-</u> ∔-}		-H-H-P
Mn		2000	400	400	500	300	++	100	++	200	500	500	500	200			150	250	400	3000
Y	с.	10000	4000	1000	5000	1000	3000	600	500	500	5000	700	5000	4000	450	450	80	++++	+++	┿┢┽
La		2000	1200	300	1000	800	2000	3000	1000	2000	300	3000	200	2000	1300	1350	200	1000	2000	3000
Sr		800	1000	1500	2000	800	+++		+++	1000	500	500	500	400	4000	4000		350		320
Pb		*	10	35	~	-									15	15	10	46		*
Ba		17 1	30	15	5	5	+		+	5	100	귀는	20	90	30	30		50		46
Kb		*		Ť	36	*	35	46	*	*	*	*	*		*	¥				

*Denotes that the element was looked for but was not present above the sensitivity limit.

A ceries of crosses indicates a quantitative analysis was not carried out, and represents the intensity of the spectral line.

TABLE XI (Continued)

1. Apatite from coarse hybrid material (317) between granophyre & olivine gabbro of western border group, Skaergaard (Wager & Mitchell, 1951).

2. Apatite from late fayalite ferrogabbro (4142), Skaergaard (Wager & Mitchell, 1951).

3. Apatite from earlier gabbro (3649), Skaergaard (Wager & Mitchell, 1951).

4. Apatite from main gabbro, Garabal Hill-Glen Fyne complex (Nockolds & Mitchell, 1948).

5. Apatite from coarse appinitic diorite, Garabal Hill-Glen Fyne complex (Nockolds & Mitchell, 1948).

6. Apatite from medium appinitic diorite, Garabal Hill-Glen Fyne complex (Nockolds & Mitchell, 1948).

7. Apatite from porphyritic graniodiorite, Garabal Hill-Glen Fyne complex (Nockolds & Mitchell, 1948).

8. Apatite from tonalite, Morven-Strontian complex (Nockolds & Mitchell, 1948).

9. Apatite from granodiorite, Morven-Stronian complex (Nockolds & Mitchell, 1948).

10. Apatite from adamellite, Morven-Strontian complex (Nockolds & Mitchell, 1948).

11. Apatite from porphyritic outer granodiorite, Ben Nevis (Nockolds & Mitchell, 1948).

12. Apatite from muscovite-biotite adamellite, Moy, Inverness (Nockolds & Mitchell, 1948).

13. Apatite from ophitic basalt, Keweenawan, Michigan (Cornwall & Rose, 1957).

14. Apatite from upper part, Black Jack teschenite sill, N.S.W. (Wilkinson, 1959).

15. Apatite from upper part, Black Jack teschenite sill, N.S.W. (Wilkinson, 1959).

16. Apatite from hypersthene-pyroxenite dyke, Madras (Howie, 1955).

17. Apatite from charnockite, Madras (Howie, 1955).

18. Apatite from charnockite, Madras (Howie, 1955).

19. Apatite from charnockite, Madras (Howie, 1955).

from the igneous and pegmatitic environment, on the grounds at that time that they might be hydrothermal, derived from igneous processes.

25 samples were classified as occurring within a metamorphic environment, and formed by metamorphic or metasomatic processes. The majority of the samples in this group (20 samples) came from pegmatitic skarns and veins associated with marbles and pyroxenites in the Grenville province of the Canadian Precambrian Shield.

The analytical results are listed in Appendix 2, and physical parameters of the samples are in Appendix 3. The symbol tr means that the spectral line for that element was present, but was too weak to measure; for statistical purposes a value of one half the sensitivity limit was used (see Table II). The symbol nd indicates that the spectral line for that element was absent.

The possibility that inclusions of a foreign mineral phase are contributing to the trace element content of the sample is discussed in some detail in a later section, using samples from a single apatite specimen to evaluate this effect. These results show that the most common inclusions in apatite (calcite and fluorite) do not contribute significantly to the trace element content. Biotite, which occurs in some samples, will contribute mainly to the Fe, Mg, Si, K, and Al content of the apatite. Since the Si content of most apatite samples is of the order of several thousand ppm, i.e. far greater than can be explained on the basis of included silicates, the contribution to the total Si content by these inclusions is not sufficient to affect the results. In most samples, the greater bulk of the Si must be in the apatite structure.
FIGURE 8

Fe content of apatite samples plotted against degree of brown Fe-oxide and hydroxide staining on fractures in the samples.



Inclusions, particularly biotite, probably contribute significantly to the Al content of the sample. Five samples of apatite that were very pure (samples A6, All, Al3, Al8, and A28) contain very little Al (less than 70 ppm).

A plot of Fe content in the sample against the degree of staining suggests a correlation in the lower ranges of Fe content (Fig. 8). There appears to be little doubt that reddish brown Fe oxide and hydroxide staining on fractures within the mineral sample is contributing significantly to the Fe determined by analysis. A number of samples contain high Fe, but show no appreciable staining under the microscope. Some of these samples contain minute inclusions of opaque minerals, probably Fe oxides. The variation in the Fe content within the single apatite crystal suggests that biotite may contribute to the Fe content of the sample, but that not all the Fe can be explained in this way. It appears, therefore, that some Fe is incorporated in the apatite phase, but that in many samples much of the Fe is due to staining on fracture surfaces and to inclusions of Fe oxides and biotite.

Mg is probably also associated with inclusions of biotite. Table XIV shows a significant linear correlation between Fe and Mg content of 25 metamorphic apatites, although the correlation is weaker and not significant for the apatites from igneous rocks. The very pure apatite samples that contain low Al contain only trace amounts of Mg also, except for Al3. This latter sample is from an ultrabasic environment and contains 1326 ppm Mg, although it appears to be very pure under the microscope. The evidence is strong, therefore, that Mg is present in

FIGURE 9

Example of good correlation, between Ce and La, for 2L apatites from igneous environments, r = 0.970.



FIGURE 10

Example of no correlation, between Mg and Al, for 21 apatites from igneous environments, r = 0.030.

.



٦.-

the structure of the apatite, in this sample.

The major cations in apatite are Ca^{2+} and P^{5+} , and it might be expected that apatite will be enriched in trace elements that

- i) are capable of readily substituting for Ca or P at lattice sites, i.e., a crystal chemical control,
- and ii) are present in the environment at the time of formation of the apatite, i.e., an environmental control.

Tables XVIII, XIX and XX compare the average abundances of the trace elements in apatite with their crustal abundances. Apatite from igneous and metamorphic environments are enriched in Ce, Sr, La and Y. Mn is enriched in apatite from igneous environments, although examination of the individual analyses shows that this only applies to those apatites from granitic pegnatites.

The analyses show that the range in trace element composition of apatite is so great, even for samples from similar environments, that it is seldom valid to make generalisations regarding their trace element content. The concept of the composition of an "average" apatite from any one environment is particularly meaningless.

Discussion of individual elements

i) Rare earths

Only the "major" clements of the rare earth group were determined in this study, i.e., Ce, La and Y.

The rare earth elements comprise a group of elements from atomic numbers 57 - 71, normally referred to as the lanthanides. These elements are very similar in properties and occurrence due to their very similar electron configurations. The outer 5s, 5p and 6s shells are identical for all the elements, and differences in configuration occur deep in the electron shells (i.e., in the 4f shell), with corresponding reduced ability to modify the properties of the individual elements. There is a regular decrease in ionic radius from Ce and Le at the head of the series to Lu at atomic no. 71. The stable valency state in the series is 3+, although differences in the stability of the oxidation states is a major factor in fractionating certain of the elements (i.e., Eu) in natural environments.

Y has an outer electron configuration of $4d^{1}5s^{2}$, and although it has an atomic number of 39, this configuration is similar to the lenthanides but in a lower series of electron shells. The ionic radius of Y is similar to the elements in the middle of the lanthanide series, and this similarity is reflected in similarities in occurrence and properties. Y is, therefore, often classed with these lanthanides from atomic numbers 64 (Gd) to 71 (Lu), and the group is referred to as the "yttrium earth elements". Similarly the elements from La (atomic no. 57), through Ce (58) to Sm (62) are often referred to as the cerium earth elements". Europium, of atomic no. 63, has a natural divalent oxidation state which separates it in behaviour scnewhat from the other rare earths, although it is often included in one of the other groups.

Although the rare earth elements exhibit a marked degree of geochemical coherence, anomalous assemblages are found in the minerals that contain abundant amounts of these elements (i.e., through apatite to the minerals in which the rare earths are essential constituents). The primary fractionation is between the Ce and Y earths, and then into

FIGURE 11

Lanthanide assemblages in apatite and other minerals (from Rankama & Sahama, 1950, after Goldschmidt & Thomassen, 1924).



variations in the relative abundances of individual elements within these groups. Goldschmidt & Thomassen (1924) showed that selective incorporation of the Y or Ce earth metals occurs when these elements form separate rare earth bearing minerals in the later stages of pegmatitic crystallisation. The Ce earths form monazite and allanite, and the Y earths form xenotime and other minerals. Fig. 11 shows the classification of the abundances of the rare earth elements into the various assemblages proposed by Goldschmidt & Thomassen. In apatite, the elements are not normally present as major constituents, and form a complete assemblage, without any marked fractionation. Bjørlykke (1937) came to similar conclusions from studying rare earth rich granite pegmatites in southern Norway. He considered that in the Ca-rich pegmatites the Ce earths might become somewhat enriched in apatite, as monazite became unstable with increasing Ca content:

Monazite + Ca-silicates -----> apatite + orthite.

Tables XII to XVII inclusive show the degree of correlation between Ce, La and Y for the apatite samples analysed in this present study. The correlation coefficients were calculated on the data expressed in arithmetic units, and also in units of log₁₀ ppm. for all 46 apatites taken together, and for the igneous and metamorphic groups separately. Ce and La, both members of the cerium earth group, show strong correlation with each other in every case. The correlation between Ce and Y is much weaker, and there is no aignificant linear correlation at the 2% level between Ce and Y in the igneous apatites. The correlation between Y and La is less marked in all groups than the correlation between Ce and Y.



FIGURE 13

Plot of Y/Y + Ce + La against total Y + Ce + La in apatite.

. .



Over a wide range of environments, therefore, the tendency for Ce and La to behave with a high degree of geochemical coherence is established in apatite, as is the tendency for some fractionation between the Ce earths and Y to occur.

The ratios of Ce:La:Y in the apatites are plotted on triangular co-ordinates in Fig. 12. Except for the pegnatite apatites there is a fair constancy of the ratios in the magnatic and metamorphic environments, and it is not possible to distinguish between the two groups. There has apparently been little fractionation of the elements in deep-seated crustal processes, therefore, although a fractionation between the Ceearths and Y occurs at the pegmatitic stage. All the pegmatite samples have an appreciably higher Y/Y+Ce+La ratio, except one sample from a granodiorite pegmatite at Strickland, Conn. (A9). The sample classified as contact metamorphic-metasomatic from Crestmore, California (A42) falls well in the pegmatite field. This is probably not unreasonable as it is formed by contact metasomatic processes in limestone from high level intrusives. The composition of the mineralising solutions at Crestmore are probably more akin to late stage pegnatitic solutions than the solutions producing the apatite skarns in the deep seated regional metamorphic environment of the Precambrian Shield.

An apatite from Center Strafford, N.H. (A19) was originally classified for correlation purposes in the metamorphic group. Stewart (1939), in a paper mentioned in the section on Environment and Occurrence, describes the occurrence of apatite at Center Strafford in contact metasomatic deposits in a limestone adjacent to a granitic intrusion.

Switzer (1938) describes manganapatite in a large granite pegnatite at Center Strafford, formed at a high temperature pneumatolytic stage. The exact locality of the sample analysed is not known, but it now appears that it is more related to granitic pegnatite processes, possibly coming from within the pegnatite proper.

The ratio of Y/Y+Ce+La against total Y+Ce+La is plotted in Fig. 13. Pegmatite apatites tend to have lower total Y+Ce+La content than the magmatic and metamorphic apatites, although a single sample (A47) from gabbroid pegmatites at Bamle, Norway, has a high total Y+Ce+La content.

I and the lanthanides have a marked affinity for P and F (Rankama & Sahama, 1950, p.518) which explains in part the concentration of these rare earth elements in apatite from igneous rocks, replacing Ca^{2+} in the lattice. Small amounts of rare earths are probably incorporated in other Ca minerals, but the bulk of the rare earths remain in the melt to form separate rare earth minerals and to be further incorporated in apatite and fluorite at the pegmatitic stage.

In silicic igneous rocks, however, the crystallisation of K-felspars, and monazite and allanite as accessory minerals, will cause the separation of the Y earths from the Ce earths. Monazite-allanite assemblages contain the Ce earth elements (Fig. 11) and Ce earths are preferentially incorporated in the K^+ position of the felspar structure. The ionic radius of K^+ (1.42Å) is closer to the ionic radii of the larger members of the lanthanides, the Ce earths, than the smaller Y^{3+} ion. The rare earths remaining in the solution after the primary phase

of granitic crystallisation will be enriched in Y. Continuation of this separation between the Y earths and the Ce earths can be expected to continue at the pegmatitic stage of crystallisation also. The total content of rare earths in the later stages will be decreased as the felspars and monazite-allanite have taken the bulk of the elements out of solution.

Some data by Gavrilova & Turanskaya (1958) on the rare earth content of minerals from Ukrainian granites are presented in Table XXI. Examination of their data shows that the bulk of the rare earth content of the granite is bound up in the felspars and accessory monazite, and the ratio of Ce earths to Y earths in these minerals is high. This would be in complete accordance with the mechanism outlined above to explain the anomolous rare earth assemblage shown in pegnatite apatites from this study.

ii) Strontium and Barium

Sr and Ba show close similarities in their chemical properties but do not show a marked geochemical coherence in their occurrence in minerals. Similarities in chemical properties and ionic radii between Sr and Ca cause Sr to readily occur in Ca minerals. This relationship persists in apatite, and it is expected that the Sr^{2+} ion substitutes for Ca²⁺ in the structure. Ba²⁺, on the other hand, with a larger ionic radius, can only do so with difficulty.

The presence of 11.60% SrO in apatite from veins in a sympite dyke in Montana has been noted in an earlier section. Apatite from the Khibina pluton (sample A5) analysed in this present study contains over 7.3% Sr, which is in accord with the results of Volkova & Melentiev (1939), also noted earlier.

All the analysed apatite samples contained Sr, although one sample (A41) from a calcite-apatite skarn in Ontario contains only 8 ppm. The range in composition of Sr in apatite is therefore very great. The arithmetic mean of the Sr analyses for the metamorphic apatites is lower than the mean for igneous apatites (Tables XIX and XX), although the high value of 7.3% Sr greatly affects the igneous mean value. The geometric means show the Sr content in the igneous apatites to be lower than in the metamorphic group. These figures, however, are probably somewhat meaningless as there can be a large variation in the Sr content of apatite from similar localities and environments. The apatite sample from Monmouth Township, Ontario, noted above, contained only 8 ppm Sr, while a further sample from the same Township (A18) and presumably from a similar environment, contained nearly 15 Sr. Apatite from a vein in a Norwegian eclogite (A44) contained over 2.6% Sr, although apatite separated from the eclogite (A45) contained only 6125 ppm. Larsen et al (1952) noted that whereas apatite from a vein in a syenite dyke contained 11.60% SrO, apatite within the syenite rock contained no appreciable Sr. It would appear, therefore, that Sr in apatite is subject to extreme variation within slightly different environments at one locality.

A plot of Sr vs. La in apatite from the igneous environments, Fig. 14, shows a wide range of values. Although Sr in apatite from granitic pegnatites varies from 35 ppm to over 13000 ppm, most of the pegnatitic apatites have less than 1000 ppm. Sr (and less than 1000 ppm. La), and apatite from the plutonic intrusives contains more than 1000 ppm Sr. The highest content of Sr in apatites from the plutonic

FIGURE 14_

Plot of Sr against La in apatite from igneous intrusives and pegmatites.



environment is in apatite from the ultrabasic rocks, and decreases with increasing acidity of the rock. The results of Nockolds & Mitchell (1943) also show this tendency (Table XI).

It is apparent, however, that regional differences are more pronounced than petrological differences. Apatite will readily incorporate any Sr that is available. Apatite from a geochemical province rich in Sr will contain more Sr than apatite from a Sr-poor province, regardless of its petrological occurrence.

Barium is impoverished in apatite. Most of the samples contain Ba in the tr-10 ppm range, with little difference between the igneous and metamorphic groups. Two samples, however, contain significantly high concentrations of Ea (A5 & A46). Both of these samples are from igneous rocks of peculiar composition and alkalic affinities, a nepheline-apatite rock from Kola and a carbonatite from Quebec. Sr is also high in these samples, and Table XVI shows a significant correlation between Sr and Ba for the igneous apatites. Von Eckermann (1952) found apatite from the Barich alkalic and carbonatite province of Alnö to be rich in Ea, samples from apatite-rich sövites containing up to 1790 ppm Ba.

It is apparent, therefore, that although Ba is incorporated in apatite far less readily than Sr, a significantly high content of Ba in the environment will be reflected in the composition of the apatite. Ba is often enriched in apatite from alkalic igneous complexes and carbonatites.

iii) Iron, Magnesium and Aluminum

These three elements are dealt with together, as it is probable that the bulk of the Fe, Mg and Al in the apatite analyses is due to inclusions of Fe- and Mg-aluminosilicates, Fe-oxides, and Fe-hydroxide

staining.

The ionic radii of Fe, Mg and Al are too small to enable them to substitute for Ca, without distortion of the structure. A distinctive feature of the apatite mineral group, however, is the stability of the apatite lattice to anion and cation defects. This has been discussed in some detail in earlier sections. Cationic defects in the Ca position will create local distortions and charge imbalance, but the lattice is still stable. Similar considerations also apply to defect structures where excess cations are stuffed into intermediate lattice positions. It is important to note that the major factor here is not the degree of "openness" of the structure, but how well the local distortions caused by these defects can be assimilated by the rest of the structure. The extent to which the excess ions can be incorporated cannot be determined simply by calculating the density of atoms within the lattice.

These elements are, however, markedly impoverished in apatite, by virtue of the difficulty of accommodating them in the structure. The occurrence of relatively high Mg in sample Al3 (1326 ppm) from an ultrabasic rock, and the absence of impurities in this sample, suggests that under conditions of high Mg in the environment this element will become trapped in the lattice. It is only possible to correlate such high Mg content with environment when the sample is extremely pure, which unfortunately is seldom the case.

Similar considerations would probably apply to Fe. A very pure gem quality apatite (A6) from Durango, Mexico is associated with replacement Fe-ores (p.80) and contains 1200 ppa.

iv) Silicon

The substitution of the small Si^{4+} ion for P^{5+} in the apatite lattice is well substantiated. The occurrence of high Si-bearing apatites has been discussed in some detail previously (pp.73 & 76). A Si-bearing apatite from Crestmore, California was analysed by wet chemical methods in the present study and contained 14.7% SiO₂.

The determination of S was not feasible using the spectrographic methods of this study, but, apart from the specimen from Crestmore, the Si content of the other apatite samples was fairly low. Sample A34, from the Grenville, contained over 1.8% Si, although it contained numerous microcrystalline inclusions of biotite, sphene and some pyroxene, and there is little doubt that much of the determined Si was not in the lattice.

There appears to be no readily apparent trend or grouping of the apatites with regard to their Si content. This is not surprising as Si would be readily available to the apatite from all the localities, and could be incorporated in the lattice.

FIGURE 15

Plot of Ce against Si in apatite from igneous intrusives and pegnatites.



The inter-element correlations show a marked lack of correlation between Si and any other element. A weak non-linear correlation (using logarithmic data) between Si and Ce occurs for the igneous apatites (Table XVII). In view of the suggestion by Vasileva (1958) that charge balance can occur by the coupled substitution $TR^{3+} \longrightarrow Ca^{2+}$, and $Si^{4+} \longrightarrow P^{5+}$, this is particularly interesting. This correlation is plotted on linear co-ordinates to determine the type of relationship in Fig. 15. The correlation is indeed poor, although the tendency for the pegnatitic apatites to be lower in Si (and Ce) than the magnatic apatites is seen!

There is no evidence, therefore, that there is a coupled substitution between Si and rare earths in apatite, with Si in concentrations of a few thousand ppm. In view of the marked stability of the apatite lattice to defects, it is unlikely that coupled substitutions to balance charges are necessary for elements at concentrations less than 1%.

v) <u>Manganese</u>

The incorporation of Mn in Ca minerals is well known, and in igneous rocks Mn^{2+} , the stable oxidation state in this environment, is incorporated in Fe and Mg minerals, and to a lesser extent in Ca minerals. The ionic radius of Mn (0.80Å) is closer to Fe²⁺ (0.74Å) and Mg²⁺ (0.66Å) than it is to Ca²⁺ (1.03Å), and Mn shows a greater degree of geochemical coherence with Fe than with Ca. According to Rankama &

¹The validity of this must, however, be questioned as the process of separating fine grained apatite from igneous rocks is more likely to cause contamination by silicates, than for large crystals obtained from pegnatites.

Sahama (1950), Mn may be enriched in the pegnatitic stages of crystallisation. Mn minerals are certainly known in pegnatites and hydrothermal veins, and do not generally form from igneous melts. As noted previously, the apatites from metamorphic environments are impoverished in Mn, compared with the crustal abundance of the element, and the apatites from igneous environments are somehwat enriched (Tables XIX and XX). The analyses show, however, that the average content of Mn in the igneous group is heavily weighted by very high Mn contents (of the order of several % Mn) in many granite pegnatites.

In apatite separated from magnatic rocks the Mn varies from 191 ppm to 1028 ppm, the highest value being recorded from a Norwegian larvikite (A24) and the lowest from a Norwegian eclogite (A45). A granite apatite (A27) also contains a relatively high Mn content of 1000 ppm. The unrelated parentage of the magnatic rocks does not permit further comparison between rock type and Mn content of the contained apatite. Apatite from the metamorphic environments contain Mn within the same range of concentration.

The high Mn-bearing apatites (> 2.5% Mn) are all from granitepegnatites, although not all the granite pegnatite apatites have a high Mn content. Apatite from the granite pegnatite at Harding, New Mexico (AlO) contains only 781 ppm Mn, for example. The reason for this strong enrichment of Mn in some granite pegnatite-apatites is not clear. Excluding the granite-pegnatite environment, the Mn content of the apatite varies within narrower limits than for any of the other trace elements present in appreciable concentrations.

A recent paper by Vasileva (1953), unfortunately only seen in abstract, uses X-ray techniques and the optical absorption curves of Mn bearing apatites to determine the oxidation state and environment of this element in the minorals. Vasileva found that Mn^{2+} and Mn^{3+} were present, replacing Ca²⁺ in the apatite lattice. Of particular interest was his conclusion that Mn^{7+} enters the lattice as $(MnO_4)^-$ substituting for the $(PO_4)^{3-}$ groups. The charges are presumed to be balanced in the latter substitution by F⁻ and OH⁻ ions being replaced by O^{2-} . Such high oxidation states of Mn would require highly oxidising environments, certainly more in accord with some pegnatitic and late stage conditions than with magnatic crystallisation.

vi) Zirconium

The high charge and ionic radius (0.79%) of Zr^{4+} make it unlikely that it will substitute for Ca^{2+} or P^{5+} in the apatite lattice. Most of the specimens did not contain detectable Zr, although some of the samples, from the magnatic rocks in particular, contain appreciable Zr. Two apatite samples from the larvikite sequence in the Oslo region of Norway (A24 & A26) contain more Zr than could be measured, i.e. greater than 1000 ppm, and an apatite (A25) from the same province also contains significantly high Zr content (94 ppm). An apatite from the alkaliccarbonatite complex of Oka, Quebec (A46) contains 93 ppm Zr.

It would appear at first sight that apatite from alkalicmagmatic provinces are significantly high in Zr, although a granite from British Columbia contains 312 ppm Zr (A27) and two samples from the Grenville (A35 & A42) contain appreciable Zr. Many of the analyses in

Table XI also show high Zr, particularly those of apatites from the Caledonian igneous rocks (Nockolds & Mitchell, 1948). The possibility that the high Zr content of these apatites are due to small inclusions of zircon, or that zircon grains have been included in the mineral concentrate from these rocks, is great. All the high Zr samples are indeed fine-grained concentrates, except for A42, which contains small high relief inclusions, some of which might be zircon. If as little as one grain of zircon in 1000 is included in the sample, the contribution to the analysis will be approximately 500 ppm Zr. The nature of the inclusions in the samples are listed in Appendix 3, and most of the high Zr-bearing samples contain numerous varied inclusions, some of which were tentatively identified as zircon. Sample A26 was fairly pure, however, but contains 94 ppm Zr. This could correspond to a zircon content of about 1 grain in 5000 in the sample, which might easily have been overlooked.

The indications are strong that Zr is not present in the apatite structure but occurs as inclusions of the mineral zircon, which would explain the high concentrations of Zr in many magnatic apatites, where the possibility of incorporating a few grains of zircon with the apatite concentrate is greatest.

vii) Nickel and Copper

Considerations of ionic radii suggest that Ni (0.69Å) and Cu (0.72Å) will not readily be incorporated in the apatite lattice, except as "trapped ions" if the environment is rich in either of these elements, as proposed for Fe and Mg.

Ni was not detected in most of the samples or was present in small amounts (less than 5 ppm), although three samples contain between 10 and 17 ppm Ni (A5, A15 & A38), and one sample (A45) contains 63 ppm Ni. A15 is from a vein in basic volcanic rocks, associated with Cu sulphides, and this might be a likely environment to contain Ni also. This sample also contains appreciable Cu (greater than 120 ppm) and it would appear that

i) the formation of the apatite was cogenetic with the sulphides,

ii) later alteration permitted Cu and Mi to be released from the sulphides and incorporated in the apatite,

or

or iii) sulphides are present as contaminating inclusions in the sample.

A sample from the Ashio Mine, Japan (All) also associated with Cu sulphides, contains no Ni, however, and only 2 ppm Cu. This sample is very pure and free of inclusions. The reasons for the Ni in samples A38 and A5 are not clear. A45 is an eclogite from Norway and the Ni content in the environment is probably high, although Ni was not detected in apatite from a vein in the eclogite (A44).

The conclusion of the writer is that although care must be taken in interpreting analyses of Ni in apatite because of possible contamination, some Ni can be trapped in the lattice if available at the time of crystallisation.

Somewhat similar conclusions would also apply to Cu in apatite. All the samples appear to contain at least traces of Cu, and the analytical method was very sensitive for this element. The difficulty in obtaining spectrographic materials completely free of this element is well known,

and it is probable that the Cu analyses represent little more than contamination where the concentration of Cu in the sample is less than about 2 ppm.

Apatite, therefore, is considerably impoverished in Cu, although it would be expected that Cu was present in many of the environments. Shaw (1960b, p.275) writes, regarding the impoverishment of Cu in scapolites, that this indicates "to what degree a mineral can exclude a trace element which cannot be accommodated". It would appear that this observation could apply equally to apatite.

viii) Vanadium and Arsenic

These elements are dealt with together as they are both capable of substituting for P in the apatite lattice, by virtue of similar radius and charge, i.e. $As^{5+} = 0.44$, $V^{5+} = 0.56$ and $P^{5+} = 0.33$. The pyromorphite and svabite series of the apatite group of minerals contain As and V as major elements, completely replacing P in the structure (see Table III).

It might be expected that apatites containing appreciable contents of V and As would be found among the 46 samples, if there was any degree of isomorphism between P and these elements. All the samples analysed were checked for their As content, but the element was not detected in any. In common with most spectrographic techniques, the method used in this study has a very poor sensitivity for As and it could not be determined at concentrations less than about 300 to 400 ppm. It is significant that none of the samples contained As even at this concentration, and the As content is probably very much lower. Gileva & Melentiev (1939) used wet chemical methods to determine the As content of apatite from the Khibina rocks and found from 0.6 to 2.4 ppm As.

The method is, however, quite sensitive (at 8 ppm) for V, and in most of the specimens V was not detected or the spectral line was too weak to measure. The highest content of V was 807 ppm in an apatite of peculiar composition from Crestmore, California (A42), which has much of the P in its structure replaced by Si.

Five other samples of apatite (A3, A5, A14, A36 & A 46) contain small amounts of V, from 32 to 93 ppm. There is no apparent correlation between environment and the V content. The samples come from the Khibina pluton, skarns from the Grenville and the USSR, and a carbonatite.

There are not significantly high concentrations of As or V in most apatites from igneous and metamorphic environments, therefore, and the question arises whether this is due to environmental or structural control. Vanadinite, the V-bearing member of the pyromorphite series, has an apatite structure, but contains Pb as a major cation constituent instead of Ca. It is possible that the expansion of the structure due to the larger Pb²⁺ ion permits ions larger than P⁵⁺, such as V^{5+} and As^{5+} , to be accommodated readily in the lattice. Si⁴⁺, however, with an ionic radius of 0.40Å, being smaller than V or As, can enter the lattice readily when Ca²⁺ is the major cation. There is less difference between As^{5+} and P^{5+} than between V^{5+} and P^{5+} , and under conditions of high As in the environment, this element might be incorporated in the lattice. Bauer & Berman (1930) found an apparent series from apatite containing no As, through apatite containing 16.2% As_2O_5 to symbite containing 35.24% As at Franklin, N.J. It is difficult to believe that in the environments of most of the apatites analysed in this study, V or As would be present in very high concentrations, except possibly for the eclogites. The abundance of V in apatite is much lower than the crustal abundance, however, and it would appear that apatite is rejecting V in preference for P. The apatite, therefore, seems to be more selective in the choice of ions to occupy the small P position in the structure than for those which can occupy the larger Ca position.

ix) <u>Uranium</u>

The analytical techniques used in this study did not permit the accurate determination of small amounts of uranium. The geochemistry of uranium in apatite, however, has been more extensively studied than probably any other trace element. The most exhaustive is that of Altschuler, Clarke & Young (1958) in a study of the geochemistry of uranium in apatite and phosphorite. These workers analysed many samples of apatite and phosphorite, and some of their analyses are reproduced in Table XXII.

All analyses were done by fluorimetric methods, and accuracy is quoted as being in the range of 15% of the uranium present. All analyses are considered to be of pure apatite concentrates.

Fig. 16 is taken from the same publication to show the relation between the total U in igneous rocks of the Boulder Eatholith and the total U in the separated apatite. Altschuler <u>et al</u> consider that the close relation between total U and U in apatite indicates that the partition of U between apatite and the crystallizing magma maintains

TABLE XII

	Inter-element correlation coefficients, r. for all 46 apatite samples.										
				with data expressed in units of k				-			
	Сө	Sr	La	Si	Al	Mg	Fe	Mn	Y	Ba	
Ce	1.000	-0,019	0.937	-0.084	-0.131	-0.051	-0.044	-0.290	0.364	0.184	
Sr		1,000	0.049	-0.090	0.215	-0.014	-0.137	-0.152	0.174	0.678	
La			1.000	0.090	-0.166	-0.058	-0.105	-0.288	0.263	0.219	
Si				1.000	-0.068	0.104	-0.104	-0.094	-0.014	0.004	
Al					1.000	0.101	0.129	-0.020	-0.090	0.190	
Mg						1.000	0.274	-0.184	-0.036	0.180	
Fe							1.000	0.616	0.000	0.002	
Mn								1.000	-0.177	-0.094	
Y									1.000	-0.127	
Ba										1.000	

"k = analytical result in ppm.

r is significant at the 2% level if the value falls outside the range +0.342 to -0.342. Significant correlations are underlined.

116

TABLE XIII

	Inter-element correlation coefficients, r, for all 46 apatite samples,										
	with data expressed in units of log10k*										
	Ce	Sr	La	Si	A1	Mg	Fe	Mn	Ϋ́	Ba	
Сө	1.000	0.471	0.969	0.314	-0.193	-0.011	0.194	-0.494	0.792	0.284	
Sr		1.000	0.511	0.161	-0.129	0.280	-0.027	-0.408	0.341	0.313	
La			1.000	0.331	-0.256	0.000	0.158	-0.506	0.767	0.311	
Si				1.000	0.243	0.380	-0.066	-0.542	0.507	0.157	
AL					1.000	0.245	0.266	0.218	-0.111	0.119	
Mg						1.000	0.295	-0.232	0.041	0.140	
Fe							1.000	0.326	0.055	0.068	
Mn								1.000	-0.488	-0.298	
Y									1.000	0.103	
Ba										1.000	

"k = analytical result in ppm.

r is significant at the 2% level if the value falls outside the range +0.342 to -0.342. Significant correlations are underlined.
I	inter-elemen	t correla	tion coe:	fficients	r, for	25 apatit	as from m	etamorphi	c environ	ments,
			<u>W:</u>	ith data	expressed	in units	of k*			
	Ce	Sr	La	Si	Al	Mg	Fø	lín	Y	Ba
Ce	1.000	0.031	0.910	-0.218	-0.158	-0.265	0.043	-0.198	0.639	-0.064
Sr		1.000	0.298	-0.291	-0.275	0.113	0.173	-0.066	-0.348	0.116
La			1.000	-0.235	-0.216	-0.214	0.120	-0.181	0.486	-0.076
S1				1.000	-0.056	0.110	-0.163	-0.174	-0.151	0.097
AL					1.000	0.088	0.420	0.893	0.087	-0.157
Mg						1.000	0.548	-0.012	-0.241	-0.177
Fe							1.000	0.276	0.000	-0.016
Mn								1.000	0.105	-0.061
Y									1.000	-0.160
Ba										1.000

TABLE XIV

*k = analytical result in ppm.

r is significant at the 2% level if the value falls outside the range +0.462 to -0.462. Significant correlations are underlined.

			wit)	n data exp	pressed in	n units of	[log ₁₀ k*			
	Cə	Sr	La	Si	Al	Mg	Fe	Mn	Y	Ba
Ce	1.000	0.193	0.942	-0.250	-0,113	-0.345	0.302	0.242	0.754	-0.167
Sr		1.000	0.250	-0.061	-0.021	0.295	0.159	0.167	-0.121	-0.122
La			1.000	-0.147	-0.221	-0.285	0.220	0.131	0.700	-0.163
Si				1.000	0.218	0.516	-0.052	-0.441	0.086	-0.072
Al					1.000	0.372	0.555	0.403	-0.030	-0.109
Mg						1.000	0.367	0.078	-0.341	-0.143
Fe							1.000	0.540	0.183	-0.145
Mn								1.000	0.177	-0.104
Y									1.000	-0.281
Ba										1.000

TABLE XV

k = analytical result in ppm.

r is significant at the 2% level if the value falls outside the range +0.462 to -0.462. Significant correlations are underlined.

	Inter-elem	ent corre	lation co	Defficient	s, r, for	r 21 apat:	ites from	igneous o	nvironner	nts,
	with data expressed in units of k*									
	Сө	Sr	La	Si	Al	Mg	Fe	Mn	Y	Ea
Ce	1.000	0.024	0.970	0.473	0.029	0.252	0.057	-0.340	0.245	0.371
Sr		1.000	0.108	-0.126	0.213	-0.081	-0.279	-0.231	-0.160	0.684
La			1.000	0.424	0.081	0.218	-0.021	-0.314	0.158	0.488
S1				1.000	0.320	0.597	0.178	-0.412	0.500	0.207
Al					1.000	0.030	-0.208	-0.245	-0.131	0.141
Mg						1.000	0.145	-0.362	0.091	0.286
Fe							1.000	0.603	0.028	-0.121
Hn								1.000	-0.193	-0.188
Y									1.000	-0.120
Ba										1.000

TABLE XVI

"k = analytical result in ppm.

r is significant at the 2% level if the value falls outside the range +0.503 to -0.503. Significant correlations are underlined.

120

TABLE XVII

	Intor-elem	ent corre	lation co	efficient	s, r, for	21 apat:	ites from	igneous d	environme	nts,
			With	data expi	ressed in	units of	10g10k-			
	Сө	Sr	La	Si	Al	Mg	Fe	Mn	Y	Ba
Ce	1.000	0.546	0.975	0.513	0.014	0.489	0.347	-0.575	0.767	0.678
Sr		1.000	0.573	0.231	-0.070	0.442	-0.053	-0.538	-0.448	0.655
La			1.000	0.443	-0.028	0.436	0.353	-0.521	0.736	0.700
Si				1.000	0.593	0.473	0.049	-0.551	0.646	0.435
A1.					1.000	-0.138	-0.126	-0.091	0.108	0.188
Mg						1.000	0.112	-0.766	0.529	0.424
Fe							1.000	0.160	0.169	0.156
i-in								1.000	-0.523	-0.545
Y									1.000	0.385
Ba										1.000

"k = analytical result in ppm.

r is significant at the 2% level if the value falls outside the range +0.503 to -0.503. Significant correlations are underlined.

TABLE XVIII

Means and ranges of analyses for all 46 apatite samples

Element	Crustal abundance ppm#	Arithmetic mean, ppm	Geometric mean.	ppm Range, ppm
Ce	40	4329	1545	nd - 13,940
Sr	450	6320	2106	8 - 73,558
La	20	2420	769	nd - 7,367
Si	25.8%	5460	2775	tr - 6.86%
A]	8.1%	700	316	tr - 3,029
Mg	3.1%	1177	668	nd - 6,083
Fe	6.5%	1588	896	28 - 5,792
Mn	1000	3858	570	24 - 6.14%
Y	40	1629	696	nd - 12,181
Ba	250	15.4	2.8	nd – 200
Cu	70	3.1	-	tr - 120
NH	80	-	-	nd - 63
V	100	-	-	nd - 807
Zr	156	-	~~	nd - 1,000

*Compiled from various sources by Shaw, 1960b.

TAB	LE	XIX
-		

Means and ranges of analyses for 25 apatite samples from metamorphic environments

Element	Crustal abundance pp	m [#] Arithmetic mean, ppm	Geometric mean,	ppm Range	e. ppm
Ce	40	5117	3031	85 - 3	13940
Sr	450	4365	2872	8 -	9839
La	20	3029	1834	40 -	7132
Si	25.8%	695 9	3734	826 -	6.86%
Al	8.1%	3 23	163	tr -	2000
Mg	3.1%	1023	512	nd -	6647
Fe	6.5%	984	661	59 -	2847
Mn	1000	424	300	24 -	2607
Y	40	1717	1223	70 -	4965
Ba	250	6.1	2.2	nd –	59
Cu	70	2.8	-	tr -	120
Ni	80	-	-	nd -	10
v	100	-	-	nd –	807
Zr	156	-		nd –	134

*Compiled from various sources by Shaw, 1960b.

TABLE XX

Means and ranges of analyses for 21 apatite samples from igneous environments

Element	Crustal abundance ppm*	Arithmetic mean, ppm	Geometric mean, ppm	Range	, ppm
Ce	40	3391	693	nd -	13652
Sr	450	8647	1449	35 -	73558
La	20	1696	277	nd -	7367
Si	25.8%	3675	1948	tr -	11013
Al.	8.1%	1158	694	12 -	3029
Mg	3.1%	1361	917	tr -	6083
Fe	6.5%	2308	1286	28 -	5792
Mn	1000	8936	1224	58 -	6.14%
Y	40	1523	356	nd –	12181
Ba	250	26.5	3.8	tr -	200
Cu	70	3.4	-	0.5 -	120
Ni	80	-	-	nd -	63
V	100	-	-	nd -	248
Zr	156	-	-	nd -	1000

*Compiled from various sources by Shaw, 1960b.

TABLE XXI

The distribution of rare earths in minerals from the Kirovograd granite (after Gavrilova & Turanskaya, 1958)

<u>Mineral</u>	<u>% by weight</u> mineral in rock	<u>% rare</u> earths	Z rare earths in the mineral. to total rare earths in rock	% of so the min earths	ome rare neral to in rock	earths in total rare
				La	Се	Y
Felspars [*] Quartz	94•77 ^{##}	0.01	29.23	6.7	14.6	-
Biotite	4.82	0.06	8.92	2.07	4.05	
Chlorite	0.57	0.06+	0.62			
Garnet	0.80	0.03	0.62	-	0.035	0.066
Apatite	0.13	0.5	2.15	0.11	0.40	0.575
Monazite	0.038	50.0	58.46	15.5	26.9	-
Zircon	0.007	nd	-			
Opaque mins.	0.103	nd	-			
TOTAL	100.92		87.84			

Mainly microcline, some plagioclase.

""Undifferentiated between quartz and felspar.

[†]Used same figure as for biotite.

FIGURE 16

Content of U in apatite as a function of U in total rock for igneous rocks of the Boulder Batholith (after Altschuler, Clarke & Young, 1958).



a fairly constant ratio during differentiation. It can also be noted from Fig. 16 that the relative concentrations of U in apatite is of the order of 30 times that in the total rock. U is thus relatively concentrated in the apatite of igneous rocks.

The authors believe U^{4+} is replacing Ca^{2+} in the lattice, from the similarity in ionic radii $(U^{4+} = 0.97^{\circ} \& Ca^{2+} = 0.99^{\circ})$. A coupled substitution is not necessary as the structure can readily tolerate the slight electrical imbalances caused by such a low concentration of U.

Altschuler <u>et al</u> used an analytical technique enabling then to analyse for U^{4+} as well as total U. The igneous apatites were found to contain from 10-66% of the U as U^{4+} . The rest of the U is present in a higher oxidation state, probably as $(UO_2)^{2+}$. Although a wide spread of U^{4+} /total U occurs, it appears from their results that this ratio is relatively constant for apatites from one igneous source. They consider the possibility that the ratio U^{4+}/U^{6+} may have been fixed at the time of initial crystallization and remain unchanged, i.e., the uranium in plutonic rocks reflects the overall oxidation capacity of the magna, and that the U^{4+}/U^{6+} ratio changes accordingly in a series of related rocks. The effects of external oxidation and radioactive decay may, however, be important on the present-day ratio.

Their study also contains a large bibliography on uranium and phosphorites, and discusses the geochemistry of U in phosphorites in detail.

Although U is concentrated in apatite from igneous rocks, as noted earlier, its contribution to the total U in the rock is small. This is partly because the content of apatite is very low in igneous rocks, and partly because other accessory minerals, such as sphene and zircon, may concentrate U several orders of magnitude more strongly than apatite. The partitioning of U between the various mineral phases of the Susamyr granite batholith in the central Tien Shan has been studied by Leonova & Tauson (1958). The apatite contributes from 0.25-2.8% of the total uranium in the rock. Table XXIII shows the partition of U between the various mineral phases in several of the batholith rocks. Except for No. 4, which contains uranothorite, the values of U in these cogenetic rocks fall within a narrow range, and are of the same order as those obtained by Altschuler, <u>et al</u>. It appears, therefore, that U in apatite from the acid igneous rocks is relatively constant within a single series of cogenetic rocks, and also from those of different areas, and is of the order of 10-100 ppm.

Notes on some other elements

As discussed in the section on analytical techniques, a major problem in the analysis of the apatite samples was the coincidence of lines from the rare earth elements, many of which have complex spectra. This problem was resolved satisfactorily for the elements already discussed, but a detailed comparison of individual rare earth spectra, with the spectra of these elements was necessary. The standard wavelength tables were only useful as a general guide as variations in matrix and arcing conditions give rise to large variations in spectral line intensities.

In the apatite samples Be is apparently either absent or present

TABLE XXII

<u>Content of U. in ppm, in apatite</u> (from Altschuler, Clarke & Young, (1958))

Host rock	Locality	Total U
Granodiorite		69
Quartz Monzonite		53
Quartz Monzonite		78
Quartz diorite	All from Boulder	49
Granodiorite	Creek Batholith,	11
Quartz Monzonite	Colorado	48
Quartz Monzonite		44
Granite		23
Quartz diorite		5
Granite dike	"Silver Plume" dikes	4.4
Granite dike	intrusive into Boulder	22
Granite dike	Creek batholith	17
Diorite		59
Diorite	All from Idaho	32
Diorite	Batholith	15
Gneissic granite		13
Quartz diorite	S. California batholith	120
Gabbro	Henderson, N.C.	6.6
Syenite	Renfrew, Ontario.	23
Quartz-monzonite	Shelby, N.C.	61
Quartz-monzonite	Shelby, N.C.	65
Apatite rock	Kola Peninsula, USSR	10
Shonkinite	Lt. Pass, California	49
Apatite-magnetite rock	Durango, Mexico	10
Apatite-magnetite rock	Mineville, N.Y.	790

....

TABLE .	XXIII
---------	-------

Distribution of	Uraniu	a, in ppn,	in mine	rals from	the Susar	vr batholith
	(aft	er Leonova	a and Tau	ison (1958	2	
Mineral	1	2	З	1.	5	6
MINELAL	*	~)	4)	0
Quartz	1.5	0.3	1.4	1	0.35	0.35
Potash felspars & plagioclase	31	0.5	1	0.5	0.25	0.22
Biotite	8	5	15	25	5	5
Hornblende	5	4	-	-	4	4.2
Magnetite	8	-	15	10	8	4
Zircon	1500	1000	1400	2500	1000	1000
Sphene	350	300	150	200	170	170
Allanite	150	150	200	4100	50	240
Apatite	64	55	45	2400	30	30
Uranothorite				60000		

1 2Porphyritic Adamellite. 3Porphyritic tonalite. 3Plagiogranite. 5Leucocratic granite. 6Coarse-grained granite. Coarse-grained granite.

in very low concentrations (less than a few ppm), but over the range of wavelengths used, quantitative analysis of Be in very low concentrations was not possible, owing to line coincidences. Similar considerations would apply to Ti and Sn, although the lines for these elements were checked on each analysis to determine if appreciable amounts (i.e., greater than 15 to 25 ppm) were present. This did not appear to be the case in any of the samples. Cr and Ag were also checked on each analysis but were always absent.

The sensitivity of the method was poor for Pb and Zn, and Pb determinations were complicated by line coincidences. However, neither Pb or Zn appeared to be present above the limits of detection (approx. 100 ppm for each element).

Conclusions

Apatite from igneous and metamorphic environments is enriched in Ca, P, Ce, La, Y, and Sr compared with the crustal abundances, and apatite from granite pegmatites is also enriched in Mn. Ce, Y, La, Sr and Mn all probably replace Ca in the apatite lattice.

Although the qualitative assemblage of trace and minor elements in apatite is fairly constant, there is a great range in the concentration of these elements in the mineral. The lattice can support marked cation defects in the Ca position, and this enables the mineral to absorb trace elements from its environment into lattice voids and Ca positions, although apatite is impoverished in Fe, Mg, Al, and Si, and the elements which normally follow Fe and Mg in minerals. The impoverishment of Fe and Mg, and possibly Al, is greater than the analyses indicate, as the bulk of

these elements are present in inclusions, and, in the case of Fe, also in stains on fracture surfaces. In environments rich in Fe and Mg, such as iron ore deposits or serpentine rocks, appreciable amounts of these elements can be trapped in the lattice.

Although Ca position defects are stable, the P position supports fewer defects and will normally reject slightly larger ions, i.e., As and V which could be incorporated in diadochic substitution with P. The lack of As in the apatites is probably due mainly to the lack of this element in the environment, but some degree of structural control appears to govern the incorporation of the larger V^{5+} ion in the structure.

At the concentrations of most minor and trace elements in apatite it is not likely that coupled substitutions to restore electrical neutrality are necessary, in view of the apparent stability of the lattice to charge imbalances. Charge balancing by anion replacements, particularly 0^{2-} , have, however, not been investigated.

The ratio of Ce:La:X is fairly constant in apatite from deepseated regional and plutonic magnatic environments, reflecting the close degree of geochemical coherence of these elements, but in the pegnatite environment the total rare earth content decreases, but the ratio of X to Ce and La increases markedly. This fractionation is probably due to the selective incorporation of Ce and La in K-felspars, and in monazite, at the granitic and pegnatitic stage of differentiation, enriching the solutions in X.

Sr in apatite shows extreme variation, even between samples from the same locality and probably reflects slight environmental differences greater than the other elements.

It is generally difficult to correlate the trace element content of igneous apatite with the rock type for igneous rocks of unrelated parentage. The apatite strongly reflects the nature of geochemically distinct provinces (i.e., the anomalous high rare-earth content, particularly the high Y, in the Bamle apatite (A47) probably reflects the overall high abundance of these elements at this locality), and these differences are often greater than the differences between rock types. However, certain distinctions may be noted. Many apatites from granite pegnatites contain high Mn, a high Y/Ce+La ratio and low total Y+Ce+La, in contrast with apatite from plutonic igneous intrusives and metamorphic environments.

Apatite from igneous intrusivestends to have higher Sr (greater than 1000 ppm) than apatite from granitic pegnatites, and apatite separated from ultrabasic rocks, alkalic rocks and carbonatites may contain over 1% Sr. Apatite from alkalic complexes and carbonatites is also enriched in Ba.

TRACE ELEMENT VARIATIONS WITHIN A SINGLE APATITE CRYSTAL

XI

While the present study of the variations in the trace element contents of apatites from different environments and localities was in progress, a large crystal of fluorapatite was sampled to determine the variation, if any, of the trace elements within a single crystal. A major element analysis of this apatite is given in Table XXIV.

If the trace and minor element content of a single crystal is not homogeneous and variations do occur, they might be related to environmental changes during the growth of the crystal, or to some form of crystallographic or mineralogical control. Alternatively the presence of impurity elements in the crystal might itself exert a control on the growth of the crystal. The theoretical arguments for such compositional variations are sound, and are presented in some detail in the following sections.

Purposes of the study

i) To determine if the trace element content of a crystal is, or is not, homogeneous within the body of the crystal.

To the writer's knowledge there are no previous available data to answer this question. The regular variation of the major elements within a crystal is well established, i.e. "zoning" in felspars. Variations in the major element content often produce pronounced optical effects, which when suitably correlated, can be used to determine

TABLE XXIV

Major	element analy	rsis of t	he single	apati	te crystal	
			lit.	% oxi	de	
	Si0,			0.75		
	AloOg			0.09		
	Feooa			nil		
	FeO			0.04		
	MnO			0.014		
	MgO			1.2		
	CaO		4	53.7		
	P205			38.4		
	II_0+			0.12		
	H_0-			nil		
	cõ			2.01		
	CL			0.04		
	F			3.45		
	Less $0 = H$, Cl		1.47	Analyst J. Muysson,	
	SUM		-	98.34	McMaster University Rock Analysis Lab.	
	Ener anadi		determine	ant ion		

From spectrographic determinations:

Ce ₂ 03	0.96
Y ₂ Õ ₃	0.18
$La_{2}O_{3}$	0.35
SrO*	0.12
momt 7	00.05
TOTAL	99.95

"Semi-quantitative determination.

Formula

í.

^{Ca}9.58^{Mg}0.30^{Ce}0.06^I0.02^{La}0.02^{Sr}0.01 ^{Al}0.02^{/P}5.41^C0.46^{Si}0.13⁰24^{-7F}1.82^{Cl}0.01^{OH}0.13 ^{#M}Calculated from the analysis on the basis that P + C + Si = 6000 gm/atoms x 104. compositional variations. Optical changes are seldom produced by trace elements to a degree which enables these changes to be measured in the laboratory. The colour of a crystal could be useful in this regard for some elements, but if several impurities are present, each contributing to the optical absorption in the visible region (as appears to be generally the case), it is not possible to make accurate correlations between these optical changes and variations in composition. A direct analytical method therefore seems to be the only possible approach.

Some of the apatite samples used in the general study of apatite geochemistry were fragments broken from a larger crystal, particularly for many of the large pegmatite crystals. This method of sampling large crystals is common in analytical determinations of trace element contents, and appears to be intuitively satisfactory if there is reason to believe that the crystal grew in a homogeneous medium. If colour or optical variations suggested, however, that the crystal was "zoned", this method would obviously not be used. The crystal analysed in this present study gave no indication that it should be other than homogeneous, and these analyses were made, therefore, to determine if this method of sampling is satisfactory.

ii) To determine if the trace element distribution could be related to the distribution of micro-inclusions within the crystal.

Special techniques that measure the electronic energy lovels of an element in the solid state would enable the geochemist to determine the atomic environment of a trace element in a crystal. Such techniques are not generally available and it is necessary to use indirect methods to determine the site of trace elements in a mineral.

It is not even possible to determine from a chemical analysis if the element is present in the mineral phase under investigation, or if it is present in a separate included phase, as:

- a) macro- or microcrystalline inclusions or intergrowths of a foreign mineral
- or b) as a discrete foreign mineral phase, but below the limits of optical resolution under the microscope.

One method of determining if inclusions of type (a) are contributing to the trace element content of the mineral as a whole is to measure these inclusions for different samples, and see if there is any correlation between the number and type of inclusions and the trace element content. While generally satisfactory, this has the disadvantage that the composition of an inclusion in sample A might not have the same composition as an inclusion of the same mineral in sample B from another locality or environment. This will lessen any correlation that might exist. The present study, using samples all from one crystal, should give minimum variation in composition and type of inclusions, and enable correlations of this sort to be made under more closely controlled conditions.

The type (b) inclusions pose a problem in attempting this type of correlation, but there are several factors that minimise the possibility of obtaining a wrong correlation because of inclusions that could not be counted.

Consider the case that microcrystalline inclusions of fluorite are counted for each sample, and it is assumed that there are a number of inclusions of fluorite in the sample that are below the limits of optical resolution, and hence cannot be estimated. Within the crystal as a whole (i.e. the whole finite population), there will be a distribution of sizes of the fluorite inclusions. If a sample from the population is taken, and that sample is large enough, it is reasonable to expect that the size distribution in the sample approaches that of the whole population (the crystal). In another sample taken from the crystal this will also be true, and hence the distribution of sizes will be relatively constant between samples. The ratio of inclusions counted to inclusions not counted will be constant between samples, and although the numerical value of this ratio is not known, the validity of attempting to correlate fluorite inclusions counted to, say, Y content of the sample, is estabished. Y is commonly found in fluorite at significant concentrations.

If, however, the individual samples are from different populations, a serious error could arise from attempting this sort of correlation. Errors which could arise in the case of this single crystal study are:

- a) if the population is not homogeneous (i.e. if the conditions of crystallisation varied sufficiently during the growth of the crystal that the size distribution of the inclusions was not constant from sample to sample,
- and b) if the sample size was not large enough to reflect the distribution of the whole population.

Neither of these considerations are expected to be important enough to affect the results in this case, however.

It is of interest to note here what might be the minimum size of a particle that could exist as a separate phase. The concept of a critical nucleus is well established from energy considerations. If a crystalline particle is below a critical size it can only reduce excess

free energy between the particle and the solution by dissolving. If it is above the critical size, it will reduce it by growing. Theoretically one can obtain an estimate of this critical size by determining the limit of formation of an intact body in a solid-liquid transition. This limit is set when the bulk energy of the molecules separating from the solution is equal to the surface energy:

$$\frac{4}{3}\pi r^{3}dL = 4\pi r^{2}\varepsilon$$

where r is the radius of the critical sphere, d is its density, L is the latent heat of the transition and s the specific surface energy. L may be of the order of 100 cals./gm. and s is of the order of 100 ergs/cm². The diameter of the minimum particle is then about 20Å. Experimental work suggests that in practice the minimum particle formed under ideal conditions for the separation of a very finely dispersed phase is much greater than this theoretical value. Van Hook (1%1) quotes the experimental work of Ostwald, who determined the minimum effective particle of salol (phenyl salicylate) in supersaturated solution as being equivalent to a sphere several microns in diameter.

iii) To determine if there is any relationship between trace element content and crystallcgraphic orientation or habit.

A mechanism for the crystallographic control of the incorporation of trace elements (impurity elements) and the effect on the habit of the resulting crystal is presented here.

The ability of impurities in solution to modify the habit of growing crystals is well known. The uncertainties regarding growth mechanisms in crystals make it more difficult to correlate this habit modification with the atomic structural picture. There are several models for crystal growth from solution. It is possible to explain the effect of impurity incorporation on the habit using some of the models, although it should be realised that difficulties and breakdowns of the theory will arise in some cases, due to insufficient knowledge of all the parameters of crystal growth.

NaCl crystallising from an aqueous solution typically develops the faces of a cube, but the addition of a small amount of urea (> 5%)to the solution results in the development of octahedral faces. Mumerous workers have found that the addition of various impurities to a saturated solution have markedly retarded crystallisation or modified crystal habit. Good reviews of these experiments are given in Buckley (1951), Van Hook (1961) and Mullin (1961). The effect of organic dyestuffs as habit-modifyers on the crystallisation of inorganic salts from saturated solutions is summarised by Buckley (1951). Only those dyestuffs that colour the crystal (i.e. are incorporated in it) act as habit modifyers. The significance of metal cations in this regard has been studied by Spangenberg (1920), who found the Hg²⁺ ions in a salt solution caused the salt crystals to develop dodecahedral faces. Yamanato (in Van Hook, 1961), found that Mn²⁺, Pb²⁺, Sn²⁺, Zn²⁺, and Cd²⁺ acted as catalysts for the growth of NaCl crystals, and Booth (1951) showed that Bi³⁺, En²⁺, Zn²⁺, and Pb²⁺ tended to be adsorbed on the (111) faces of NaCl. The dominant prism faces of tetragonal NH H PO are replaced by curved tapering faces converging along the c-axis by the following cation concentrations in the solution (Kolb & Komer, in Buckley, 1951):

FIGURE 17

Effect of sodium dodecylbenzene sulphanate (SDBS) and trimethyldodecylanmonium chloride (TDMAC) on the specific growth rates of various faces of adipic acid (after Michaels & Colville, 1960).



F 1

. .	_
Sn ³⁺	4.4 x 10^{-5} moles/litre.
C r³⁺	1.8 x 10 ⁻³
Fe ³⁺	1.8×10^{-3}
Ti ⁴⁺	2.0×10^{-3}
Au ³⁺	2.0×10^{-3}
л1 ³⁺	4.0×10^{-3}
Be ²⁺	1.1×10^{-2}

A recent paper by Michaels & Colville (1960) on the habit modification of monoclinic adipic acid, $(GH_2)_4(GOOH)_2$, in supersaturated solutions, by sodium dodecylbenzenesulphonate (SDES) and trimethyldodecylammonium chloride (THDAC), showed the effect of additives on the specific growth rates of various crystal faces. The long axes of the linear dicarboxylic acid molecule are aligned parallel to the (OlO) face, so that the (OO1) face is composed entirely of carboxyl groups, while the (OlO) and (110) faces contain both carboxylic and hydrocarbon portions of the molecule. Fig. 17 shows the effect of adding TMDAC and SDES at concentrations of 50-100 ppm on the growth rate of the faces, with varying degrees of supersaturation.¹

Inhibition of all the faces occurs with the additives, but TMDAC is far more effective in controlling the development of the (001) face, and the SDBS is more effective in inhibiting the (110) and (010) faces. This is believed to be due to the adsorption of the SDBS preferentially on crystal faces with a low hydroxyl density, due to the anicnic nature of the reactant, while the TDMAC, a cationic reactant, is preferentially

 $1/\ln S$ is used as a measure of the degree of supersaturation, as: $R = Ke^{A}/\ln S$, where R is the growth rate of a face in mg./min/cm², S is the supersaturation ratio in the solution, A and K are constants.

adsorbed on the planes with the greatest hydroxyl density.

The action of impurities influencing the habit of crystals by retarding growth rates was regarded by Freundlich (1922) as an adsorption phenomenon. He believed that the impurity ions were adsorbed onto the surface of the growing crystals. Possibly the impurity may compete for and enter the lattice site, but, in any case, the number of sites available for surface nucleation or solute deposition on the face are reduced, and growth is impeded.

Several other workers have explained the impedance of crystal growth by the adsorption mechanism of Freundlich. The development of octahedral faces on crystals of NaCl, noted above, is due to the preferential adsorption of polar organic molecules on the {111} faces of the crystal. The planes of the {100} faces of the NaCl lattice are occupied by alternating Na⁺ and Cl⁻ with a net charge of zero, whereas the {111} planes are occupied only by ions of like charge. The latter planes therefore would preferentially adsorb appropriate polar materials. This adsorption reduces the available sites for new growth or nucleation, and the face is impeded in its crystallisation. The slowest growing faces are the ones best developed in the crystal, as will be shown below, and consequently the {111} faces become well developed in the final product.

It can be shown simply and diagramatically that in a growing crystal, the fastest growing faces will be the ones that are quickly eliminated from the form, whereas the faces that are inhibited in their growth are persistent and become best developed in the final form. The following treatment is from Azaroff (1960):

Two vectors (OP and OR), representing the growth velocity of two crystal faces (PQ and RQ), are drawn from a common origin, 0, in Fig. 18A. The intersection of the faces is connocted to 0, and a line, pr, contructed to intersect the growth velocity vectors normal to the construction line, OQ. OPQ and Oqp are similar right triangles and the following relations hold:

$$OP:Oq = OQ:Op$$

and $OR:Oq = OQ:Or$

Therefore

$$Op = \frac{1}{OP} (OQ.Oq)$$

and
$$Or = \frac{1}{OR} (OQ.Oq)$$

Op and Or are therefore proportional to the reciprocals of the growthvelocity vectors and are called "index vectors". Fig. 18B shows a new face added at S. The index vector of this face, Os, is constructed, and:

$$0s = \frac{1}{0S} (00.0q)$$

The new face OS is drawn at the limiting condition where it will just appear or disappear and hence Os terminates on the line pr. If Os is within the triangle Opr, the new face will not intersect the faces CP and QR and hence will not appear. If it lies outside the triangle it will intersect these faces and will appear. Whether the new face appears or disappears depends on the length of the index vector, which is inversely proportional to the growth velocity. Hence the fastest growing faces will be eliminated, whereas the slowest growing faces will be preserved. A diagrammatic representation of the growth stages of an octahedral crystal in a supersaturated solution is shown in Fig. 18C.

FIGURE 18

30

Representation of the effect of growth velocity on the development of crystal faces. (18A & 18B after Azaroff, 1960, 18C after Buckley, 1951).





The {111} faces are growing more rapidly than the {100}. faces and hence are rapidly eliminated.

It has been previously noted that the unsatisfied charges existing on the surface of the crystal plane will be important in determining the attraction of other atoms or molecules to that surface. If different faces have different atomic arrangements on their surfaces (as in the case of the NaCl planes noted previously) selective incorporation of new "building units" will occur. This has to be taken into account, but for many complex crystals the development of faces can be predicted from the plane packing density of atoms on the crystal surface. These planes with the greatest packing density will grow more slowly as it requires more material to build up a new layer of the face. A difficulty arises here as it is not possible to define precisely the plane of the crystal surface with reference to the atomic structure. A plane taken at any direction in the structure will not pass exactly through the centres of all the atoms in the neighbourhood of that plane. The calculation of the plane packing density cannot be done simply, as it is difficult to know which atoms should be considered as contributing to this density. However, the use of lattice points, which all lie on a plane, can be used, so that instead of defining the plane density of atoms, it is simpler to define the plane density of lattice points. This is possible, of course, because each lattice point is associated with an identical atomic environment.

This kinetic approach, formulated by Bravais and modified by Donnay & Harker, is sometimes referred to as the Bravais-Donnay-Harker rule. It should be noted here that it is possible to predict the development of crystal faces by a thermodynamic reasoning, based on the Gibbs criterion of surface energy of the face. Van Hook summarises this reasoning as follows (1961, p.21):

> If alternative arrangements are available in a crystal face, that one will appear in which the greatest decrease in free energy is involved. This maximum change will be realised with the establishment of greatest bond strength, which is at the site which offers the greatest area of attachment between crystal and accreting molecules.

iv) To determine if there is a regular variation in the minor element distribution within the crystal, possibly related to fluctuations in the supply of material during the growth period.

A regular variation in the minor element content of a crystal could occur by fluctuations in the composition of the solutions feeding the crystal. The existence of crystals zoned in their major element content has already been noted in this regard.

There is evidence that the Mn content of successive generations of apatite from some pegnatites may decrease as the solutions pass from the pegnatitic stage to high and low temperature hydrothermal stages, (see p.67).

Similar zoning in the minor and trace element content of the crystal might be related to a mechanism of this type and may throw light on the crystallisation process.

Natural environment of the apatite crystal

A large single crystal of apatite, measuring approximately 6" in length (parallel to the c-axis) and 4" in diameter (in a plane cut normal to the c-axis) was kindly supplied by Dr. D. M. Shaw. This crystal was collected by Dr. Shaw from the Belisle zone, Yates Uranium Mines Incorporated, lot 18, range IV, Huddersfield Township, Quebec.

At this locality large green apatite crystals are associated with 6-inch books of amber mica in pyroxenites of the Grenville sub-province of the Canadian Pre-Cambrian Shield (Shaw, 1958). Shaw describes the pyroxenites as skarns of three main types:

- i) a green diopsidic pyroxenite with green tremolite, calcite, scapolite, amber mica and sphene,
- ii) a similar type to (i) except that calcite is the major constituent,
- and iii) a scapolite-diopside rock, with large scapolites (up to 2" long).

Granites, migmatites and sillimanite-gneiss are associated with the pyroxenites, and the skarns contain radioactive minerals, i.e., thorianite, uranothorite, uranophane and allanite. The Belisle zone is only weakly radioactive. Writing of this property, Shaw (unpublished) states:

> There is extensive variation in lithology over short distances, a considerable variety of skarns and marbles being present. The grain-size is also very variable, from medium and coarse marbles to very coarse vein or pegnatitic skarn.

Shaw's interpretation of the origin of these rocks as an interplay of the various processes of metamorphism, metasomatism and igneous activity has already been noted (pp.71-72). He considers the pyroxenite skarns to have been formed in depth by fluids rich in CO_2 , H_2O , Cl and SO_4 with local concentrations of F and P. These fluids reacted with country rocks, mainly marbles, and produced the skarns and vein and pognatite assemblages by processes of in situ metasomation, vein deposits and replacements. The biotite-apatite deposits of Quebec were considered by Landes (1938) to be essentially pegnatitic and hydrothermal from the deep seated crystallisation of a P-rich granite magan. Landes' approach consider the apatite to have formed by direct crystallisation from a derivative granitic fluid, while Shaw's approach includes the possibility of growth by diffusion of fluids through the rock to supply rapidly growing crystal nuclei.

Nethod of study

The large apatite crystel was cut in half normal to the c-axis and the cut section was ground to smoothness, to give a basal section 11 cms. x 14 cms. (Plate I). The half-crystal was then mounted in polylite cold plastic with only the ground face exposed. A grid, of squares 1 cm. x 1 cm., was then placed randomly over the cut face. The left-hand and lower sides of each individual grid square were divided equally into 10 units of 1 mm. each, so that a co-ordinate system was set up with the origin 0,0 at the bottom left-hand corner of each square. Using a Table of random two-digit numbers (Table A-1, Dixon & Massey, 1957), a sampling point was located in each square. For example, if the random number chosen was 42, the campling point was located by reading off 4 units on the x-axis and 2 units on the y-axis. This was done for each individual square of the grid.

An autoradiograph of the crystal was made to determine if their were any local concentrations of U or Th, or their radicactive decay products. The cut face of the crystal was placed on a sheet of Kodak Ko-Screen X-ray film, being separated from immediate contact with the film by a sheet of black paper. It was kept in a light tight box and two separate exposures made, one for 7 days and the other for 15 days. The

natural radioactivity of the crystal was not intense enough to affect the film appreciably for the 7 day exposure, but the 15 day exposure produced a good autoradiograph (Plate II). The background radioactivity of the crystal gave an image with the crystal outline readily visible. The highly radioactive spots on the film (light patches on the print in Plate II) can be correlated with minute black and reddish-brown, opaque inclusions of unknown composition, visible under the binocular microscope. Larger calcite inclusions within the apatite are not radioactive and show up as dark areas on the print. The fracture pattern of the crystal is easily distinguishable on the print, and may be due to a slightly radioactive secondary coating on the fracture surfaces. There is also the possibility that radon gas may leak from the interior of the crystal along the fractures.

Samples of the apatite were then taken at each of the sample points on the grid. A small coring diamond drill bit was made to specifications for this purpose by J. K. Smit and Sons of Toronto (Cruft & Shaw, 1962). A core sample of 3.4 mm. diameter, and approximately 1 cm. long, was obtained using the coring bit mounted in the chuck of a drill press. It was necessary to use a water swivel mounted between the bit and the drill chuck so that a flow of water could be maintained through the interior of the bit to wash away cuttings (Plate III). The diamonds of the bit are set in a tungsten alloy matrix, and there was no contamination of the sample using this technique. Altogether 102 core samples were taken over the surface of the crystal (Fig. 19).
The core samples were examined under the binocular microscope to determine the degree of fracturing and any staining present, and large inclusions of calcite and biotite (if present) were removed by breaking and hand picking. The degree of fracturing was recorded using the coding system outlined in the section on "Sample Preparation".

The core sample was then crushed and a small portion of the sample sieved using nylon mesh screens and the 150-250 mesh fraction was collected. A known volume, weighing approximately 3 mg., of this size fraction was then obtained using a graduated glass capillary tube, and put on a microscope slide. Refractive index oil (n = 1.632) was added to the sample and the total number and type of all inclusions counted. Calcite was the most common inclusion, followed by fluorite and biotite (see Appendix 5). The remainder of the sample was further ground, mixed 1:1 with graphite and 0.08% PdCl₂, and analysed using the same spectrographic methods as for the general series of apatites.

The samples were analysed in triplicate, except for C4 and J6 (Fig. 19), which were analysed in duplicate owing to losses during experimentation and arcing. The samples were arced in a random order to climinate the effect of any experimental "drift" with time, and analysed for Si, Al, Fe, Mn, Y, Ce, and La. It was originally intended to analyse also for Sr, Ba and Cu. Ba, however, was present in amounts just below the limit of sensitivity and could not be read with any accuracy, and Sr could not always be read on the same spectral line. The intensities of the Sr lines did not always permit the transmission readings to be taken within the 5%-95% range necessary for accurate photodensitometer response,

and it was also necessary to change from one spectral line to another. Cu determinations were not continued when it was realised that the analytical variation was too great to pick out small differences between samples. As the level of Cu content was of the order of a few ppm, it is possible that Cu contamination was affecting the results. The transmission data were converted to analysis results, punched on IEM data processing cards and the arithmetic means of the triplicate analyses obtained using Bendix G-15 computer programs prepared by the writer. The analytical results are given in Appendix 4.

A single classification analysis of variance of the triplicate analyses was then carried out, with the data expressed in units of \log_{10} , using a Bendix G-15 Computer program prepared by Mr. A. M. Kudo²

The means of the analyses were plotted and the diagrams contoured. The percentage of microcrystalline inclusions was also plotted for each sample, and contoured to enable comparisons to be made. These diagrams are reproduced in Figs. 20-30.

In order to determine how objective the contouring of these analysis results could be, the data for Ce were given to three other independent operators to contour. Their contoured maps are reproduced in Figs. 31-33.

²For some elements the analytical data expressed in ppu were also used to compare the effect of the logarithmic conversion on the results.

DISCUSSION OF RESULTS

XII

The results of the single variable of classification analysis of variance computations are presented in Table XXVI. The concentrations (k ppm) were converted to logarithms₁₀ prior to computation, although this appears to have been unnecessary, since the analysis of variance for Si and Mn was also carried out with arithmetic data and the F-ratios show only a very slight difference between the two sets of data. This is probably due to the poor separation between the normal and lognormal distribution curves when the coefficient of variation, $\frac{S}{K} \times 100$, is less than about 20% (Shaw, 1961). The coefficients of variation are listed in Table XXV.

The observed F-ratios are much higher than the tabulated function, $F_{0.995(99,200)}$, for all the elements which were analysed over the whole crystal, i.e., Si, Al, Fe, Mn, Y, Ce and La. The level of significance had been chosen at 2.5% prior to undertaking the experiment, but the results show that the means are significantly different even at the 0.05% level. The grand means, standard deviations and coefficients of relative variation for each element, are given in Table XXV.

It is apparent therefore, that a small fragment from this apatite would not give a result which would efficiently represent the overall content of the trace and minor elements within the crystal. The total variation between samples from the single crystal is much less than

the variation between apatite samples from different localities. However, if an experiment were set up to determine the variation in the trace element content within apatites from, say, a single pegmatite vein, where differences might be expected to be slight, inhomogeneity of the individual crystals could significantly affect the result, unless proper precautions were taken when sampling.

Comparison of the contours for Ce content of the crystal by the four independent workers, JHC, EFC, AEK and GS, shows fair agreement, although one of the operators chose to join some of his contours to accentuate. E-W trends. whereas the other operators have accentuated N-S trends, and produced more or less marked zonal pattern. Contouring the analytical values, however, is justified, as the high and low values aro concentrated in definite belts or clusters. If large significant variations in the composition had occurred somewhat randomly over very small distances, the scale of sampling would have precluded obtaining definite compositional zones or belts within the crystal. This is not the case, however.

The percentage of various inclusions in the crystal were plotted and contoured (Figs. 28-30). There is no similarity between the distribution of the elements and the percentage of calcite inclusions. Lapkowsky (1959) analysed calcite from the same property as the apatite crystal and found 1400 ppm Fe, 650 ppm Mn and 860 ppm Si present. The maximum percentage of calcite included in any sample from the apatite was in sample K9 (2.5% calcite). The maximum contribution of Fe, Mn and Si from the calcite to this apatite sample would be approximately 30 ppm

Fe, 15 ppm Mn and 20 ppm Si. The sample K9 actually coincides with low values for the elements in question.

A similar lack of spatial correlation exists between the trace elements and the percentage of fluorite inclusions. Biotite inclusions are generally absent over much of the crystel, but several samples contain as much as 0.3% biotite inclusions. Values in the lower ranges show no correlation between the elements and the percentage biotite, but there is a spatial relationship between the high values of biotite and the high values of Fe, Al and Si. All the samples containing 0.3% biotite coincide with Fe values greater than 300 ppm, although high Fe values do not necessarily coincide with high observed contents of biotite. It is interesting to note that these Fe highs correlated with high biotite tend to occur in isolated samples without any well defined trend. The most extensive trend in high Fe content, in a SW-NE belt, just below the centre of the crystal, is not spatially coincident with high biotite concentrations. It appears, therefore, that Fe is present within the apatite mineral phase, in well defined zones, but that there is a contribution to some of the high values from included biotite. Somewhat similar considerations would apply to Al, although the correlation is less evident. It is also much less evident with Si, although this is because Si occurs in a much higher concentration range (1800-4400 ppn).

^LThe method of counting inclusions under the petrographic microscope is based on an area counting technique. Insofar as biotite occurs in thin plates, the percentage estimate of the biotite content is probably somewhat high. The relative variation from sample to sample should, however, not be affected.

There is no readily apparent correlation between a crystallographic direction within the crystal and the trace element content. although there is a possible correlation between the crystal habit and the composition for a few elements. There is a greater area of high Ce content near the faces c, d and f (particularly with d). Ce is present in a concentration range from 6359 ppm (considering the 4948 ppm value as possible analytical error) to a high of 10339 ppm. It therefore was relatively abundant in the growth solutions, and it fits into the apatite lattice readily. It is a trivalent ion and might be expected to become readily adsorbed on the face of the crystal, but its incorporation in the Ca²⁺ position of the structure will create a slight distortion (ionic radii of Ca²⁺ and Ce³⁺ are 1.03 and 1.11A respectively) and an increase in the local positive charge accumulation on the surface. Ce^{3+} has a higher electronegativity than Ca²⁺ (160 Kcal/gm. atom as against 137 Kcal/gm. atom), and a higher EK value (922 for Ce³⁺ and 477 for Ca²⁺). The incorporation of the Ce^{3+} ion in the place of Ca^{2+} will have the effect of increasing the lattice energy and forming a somewhat weaker The number of sites available for further nucleand less ionic bond. ation and growth are reduced, and from reasoning on kinetic and energy grounds, presented in the previous section, the crystallisation of the face will be impeded. Therefore, if the habit modification is due to the incorporation of impurities, an impurity with the parameters of Ce³⁺ and in relatively high concentration would be effective. It is probable that the most important of the parameters here is concentration. The other elements, including other rare earths, are present in lower

concentration than Ce, and would be far less effective in inhibiting growth.

The good development of the faces c, d and f in the crystal, and the higher concentrations of Ce near these faces, are compatible with a slow growth rate. The evidence is, however, indicative and not conclusive. Other factors, such as impedance by pressures in the medium, might be important, although growth pressures of crystal faces are of the order of several kilograms/cm², and the effect of impurities as habit modifyers seems to far outweigh other factors in artificial systems.

The poor development of face e, and the good development of face b cannot be simply related to Ce concentrations. A further difficulty arises in considering why the Ce should be preferentially attracted to faces c, d and f. The atomic environment of the hexagonal prism faces of the growing apatite should be almost identical, and it would be necessary to postulate a mechanism that created a greater concentration of Ce on one side of the crystal than the other. Growth from a homogeneous fluid under open space conditions would obviously not do this, although this type of deposition would not be expected in the Grenville province at depths of probably 15-25 km. If a model of diffusion of elements to crystallizing nuclei is used, this mechanism would involve a direction of flow of the "solutions" through the pore spaces of the rock. If the direction of diffusion was from the E to the W (using these terms only in reference to the trace element "maps" of Figs. 20-27), local concentration gradients could arise by the rapid adsorption of charged Ce^{3+} ions on the nearer faces, i.e., c & d, of the apatite crystal.

There is a well defined belt of low Fe values near the a face, although the concentration of Fe in the crystal is so low that it does not seem feasible to correlate the face development with Fe impurity in the same way as was done for Ce.

Variation in the supply of an element during the growth period is suggested for some elements. This is particularly so for Ce. Fig. 25 shows a zone of low Ce values within the crystal, roughly parallel to the crystal outline. Similar zones of less definite character are also seen for Mn and Al. The low values can be correlated with a belt of calcite inclusions and stringers within the crystal that probably represent a halt stage in the crystallisation. This zone of inclusions is particularly marked parallel to face d, and most trace elements occur in low values here. That this is not due to a high content of calcite in the samples can be seen from Fig. 28, which shows the microcrystalline inclusions to decrease somewhat in this part of the crystal. It appears that the zone is marked by large macrocrystalline calcite inclusions only. Mn, Fe and Al are particularly low in this zone, although all the elements except La are low to a somewhat lesser degree. Variations in the supply of the solutions probably occurred during the growth of the crystal, and this is reflected by variations in the trace elements incorporated in the crystal.

The correlation between pairs of elements in the crystal can be seen from Figs. 20 to 26. A statistical measure of this correlation was also obtained by computing the value of the correlation coefficient, r, for all possible combinations of the elements (Table XXVII). At the

Lé level of significance most pairs of elements show the population correlation coefficient to be significantly different from zero. This implies that the general level of concentration of trace elements in the growth medium was varying as a whole, rather than as individual elements. It should be point out, however, that most of the correlations are weak, although significant (for $\rho = 0$) and random fluctuations must have occurred. Another possibility which must be considered, however, is that variations in the physical conditions (i.e., temperature, pressure) occurred throughout growth of the crystal, and these variations permitted the crystal to incorporate a wider variety of trace elements within its structure at one time than at others. A lack of information on this aspect of crystal growth prevents adequate discussion of this possibility, but it is doubtful if such effects are significant enough to produce the degree of variation observed.

Particularly surprising is the poor correlation, or absence of significant correlation, between Ce, Y and La in this crystal. Ce and Y are only somewhat weakly correlated (r = 0.390) and there is no significant correlation between Ce and La, a pair of elements of similar properties and close geochemical cohorence. This is in opposition to the results obtained from the study of apatite from widely varied environments where Ce and La show a very strong correlation, and Ce and Y a much weaker correlation.

It might be expected that elements with a great similarity in chemical properties would show a greater degree of coherence in one particular environment, than in different environments. If fractionation

could occur it would be contradictory for it to occur more readily with slight changes in physical conditions than with marked changes, i.e., assuming temperature (as an example) to be the main factor controlling the concentration of two elements in a mineral phase, fractionation occurs (in this case) when a temperature change produces different degrees of concentration of the two elements in the phase. A small change in temperature produces less fractionation than a great change in temperature. It may be safely assumed that the differences in conditions of formation between individual samples of the single apatite crystal were much less than between samples of the general series of apatites from various localities and environment. Yet Ce, Y and La show less coherence within the single crystal.

The conclusion must be, therefore, that over a broad range of environments, Ce and La (and Y to some extent) show a marked cohorence but slight random fluctuations will occur. This single crystal study, by working in such a narrow range of conditions, has had the broad coherence of these elements largely obliterated within this range by the effect of minor fluctuations in the abundances of the rare earths.

In view of the somewhat sympathetic variation of the elements in the growth medium, it was decided to obtain a function for each sample which represented the degree of enrichment of all the elements. Each of the seven elements in every sample was divided by its mean value for the whole crystal and the sum of these ratios taken. For any sample, therefore, the value of $\sum_{i=1}^{i=7} \frac{k_i}{z_i}$ is obtained, where k_i is the concentration of element i in ppm, and X_i is the mean in all the samples (Table

XXVIII). Fig. 27 shows this function contoured, and zones are apparent, although a regular pattern is less marked than for Ce alone. Fig. 27, therefore, is a representation of the way in which all the seven elements are varying together in the crystal.

Finally, it should be noted that the results are obtained on a section through the crystal, and are therefore 2-dimensional. For the aims stated, this method of sampling is valid, although there is no information regarding variation within the crystal along the direction of the c-axis. It is doubtful, however, if this would contribute significantly more to the results.

Conclusions

The conclusions resulting from this study of the variation of minor elements may be summarised as follows:

i) The apatite crystal is inhomogeneous in its content of all the trace elements analysed for, i.e., Si, Al, Fe, Mn, Y, Ce and La. For each element there occur well defined zones within the crystal that are significantly different in composition.

ii) This variation could affect the results of a geochemical study where minor variations in trace element content are significant, unless proper sampling precautions are employed.

iii) Ce, Y, Ia, Mn and the bulk of the Si are incorporated within the apatite structure, probably at lattice sites. Some of the Fe. Al and Si is incorporated in inclusions of biotite, and the effect of the contribution to the total Fe from the inclusions is sufficient to significantly affect the distribution of Fe in the apatite. Similar considerations might apply to Al, but the evidence is less clear.

iv) Habit modifications within the crystal might be related to the incorporation of up to 1.0%Ce. This would imply local concentration gradients in the growth solutions over short distances caused by the crystal faces in the direction of flow of the solutions selectively removing Ce by adsorption.

v) Fluctuations in the supply and composition of the growth solutions occurred, giving rise to compositional variations within the crystal.

TABLE XXV

Element	F-ratios*	<u>Mean, k</u>	<u>s</u>	$R = \frac{S}{k} \times 100$
Si	7.51	2813.2	464.7	16.52%
Al	3.66	115.5	13.4	11.60%
Fe	12.90	260.9	55.0	21.08%
Mn	4.26	83.2	11.4	13.70%
Y	4.25	1412.3	165.9	11.75%
Ce	7.90	8228.6	826.6	10.05%
La	5.12	3002.5	549•7	18.31%

Statistical parameters for analyses of single apatite crystal

All parameters, except mean, calculated on data expressed in units of log₁₀k.

S = standard deviation about means of individual samples.

R = coefficient of relative variation.

*Ratios of the observed F value to the tabulated F0.995(99,200) value.

TABLE XXVI

Single variable of classification analysis of variance tables for triplicate analysis of 100 samples from a single crystal of apatite

1. Si (logarithmic)

	Sun	of squares	df	Mean square	F
Abou	t means	1.69660	99	0.017137	$F = \frac{0.017137}{0.001483} = 11.56$
with	in groups	0.29668	200	0.001483	$F_{0.995(99.200)} = 1.54$
To	tal	1.99328	299		
2.	Si (arithme	tic)			100170 07
		68572357.6	5 99	692650.07	$\vec{F} = \frac{692650.07}{58129.42} = 11.92$
		11625884.]	L 200	58129.42	$F_{0.995(99.200)} = 1.54$
		80198241.7	7 299		
3.	Al (logarit	hmic)			
		0.93888	99	0.009483	$F = \frac{0.009483}{0.001632} = 5.64$
		0.33638	200	0.001682	$F_{0.995(99,200)} = 1.54$
		1.27526	299		
4.	Fe (logarit	hmic)			
		3.89785	99	0.039372	$F = \frac{0.039372}{0.001980} = 19.88$
		0.39609	200	0.001980	$F_{0.995(99,200)} = 1.54$
		4.29394	299		
5.	Mn (logarit	hmic)			0.010001
		1.29601	99	0.013091	$F = \frac{0.013091}{0.001995} = 6.56$
		0.39907	200	0.001995	$F_{0.995(99.200)} = 1.5l_{\odot}$
		1.69508	299		
6.	Mn (arithme	tic)			F03 4F
		52655.3	99	531.87	$F = \frac{531.87}{89.47} = 5.94$
		17893.5	200	89.47	$F_{0.995(99.200)} = 1.54$
		70548.8	299		
7.	Y (logarith	mic)			0.00010/2
		0.931220	99	0.0094063	$\mathbb{F} = \frac{0.0094053}{0.0014380} = 6.54$
		0.287591	200	0.0014380	$F_{0.995(99.200)} = 1.54$
		1.218611	299		

TABLE XXVI (Continued)

8. <u>Ce (logarithmic)</u>

...

		Sum of squares	df	Mean square	F
Abo	ut means	0.635980	99	0.0064204	$F = \frac{0.0064204}{0.0005280} = 12.16$
wit	hin groups	0.105591	200	0.0005280	$F_{0.995(99,200)} = 1.54$
T	otal	0.741571	299		0.,,)(,),200,
9.	La (logar	ithmic)			
		2.229972	99	0.0225250	$F = \frac{0.0225250}{0.0028582} = 7.88$
		0.571638	200	0.0028582	$F_{0.995(99,200)} = 1.54$
		2.801610	299		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
10.	*Cu (logar	ithmic)			
		0.421527	23	0.0183273	$F = \frac{0.0183273}{0.0094449} = 1.94$
		0.453355	48	0.0094449	$F_{0.975(23.48)} = 1.95$
		0.874882	71		
-					

[±]Cu was determined in 72 analyses only.

TABLE XXVII

			with data	expressed in		oundre apre	200 01,0001
	Si	Al	Fe	lán	Y	Ce	La
Si	1.000	0.650	0.327	0.435	0.640	0.118	0.183
٨l		1.000	0.359	0.373	0.826	0.491	0.266
Fe			1.000	0.497	0.068	0.214	-0.218
Mn				1.000	0.083	-0.041	-0.246
Y					1.000	0.390	0.506
Ce						1.000	0.100
La							1.000

The correlation is significant at the 1% level if the value of r falls outside the range +0.239 to -0.239.

Significant values are underlined.

.

TABLE XXVIII

Sample No. $\sum_{i=1}^{i=7} \frac{k_i}{\bar{x}_i}$ Sample No. $\sum_{i=1}^{i=7} \frac{k_i}{\bar{x}_i}$ Sample No. $\sum_{i=1}^{i=7} \frac{k_i}{\bar{x}_i}$ A36.25E56.30H88.06A46.27E67.85H96.01A55.90E77.19H107.52A67.81E87.30H116.71A76.67E97.60I36.63A87.74E106.47I46.19A96.16E118.40I56.54B25.97F27.88I65.93B36.30F37.15I76.63B46.07F46.67I86.63B57.88F57.31I95.38E76.48F67.94I107.32B87.79F77.18I117.10B97.58F86.37J36.94C26.71F97.26J47.27C37.48F106.08J55.87C49.39F115.41J67.04C57.10F126.57J78.07C67.61G27.25J87.77C76.90G36.41J97.14C86.54G45.98J107.64C97.00G57.12K36.90C49.39F115.41J6 <th>Values of</th> <th>i=7 <u>ki</u> i=1 ī</th> <th>for samples</th> <th>from th</th> <th>e single apa</th> <th>tite crystal</th>	Values of	i=7 <u>ki</u> i=1 ī	for samples	from th	e single apa	tite crystal
A3 6.25 E5 6.30 H8 2.06 A4 6.27 E6 7.85 H9 6.01 A5 5.90 E7 7.19 H10 7.52 A6 7.81 E6 7.30 H11 6.71 A7 6.67 E9 7.60 I3 6.68 A8 7.74 E10 6.47 I4 6.19 A9 6.16 E11 8.40 I5 6.54 E2 5.97 F2 7.88 I6 5.93 B3 6.30 F3 7.15 I7 6.93 B4 6.07 F4 6.67 I8 6.63 E5 7.38 F5 7.31 I9 5.38 E7 6.46 F6 7.94 I10 7.32 B8 7.79 F7 7.18 I11 7.10 B9 7.58 F6 6.37 J3 6.94 C2 6.71 F9 7.26 J4 7.27 C3 7.48 F10 6.08 J5 5.87 C4 9.39 F11 5.41 J6 7.04 C5 7.10 F12 6.57 J7 8.07 C6 7.61 G2 7.25 J8 7.77 C7 6.90 G3 6.41 J9 7.14 C8 6.54 G4 5.98 J10 7.64 C9 7.00 G5 7.12 K3 6.90 C10 6.66 G6 7.14 K4 7.37 D2 7.06	Sample No.	$\sum_{i=1}^{i=7} \frac{k_i}{\bar{x}_i}$	Sample No.	$\sum_{i=1}^{i=7} \frac{k_i}{\bar{x}_i}$	Sample No.	$\sum_{i=1}^{i=7} \frac{k_i}{\overline{x_i}}$
	A3 A4 A5 A6 A7 A8 A9 B2 B3 B4 B5 B7 B8 B9 C2 C3 C4 C5 C6 C7 C6 C7 C6 C9 C10 D2 D3 D4 D5 D6 D7 D8 D9 D10 E3	6.25 6.27 5.90 7.61 6.67 4.16 5.97 6.307 7.68 7.76 6.77 6.48 7.758 7.761 7.610 6.54 7.00 6.68 7.00 6.68 7.31 7.50 6.797 6.70 6.68 7.50 6.70 6.68 7.50 6.70 6.70 6.70 6.70 6.70 6.70 6.70 7.610 7.60 6.54 7.00 6.68 7.50 6.70 7.50 6.70 6.70 6.70 6.70 6.70 6.70 6.70 7.50 6.70 6.70 6.70 7.50 6.70 6.70 6.70 6.70 7.50 6.70 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50 6.70 7.50	E5 E6 E7 E8 E9 E10 E11 F2 F3 F4 F5 F6 F7 F8 F9 F10 F11 F12 G2 G3 G4 G5 G6 G7 G8 G9 G10 G11 G12 H3 H4 H5 H6	6.30 7.85 7.30 7.607 6.4708 7.197 6.671 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.9487 7.947 7.986 7.177 7.986 7.9867 7.977 6.677 7.9867 7.9877 7.9877 7.9877 7.9867 7.9877 7.9777 7.9777 7.98777 7.98777 7.98777 7.97777 7.987777 7.987777 7.987777 7.987777 7.9877777777777777777777777777777777777	H8 H9 H10 H11 I3 I4 I5 I6 I7 I8 I9 I10 I11 J3 J4 J5 J6 J7 J8 J9 J10 K3 K4 K5 K6 K7 K8 K9 L5 L6 L7 L8	8.06 6.01 7.52 6.71 6.63 6.19 6.54 5.93 6.93 6.63 5.38 7.32 7.10 6.94 7.27 5.87 7.04 8.07 7.714 7.64 6.90 7.37 8.47 8.03 6.35 6.15 5.61 6.59 6.63 7.74 6.59 6.35 7.74 7.73 7.18

FIGURE 19

4

ĸ.

Key to core sample locations in the single apatite crystal.



0

Letters a,b,c,d,e and f, are used to refer to crystal faces in text.

Corner between a and f faces broken, and faces projected in crystal diagrams.

FIGURES 20-30

Contoured diagrams of element distributions and inclusions in the single apatite crystal.

20.	Si	26.	La.
21.	AL	27.	Contours of the
22.	Fe		function $\sum_{i=1}^{L} \frac{k_i}{\bar{x}}$
23.	Mn	28.	Calcite inclusions.
24.	Y	29.	Biotite inclusions.
25.	Се	30.	Fluorite inclusions.

Stippled patches in the diagrams are large calcite inclusions.

For discussion purposes in the text, the top of the page is considered north. This does not coincide with the field orientation of the sample. 20. S.ILICON





> 3500 ppm. 3000-3499 ppm. 2500-2999 ppm. 2000-2499 ppm. < 1999 ppm.</pre>

21. A L U M I N U M





ĩ

22. I R O N





23. MANGANESE





24. YTTRIUM





> 1700 ppm. 1500-1699 ppm. 1300-1499 ppm. 1100-1299 ppm. < 1099 ppm.</pre> 25. CERIUM

 λ_{2}



> 10,000 ppm.
9000-9999 ppm.
8000-8999 ppm.
7000-7999 ppm.
< 6999 ppm.

26. LANTHANUM





27. CONTOURS OF THE FUNCTION $\sum_{i=1}^{i=7} \frac{k_i}{x_i}$

.





28. CALCITE INCLUSIONS





Included large calcite crystals > 2.0% calcite inclusions 0.9%-2.0% calcite inclusions

< 0.9% calcite inclusions

29. BIOTITE INCLUSIONS





> 0.05% biotite inclusions 0.05%-0.20% biotite inclusions 0.20%-0.30% biotite inclusions

30. FLUORITE INCLUSIONS





> 0.70% fluorite inclusions 0.50%-0.70% fluorite inclusions 0.30%-0.50% fluorite inclusions 0.05%-0.30% fluorite inclusions < 0.05% fluorite inclusions</pre>

FIGURES 31-33

Contours of Ce values in the single apatite crystal by three independent operators, JHC, AMK and GS.











163	> 10,000 ppm.
5.1	9000-9999 ppm.
	8000-8999 ppm.
	7000-7999 ppm.
	< 6999 ppm.

CERIUM Operator GBS

į.





.1

PLATE I

Cut-section of the single apatite crystal, normal to the c-axis, prior to mounting and sampling.


PLATE II

Photographic print from a 15-day autoradiograph of the single apatite crystal (natural size). Very light spots on the edges of the crystal are from U-oxide added for alignment purposes.

.



PLATE III

:

Single apatite crystal, showing mounting and drill assembly during core-sampling.

-



APPENDIX 1

.

.

Apatite samples localities

Sample No.	Donor and Sample No.	Locality	Environment
A2	RO11 [#] M13191	Turners Island, Sebastopol Twp., Renfrew Co. Ontario.	,Metamorphic (Grenville)
A3	R01 -	N. Burgess, Lanark Co., Ontario.	Metamorphic (Grenville)
A4	HOM M6630	Ticonderoga, Essex Co., N.Y.	Netamorphic?
Λ5	ROM 1417148	Kukisaumchoor, Khibina, USSR.	Nagmatic-alkalic
AG	ROM 1/21549	Durango, Mexico.	Metasomatic? from replacement
			Fe-ore deposit.
A7	R011 -	Wakefield Twp, Quebec.	Metamorphic (Grenville)
A8	RON 1911902	Snarua, Norway.	Ultrabasic association
Λ9	ROM 1124078	Strickland Quarry, Portland, Connecticut.	Granodioritic-pegmatite
A10	r.011 1122945	Harding Hine, Dixon, N. Hexico.	Granitic pegnatite
V11	ROLI 1414385	Ashio Mino, Shimotsuke, Japan.	Hydrothermal? with Cu sulphides
N12	ROM E1025	Dacy's line, Frontenac, Quobec.	Netamorphic (Grenville)
A13	ROM 1422179	Holley Springs, Georgia.	Fagmatic-ultrabasic
VII'	ROM 1423046	Slyudyanka, Transbaikal, USSR	Retamorphic skarn
A15	FOII 1-13903	Leroy Lake, Gowganda, Ontario.	Hydrothermal? with Cu sulphidos
A16	f.0.1 M23328	Hugo Mine, Keystone, S. Dakota.	Granitic pegmatito
A17	ROT 1414586	Greenwood, Maine.	Granitic pegnatito
A18	ROM 1118955	Mornouth Twp., Ontario.	Netamorphic (Grenville)
K19***	a011 1119758	Center Strafford, N. Hampshire.	Granitic pogmatite?
ń20	ROM 116669	Stonehan, liaine.	Pegnatite?
<u>121</u>	NOI: 195 88	Varutrack, Sweden.	Granitic pegmatite
A22	RUM 1123429	Heyers manch Pegmatite, Guffey, Colorado.	Granitic pegmatite
A23	H.D. Wright	Bolton, Lass.	Pegnatite?
A24	11.D. Vright	Agardslia, Norway.	Lagmatic-larvikite
A25	H.D. Uright	Langendarlen, Norway.	lagmatic-lardalite
A26	H.D. Wright	Hatnosa, Korway.	Magmatic-kjolsasite
A27	J.H. Leesor	Horsethiof Eatholith, B.U.	Hagmatic-granite
A28	DHS† ()—16a	Con. 5, Huddersfield Twp., Quebec.	Fluor-cte-ap gnoiss
A29	DIIS 011-30b	Fiscion line, Loss 4/0, Con-21, Cardin	cte-fluor-ap gneiss
- •		Tup., Untario.	

186

•

APPENDIX 1 (Continued)

Sample No.	Donor and Sample No.	Locality	Environment
A30	DAS ON-57	Lot 9, Con.21, Cardiff Twp., Ontario.	Cte-fluor-ap gneiss
A31	DMS ON-61	Lots 27/28. Con. 15. Glamorgan Typ., Ontario.	Cte-ap rock
A32	DIS CA-65	Range 6. Lot 33. Calumet Island. Quebec.	Sphene-px-scap rock
A33	DMS 011-59-1	Lot 17. Con.6. Glamorgan Two., Ontario.	Qtz-cte-ap vein
A34	DMS CA-92b-24	Range 7. Lots 29/30. Calumet Island, Quebec.	Cte-ap-fluor rock
A35	DMS CA-74-b	Range 8, Lot 32, Calumet Island, Quebec.	Fluorite-scapolite skarn
A36	DMS ON-31	Lot 17, Con.6, Glamorgan Tup., Ontario.	Cte-ap rock
A37	DMS CA-81	Range 8, Lot 32, Calumet Island, Quebec.	Fluor-cte-ap vein
A38	DMS CA-55	Range 7, Lot 30, Calumet Island, Quebcc.	Fluor-cte-ap vein
A39	DMS ON-26	Lot 17, Con.12, Monmouth Twp., Ontario.	Cte-ap-px-scap (pegnatitic?)
A40	DMS CA-92b-5-	Range 7, Lots 29/30, Calumet Island, Quebec.	Fluor-ap-sulphide vein
	22		
A41	DMS ON-60	Probably Lot 17, Con.12, Monmouth Twp., Ont.	Cte-ap-hb rock
A42	A.B. Carpenter	Crestnore, California.	Contact-metacomatic skarn
A43	McMaster Univ.	Lot 28, Con.10, Glamorgan Twp., Ontario.	Metamorphic (Grenvillo)
A44	H.H. Schmitt	Eiksundjosak, Norway.	Omphacite-diopside-apatite vein in oclogite
N15	H.H. Schmitt	Eiksundjesak, Norway.	Magnatic-eclogite
N46	D.P. Gold	St. Laurence River Mines, A ore zone, Oka, Quebec.	Magnatic-carbonatite
A47	H.D. Wright	Bamle, Norway.	Gabbroic-pegmatite

^{*}Noyal Ontario Musoum, Toronto, Ontario. ^{**}Originally classified as contact metasomatic skarn for correlations, but reclassified as granitic pegnatite. †Prof. D. M. Shaw, McMaster University. Samples A23-A41 inclusive are from the PreCambrian Gronville province of Ontario and

Quebec. Details of the individual occurrences were supplied by Prof. D. H. Shaw.

	D	D .	111	T	F	2
HL	-	Ľ.	IND.	1	7	2

.

	Analyses of apatite samples													
	Si	Al	v	Mg	Ni	Cu	Fe	Zr	lín	Y	Ce	Sr	La	Ba.
r(A)	0.40	0.51	0.56	0.66	0.69	0.72	0.7 <i>1</i> ,	0.79	0.80	0.92	1.11	1.16	1.18	1.43
Sampl	.0	*********		and the second			and Associate Stocks							
A2	5346	170	nd	1232	tr	10.2	1933	nd	4.05	1231	6459	5768	5297	8
A3	3376	325	32	1281	nd	1.3	864	2	347	346	1979	7645	1119	8
N.	3388	241	nd	3125	nd	2.7	1727	tr	741	1956	4073	7685	3967	tr
A5	1534	3029	93	tr	17	1.8	218	tr	1,45	542	3072	73558	24,80	214
Λ6	1379	69	tr	ir	tr	1.7	1200	tr	269	1083	4433	8898	5129	tr
A7	3128	192	tr	2036	nd	2.0	6'70	tr	624	397	950	7712	545	9
A8	6115	1500**	nd	1145	nd	4.6	3772	tr	231	2028	2061	20255	1137	10
A9	679	890	tr	tr	nd	1.2	5792	\mathbf{tr}	5.10%	44	183	113	377	3
ALO	124,9	1000^{3}	nd	675	nd	1.5	28	tr	781	tr	tr	156	tr	tr
All	\mathbf{tr}	37	nd	932	nd	2.0	757	tr	1696	- 99	191	17219	305	3
A12	1,90	179	nd	1555	tr	2.9	863	3	378	164	866	5700	481	1.7
A13	556	12	nd	1326	tr	0.5	683	nd	622	208	197	1118	62	tr
114	3243	21,4;	33	787	nd	9.8	274	tr	148	70	85	2432	40	3
A15+	6786	1144	nd	1563	15	S	5370	tr	457	3545	10033	2638	3249	15
A16	4836	2500"	nd	tr	nd	2.3	192	nd	4572	tr	tr	95	tr	tr
A17	4776	2000	tr tr	1135	\mathbf{tr}	2.2	590	23	4917	559	tr	13486	tr	1.2
Als	826	48	ir	tr	\mathbf{tr}	1.7	109	nd	639	645	2845	9839	3255	4
A19	3163	2000*	tr	tr	\mathbf{tr}	2.0	1649	7	2607	1987	776	552	287	1.15
A20	\mathbf{tr}	61 8	\mathbf{tr}	tr	nd	2.0	5158	nd	6.14,5	nd	nd	41	nd	tr
A21	tr_{0}	416	tr	tr	nd	2.0	3361	nd	25417	tr	tr	35	tr	tr
A22	1000°	* 299	nd	600	' tr	2.6	4688	tr	2.52,5	2742	1236	313	573	1.0
A23	2007	1838	nd	2915	nd	4.4	334	nd	383	977	89	721	27	3
124	8786	1,10	nd	700***	tr	5.8	2666	5	1028	2229	7129	1823	3758	7
A25	4310	1700*	nd	1045	tr	2.4	1058	94	493	2435	13652	234,8	7304	11
A26	3172	871	nd	1363	tr	4.1	2500	210	760	1285	5697	1779	2815	5
A27	2372	639	tr	757	tr	4.9	1145	213	T000.	-1947	2853	1976	1654	tr

r(Å)	Si 0.40	A1 0.51	V 0.56	Mg 0.66	Ni 0.69	Cu 0.72	Fe 0.74	Zr 0.79	Mn 0.80	¥ 0.92	Ce 1.11	Sr 1.16	La 1.18	Ba 1.43
Samp	le													
A28	3960	62	tr	tr	tr	tr	163	nd	220	2293	13940	3872	7132	tr
A29	2784	tr	nd	tr	tr	tr	140	nd	525	4851	9339	1810	4613	tr
A30	4090	469	tr	tr	tr	2.6	473	nd	511	4965	10218	3247	5504	5
A31	906	75	\mathbf{tr}	nd	nd	\mathbf{tr}	1258	nd	438	1402	5592	6335	3197	59
A32	7047	253	nd	656	\mathbf{tr}	2.0	1294	nd	221	1784	7780	5925	4143	6
A33	3170	84	tr	\mathbf{tr}	\mathbf{tr}	3.7	351	nd	126	1968	2644	2583	2039	nd
A34	18841	1380	\mathbf{tr}	2528	nd	4-5	2847	nd	497	2106	9996	5163	5216	tr
A35	3790	490	tr	820	nd	4.7	1526	60	284	2482	2042	1870	629	tr
A36	11530	653	93	6647	nd	tr	2231	tr	308	858	1730	3300*	*1431	\mathbf{tr}
A37	4407	234	\mathbf{tr}	nd	tr	tr	643	nd	271	2491	11082	5277	6643	\mathbf{tr}
Л38	2589	131	nd	nd	10	2.9	207	nd	93	1952	10290	2377	4662	4
۸39	1867	67	nd	tr	tr	2.2	1668	nd	217	1199	7713	5567	5131	8
A40	12119	287	\mathbf{tr}	1011	\mathbf{tr}	S	1361	nd	263	3435	7430	2264	2526	3
Λ41	1602	47	nd	\mathbf{tr}	nd	3.4	164	nd	214	1250	2361	2572	785	8
A42	6.86%*	43	807	1247	nd	2.1	59	134	24	620	116	727	269	\mathcal{U}_{\flat}
A43	1338	121	nd	nd	\mathbf{tr}	2.8	573	nd	225	1380	3194	8	1680	10
A44	\mathbf{tr}	59	nd	1798	nd	3.5	1315	nd	226	199	4604	26114	1611	7
N45	11013	2719	nd	6083	63	12	5308	11	191	121	3027	6125	1471	8
A46	7294	239	248	3203	tr	3.6	1888	93	863	709	13203	11522	7367	S
A47	9705	508	tr	2096	tr	4.7	1584	nd	58	12181	3859	155	1411	7

APPENDIX 2 (Continued)

Values are arithmetic means of triplicate analyses and are expressed in ppm, except where listed as %.

"From wet chemical analysis, analyst J. Muysson, McMaster University Rock Analysis Laboratory.

thingle analysis only; insufficient material for triplicate. S intensity of spectral line too strong to measure.

APPENDIX 3

Physical parameters of apatite samples

No.	Colour	Fracture	Lustre (Cleavage	Staining	Transparenc	Inclusions ^{##}
A2	10R4/6	3.5	Vitreous	4.0	4.5	3.0	2.0 - mainly haematite and opaque orides.
A3	10GY6/4	2.5	Vitreous	3.0	1.5	2.5	2.5 - haematite, opaque oxides & biotite.
A4	10GY5/4	2.5	Sub-resinous	3.5	1.5	3.0	2.0 - opaque oxides & graphite?
A5	1018/2	1.5	Vitreous	1.5	1.0	1.5	2.0 - minor hornblende?
A6	10Y8/2	2.0	Vitreous (ger	m) 1.5	1.5	1.5	1.0 - pure.
A7	567/2	3.0	Sub-resincus	3.5	1.0	3.0	2.5 - calcite, fluorite?, & needle-like unknowns.
84	N8	4.0	Dull	3.0	4.0	4.5	3.0 - hornblende, opaque oxides.
Λ9	5BG4/2	2.5	Sub-resinous	3.0	1.0	3.5	4.5 - numerous oriented needles & fluid? inclusions.
Alo	6B6/2	3.0	Vitreous	2.5	1.0	3.0	2.5 - tourmaline? needles & fluid inclusions.
A11	N9	2.0	Vitreous	1.5	1.0	3.0	1.0 - pure.
A12	5B5/1	3.5	Vitreous	3.0	1.0	3.0	3.5 - calcite, biotite, opaque oxides & oriented needle- like unknowns.
A13	5GY7/4	1.5	Vitreous (ge	m) 1.5	1.0	2.0	1.0 - pure.
AI4	567/2	3.0	Sub-resinous	3.5	2.0	3.0	5.0 - oriented needle-like unknowns & pink hexagonal inclusions, opaque oxides.
A15	5R4/6	3.0	Dull	3.0	1.5	4.0	2.0 - haematite, opaque oxides (& sulphides?)
A16	5B5/6	3.0	Sub-resinous	2.5	1.0	3.5	2.5 - dark needles (tournaline?), fluid inclusions fluorite?
A17	5P6/2	2.5	Sub-resinous	2.5	2.0	3.0	2.5 - needle-like unknowns, opaques,
A18	10GY5/1	1.0	Vitreous (ge	m) 1.0	1.0	5	1.0 - pure.

Sample No.	Colour	Fractur	Lustre	Cleavage	Staining	Transparency	Inclusions
A19	N9	3.5	Dull	3.0	4.0	3.5	4.0 - haematite, muscovite?, fluid?
A2 0	5G4/1	3.0	Sub-resincus	3.0	1.5	3.5	3.5 - biotite, haematite, opaques & v. minor high relief
A21	5G2/1	3.0	Vitreous	3.0	2.0	4.0	2.5 - 002000 excelor in planes
A22	10GY4/l	2.0	Vitreous	2.5	1.5	3.0	2.0 - feldenan? & one one one of the
A23	5BG7/2	3.0	Vitreous	2.5	1.0	3.0	2.5 - minute dark needles or high relief prismatic unknowns.
A24*	-		-	-	-	-	2.5 - zircon?, sphene, pyroxene? & opaques.
A25"	-	-	-	-	•	-	1.5 - fairly pure, mainly pyroxene? grains.
A20"		-	-	-	-	- :	2.5 - biotite?, sphene?, pyroxene grains & opaques.
A2/"		-		-	-	-	2.5 - opaques, zircon?, sphene?
A28	9 GI7/4	2.5	Vitreous	2.0	1.5	2.5	1.0 - pure.
A29	10615/4	. 3.0	Vitreous	3.0	2.5	3.0	3.0 - haematite?, fluorite.
A30^	1018/2	2.07	Vitreous	2.0?	2.5	2.5?	3.0 - haematite, fluorite, sphene?
A31	10R5/4	3.0	Vitreous	3.0	4.0	3.5	3.0 - fluorite, haematite, opaques, calcite. scapolite?
A 32	10R5/4	3.0	Sub-resinous	3.0	3.0	3.5	4.0 - haematite, oxides, calcite, fluorite?
A33	10GY6/4	2.0	Vitreous	2.0	1.5	2.0	2.0 - scapolite?, calcite, fluonite
A34	10GY5/4	. 5.0	Vitreous	3.5	2.5	3.5	5.0+ - numerous sphene, molybdenite?, fluorite, biotite, calcite, pyroxene?
A35*	10617/2	-	-	-	-		3.0 - fluorite, sphene?, opaques, needle-like unknowne
A36	10GY7/2	3.0	Sub-resinous	3.5	1.0	3.0	3.0 - mainly scapolite and/or cal-
A37*	518/1		-	-		3	3.5 - fluorite, sphene?, opaques.

APPENDIX 3 (Continued)

.

T6T

۱

Ξ.

Sampl No.	Colour F	racture	Lustre	<u>Cleavage</u>	Staining	Transparenc	Inclusions
A 38	1017/4	3.0	Vitreous	3.5	2.5	3.0	2.5 - fluorite, haematite, calcite, scapolite?
A39	107/4 (variable)	4.0)	Sub-resincus	3.0	5.0	3.5 (variable)	4.0 - haematite, opaques, v. minor fluorite?
A 40	10GY5/2	2.5	Vitreous	3.0	1.5	3.5	4.5 - fluorite, biotite, opaques, dark oriented needle-like unknowns.
A41	10617/2	3.0	Vitreous	3.0	2.0	3.0	3.0 - calcite, scapolite?, biotite?, sphene?, opaques.
A42	1017/4	2.0	Vitreous	3.0	1.0	3.5	3.0 - calcite mainly, occ. oriented needle-like unknowns, & high relief.
A43	10GY6/4	3.0	Vitreous	3.5	3.0	3.0	2.0 - fairly pure, haematite, opaques
АЦЦ	1016/4	4.0	Sub-resinous	s 3.0?	3.5	3.0	3.0 - dendritic black oxides? in planes, & black needle-like unknowns.
A45*	1016/4	3.0?	Sub-resinou	s 3.0?	3.5	3.0	3.5 - opaques, needle-like unknowns, pyroxene?
A46*	-	-		-	-	-	5.0 - opaques, calcite & pyroxene? grains, mainly from separa- tion of concentrate.
л47	N\$	3.0	Dull	2.5	3.0	5.0	4.0 - all sub-microscopic dusty opaques.

APPENDIX 3 (Continued)

Coding system for colour, fracture, cleavage, staining and transparency is discussed in text in section on "Sample preparation".

*Apatite concentrated from host rock; difficult or impossible to determine many physical parameters.

**Inclusions are coded according to the following scheme:

.

1.0 - 1 grain of inclusion in 1000 grains of sample													
2.0	-	approx.	5	grains	of	inclusion	in	1000	grains	of	sample		
3.0		- H	10	11	11	11	18	11	18	н	11		
4.0	-	11	20	N	n	н	16	н	n	H	11		
5.0	-	N	30	Ħ	n	13	Ħ	tt	n	Ħ	11		

	Anal	yses of	samples	from the	single	apatite	crystal	
Sample	No.	Si	Λl	Fe	Mn	Y	Ce	La
A3		2521	114	207	90	1195	8398	1869
AL,		2804	114	124	78	1541	6359	3033
A5		2570	94	177	61	1255	7319	2964
A6		2789	118	373	92	1437	8828	3513
A7		2531	114	272	63	1381	7894	2971
A8		3067	124	366	79	1521	8675	3295
A9		2458	92	283	64	1194	7782	2536
B2		2361	95	189	77	1214	8147	2420
B3		2787	107	139	88	1322	7979	2661
B4		2129	94	240	77	1187	8173	24,63
B5		3094	135	313	91	1637	8707	3316
B7		2000	105	310	77	1262	3407	2509
BS		3036	134	309	87	1620	8378	3458
B9		2934	127	279	65	1650	9205	3902
C2		2954	120	125	76	1549	8265	3377
C 3		3226	120	253	106	1544	7622	3110
CT *		4336	159	537	129	1753	7253	2235
C5		21.76	117	290	98	1325	9299	2552
C6		2895	131	3/2	97	1438	9110	2535
00		2850	112	271	90	1363	7588	2693
07		3211	103	260	76	1235	7724	2359
co		3093	105	301	81	1213	7751	2153
cio		2607	103	252	78	1363	9076	2624
010		21 80	110	278	81.	139/	8737	2606
D2 D2		2211	137	283	96	1711	90/6	3767
עע		21.25	106	178	62	1347	7802	2703
דע דב		1903	100	253	82	1103	6698	21.96
D) D(2600	131	259	02	1600	6386	3166
סע		2570	120	2006	70	1566	8361	351.6
		2)10	120	200	70	1671	6033	3006
20		2012	174	290	סן רת	1602	0561	2551
D9		2714	110	272	(12	1008	0304	5271
DTO		2077	111	2/2	04	1290	())(2625
25		2312	100	207	90	1922	6495	2000
164		2900	128	205	72	1464	8917	2700
155		2005	115	199	11	1404	7961	2())
E6		3621	140	243	82	1759	830L	3548
722		2592	110	398	93	1204	0540	2337
ES.		3290	118	231	75	1664	7735	3621
£9		2952	122	198	87	1380	8724	4948
E10		2649	98	283	71	1243	7943	2684
E11		3244	148	390	85	1649	9837	3251
F2		4297	105	368	126	1309	7012	2231
F3		3031	120	198	94	1447	8713	3182
F4,		1994	110	278	103	1177	7971	2524
F5		3152	128	209	94	1647	7638	3158

APPENDIX 4

APPENDIX 4 (Continued)

Sample No.	F6 F7	178 178	C12	FLI	FL2	G2	5	G5	G6	G7	GB	G9	CIO		275	5	1-1-1 1-1-1	HG HG	ET CH	II3	H9	OTH	TTH	B	Ŕ	I5	9T).T	TO TO			J3	JI4	J5,	J6"	7.0	20	סתי	02	104	K5
Si	3617 2889	2448	707 770 L	2227	2313	3787	6652	2762	2301	2772	24,34	2917	3296	3224	0110	2726	2387	3568	2586	3188	2271	3293	2214	2449	2221	2326	2453	0442	2270	31.01	2698	2473	2893	1846	2641	2222	COV5	3218	2534	2677	3033
TV	142	320		10	011	101	LOT	911	911	16	511	109	29		277		133	620	121	135	100	123	121	8	101	60T	16	ACT -	50T	131	120	105	132	22	101	HOT I	171	211	125	116	132
Fe	271 208	282	200	195	163	367	2970	275	309	227	364	250	275	24:5		00T	010	281	373	343	161	281	323	255	205	296	191	717	122	262	251	216	242	193	339	0.92	412	300	227	225	614
n'n	011 86	06	27	30	17	132	200	106	96	72	36	76	8			22		8.5 2.5	れ	33	66	22	22	82	ខេន	201	120	0 0) û	67	71	68	78	2	2			40 12	1 19	84	TOL
д	1503	OOTT	7017	1098	1421	2001	1080L	1345	1263	1297	1283	1399	1584	1241	2121	1329	C04L	1602	THET	1575	1133	1563	1203	1316	8777	0/21	2711	0021	2007	11.66	1504	1397	1579	1263	1286	1629	Teht	65/T	1581	1573	1492
Co	8764 8687	7677	1277	6102	84,20	4,94,8	1411.1	7989	8652	6546	8204	6671	9632	6068	1201	1000	1749	8005	1416	9372	6723	8561	6088	8836	7518	8444	6250	200	6720	9537	8950	8014	8906	7830	0340	2961	8630	10330	97196	0196	9223
Ia	2796 3169	2489	2047	2270	3106	1869	2012	2636	3099	4384	2353	2410	3323	2869	1102	3135	3763	3103	2554	3224	14243	3409	2324	2930	2368	COTZ	14/12	0402	CYIC	21,00	3284	4631	3097	2473	2454	3265	3137	3451	2852	3513	3081

194

.

			5416 H 10	ono mucu.	2		
Sample No	. Si	Al	Fe	Mn	Y	Cə	La
к6	3414	127	291	81	1818	7907	4222
К7	2769	94	282	63	1276	7569	2676
KS	2669	113	172	64	1402	7576	2655
K9	2242	89	164	69	1231	6686	2705
L5	2503	117	275	79	1338	8161	2231
L6	2685	106	193	64	1363	6616	4591
L7	2702	131	300	92	1643	8974	3412
LS	2926	110	222	81	1361	8390	2789
L9	3070	131	219	70	1623	8539	3263
M6	2977	126	216	71	1612	8580	3611

APPENDIX 4 (Continued)

"Mean of duplicate analysis.

APPENDIX 5

Sample No.	5 Total	% Calcite	% Fluorite	5 Biotite	% Opaques	7
benipite no.	Inclusions	Inclusions	Inclusions	Inclusions	& "Clays"	Fracture
A3	0.6	0.4	0.2	-	-	1.0
A4	1.6	0.7	0.7	0.1	0.1	4.5
A5	1.2	1.0	0.1	0.05	0.05	1.5
AG	0.8	0.7	-	9.1	-	4.0
A7	0.4	0.4	-	-	-	3.0
A8	1.2	1.2	-	-	-	3.0
A9	1.0	1.0	-	-	-	4.0
B2	0.6	0.3	-	-	0.3	3.0
B3	0.7	0.4	0.3	-	-	2.0
Б4	0.7	0.7	-	-	-	1.5
B5	1.5	0.9	0.3	0.2	0.1	4-5
B7	1.3	0.9	0.4	-	-	3.0
BS	1.2	1.2	-	-	-	4.0
B9	1.4	1.0	0.3	-	0.1	4.0
C2	0.4	0.2	0.2		-	3.0
C3	1.0	1.0	-	-	-	5.0
C4	0.6	0.3	-	0.3	-	
C5	1.3	1.2	0.1	-	-	4.0
C6	1.9	1.0	0.5	0.1	0.3	3.0
C7	2.0	1.8	-	0.1	0.1	2.0
68	0.6	0.5	0.1	-	-	1.5
C9	0.5	0.4	-	-	0.1	5.0
C10	1.4	0.8	0.3	-	0.3	4.0
D2	1.0	0.9	0.05	-	0.05	5.0
D3	1.4	1.3	0.05	-	0.05	4.0
D4	0.7	0.3	0.4	-	-	1.5
D5	1.9	1.9	-	-	-	4.0
D6	2.2	0.9	0.9	0.2	0.2	3.0
D 7	1.9	1.6	-	0.15	0.15	2.0
DS	1.2	0.6	0.6	-	-	2.5
D 9	1.8	0.8	0.7	0.1	0.2	3.0
D 10	2.0	1.9	-	-	0.1	2.0
E 3	0.8	0.4	0.4	-	-	4.0
E4	1.7	1.0	0.3	0.2	0.2	3.0
E5	1.4	0.4	1.0	-	-	3.0
E6	2.0	1.0	0.8	0.1	0.1	3.0
E7	1.3	1.0	-	0.3	-	5.0
ES	0.3	0.2	0.05	0.05	-	5.0
E9	2.2	1.8	0.2	0.2	-	1.0
EIO	1.8	1.2	0.2	0.2	0.2	4.0
E11	1.7	1.7	-	-	-	5.0
F2	1.8	0.8	0.6	0.3	0.1	/
F3	1.8	1.4	0.3	0.05	0,05	1.0
F4	1.5	0.6	0.8	-	0.1	1.5
F5	0.9	0.4	0.4	0.1		1.0
	-		-			M

Sample No.	<u>% Total</u> Inclusions	<u>% Calcite</u> Inclusions	% Fluorite Inclusions	<u>5 Biotite</u> Inclusions	5 Opacuas & "Clays"	Fracture
F6	1.4	0.9	0.5	-	_	2.0
F7	2.4	2.2	-		0.2	2.0
F8	1.3	1.3	-	-	-	4.0
F9	1.1	0.8	0.3	_	-	3.5
FIO	0.6	0.5	-	-	0.1	4.5
FII	1.3	0.5	0.5	0.15	0.15	4.0
F12	1.0	1.0	-	-		3.0
G2	1.5	0. <i>b</i> .	0.7	0.3	0.1	
G3	1.4	0.7	0.7	-	-	2.0
GL	1.4	0.7	0.7	-	-	1.0
G5	1.1	1.1	-	-	-	3.0
G6	2.0	0.8	1.2	_	-	4.5
G7	1.4	0.9	0.4	-	0.1	5.0
G8	0.8	0.1	0.3	-	0.1	3.5
G9	1.2	1.1	-	0.1	-	2.0
GIO	1.0	0.7	0.2	-	0.1	3.5
GII	1.4	0.7	0.6	0.05	0.05	2.0
612	0.6	0.6	-	-	-	5.0
H3	1.2	0.3	0.9	-	-	2.0
HA	0.6	0.6	-	-	-	3.5
HS	1.2	0.7	0.5		-	3.0
86	1.8	0.8	0.8	-	0.2	3.0
H7	1.9	0.9	0.9	0.05	0.05	3.(
HA	1.6	1.4	_	0.05	0.15	3.5
H9	1.0	0.8	-	0.2	-	1.0
H10	1.6	1.2	0.2	-	0.2	5.0
817	1.4	0.3	0.9	0.05	0.15	4.5
T3	1.6	1.3	0.2	-	0.1	4.0
т.	0.8	0.7	-	0.1	-	3.0
15	2.0	0.9	0.8	-	0.3	5.0
T6	1.0	0.8	0.1	0.05	0.05	3.0
17	0.6	0.6	-	-	-	4.0
TR	1.6	1.0	0.6	-	-	2.0
19	0.6	0.6		-	-	2.0
no	2.0	1.0	0.5	0.15	0.35	5.0
111	3.0	2.0	0.6	0.3	0.1	4.0
<u>J</u> 3	1.3	1.3	~~	-	-	3.0
JL	0.9	0.7	0.2	-	-	3.0
J5	0.9	0.8	0.1	-	-	3.5
J6	1.0	0.9	-		0.1	5.0
J7	0.7	0.6	-	-	0.1	3.0
JB	1.0	1.0	-	-	-	2.0
J9	1.5	1.4	-	0.05	0.05	3.0
no	0.6	0.3	-	0.3	-	2.5
K3	1.3	0.6	0.0	0.05	0-05	3.0
KL	1.3	1.0	0.2	0.05	0-05	3.0
K5	2.0	1.6	0.1	0.1	0.2	1.5

APPENDIX 5 (Continued)

APPEDIX 5 (Continued)

Sample No.	% Total Inclusions	<u>% Calcite</u> Inclusions	% Fluorite Inclusions	<u>% Biotite</u> Inclusions	5 Opaques & "Clays"	Fracture
K6 K7 K8 K9 L5 L6 L7 L8 L9 M6	1.6 1.0 1.1 2.5 0.7 2.1 0.8 1.6 1.4 0.6	1.3 0.7 1.0 2.5 0.6 1.8 0.7 1.0 1.0 0.3	0.1 0.2 - 0.1 0.2 0.1 - 0.2 0.2	0.1 0.1 - - 0.05 - 0.15 0.05	0.1 0.1 - 0.05 0.45 0.15 0.1	4.0 2.5 5.0 4.5 5.0 4.0 1.0 1.5 3.0 2.0

BIBLIOGRAPHY

- Abrard, R. (1923). Presence de l'apatite dans les pegnatites des environs de Dinard. Bull. Soc. Franc. Min., vol. 46, p.5.
- Adams, F. D. (1926). A Visit to the Gem Districts of Ceylon and Burma. Bull. Can. Inst. Mining Metall., No. 166, pp.213-246.
- and Barlow, A. E. (1910). Geology of the Haliburton-Bancroft Areas. Men. Geol. Surv. Canada, Vol. 6.
- and Lawson, A. C. (1888). On some Canadian Rocks containing scapolite, with a few notes on rocks associated with the apatite deposits. Can. Rec. Sci., vol. 3, pp.186-201.
- Afanasev, G. D. (1948). On strontium in minerals of pegmatitic and hydrothermal origin in Caledonian intrusions of western Caucases. Doklady Acad. Sci. USSR, vol. 62, pp.677-679 (in Min. Abs., 10-566).
- Ahlfeld, F. (1931). The tin ores of Uncia-Llallagua, Bolivia. Econ. Geol., vol. 26, pp.241-257.
- Ahrens, L. H. (1961). Spectrochemical Analysis, 2nd ed. Addison-Wesley Publishing Co. Inc., Reading, Mass.
- Altschuler, Z. S., Cisney, E. A. & Barlow, I.H. (1952). X-ray evidence of the nature of carbonate-apatite. Bull. Geol. Soc. Am., vol. 63, pp.1230-1231.
 - . (1953). X-ray evidence of the nature of carbonate apatite. C.R. XIX Congr. Geol. Internat. Alger., fasc. XI, p.9.
- , Clarke, R. S., Jr. & Young, E. J. (1958). Geochemistry of uranium in apatite and phosphorite. U.S. Geol. Surv., Prof. Paper 314D, pp.45-90.
- Ames, L. L. Jr. (1959). The genesis of carbonate apatites. Econ. Geol., vol. 54, pp.829-841.
- . (1960). Some cation substitutions during the formation of phosphorite from calcite. Econ. Geol., vol. 55, pp.354-362.

Antonov, L. B. (1934). The apatite deposits of Khibina tundra. State Chem. Tech. Publ., Leningrad, vol. 7, (in Min. Abs., 6-312).

Azaroff, L. V. (1960). Introduction to solids. New York: McGraw Hill Inc.

Bateman, A. M. (1950). Economic Mineral Deposits. 2nd ed. New York: Wiley & Sons.

Bauer, L. H. & Berman, H. (1930). Notes on some Franklin minerals. Am. Min., vol. 15, pp.340-348.

Beevers, C. A. & McIntyre, D. B. (1945). The atomic structure of fluorapatite and its relation to that of tooth and bone material. Min. Mag., vol. 27, pp.254-257.

Belov, N. V. (1939). On some isomorphic substitutions in the apatite group. C.R. Acad. Sci. USSR, vol. 22, pp.89-92.

Bezrukov, P. L. (1939). On the contact metemorphism of phosphorites. C.R. Acad. Sci. USSR, vol. 24, pp.282-284.

Bjørlykke, H. (1937). The granite pegmatites of Southern Norway. Am. Min., vol. 22, 241-255.

Boeggild, O. B. (1903). Medd. on Grønland, vol. 26, in Min. Mag., 14-398.

Booth, A. H. (1951). Anomalous co-crystallisation of radioactive trace quantities of foreign ions with sodium chloride crystals. Trans. Faraday Soc., vol. 47, pp.633-645.

Eorgström, L. H. (1932). Syntetisk NaCl-apatit. Finska Kemistsamfundets Meddelanden, No. 2, pp.51-54 (in Min. Abs., 5-260).

Borneman-Starinkevitch, I. D. (1924). On the presence of rare earths in apatites. C.R. Acad. Sci. Russ., pp.39-41 (in Min. Abs., 2-408).

> . (1938). On some isomorphic substitutions in apatite. C.R. Acad. Sci. USSR, vol. 19, pp.253-255.

. (1953). On carbonate apatites. Doklady, Acad. Sci. USSR, vol. 9, pp.89-92 (in Min. Abs., 12-224).

and Eelov, N. V. (1940). Isomorphic substitutions in carbonate-apatite. C.R. Acad. Sci. USSR, vol. 26, pp.804-806 (in Min. Abs., 8-380).

- Brasseur, H. (1954). Note sur les constantes reticulaires et les indices de refraction des fluor-, chlor-, et hydroxyapatites. Proc. Internat. Symposium on Reactivity of Solids, Gothenburg, Pt. I, pp.363-367.
 - . (1958). Considerations nouvelles sur la constitution possible de phosphate tricalcique hydrate. Bull. Acad. Roy. Belgique, Classe Sci., Ser. 5, vol. 44, pp.507-513.
- لت Dallemagne, M. J. (1949). La synthese des apatites. Bull. Soc. Chim. France, pp.D135-D137.
- Brauns, R. (1916). Uber dem Apatit aus dem Laacher Seegebiet. Sulfatapatit und Carbonatapatit. Neues Jahrb. Min. Beilage Band 41, pp.60-92.
- Bredig, M. A., Franck, H. H. & Fuldner, H. (1933). Beitrage zur kenntnis der kalk-phosphorsaure Verbindungen. II. Zeits. Elektrochem., vol. 39, pp.959-969.
- Buckley, H. E. (1951). Crystal Growth. New York: John Wiley & Sons.
- Cayeux, L. (1934). The phosphate nodules of Agulhas Bank. S. African Mus., Ann., vol. 31, pp.105-136.
- Chaudron, G. & Wallaeys, R. (1949). Synthese des apatites pare reaction dans l'etat solide. Bull. Soc. Chim. France, pp.D132-D134.
- Chirvinsky, V. N. (1919). Materials for the knowledge of the natural productive forces of Russia. No. 30, The phosphorites of the Ukraine. Petrograd, USSR, 52 pp. (in Min. Abs., 2-54).
- Cornwall, H. R. & Rose, H. J. Jr. (1957). Minor elements in Keweenavan lavas, Michigan. Geochim. et Cosmochim. Acta, vol. 12, pp.209-224.
- Correns, C. W. (1956). The geochemistry of the halogens. Physics & Chemistry of the Earth. Vol. 1. New York: McGraw Hill Inc.
- Cruft, E. F. & Shaw, D. M. (1962). A diamond drill for coring mineral samples in the laboratory. In press, Canadian Mineral-ogist.
- Currie, J. B. (1951). Mica and apatite deposits in S.E. Ontario. Econ. Geol., vol. 46, pp.765-778.

Dadson, A. S. (1933). A study of some Canadian apatites. Univ. Toronto Studies, Geol. Ser., No. 35, pp.51-59.

Dallemagne, M. J., Brasseur, H. & Melon, J. (1949). Le constitution de la substance mineral de l'os et la synthese des apatites. Bull. Soc. Chim. France, pp.D138-D145.

- Daly, J. W. (1935). Paragenesis of the mineral assemblage at Crestmore, Riverside County, California. Am. Min., vol. 20, pp.638-659.
- Davies, K. A. (1947). The phosphate deposits of the Eastern Province, Uganda. Econ. Geol., vol. 42, pp.137-146.
 - . (1956). Geology of part of S.E. Uganda. Geol. Surv. Uganda, Hem. 8, 76 pp.

Dawson, J. W. (1876). Note on the phosphate of the Laurentian and Cambrian rocks in Canada. Q.J.G.S., London, vol. 32, pp.285-291.

Deans, T. (1938). Francolite from the Coal Measures. Min. Mag., vol. 25, pp.135-139.

Delecourt, J. (1955). Application de la notation equivalentaire a l'etude des roches phosphateos.

Dietz, R. S., Emery, K. O. & Shepard, F. P. (1942). Phosphorite deposits on the sea floor off Southern California. Geol. Soc. Am. Bull., vol. 53, pp.615-847.

Dihn, P. & Klement R. (1942). Isomorphe Apatitarten. Zeits. Elektrochem. angeu. physik. Chem., vol. 48, pp.331-333 (in Min. Abs., 9-13).

Dittler, E. (1932). Uber chemische Untersuchungen an Mineralien von den Totenkopfer im Stubachtale. Min. Petr. Mitt. (Tschermak), vol. 43, pp.71-74.

Dixon, W. J. & Massey, F. J. (1957). Introduction to Statistical Analysis. New York: McGraw-Hill Inc.

Du Toit, A. L. (1931). The genesis of the pyroxene-apatite rocks of Palabora, eastern Transvaal. Trans. Geol. Soc. S. Africa, vol. 34, pp.107-127.

Eakle, A. S. & Rogers, A. F. (1914). Wilkieite, a new mineral of the apatite group, and okenite, its alteration product, from S. California. Am. Jour. Sci. Ser. 4, vol. 37, pp.262-267.

- Eckermann, H. von. (1922). The rocks and contact minerals of the Mansjö mountain. Geol. För. Förh. Stockholm, vol. 44, pp.203-410.
 - . (1952). The distribution of barium and strontium in the rocks and minerals of the syenitic and alkaline rocks of Alno Island. Arkiv for min. och. geol., Edl. 13, pp.367-375.
- Eisenberger, S., Lehrman, A. & Turner, W. D. (1940). The basic calcium phosphates and related systems. Some theoretical and practical aspects. Chem. Review, vol. 26, no.2, pp.257-296.
- Eitel, W. (1958). Structural conversions in crystalline systems. Geol. Soc. Am., Special Paper 66, 183 pp.
- Forsman, A. E. (1924). Sur la presence des terres rare dans les apatites des gisements divers. C.R. Acad. Sci. Russ., pp.42-45 (in Min. Abs., 2-409).
 - . (1926a). Minerals of the Kola Peninsula. Am. Min., vol. 11, pp.289-299.
- . (1926b). Die mineralien der Chibina und Lujaur -Tundren auf der Halbinsen Kola. Neuss Jahrbuch Min., Abt. A, vol. 55, pp.36-46.
- . (1929). The apatite-nepheline problem of the Khibinsky tundra. Materials for chemicalising the national economy. Leningrad, USSR, No. 5 (in Min. Abs., 6-232).
- Fischer, R. B. & Ring, C. E. (1957). Quantitative infra-red analysis of apatite mixtures. Anal. Chem., vol. 29, pp.431-434.
- Fisher, D. J. (1958). Pegmatite phosphates and their problems. Am; Min., vol. 43, pp.181-207.
- Fleet, W. F. & Smithson, F. (1928). On the occurrence of dark apatite in some British rocks. Geol. Mag., vol. 65, pp.6-8.
- Foshag, W. F. (1929). Mineralogy and geology of Carro Mercado, Durango, Mexico. Proc. U.S. Nat. Mus., vol. 74, art. 23, 27 pp.
- Fouretier, G. (1937). La precipitation du phosphate tricalcique et l'hydroxyapatite. C.R. Acad. Sci. Paris, vol. 205, pp.413-415.

Franck, H. H., Bredig, M. A. & Frank, R. (1936). Untersuchungen uber Kalk-Alkali Phosphate. I. Ein Eeitrag zur Kenntnis des Rhenaniaphosphates. Zeits. Anorg. Chem., vol. 230, pp.1-27.

. (1938), Untersuchungen über Kalk-Alkali Phosphate. II. Über Calcium-Kalium-Phosphate. Zeits. Anorg. Chem., vol. 237, pp.49-78. Freundlich, H. (1922). Colloid and capillary chemistry. New York: E. P. Dutton and Co. Frondel, C. (1943). Mineralogy of the calcium phosphates in insular phosphate rock. Am. Min., vol. 28, pp.215-232. and Prien, E. L. (1942). Carbonate apatite and hydroxylapatite in urinary calculi. Science, vol. 95, p.431. Gavrilova, L. K. & Turanskaya, R. V. (1958). Distribution of rare-earths in rock-forming and accessory minerals of certain granites. Translation in Geochemistry, No. 2, pp.163 170.

Geiger, Th. (1950). Kennzeichnung einer Reihe technisch verwendeter Rohphosphate und deren Verhalten bei thermischer Behandlung. Schweiz. Min. Petr. Mitt., vol. 30, pp.20. 218.

Geijer, P. (1931). 'The iron ores of the Kiruna type. Sveriges Geol. Undersökning, Ser. C, No. 512, Arsbok 24, No. 4, Stockholm.

Gerasimovsky, V. I. (1937). Erikite from the Lovozersky tundras. Trans. Lomonossov Inst. Acad. Sci. USSR, Ser. Min. No. 10, pp.29-36 (in Min. Abs., 8-222).

Gevers, T. W. & Frommurze, H. F. (1930). The tin bearing pegmatites of the Erongo area, S. W. Africa. Trans. Geol. Scc. S, Africa, vol. 32, pp.111-149.

Gileva, Z. M. & Melentiev, B. N. (1939). Arsenic in the apatites of the Khibiny turdras. C.R. Acad. Sci. USSR, vol. 25, pp.118-119 (in Min. Abs., 6-141).

Goldschmidt, V. M. (1954). Geochemistry. Oxford: Clarendon Press.

and Thomassen, L. (1924). Geochemische Verteilungesetze der Elemente. III. Röntgenspektrographische untersuchungen über die Verteilung der seltenen Erdmetalle in Mineralien. Skr. Vidensk. Selk. Christ., vol. 5, pp.1-50.

Groves, A. W. & Mourant, A. E. (1929). Inclusions in the apatite of some igneous rocks. Min. Mag., vol. 22, pp.92-99.

- Gruner, J. W. & McConnell, D. (1937). The problem of the carbonate apatites. The structure of francolite. Zeits. Krist., vol. 97, pp.208-215.
- Gutkova, N. N. (1925). Apatites of Khibinsky tundra. Bull. Acad. Sci. Russ., Ser. 6, vol. 19, pp.123-132 (in Min. Abs., 3-102).
- Hägele, G. & Machatschki, F. (1939). Britholith ein Cererdensilikatapatit. Naturnissenschaften, vol. 27, pp.132-133 (in Min. Abs., 7-395).
- Harada, Z. (1938). Beiträge zur Kenntnis der optischen und chemischen Eigenschaften des Apatits von Kurokura, Kanagawa Prefecture. Jour. Fac. Sci. Hokkaido Univ. Sappero, Ser. 4, pp.11-16 (in Min. Abs., 7-351).
- Harrison, G. R. (1939). M.I.T. Wavelength Tables. New York: Wiley & Sons Inc.
- Hata, S. (1938). Abukumalite, a new yttrium mineral. Sci. Papers, Inst. Phys. Chem. Research, Tokyo, vol. 34, pp.1018-1023 (in Min. Abs., 7-225).
- Hayashi, S. (1960). Analysis of the crystal structure of fluorapatite by nuclear magnetic resonance. Jour. Chem. Soc. Japan, vol. 81, pp.540-542.
- Hendricks, S. B., Hill, W. L., Jacob, K. D. & Jefferson, M. E. (1931). Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and X-ray diffraction examinations. Ind. Eng. Chem., vol. 23, pp.1413-1418.
- , Jefferson, M. E. & Mosley, V. M. (1932). The crystal structure of some natural and synthetic apatite-like substances. Zeits. Krist., vol. 81, pp.352-369.
- Hewitt, D. F. (1954). Geology of Monteagle & Carlow Twps. Ont. Dept. Mircs, Ann. Rept., vol. 63, pt.6.
- . (1957). Geology of Cardiff and Faraday Twps. Ont. Dept. Mines, Ann. Rept., vol. 66, pt.3.
- and James, W. (1955). Geology of Dungannon and Mayo Twps. Ont. Dept. Mines, Ann. Rept., vol. 64, pt.8.
- Hey, M. (1955). Chemical Index of Minerals. Brit. Museum Nat. Hist., London.

Hodder, R. W. (1958). Alkaline rocks and niobium deposits near Memegos, Ontario. Geol. Surv. Canada, Paper 57-8.

Hoffmann, J. (1938). Uber Ionen- und Atomfärbungen Kunstlich hergesteller und natürlicher Apatite. Chem. Erde, vol. 11, pp.552-575.

- Hogarth, D. D. (1957). The apatite-bearing veins of Misikkatch Lake, Saskatchewan. Can. Min., vol. 6, pp.140-150.
- Howie, R. A. (1955). The geochemistry of the charnockite series of Madras, India. Trans. Roy. Soc. Edinburgh, vol. 62, pt. 3, pp.725-763.
- Hutton, C. O. & Seelye, F. T. (1942). Francolite, a carbonate apatite from Milburn, Otago. Trans. Roy. Soc. N.Z., vol. 72, pp.191-198 (in Min. Abs., 9-34).
- Iwase, E. (1935). Uber das fluorescenzspektrum des Apatites im Ultravioletten Licht. Sci. Papers, Inst. Phys. Chem. Res. Tokyo, vol. 27, No. 567, pp.1-9 (in Min. Abs., 6-279).
- Janisch, E. P. (1927). The occurrence of phosphates in the Zoutspansberg district of the Northern Transvaal. Trans. Geol. Soc. S. Africa, vol. 29, pp.109-125.
- Jesus, A. M. de (1933). Pegmatites mangano-litiniferas daregiao de Mangualde. Communicacaoes Serv. Geol. Portugal, vol. 19, pp.65-210 (in Min. Abs., 6-440).
- Johnson, P. D. (1961a). Some optical properties of powder and crystal halophosphate phosphors. Jour. Electrochem. Soc., vol. 108, No. 2, 159-162.
 - _. (1961b). Dichroic color centres in calcium fluorophosphate. Jour. App. Physics, vol. 32, No. 1, 127-128.
- Jong, W. F. do (1926). On the mineral component of bones. Proc. Sect. Sci. K. Akad. Wetensch, Amsterdam, vol. 29, pp.870-872.
- Kind, A. (1939). Der magmatische Apatit, seine chemische Zusammensetzung und seine physikalischen Eigenschaften. Chem. Erde, vol. 12, pp.50-Sl.
- Klement, R. (1938). Basische Phosphate zweiwertiger Metalle. I. Blei-hydroxylapatit. Zeits. Anorg. Chem., vol. 237, pp.161-171.

Klement, R. (1939a). Basische Phosphate zweiwertiger Metall. IV. Strontium-Hydroxylapetit. Zeits. Anorg. Chem., vol. 242, pp.215-221.

- _. (1939b). Isormorpher Ersatz des Phosphors in Apatiten durch Silicium und Schwefel. Naturviss., vol. 27, pp.57-58.
- and Dihn, P. (1938a). Basische Phosphate zweiwertiger Motalle. II. Bariun-hydroxylapatit. Zeits. Anorg. Chem., vol. 240, pp.31-39.

. (1938b). Uber Kalk-Alkaliphosphate Benerkungen zu den gleich namigen Arbeiten von H. H. Franck und Mitarbeiten. Zeits. Anorg. Chem., vol. 240, pp.40-49.

- and Zureda, F. (1940). Basische Phosphate zweiwertiger Metalle. V. Phosphate und Hydroxylapatit des Cadmiuns. Zeits. Anorg. Chem., vol. 245, pp.229-235.
- Kohler, A. & Haberlandt, H. (1934). Lumineszenzanalyse von Apatit, Pyromorphite und einigen anderen Phosphaten. Chemie der Erde, vol. 9, pp.88-89.
- Kratochvil, F. (1952). On some minerals from the granite pegmatites between Pobezovice and Domazeice. Sbornik Ustredniho Ustavu Geologiceho, vol. 19, pp.321-328 (in Min. Abs., 12-364).
- Kraus, E. B. & Lawson, C. B. (1947). Gens and Gen Minerals. New York: McGraw-Hill.
- Krumbein, W. C. & Garrels, R. M. (1952). Origin and classification of chemical sediments in terms of pH and oxidationreduction potential. Jour. Geology, vol. 60, pp.1-21.
- Lacroix, A. (1923). La composition de la meteorite tombes a Saint Saveur (Haute Garonne) en 1914. C.R. Acad. Sci. Paris, vol. 177, pp.561-565.
 - . (1933). Contribution a la connaissance de la composition chimique et mineralogique des roches eruptives de l'Indochine. Bull. Service Geol. Indochine, vol. 20, fasc. 3, 208 pp. (in Hin. Abs., 6-21).
- Laitakari, A. (1921). Über die Petrographie und Mineralogie der Kalksteinlagorstätten von Paracinem (Pargas). Bull. Comm. Geol. Finlande, No. 54, 114 pp.

Landes, K. K. (1925). The paragenesis of the granite pegmatites of central Maine. Am. Min., vol. 10, pp.355-411. . (1929). Sequence of mineralization in the Keystone. S. Dakota, pegmatites. Am. Min., vol. 13, pp.519-530 and 537-558. (1938). Origin of the Quebec phlogopite-apatite deposits. Am. Min., vol. 23, pp.359-390. Lapkowsky, W. W. (1959). Minor elements in some carbonates. Unpublished M.Sc. thesis, McMaster University. Larsen, E. S. (1942a). Alkalic rocks of Iron Hill, Gunnison County, Colorado. U.S.G.S. Prof. Paper 197-A, 64 pp. . (1942b). The mineralogy and perrogenesis of the variscite nodules from near Fairfield, Utah. Mn. Min., vol. 27, pp.281-300. , Fletcher, M. H. & Cisney, E. A. (1952). Strontian apatite. Am. Min., vol. 37, pp.656-658. & Pardee, J. T. (1929). The stock of alkaline rocks near Libby, Montana. Jour. Geol., vol. 37, pp.97-112. & Shannon, E. V. (1930). Two phosphates from Dehrn; Dehrnite and Crandallite. Am. Min., vol. 15, pp.303. 337. Laubmann, H. (1923). Die phosphatmineralien und Ederlerden des Amberg Auerbacher Erzkorpers. Ein Beitrag zur Kenntnis bayerischer Minerallagerstätten. Geognostiche Jahreshefte, Geol. Landesunters Munchen, vol. 35, pp.193-204 (in Min. Abs., 2-522). & Steinmetz, H. (1920). Phosphatführende Pegnatite des Oberpfalzer und Dayerischen Waldes. Zeits. Krist., vol. 56, pp.90-94. Leonova, L. L. & Tauson, L. V. (1958). The distribution of uranium in the minerals of Caledonian granitoids in the Susamyr batholith (Central Tien Shan). Transl. in Geochemistry, No. 7, pp.815-826. Lindberg, M. L. & Pecora, W. T. (1955). Tavorite and barbosalite, two new phosphate minerals from Minas Gerais, Brazil. Am. Min., vol. 40, pp.952-965. Lovell, L. C. (1958). Dislocation etch pits in apatite. Acta Metallurgia. vol. 6, pp.775-778.

- Lovett, F. D. et al (1960). Authigenic apatite and clay minerals from Roger Mills County, Oklahoma. Oklahoma Geology Notes, vol. 20, No. 8, pp.190-194. (in Geosc. Abs., 3-1270).
- Lowell, W. R. (1955). Igneous intrusions and metamorphism in some phosphatic rock of S. W. Montana. Econ. Geol., vol. 50, pp.715-737.
- Machatschki, F. (1939). Sind Abutumalit und Britholith Glieder der Apatitreihe? Zentr. Min., Abt.A, pp.165-167.
- Mansfield, G. R. (1940). The role of fluorine in phosphate deposition. Am. Jour. Sci., vol. 238, pp.863-879.
- Mason, B. (1941a). Minerals of the Varuträsk pegmatite. XXIII. Some iron-manganese phosphete minerals and their alteration products, with special reference to material from Varuträsk. Geol. För. Förh. Stockholm, vol. 63, pp.117-175.
 - . (1941b). Minerals of the Varuträsk pegmatite. XXVI. Manganhydroxy-apatite. Geol. För. Förh. Stockholm, vol. 63, pp.279-284.
 - . (1942). Mangualdite is manganvoelckerite. Geol. For. Forh Stockholm, vol. 63, pp.383-386.
- McConnell, D. (1937). The substitution of SO, and SiO, groups for PO, groups in the apatite structure, Ellestadite, the end member. Am. Min., vol. 22, pp.977-986.
 - ___. (1938a). A structural investigation of the isomorphism of the apatite group. Am. Min., vol. 23, pp.1-19.

 - _____. (1939). Some isomorphic substitutions in apatite. C.R. Acad. Sci. USSR, vol. 25, pp.46-50 (in Min. Abs., 8-141).
 - . (1950). The petrography of the rock phosphates. Jour. Geol., vol. 58, pp.16-23.
 - - _. (1955). The problem of the carbonate apatites. Jour. Am. Chem. Soc., vol. 77, p.2344.

McConnell, D. (1958a). The apatite-like mineral of bones and sediments. Econ. Geol., vol. 53, pp.110-111. ___. (1958b). Letter to editor. Am. Scientist, vol. 46, p.292A. _ and Gruner, J. W. (1940). The problem of the carbonate apatites. III. Carbonate apatite from Magnet Cove. Arkansas. Am. Min., vol. 25, pp.157-167. McKeown, F. A. & Klemic, H. (1956). Rare-earth bearing apatite at Mineville, Essex Co., N.Y. Bull. U.S. Geol. Surv., No. 1046-B, pp.9-23. McLintock, W. F. P. & Ennos, F. R. (1922). On the structure and composition of the Strathmore meteorite. Min. Mag., vol. 19, pp.323-329. Mehmel, M. (1930). Uber die struktur des Apatits. I. Zeits. Krist., vol. 75, pp.323-331. . (1931). Beziehungen zwischen Kristallstruktur und chemischer Formel des Apatits. Zeits. Physikal Chem., Abt.A, vol. 15, pp.223-241. Melon, J. & Toussaint, J. (1957). Evansite et apatite du Kivu. Ann. Soc Geol. Eelgique, vol. 80E, pp.496-501. Mennell, F. P. (1946). Ring structures with carbonate cores from S. Rhodesia. Geol. Mag., vol. 83, pp.137-140. Michaels, A. S. & Colville, A. R. (1960). The effect of surface activ agents on crystal growth rate and crystal habit. Jour. Phys. Chem., vol. 64, pp.13-19. Michel, L. (1893). Bull. Soc. Franc. Min., vol. 16 in Min. Mag., 11-328. Mieleitner, K. (1921). Uber einige Mineralien von Fuchsbau im Fichtelgebirge. Zeits. Krist., vol. 56, pp.90-94. Minguzzi, C. (1941). Apatiti sintetiche con cromo trivalente ed esavalente. Periodico Min. Roma, vol. 12, pp.343-380. (in Min. Abs., 9-283). Mitchell, L., Faust, G. T., Hendricks, S. B. & Reynolds, D. S. (1943). The mineralogy and genesis of hydroxylapatite. Am. Min., vol. 28, pp.356-371. Mitchell, R. S. & McGavock, E. H. (1960). Apatite from the Morefield pegmatite, Amelia Co., Virginia. Rocks & Minerals, vol. 35, No. 11/12, pp.553-555. (in Geosc. Abs., 3-901).

Montel, G. & Chaudron, G. (1951). Synthese de la fluorapatite calcioue par voir seche a partir de differents phosphates de calcium. C.R. Acad. Sci. Paris, vol. 233, pp.318-319. Mullbauer, F. (1925). Die Phosphatpegmatite von Hagendorf i Bayern (Neue beobachtungen). Zeits. Krist., vol. 61, pp.318-336. Mullin, J. W. (1961). Crystallisation. London: Butterworth & Co. Ltd. Murdoch, J. (1955). Phosphate minerals of the Borborema pegmatite. I. Patrimonia. Am. Min., vol. 40, pp.50-63. . (1958). Phosphate minerals of the Borborema pegnatites. II. Boqueirao. Am. Min., vol. 43, pp.1148-1156. Naray-Szabo, St. (1930). The structure of apatite (CaF)Ca, (PO,)3, Zeits. Krist., vol. 75, pp.387-398. Nockolds, S. R. & Mitchell, R. L. (1948). The geochemistry of some Caledonian rocks: A study in the relationship between the major and trace elements of igneous rocks and their minerals. Trans. Roy. Soc. Edinburgh, vol. 61, pt. II, pp.533-575. Nowacek, R. (1928). Minerals of the pegnatites and surrounding rocks from Budislaw, in eastern Bohemia. Casopis Narodniho Musea, Prague, vol. 102, pp.91-95. Omori, K. & Hasegawa, S. (1953). Ittrialite and abukumalite from a pegnatite of Suisho-yama, Iizaka village, Fukushima prefecture. Jour. Japanese Assoc. Min. Petr. Econ. Geol., vol. 37, pp.21-29 (in Min. Abs., 12-443). O'Neil, R. L. & Suhr, N. H. (1960). Determination of trace elements in lignite ashes. Applied Spectroscopy, vol. 14, No. 2, pp.45-60. Otto, H. (1935). Die Holle des Mangans in den Mineralien. Min. Petr. Mitt. (Tschernak), vol. 47, pp.89-140. Palache, C., Berman, H. & Frondel, C. (1951). Dana's System of Mineralogy. 7th ed. Vol. II. New York: Wiley & Sons. Pecora, W. T. (1956). Carbonatites: a review. Bull. Geol. Soc. Mm. vol. 67, pp.1537-1556. Pehrman, G. (1939). Uber Phosphate aus dem Pegnatit von Lemnas (Kimito, S. W. Finnland). Acta Acad. Aboensis, Math. et Physica. vol. 12, No. 6, 24 pp. (in Min. Abs., 7-417).

Perdok, W. G. (1952). Die aufnahme von Fluorionen durch Zahnschmetz. Schweiz. Mschr. Zahnheilk, vol. 62, pp.249-269 (in Structure Reports, vol. 16, 1952, pp.331-332).

Perloff, A., Posner, A. S. & Diorio, A. F. (1958). Refinement of the hydroxyapatite structure. Acta Cryst., vol. 11, pp.308-309.

- Pettijohn, F. J. (1941). Persistence of heavy minerals and geological age. Jour. Geol., vol. 49, pp.610-625.
- Pierruccini, R. (1947). Sulla possibilita di introdurre alluminio, ferro, plombo o molibdeno nel reticolo delle apatiti. Atti. Soc. Toscana Sci. Nat., vol. 54, 14 pp. (in Min. Abs., 10-261).

Prior, G. T. & Smith, G. F. H. (1910). Note in Mature, vol. 83, p.513.

- Quensel, P. (1937). Minerals of the Varuträsk pegmatite. Geol. For. Forh. Stockholm, vol. 59, pp.257-261.
- Rankama, K. & Sahama, Th. G. (1950). Geochemistry. Chicago: Univ. of Chicago Press.
- Redfield, A. C. (1958). The biological control of chemical factors in the environment. Am. Scientist, vol. 46, pp.204-221.
- Reuning, E. (1923). Pegnatite und Pegnatitmineralien in Sudwestafrike. Zeits. Krist., vol. 58, pp.448-459.
- Rogers, A. F. (1912). Dahllite (podolite) from Tonopah, Nevada; voelckerite, a new basic calcium phosphate; remarks on the chemical composition of apatite and phosphate rock. Am. Jour. Sci., vol. 33, pp.475-482.
- Ronov, A. B. & Korzina, G. A. (1960). Phosphorus in sedimentary rocks. Translation in Geochemistry, No. 8, pp.805-829.
- Rose, E. R. (1960). Rare-earths in the Grenville. Geol. Surv. Canada, Paper 59-10, 41 pp.
- Rowe, R. E. (1958). Niobium (columbium) deposits of Canada. Geol. Surv. Canada, Econ. Geol. Series 18, 108 pp.
- Sandell, E. B., Hey, M. A. & McConnell, D. (1939). The composition of francolite. Min. Mag., vol. 25, pp.395-401.
- Satterley, J. (1943). Mineral occurrences in the Haliburton area. Ont. Dept. Mines, Ann. Rept., vol. 52, pt.2.

Schairer, J. F. (1926). Lithiophilite and other rare phosphates from Portland, Conn. Am. Min., vol. 11, pp.101-104.

Schleede, A., Schmidt, W. & Kindt, H. (1932). Zur Kenntnis der Calcium phosphate und Apatite. Zeits. Elektrochem., vol. 38, pp.633-641.

Shand, S. J. (1931). The granite-symplet complex of Palabora, eastern Transvaal, and the associated apatite deposits. Trans. Geol. Soc. S. Africa, vol. 34, pp.81-105.

Shannon, E. V. & Larsen, E. S. (1925). Merrillite and chlorapatite from stony meteorites. Am. Jour. Sci., Ser. 5, vol. 9, pp.250-260.

Shaw, D. M. (1958). Radioactive mineral occurrences of the province of Quebec. Quebec Dept. Mines, Geol. Rept. 80.

. (1960a). Spectrochemical analysis of silicates using the Stallwood jet. Can. Min., vol. 6, pt. 4, pp.467-482.

_____. (1960b). The geochemistry of scapolite. Pts. I & II. Jour. Petrology, vol. I, pp.218-285.

. (1961). Element distribution laws in geochemistry. Geochim. et Cosmochim. Acta, vol. 23, pp.116-134.

Silverman, S., Fuyat, R. & Weiser, J. (1952). Quantitative determination of calcite associated with carbonate bearing apatites. Am. Min., vol. 37, pp.211-222.

Simpson, E. S. (1929). Contributions to the mineralogy of western Australia. Series IV. Jour. Roy. Soc. W. Aust., vol. 15, pp.99-113 (in Min. Abs., 4-315).

Smith, G. F. H. (1952). Gemstones. London: Methuen & Co.

Smirnov, S. (1925). Preliminary report. Bull. Comm., Geol. Leningrad, vol. 43, pp.549-563 (in Min. Abs., 3-194).

Spangenberg, K. (1920). Uber die Besinflussung der Kristalltracht des NaCl durch complexionen bildende Lösungsgenossen. Zeits. Krist., vol. 59, pp.375-382.

Spence, H. S. (1920). Phosphate in Canada. Canada, Minss Branch, Pub. No. 396, 156 pp.

Starrabba, A. S. (1942). Sopra alcuni minerali pneumotolitici di Acicatena (Etna). Periodica Min. Roma, vol. 13, pp.157-174 (in Min. Abs., 9-156). Stewart, G. W. (1939). Vesuvianite and fluorescent apatite from Center Strafford, New Hampshire. Am. Min., vol. 24, pp.274-275.

Sumin, N. G. (1957). On certain features of apatite from skarn iron-ore deposits. Trans. Min. Mus. Acad. Sci. USSR, vol. 8, pp.116-121.

Svyatlovsky, A. E. & Dieterikhs, F. M. (1939). On apatitic deposits of the Khibiny tundras. Bull. Acad. Sci. USSR, Ser. Geol. No. 4, pp.80-93 (in Min. Abs., 8-29).

- Switzer, G. (1938). The paragenesis of the Center Strafford, N. H. pegnatite. Am. Min., vol. 23, pp.811-820.
- Tatarinov, P. M. (1937). Micas of the USSR. Centr. Geol. Prosp. Inst. Leningrad & Moscow. (In Min. Abs., 9-31).

Thewlis, J. (1940). The structure of teeth as shown by X-ray examination. Med. Res. Council, London, No. 238, pp.82 (in Structure Repts., 1941, vol. 8, p.207).

, Glock, G. E. & Murray, M. M. (1939). Chemical and X-ray analysis of dental, mineral and synthetic apatites. Trans. Faraday Soc., vol. 35, pp.358-363.

Trömel, G. (1932). Untersuchungen über die Bildung eines halogenfreien Apatits aus basischen Calciumphosphaten. Zeits. Physikal Chom. Abt.A, vol. 158, pp.422-432.

- Ulrich, F. (1933). Luminescence of bones and related inorganic substances in ultraviolet light. Inst. Anthrop. Univ. Charles, Prague, vol. 11, pp.227-231 (in Min.Abs., 7-529).
- Van Hook, A. (1961). Crystallisation, Theory and Practice. New York: Reinhold Publishing Co.

Vasileva, Z. V. (1958a). Sulphur-bearing apatites. Transl. in Geochemistry, vol. 4, pp.464-470.

> . (1958b). On the role of Mn in apatites. Mem. All-Union Min. Soc., vol. 87, pp.455-468 (in Min. Abs., 14-286).

Villiers, J. E. (1942). The carbonate-apatites: francolite from the Richtersveld, South Africa. Am. Jour. Sci., vol. 240, pp.443-447.

Vlodavetz, V. I. (1930). Nepheline-apatite deposits of the Khibinsky tundra. Trans. Inst. Explor. of the North, No. 46 (in Min. Abs., 6-308).

i

- Volborth, A. von (1952). Quelques phosphates rare des pegmatites de lithium d'Erajarvi (Finlande Centrale). C.R. Congres geol. intern. Alger., p.175.
- Volkova, M. I. & Melentiev, B. E. (1939). Chemical composition of the Khibiny apatites. C.R. Acad. Sci. USSR, vol. 25, pp.120-122 (in Min. Abs., 8-52).
- Wager, L. R. & Mitchell, R. L. (1951). The distribution of trace elements during strong fractionation of basic magma - a further study of the Skaergaard intrusion, East Greenland. Geochim. et Cosmochim. Acta, vol. 1, pp.129-208.
- Walker, T. L. & Parsons, A. L. (1924). Pegmatite minerals from New Ross, Nova Scotia. Univ. Toronto Studies, Geol. Ser. No. 17, pp.46-50.

. (1925). The characteristics of primary calcite. Univ. Toronto Studies, Geol. Ser., No. 20, pp.14-17.

. (1926). Apatite, lepidomelane, and associated minerals from Faraday Twp., Hastings Co., Ontario. Univ. Toronto Studies, Geol. Ser. No. 22, pp.20-25.

- Wallaeys, R. & Chaudron, G. (1950). Sur la preparation de certaines apatites mixtes. C.R. Acad. Sci. Paris, vol. 231, pp.355-357.
- Weber, I. N. (1961). The elimination of cyanogen molecular spectra by instantaneous d.c. carbon-arc excitation of geological materials in oxygen. Spectrochim. Acta, vol. 17, pp.669-671.
- Wherry, E. T. (1917). Neodymium as the cause of the red-violet color in certain minerals. Jour. Nash. Acad. Sci., vol. 17, pp.143-146.
- Wick, F. G. (1937). An experimental study of the triboluminescence of certain natural crystals and synthetically prepared materials. Jour. Opt. Soc. Am., vol. 27, pp.275-285.
- Wilkinson, J. F. G. (1959). The geochemistry of a differentiated teschenite sill, near Gunnedah, N.S.W. Geochim. et Cosmochim. Acta, vol. 16, pp.123-150.
- Winchell, A. N. & Winchell, H. (1951). Elements of optical mineralogy. Pt. II. New York: Wiley & Sons.

Winther, C. (1900). Medd. om Grønland, vol. 24 in Min. Mag., 12-380.

Zambonini, F. (1915). Sur les solutions solides des composes du calcium, du strontium, du baryium et du plomb avec ceux des terres rares. Bull. Soc. Franc. Min., vol. 38, pp.206-264.