STUDIES ON STATISTICAL INFERENCE FROM X-RAY AND OTHER SPECTROSCOPIC DATA

By

PHLISDAMON NONGKYNRIH

DEPARTMENT OF PHYSICS

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DOCTOR OF PHILOSOPHY

To

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SHILLONG - 793001
MEGHALAYA, INDIA

NOVEMBER, 1985

"The fear of the Lord is the instruction of wisdom ;
and before honour is humility"

(Proverb 15 : 33)

DEDICATED TO

MY PARENTS

Whose guidance had been the source of this goal.

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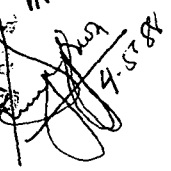

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CERTIFICATE

I certify that the dissertation entitled "STUDIES ON STATISTICAL INFERENCE FROM X-RAY AND OTHER SPECTROSCOPIC DATA" submitted by Miss Phlisdamon Nongkynrih in fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY is the outcome of a study undertaken by the candidate.

I certify that the sources from which ideas have been borrowed have been duly referred to and acknowledged.

The material in this dissertation has not been presented for award of a degree in any University before. This dissertation may be placed before the examiners for evaluation and necessary formalities.

The work for this thesis is a continuation of the candidate's M.Phil. dissertation entitled "Nuclear Techniques in Trace Element Analysis". The identification of Titanium and the observations on the Crystal Structure changes are worthy of consideration by the examiners for the award of the degree of Doctor of Philosophy.

Y.S.T. RAO
Supervisor
Physics Department
North - Eastern Hill University
SHILLONG.

November 15, 1985.

A C K N O W L E D G E M E N T S

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P. Nongkynrih.

(P.Nongkynrih)

7th. Dec. '85.

CONTENTS

CHAPTER- 0

INTRODUCTION

Physics is a branch of Science which is involved mostly with experiments. One performs the experiments, thoroughly takes the measurement and checks its reproducibility. The data obtained are analysed and consequently the theory often follows to explain and give a proper understanding of the experimental results. In any experimental study, the understanding of the system we study depends upon the precision and reliability of the measurements. In most cases, a systematic logical theory is proposed to give a picture of the phenomena which have not yet found by experiments. This systematic understanding of the physical process becomes a law. If the errors have been taken care of and also if all sorts of precautions are adopted yet if found that the experimental findings differ from the prediction of the law by many times the estimated error, then the law needs modification.

Physics deals mostly with quantitative measurements of physical properties of objects and precise relation between these properties. Hence, Mathematics plays a very important role in Physics.

As our resources are limited and that there could be some factors influencing our measurements which have not been taken into account, the theory of Errors, Analysis of Variance, Design of Experiments, Estimations or in general the science called Statistics is to be used. "By Statistics, we mean aggregates of facts affected to a marked extend by multiplicity of causes numerically expressed, enumerated according to resonable standards of accuracy, collected in a systematic manner for predetermined purpose and placed in relation to each other" as defined by Horace Secrist.

The philosophy of Statistical techniques is not well appreciated in our Sister Disciplines and more so in inter-disciplinary research. In this thesis, two problems of interest to our friends in sister disciplines- Geology and Chemistry are analysed to demonstrate what they have lost sight of and then the new results brought by the diverse physical (experimental) techniques will be discussed.

The first chapter deals with the X-Ray Fluorescence Technique (XRF) used for detecting and estimating the trace elements in samples. This technique is developed in the last few years and has become an important tool to the geologists, environmentalists, health scientists, etc.

The use of the XRF technique in analysing the trace elements in the coal fields of North-Eastern Region of India is described in the second chapter. The region has got a good reserve of coal. Coal was chosen as it is a repository of elements that are likely to be present in the neighbourhood. The analysis of coal can therefore serve as a precursor in identifying possible location of mineral wealth in the region. Further such analysis may have a bearing on geochronological studies.

The unusual finding of large quantity of Titanium in Bapung (Jaintia Hills District, Meghalaya) which all the previous workers using chemical technique have missed is an important contribution. Following our work, the Geological Survey of India has identified a rich source of Titanium in Sung Valley (Jaintia Hills District, Meghalaya) close to the fields where our study was carried out.

The third chapter deals with the studies involving the analysis of the X-Ray diffraction data of the substituted apatites. Apatites are important constituents of human bone and teeth. Their decay is due to isomorphic substitution of the constituents which affect the changes in crystal structure. The lattice of the apatites is in general hexagonal in structure. According to Vegard's Law the lattice

constants 'a' and 'c' of hexagonal lattice are expected to change linearly with the degree of substitution. So far, it appears that all experimental evidence support this law, we show that the law is violated and that two distinct and different linear behaviors in the ranges 0 - 50% and 50 - 100% degree of substitution are obtained.

The fourth chapter deals with the use of Infra Red absorption spectroscopy technique for the substituted apatites. The results confirm our conclusion that something happens around 50% degree of substitution.

The fifth and last chapter summarise the work described in the previous chapters. It also emphasizes the importance of using statistical and physical techniques in analysing results of important to sister disciplines.

CHAPTER - I

TRACE ELEMENT DISTRIBUTION IN COAL FIELDS OF NORTH-EASTERN INDIA

1.0 Introduction

The X-Ray fluorescence Technique (XRF) offers simultaneous quantitative analysis of several elements by a single scan (1.1). It has been extensively used and improved upon by several workers (1.2). It is rather an inexpensive technique and very simple to use.

1.1 X-Ray Fluorescence Technique (XRF). (Principle and Analysis)

The basic principle of the XRF is that when incoming photons from radio-isotopes or X-Ray tubes are allowed to fall on a specimen, photoelectrons are rejected creating vacancies in the inner shells of the atoms of the specimen. These vacancies are then filled by transitions of electrons from high energy orbitals leading to emission of a spectra of characteristic X-Ray. Measurement of the energies and intensities of such characteristic X-Rays is the basis of Energy Dispersive XRF technique.

The intensity I_j of the characteristic X-Ray of the j^{th} element of a given sample is related to the concentration M_j of the same element as (1.3).

$$I_j = I_o G K_j M_j A \qquad \text{------ (1.0)}$$

Where I_o = the incident photon flux on the sample

G = the geometrical factor

K_j = the relative ability to excite and detect the X-Ray line of interest.

and A = total absorption, which is due to absorption of exciting and fluorescent radiation in the sample matrix.

The matrix enhancement effects are neglected here as the sample are considered to be thin. The matrix enhancement effects occur when the fluorescent X-Rays of one element act as an exciting radiation for other elements which have absorption edges lower than the energy of the fluorescent radiation of the element. This effect is severe for thick specimens and is difficult to correct for without a prior knowledge of the specimen.

The total absorption 'A' is obtained by considering the absorption at a small element thickness in the specimen and then integrating over the entire specimen thickness. It thus follows that (1.3)

$$A = \frac{1 - e^{-(\mu_1 \operatorname{Cosec} \phi_1 + \mu_2 \operatorname{Cosec} \phi_2)m}}{(\mu_1 \operatorname{Cosec} \phi_1 + \mu_2 \operatorname{Cosec} \phi_2)m} \quad \text{----(1.1)}$$

Where ϕ_1 and ϕ_2 are the average angles of incident and fluorescent radiation with respect to the sample surface as shown in Fig : 1.1 and m is the mass of the specimen per unit area for the geometry chosen. μ_1 and μ_2 are the total absorption coefficients of the specimen for the exciting and fluorescent radiation respectively. The values of μ_1 and μ_2 are not easy to estimate for any unknown matrix. To determine μ_1 and μ_2 dilution technique has to be adopted. The method involves the dilution of the sample by mixing it with a large amount of a low Z material such as pure cellulose powder, borax etc. The diluted samples have low analytical sensitivity but the method has overriding advantages. The first advantage is that the mass absorption coefficients, μ_1 and μ_2 are the well known quantities as they are largely determined by the diluting agent (i.e cellulose etc). Secondly, the matrix enhancement effects of the diluted sample are negligence. Therefore, only relatively simple matrix

absorption corrections are required to be made according to Eqn : 1.1. In the case of thin, diluted samples, the compton scattered peak of the primary monoenergetic beam is also determined mainly by the cellulose matrix. The ratio of the fluorescent peak intensities to the intensity of the compton scattered incident beam is dependent only on the concentration of the respective element with respect to the cellulose. In this method, therefore, the system can be easily calibrated using a set of multielement standards prepared in the above mentioned manner.

The relative ability K_j is given by

$$K_j = \sigma_{k_j}\, \omega_{k,L}\left(1 - \frac{1}{J_{k,L}}\right) T f E \quad ----(1.2)$$

Where σ_{k_j} = Photoelectric cross section of the element j and of the atom in the K shell

$\omega_{k,L}$ = The fluorescent yield

$J_{k,L}$ = The jump ratio for the element j

T = Transmission of the fluorescent radiation in its path.

f = fractional intensity of the X-Ray line under analysis.

E = Detector efficiency.

The values of $\omega_{K,L}$, $J_{K,L}$, σ_{K_j} and f are known from the literature and with the known values of T, E for the detector, the factor K_j can be evaluated for given system. Now the only unknown factor is I_0G. Its value can be absolutely determined by taking one non-interfering element of known concentration which can either be added in the specimen or it can be taken as a separate specimen. The factor I_0G can then be computed from the intensity of characteristic X-Ray of known elements using Eqn : 1.0. This procedure is called one element standard method.

In some cases, the separation of the K_β line of one element with the K_α line of another has to be done. In other cases the L- X-Rays of the higher elements might overlap with the $K_{\alpha,\beta}$ rays of the lower elements. A knowledge of the intensity ratios of all the X-Ray components is required and applied to resolve them.

1.2 The Experimental Set Up

The analysis of the coal and ore samples collected from the different parts of North - Eastern Region of India, by the XRF technique was carried out at the Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay.

Figure 1.2 shows the Schematic experimental arrangement of the X-Ray-tube-excited X-Ray Fluorescence system used.

For quantitative analysis, a computer Code XRS was written. Most of the quantities given in Eqn : 1.0 are fixed. The K_j factors with respect to cellulose had been earlier fed into the programme. For coal samples, both cellulose and carbon were taken into account for the absorption coefficient while for mineral samples, the absorption coefficient is due to cellulose only, as the specimen is made up of 90% cellulose. The only variables which were to be fed were the Compton peak area (I_{comp}) and the peak areas of the elements (I_j).

X-Ray Tube Power Supply :- The High Voltage unit was made indigenously by the High Voltage section of the Variable Energy Cyclotron Centre, Calcutta. The High Voltage (H.V) Supply provides a continously adjustable source of well - regulated D.C Voltage from 0 to ± 50 Kv with a maximum current capacity of 1 m.A. The unit has 0.1% regulation, 0.1% ripple at maximum load and a stability of 0.1% for 8 hours after ½ hour warm-up time. The High voltage common is grounded through sampling resistors whose output is used to adjust the X-Ray tube current. The filament power supply is a voltage regulated D.C. supply with output

voltage varying from 0 to 5 volts. The tungsten filament is of 10 m.m diameter and has a length of about 2 cm. The error signal obtained by comparison of the output of the sampling resistance and the standard current setting reference voltage is fedback to the filament D.C supply to keep the tube current constant. A Wehlnet-cylinder type intermediate electrode is used in the X-Ray tube to focus the electron beam spot in the centre of the target anode to a size of the order of 4 to 5 m.m, so that the beam does not impinge on the stainless steel holder. The grid bias used on the cylin der is kept in the range 300 to 600 volt, without any feedback loop.

X-Ray tube :- The X-Ray tube with Molybdenum target was used for the analysis. A target voltage upto 35 Kv and a target current upto 200 μA were used. The maximum beam power of 10 watts was dissipated mostly by radiation from the anode structure. The high vacuum in the X-Ray tube does not deteriorate due to this heating. Using the voltage regulated filament and the feedback stabilisation from the target current, the tube output was found to be stable within 2% during the day, after an initial warm-up period of about half an hour. The filament voltage and filament current are of the order of 2 to 3 volts and 1 to 1.5 amperes for a tube output current of 200 μA. The intermediate electrode

potential was kept at 500 volts, which gave stable target current.

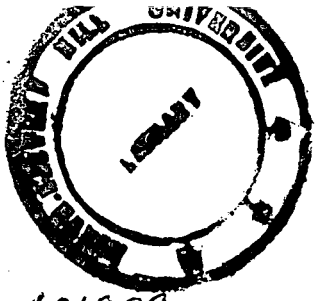
Si(Li) X-Ray Spectrometer :- The system included a cooled Si(Li) detector mounted in a vertical cryostat with a pulsed opto-feedback pre-amplifier. The Si(Li)detector employed had an area of 30 mm^2 and thickness 3 mm and this detector system gave an energy resolution of about 200 ev for 5.9 kev Mn K_α - X-Rays. This resolution is maintained upto a count rate of 20,000 cps, though the useful count rate was limited to only about 12,000 cps owing to large pile- up rejections at higher count rate. The shift in the peak position as a function of count rate was negligible. In the set up, the main amplifier (X-Ray pulse processor) had an option of inhibiting the main amplifier action to avoid overloading due to large amplitude pulses along with the pile up rejection. In the amplifier a Gaussian shaping network was used with a peak width of 15 μ Sec . The pulses from the amplifier were then fed to a 2048-channel analyser (Canberra Series 80).

1.3 XRF Calibration :- The relative factor K_j was not estimated exactly as defined in Eqn. 1.2 since the contribution of the continuum Bremstahlung radiation, in addition to the characteristic Mo- K_α -X-Rays in the X-Ray tube output, made the results less reliable. The relative factor K_j' for elements with Z in the

range 18-38 and 54-90, was determined experimentally. K_j' was determined at three target voltages-25, 30 and 35 Kv. The three different target voltages had to be operated as the analytical sensitivity was dependent on the operating conditions of the tube. Fig: 1.3 shows the experimental K_j factors (counts/ compton K_α counts/ppm) as a function of the atomic number at three different Mo-target voltages namely 25 Kv (∘ ∘ ∘), 30 Kv(• • •)and 35 Kv (× × ×). This was done using a number of thin multi-element standards with cellulose as base material. These multi-element standards were prepared by absorbing known concentrations of the elements in solutions on the cellulose powder and drying at approximately 80°C. The dried mixture was weighed and pulverised and a small amount of it was pressed into a thin pellet which was then weighed and analysed. The choice of elements in any one standard was made such that their fluorescent X-Rays were separate and the peak areas could be determined. The concentration of the elements taken was in the range of 500 to 5000 ppm, with respect to cellulose so that the absorption correction could be easily made with the use of only the cellulose mass absorption coefficients for exciting and fluorescent radiation.

In these calibration standards, the compton scattering of the excited radiation was essentially due to the cellulose matrix only. Therefore the ratio of the fluorescent peak to the intensity of Compton Scattering Mo K_{α} -X-Rays was only dependent on the concentration of the respective element in ppm units and on the desired relative excitation factors K_j. Using these multi-element standards, the experimental set up was calibrated for conversion of the ratios of fluorescent peak counts to the Compton peak counts of Mo K_{α} X-Rays, into the concentration of elements in ppm with respect to cellulose matrix. A smooth variation of these factors with Z was found. Values for the adjacent elements could therefore be obtained by interpolating this curve. The amount of the element in ppm was obtained by multiplying the ppm units by the ratio of the weight of the sample to the weight of the cellulose.

1.4 Minimum Detection Limits (m.d.l):- The m.d.l's were calculated from the observed fluorescent X-Ray spectra of thin multi-element standards. The observed m.d.l values as seen in Fig: 1.4 were found to be dependent on the target voltage. The optimised target voltage was found to be 35 Kv for a counting time of 500 secs. Fig : 1.4 shows the lowest m.d.l values as a function of atomic number Z for a target



voltage of 35 Kv and for a counting time of 500 secs. It can be inferred from Fig : 1.4 that in the low Z region the m.d.l's are typically of the order of a few ppm and the minimum value occurs around Z ≈ 30 for K-X-Rays and around Z ≈ 75 for L-X-Rays.

1.5 Sample Collection

The samples analysed were collected from selected areas of North-Eastern India. In Meghalaya, the samples were collected personally from the sites and through the Directorate of Mineral Resources. The selected coal mines included Bapung in the Jaintia Hills, Borsara in West Khasi Hills and Nongwalbibra in West Garo Hills.

The ore samples were from the Phek District of Nagaland and were obtained through the Directorate of Geology and Mining, Government of Nagaland. Some ore samples from Ukhrul in Manipur were obtained through personal contacts.

1.6 Sample Preparation :

As the absorption effects increase more rapidly for the fluorescent X-Rays than for the scattered exciting X-radiation in the case of thick samples, higher sensitivities are obtained with relatively thin samples. Thin samples were prepared by using cellulose powder (E Merck, microcrystalline cellulose used for thin layer chromotography) as the binding material. The absorption of fluorescent radiation in the cellulose was comparatively small. The samples were thoroughly homogenised by grinding to almost the size of the cellulose particles. The grounded coal and mineral samples were mixed with the cellulose in the ratios of 1:1 and 1:9 respectively by weight. The mixtures were pelletised to a size of thickness about 30 - 40 mg/cm^2. The pellets were weighed and used as the specimens.

1.7 Calculation :

The only variables present in the final equation used for the calculation of the elemental concentration were the Compton peak area (I_{comp}) and the peak areas (I_f) of all the elements. Earlier, the other

variables had been calculated according to the following steps :

(a) Calculation of the Absorption Correction

For coal samples, the absorption corrections in the matrix were calculated for cellulose and carbon, while in the case of mineral samples, they were calculated for cellulose only, as 90% of the cellulose was present in each specimen.

The absorption coefficients for coal samples (μ_{Coal}) and mineral samples (μ_{min}) were given by

$$\mu_{Coal} = (\mu_{cell} + \mu_c)/2$$

The absorption correction (A) which is of the following form :

$$A = \frac{1 - e^{-\mu x}}{\mu x}$$

was calculated by adopting an Iteration Method.

(b) Calculation of Corrected peak area (I_f')

$$I_f' = \frac{I_f}{A}$$

(c) Normalisation

For Normalising, the corrected peak areas were divided by Compton peak area.

$$\frac{I_f'}{I_{comp}} = X$$

(d) The relative ability (K_j)

The K_j factors with respect to cellulose were included in the programme.

(e) Amount of the element with respect to cellulose

The calculation of the element concentration in ppm with respect to cellulose is

$$\frac{X}{K_j} = X'$$

is calculated.

(f) Amount of the element

The calculation of the element concentration in ppm is

$$\text{Amount of element in ppm} = \frac{X' \text{ (weight of the sample)}}{\text{(weight of the cellulose)}}$$

CAPTIONS FOR THE FIGURES.

FIG : 1.1 Shows the incident and fluorescent radiation where ϕ_1 and ϕ_2, the average angles of incident and fluorescent radiation respectively.

FIG : 1.2 Shows the schematic diagram of the experimental set up of the XRF system.

FIG : 1.3 Shows the experimental values of K_j factors (counts/Compton K_α counts/ppm) versus the atomic number.

K_j at 25 Kv Mo- target voltage (o o o)

K_j at 30 Kv Mo- target voltage (· · ·)

K_j at 35 Kv Mo- target voltage (× × ×)

FIG : 1.4 Shows the minimum detection limits versus the atomic number for target voltage of 35 Kv.

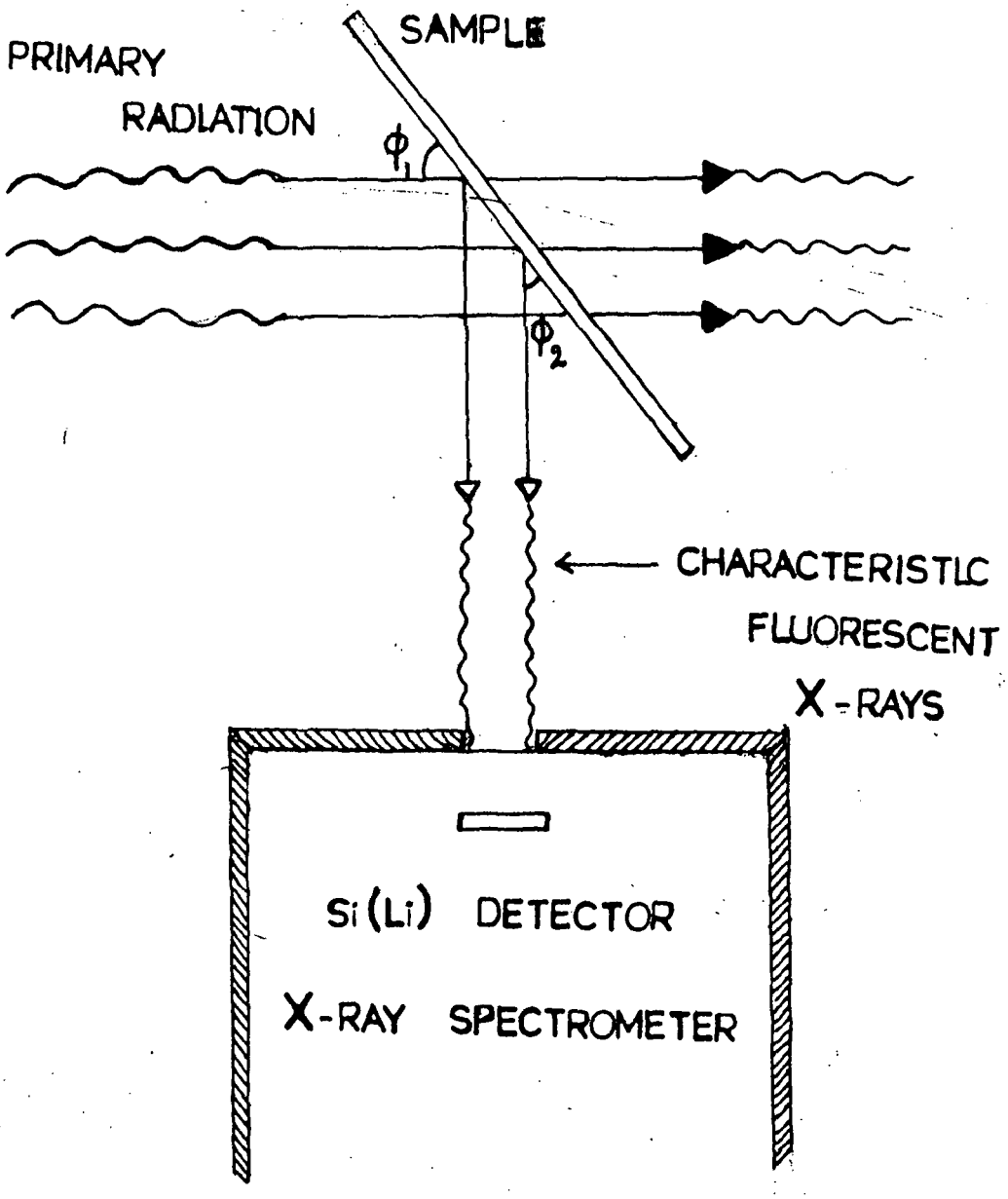

SAMPLE
PRIMARY
RADIATION
ϕ_1
ϕ_2
CHARACTERISTIC
FLUORESCENT
X-RAYS
Si(Li) DETECTOR
X-RAY SPECTROMETER

FIG:-1.1

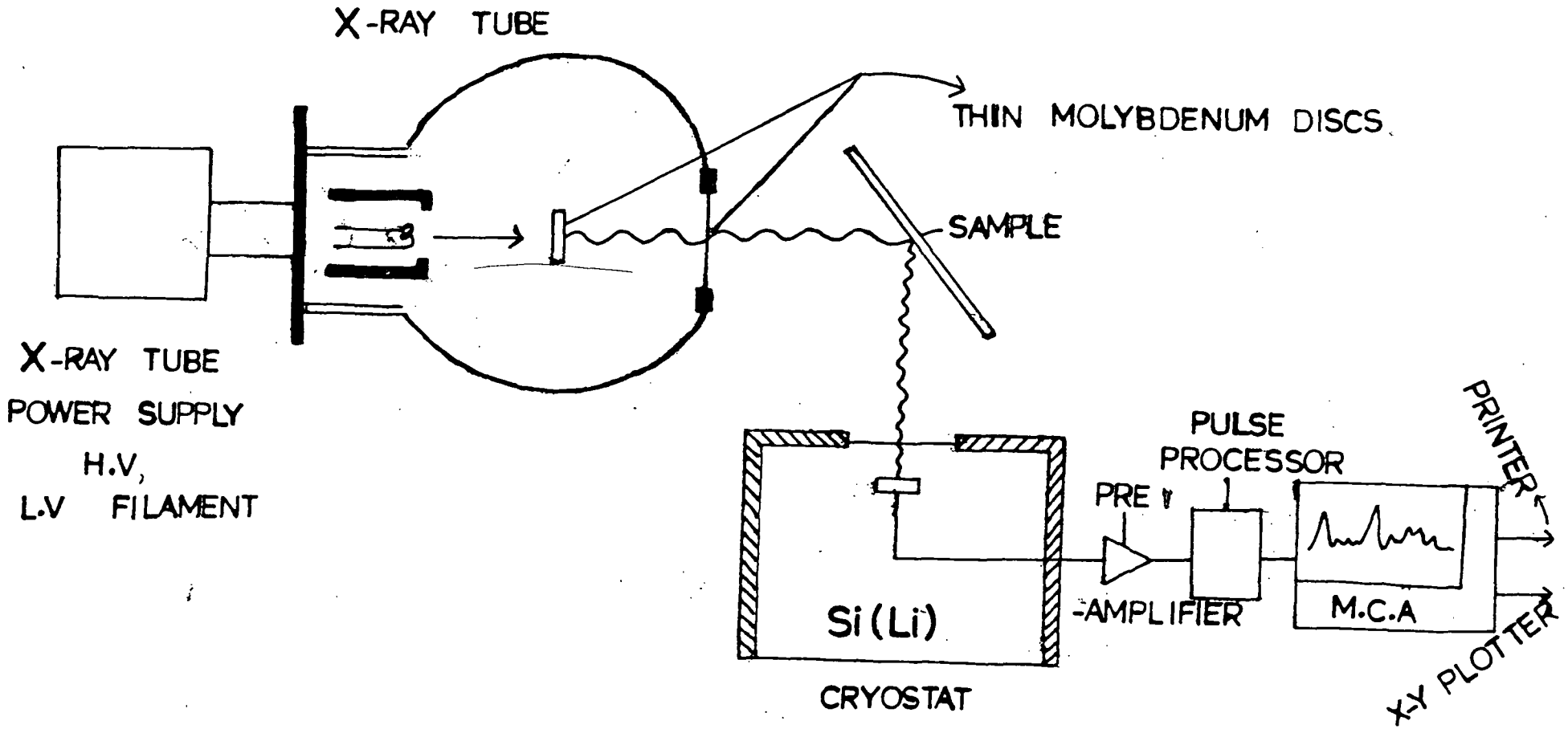


FIG:-1.2 : X-RAY TUBE EXCITED XRF SYSTEM .

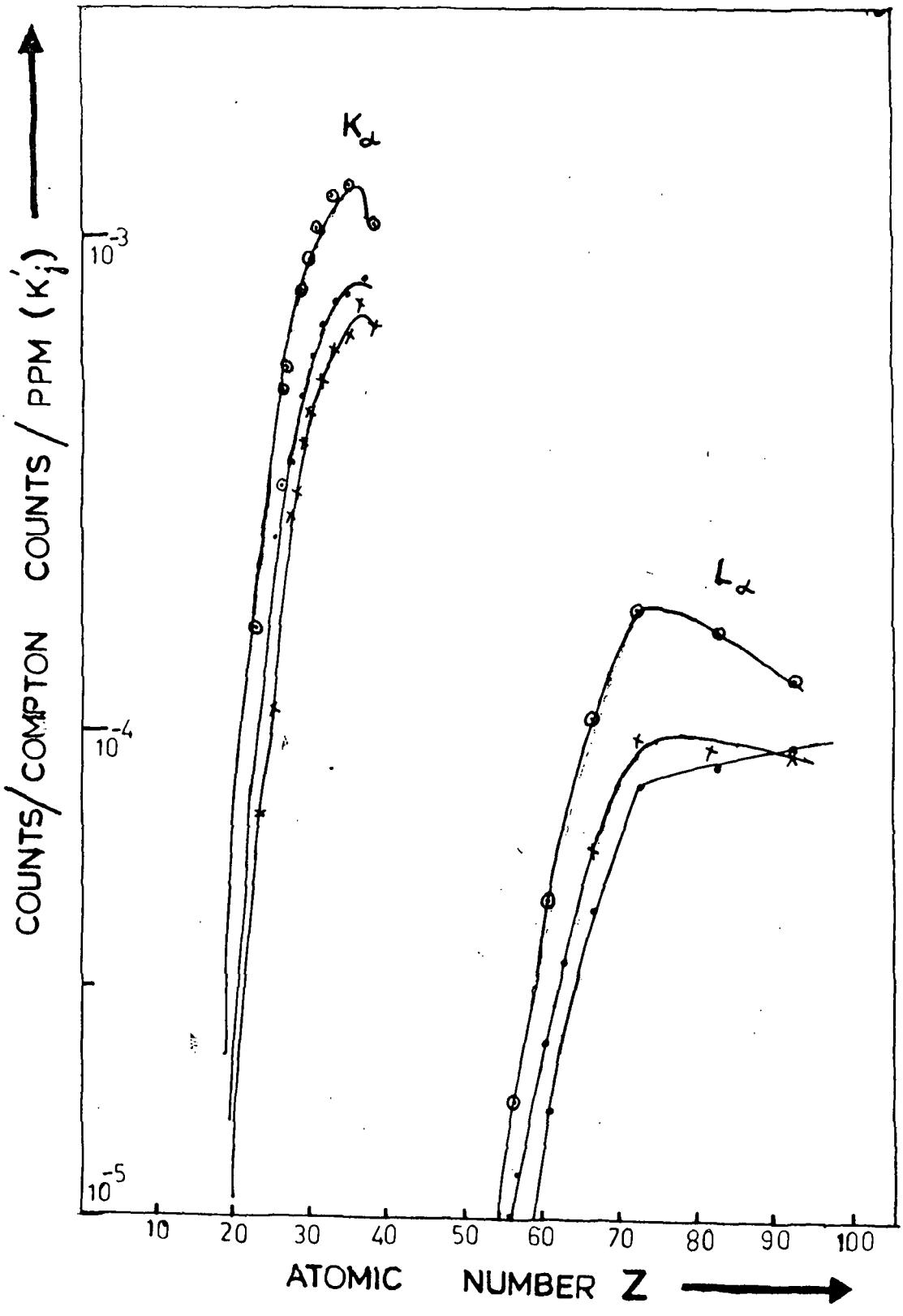

COUNTS/COMPTON COUNTS / PPM (K'i)
10^{-3}
10^{-4}
10^{-5}
K_α
L_α
10
20
30
40
50
60
70
80
90
100
ATOMIC NUMBER Z

FIG :-1-3

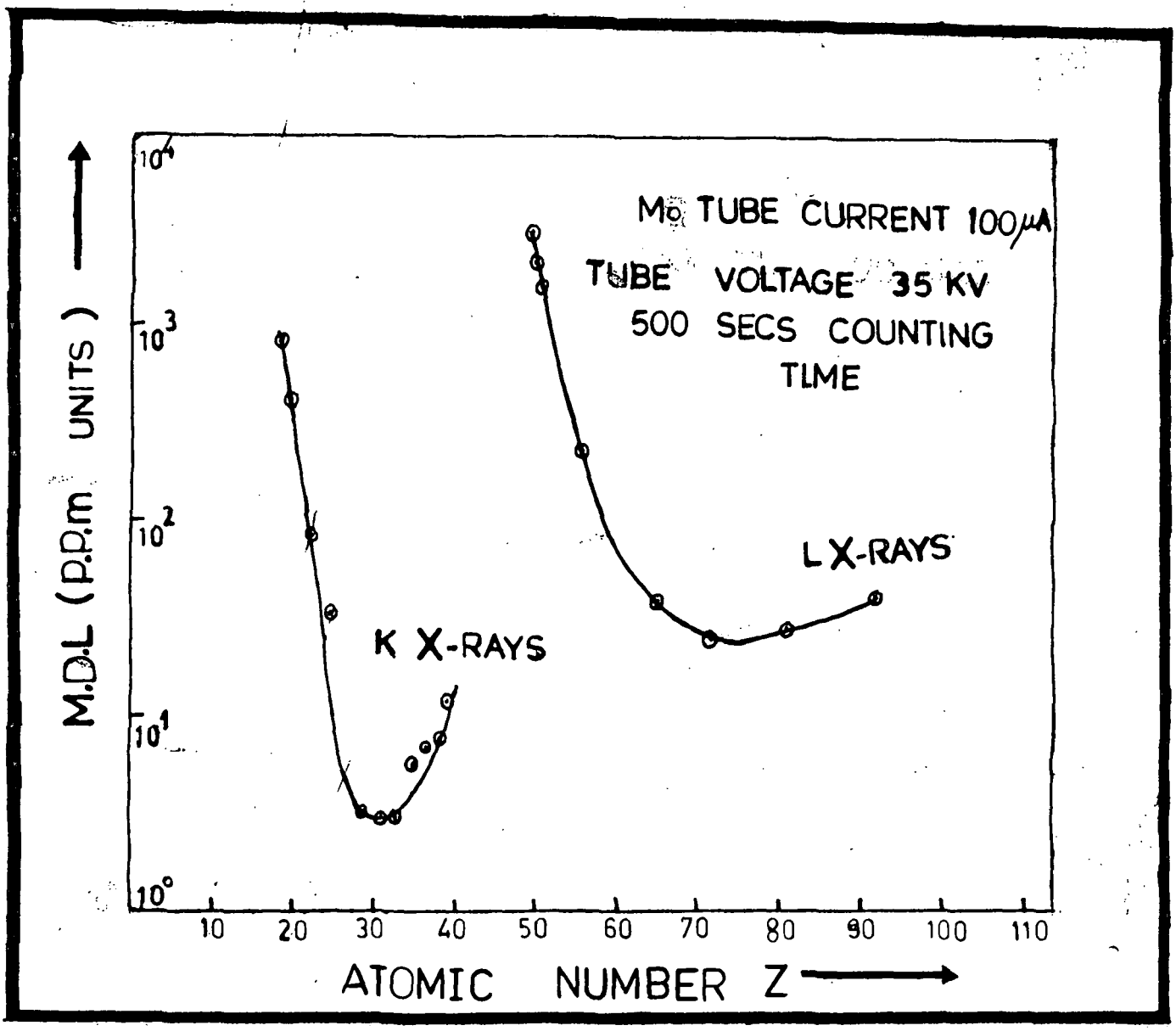

M.D.L (P.P.m UNITS)
10^4
10^3
10^2
10^1
10^0
Mo TUBE CURRENT 100μA
TUBE VOLTAGE 35 KV
500 SECS COUNTING TIME
K X-RAYS
L X-RAYS
10 20 30 40 50 60 70 80 90 100 110
ATOMIC NUMBER Z

FIG :-1.4

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CHAPTER - 2

STUDYING OF THE RESULTS OBTAINED FROM THE XRF ANALYSIS

2.0 Introduction

The selected areas of the North-Eastern Region of the country, where from the samples have been collected for study are shown in the accompanying map (Fig : 2.2).

2.1.1 Confirmation of the results by Chemical Analysis.

The samples collected from the mines of Bapung area (25^0 25' N : 92^0 19' E) in Jaintia Hills District, Meghalaya (Fig: 2.3) on being analysed by XRF technique showed a high content of Titanium (Table 2.1). Accordingly, it was thought desirable to analyse some samples by other Physico-chemical methods in order to confirm the results. The Physico-chemical method selected for the purpose is the Colorimetric determination of Titanium by following the standard procedure (2.1) using a spectrophotometer Model ECIL - (GS -866).

2.1.2 Preparation of Standard Titanium Solution.

An accurately weighed amount of 0.5 gm of reagent grade Titanium dioxide was dissolved in 1:1 H_2SO_4. The solution was heated to fuming and then cooled to room

temparature. The solution thus obtained was transferred quantitatively to a 500 cm^3 volumetric flask and the volume was made up to the mark with distilled water(1 cm^3 of the solution contains 1 mg of TiO_2).

2.1.3 Preparation of the Solution for the Standard Curve.

Four different portions namely, 1 cm^3, 2 cm^3, 4 cm^3 and 6 cm^3 of the above mentioned standard Titanium solution were pipetted out in four different 100 cm^3 volumetric flasks. To each of these flasks were added 10 cm^3 of 1:1 H_2SO_4 and 5 cm^3 of concentrated H_3PO_4 followed by the addition of above 25 cm^3 of distilled water. An amount of 5 cm^3 of 3% H_2O_2 was added to each of the flasks and the contents were shaken thoroughly. Further amount of distilled water was added to make up to the mark of the volumetric flasks. The absorbance of each solution was measured against a reagent blank. The readings recorded for absorbance were plotted against the amounts of TiO_2(mg) (Fig: 2.1).

2.1.4 Preparation of the Solutions of the Samples, under analysis.

An accurately weighed amount of 0.5 gm of a finely ground samples was taken in a small platinum bowl and the content was dissolved in 10 cm^3 of 1:1 of H_2SO_4. To this 15 cm^3 of 40% HF was added and heated to fuming . Heating was continued for a further period of 20 minutes and then cooled. The solution was diluted with 15-20 cm^3 of distilled water and then filtered. The filtrate and washing were collected in a 100 cm^3 volumetric flask and the volume was made up to the mark with distilled water. A portion of 10 cm^3 of the afore-mentioned solution was pipetted out in a 100 cm^3 volumetric flask followed by the addition of 5 cm^3 of 1:1 if H_2SO_4 and 5 cm^3 of H_3PO_4. The solution was diluted with about 20 cm^3 of distilled water and then an amount of 5 cm^3 of 3% H_2O_2 was added to it. The whole was thoroughly shaken and finally the volume was made up to the mark with distilled water.

The absorbance of the test solution was recorded at 410 $m\mu$ against the reagent blank. The test solution as well as the standard were maintained at the same temperature (27°C). The amount of TiO_2 present in the test solution was determined from the standard curve.

The following empirical relation was used to calculate the Titanium content in terms of TiO_2.

$$\% \ TiO_2 = \frac{x \times 10^{-3} \times 100 \times D.F}{\text{Weight of the sample taken}}$$

Where D.F = Dilution factor = 10 (in the present case)

x is the amount of TiO_2 in mg as determined from the standard curve.

$$\% \ Ti = \frac{\% \ TiO_2 \times \text{Atomic Weight of Ti}}{\text{Molecular Weight of } TiO_2}$$

Atomic weight of Ti = 47.9

Molecular weight of TiO_2 = 79.9

The details of the readings for the standard solutions and the readings for the test solutions are given in Table 2.2 and Table 2.3 respectively.

2.2 Analysis of the XRF Results obtained.

It is interesting to note that the results of analysis by XRF technique of the samples collected from the coal mines of Bapung area, Jaintia Hills showed not only the presence of Titanium (Table 2.1) but also its occurence in a high quantity which has escaped from the sight of previous workers (2.2, 2.3). Similar analysis on the samples obtained from various other areas of the North-Eastern Region, however showed a very low concentration of Titanium. The occurence

of Titanium was found (2.4) to be generally of the order of ppm in the two coal and five rock samples of Nongwalbibra (25° 28' N: 90° 42' E) in West Garo Hills(Meghalaya),six coal samples obtained from Borsara (25° 12' 03" N: 91° 11' 04" E) in West Khasi Hills(Meghalaya), one coal sample from Ukhrul (25° 07' N: 94° 22' E) in Manipur and eight rock samples collected from Phek (25° 42° 30" N: 94° 28' 00" E)

A perusal of the results (Table 2.1)makes it evident that while the Titanium contents in samples of West Khasi Hills and West Garo Hills lie in the region of a few hundred ppm and a few thousand ppm respectively, the element content in the samples of Nagaland and Manipur is about a few thousand ppm. On the other hand we have a percentage level of Titanium in Jaintia Hills

2.3 Geological Significance of High occurence of Titanium.

The results of our analytical studies reveal that the Titanium contents in various samples collected from the North-Eastern Region of the Country did not exceed an amount of a few thousand ppm. The samples referred to above are ones other than those obtained from the coal mines. However, it is significant to note that the samples collected from the coal mines of the Bapung area of the

Jaintia Hills District (also in North-Eastern Region) on being analysed showed not only the presence but also the occurence of Titanium to an extent of 4%. This must be considered very important because it directly indicates that there may be a reserve of Titanium nearby such an area and should be possible to explore the feasibility of locating ores of Titanium namely Rutile (TiO_2) etc.

In this section, it is worth mentioning that the Geological Survey of India (G.S.I.) has very recently detected a high occurence of Titanium in a place called Sung Valley (25 ^{o} 35' 15" N: 92^{o} 06' 55" E) which is incidentally a part of Jaintia Hills district. The report of the work of the G.S.I.is given in Appendix-A. The people of the Atomic Minerals Division had also worked in this place, Sung Valley and part of their work is given in Appendix B. (The works of other people do not form part of this thesis).

Hence, we think that the occurence of high quantity of Titanium in the Bapung coal fields may be related to the occurence of high concentration of TiO_2 in Sung Valley which are both located in Jaintia Hills District, Meghalaya. Fig: 2.4 shows parts of East Khasi Hills and Jaintia Hills (Meghalaya) where these two places,Bapung coal field and Sung Valley are situated.

2.4 Correlation Study between different Elements detected by XRF

The absolute concentration level of the elements does not provide much information. Variations in concentrations are obtained in samples taken from the same bore hole at different depths and also from the same type of sample. With the available data, the Correlation study was therefore done to check if there would be any correlation between the occurence of one element with respect to another. The formula used in finding the Correlation factor (r) is presented as follows:

$$r = \frac{\left\{ N\sum x_i y_i - \sum x_i \sum y_i \right\}}{\left\{ N\sum x_i^2 - \left(\sum x_i\right)^2 \right\}^{1/2} \left\{ N\sum y_i^2 - \left(\sum y_i\right)^2 \right\}^{1/2}}$$

where x and y are the amounts in ppm of any two elements considered in the i-th sample.

$\sum x_i y_i$ stands for the total of the product of x and y in all the samples.

$\sum x_i$ and $\sum y_i$ stand for the totals of x and y in all the samples.

$\sum x_i^2$ and $\sum y_i^2$ stand for the total of the squares of x and y respectively.

N stands for the number of the samples.

The results of the element-to-element Correlation study are given in Table 2.4. Some elements are strongly correlated irrespective of the bore holes, depths and types of the samples. Perhaps, these elements may have come from the same source. Hence, the Correlation study may throw some light on the occurance of the elements.

CAPTIONS FOR THE TABLES.

TABLE 2.1 gives the Multi - Element Analysis of the samples collected from different places of North - Eastern India by X-Ray Flourescence Technique (XRF).

TABLE 2.2 gives the Absorbance readings at 410 mμ of the prepared standard solutions of TiO_2 (in mg).

TABLE 2.3 gives the Absorbance readings at 410 mμ of the Test Solution containing Titanium.

TABLE 2.4 gives the Correlation Coefficients of the amounts of various elements detected by XRF in samples collected from Bapung Coal-field (Meghalaya) irrespective of the bore holes, depths and types of samples.

TABLE 2.1 Multi - Element Analysis by XRF in ppm

Element.	1	2	3	4	5	6	7	8
K	-	-	-	-	-	-	-	2040
Ca	254	-	184	-	-	-	2031	-
Ti	24	1944	804	44628	21145	34838	2338	1226
Cr	-	45	-	-	-	-	-	33
Mn	-	-	-	-	-	-	4632	10
Fe	20	6108	2038	37525	95012	185532	38424	11087
Ni	2	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	-	3
Zn	-	-	-	-	-	-	18	38
Ga	-	14	13	-	-	-	-	-
Ge	7	-	3	-	-	-	-	-
Br	-	-	2	-	-	-	-	-
Rb	-	-	-	6	24	38	108	144
Sr	26	29	102	42	81	37	105	99
Y	17	66	26	28	69	120	-	57
Zr	-	75	18	55	853	1950	-	55
Nb	-	-	-	13	44	45	-	-
Cs	-	-	-	-	8	50	-	-
Ba	-	-	-	22	282	325	-	-
La	-	-	-	7	42	90	-	-
Ce	-	-	-	7	241	288	-	-
Pb	-	521	32	52	413	374	448	-

Index to sample Nos.

Sample 1 - Coal sample from Nongwalbibra (West Garo Hills)
Sample 2 - Ore sample from Nongwalbibra (West Garo Hills)
Sample 3 - Coal sample from Borsara (West Khasi Hills)
Sample 4 - Coal sample from Bapung (Jaintia Hills)
Sample 5 - Ore sample from Bapung (Jaintia Hills)
Sample 6 - Sand-stone sample from Bapung (Jaintia Hills)
Sample 7 - Ore sample from Phek (Nagaland)
Sample 8 - Ore sample from Ukhrul (Manipur)

TABLE 2.2 Readings for the Standard Curve

Amounts of TiO_2 in mg.	Absorbance reading at 410 mμ
1.00	0.06
2.00	0.13
4.00	0.26
6.00	0.38
8.00	0.51

TABLE 2.3 Readings of the Test Solutions.

Sample No.	Nature	Bore hole No.	Distance from the surface	Mean Absorbance reading at 410 mμ	Amount of TiO_2 in percentage	Amount of Ti in percentage	Amount of Ti in percentage by XRF
4	Coal	21	4.9 m	0.23	7.2	4.3	4.463
5	Sand Stone	22	32.55 m to 33.85 m	0.11	335	2.1	2.115

TABLE 2.4 Correlation coefficients of the Amounts of various elements detected in Samples obtained from Bapung Coal - field by XRF.

	Ti	Fe	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb
Ti(Z = 22)	1.000	0.277	0.173	0.319	0.435	0.372	0.387	0.438	0.380	0.260	-0.161
Fe(Z = 26)		1.000	0.158	-0.062	0.202	0.459	0.165	0.256	0.330	0.077	-0.196
Rb(Z = 37)			1.000	0.356	0.558	0.786	0.671	0.638	0.774	0.742	-0.195
Sr(Z = 38)				1.000	0.526	0.430	0.657	0.668	0.672	0.724	-0.186
Y(Z = 39)					1.000	0.851	0.720	0.840	0.830	0.843	0.143
Zr(Z = 40)						1.000	0.699	0.771	0.896	0.782	-0.165
Nb(Z = 41)							1.000	0.969	0.766	0.806	-0.021
Ba(Z = 56)								1.000	0.832	0.912	0.088
La(Z = 57)									1.000	0.914	-0.100
Ce(Z = 58)										1.000	0.113
Pb(Z = 82)											1.000

CAPTIONS FOR THE FIGURES.

FIG: 2.1 shows the Calibration Curve of the Absorbance readings at 420 mμ versus amounts of TiO_2 in mg.

FIG: 2.2 shows the map of North - Eastern India with the locations of the places from where the samples are collected.

FIG: 2.3 shows the geological map of Meghalaya.

FIG: 2.4 shows the geological map of East Khasi Hills and Jaintia Hills (Meghalaya) in parts where Bapung area and Sung Valley are located.

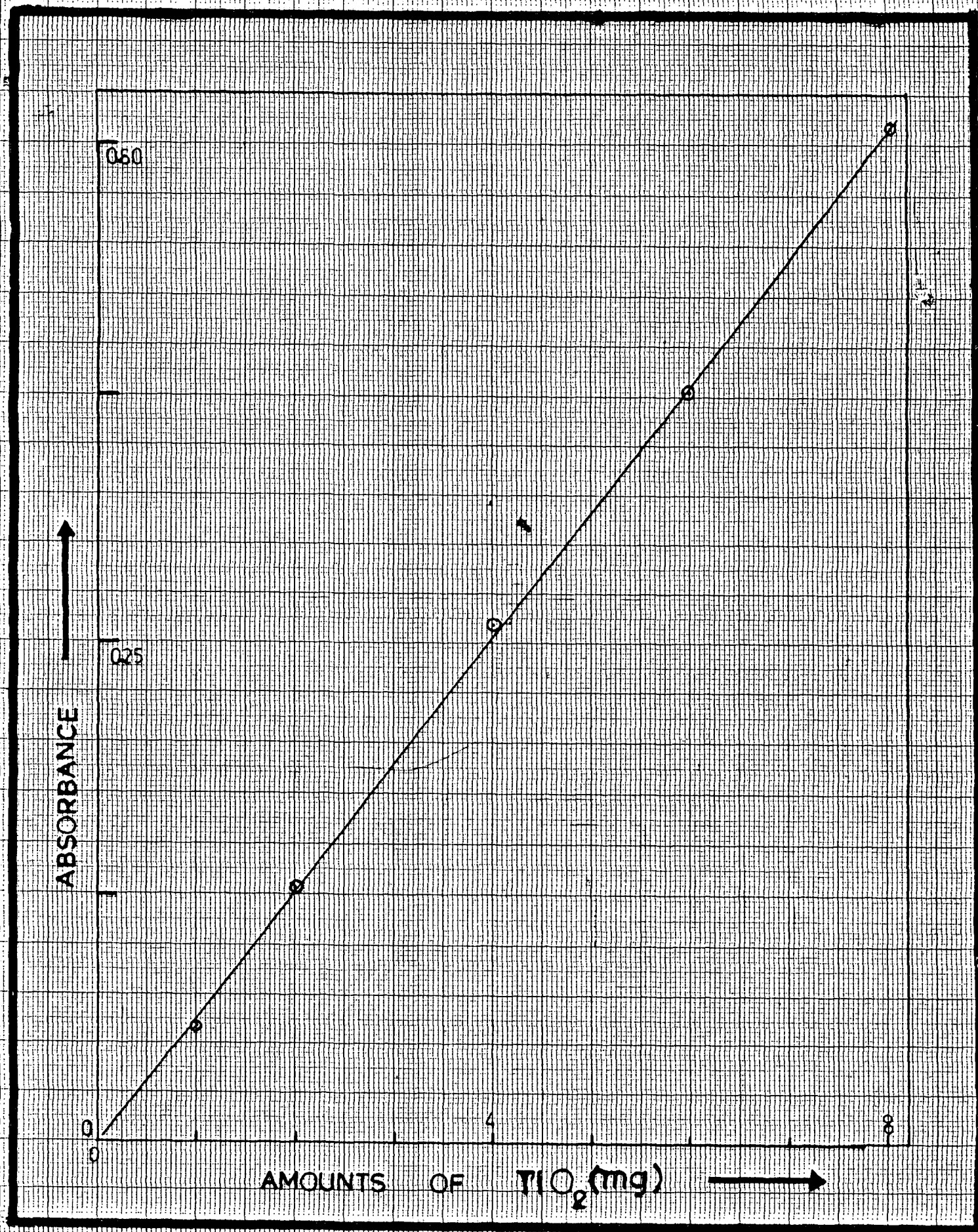


FIG :- 2.1

MAP OF NORTH-EASTERN INDIA SHOWING SAMPLE LOCATIONS

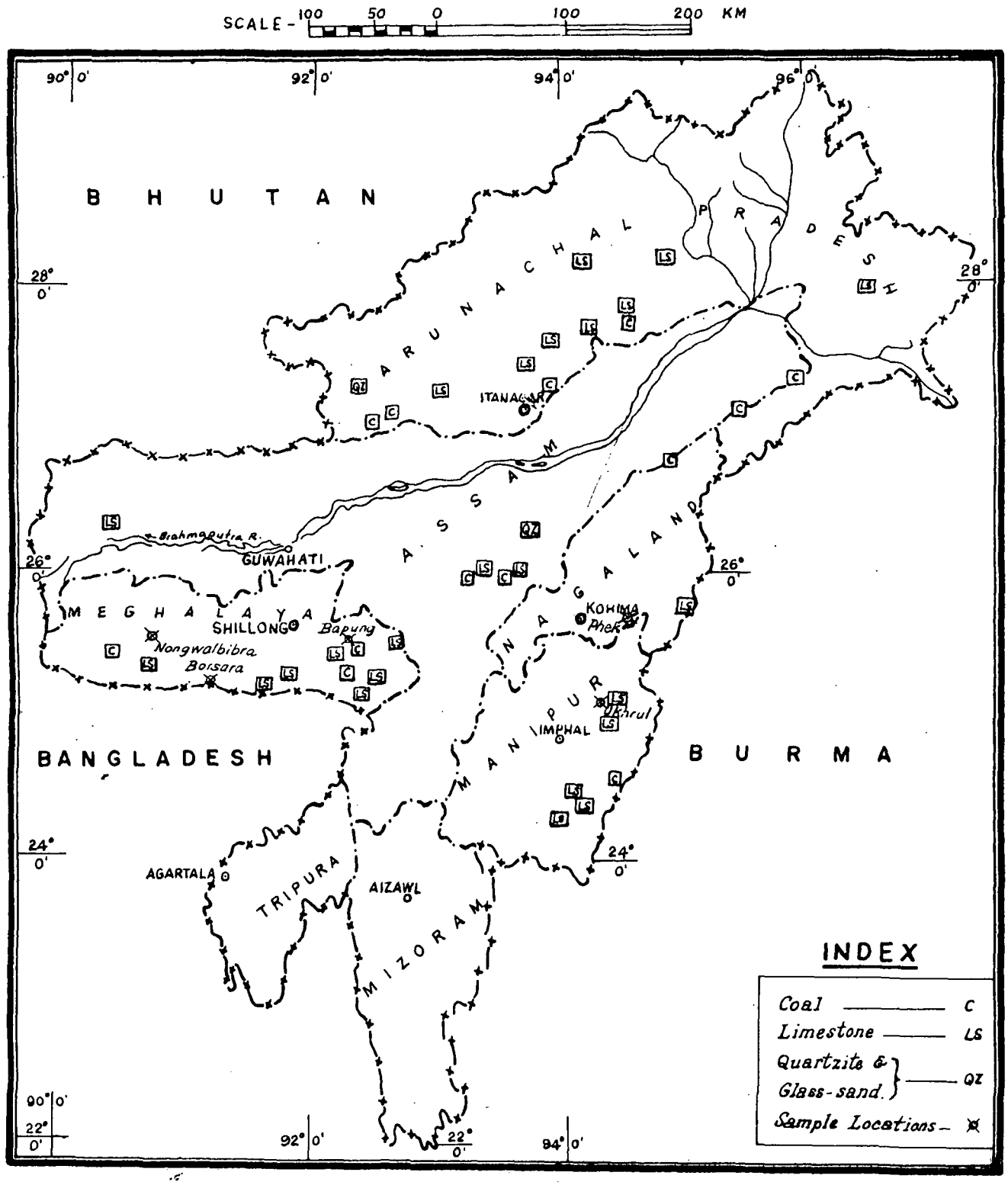
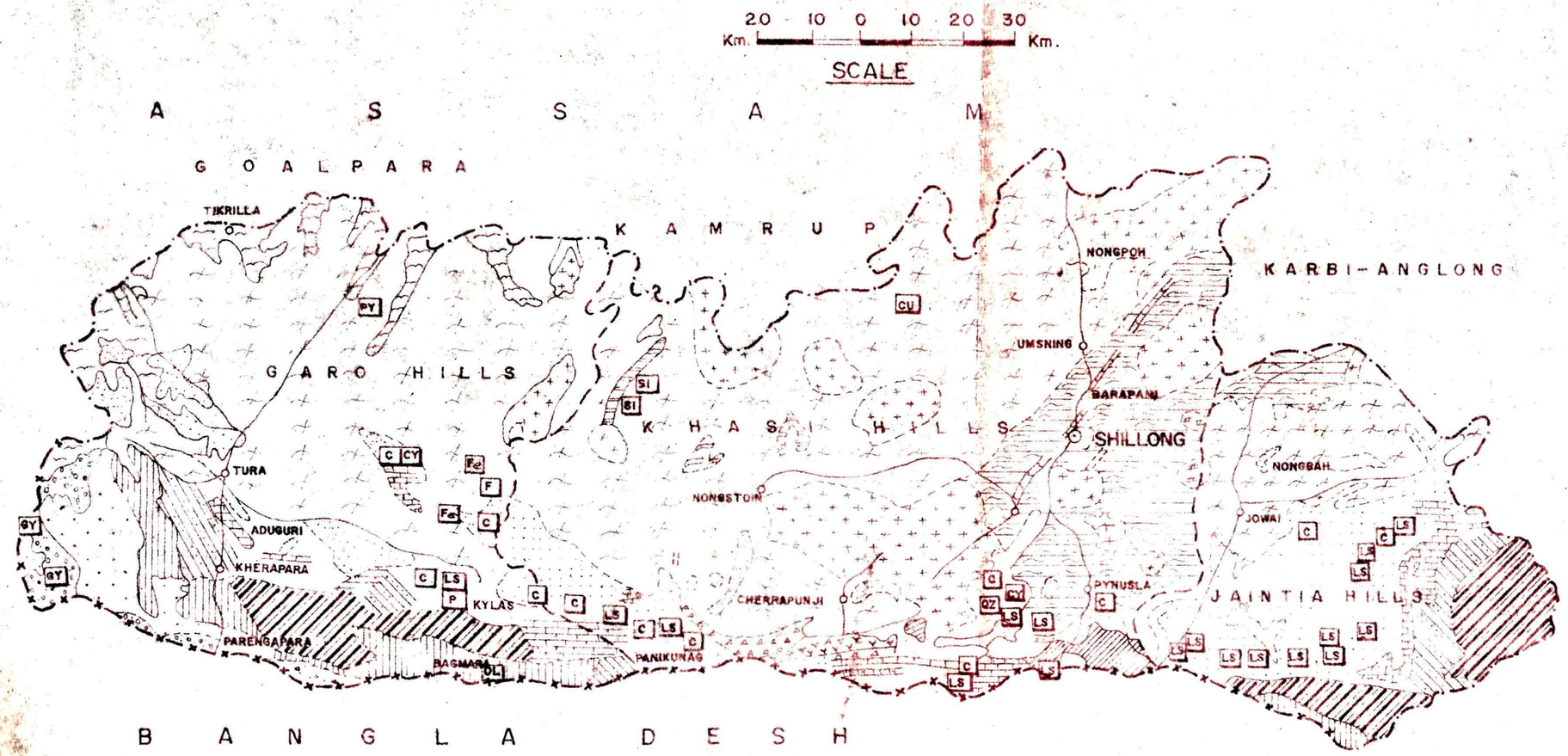


FIG. 2·2 .

GEOLOGICAL AND MINERAL MAP OF MEGHALAYA



INDEX

- Alluvium (Newer/Older)
- Dupitila Group
- Chengapara Formation (Tipam)
- Bagmara Formation (Surma)
- Simsang Formation (Barail)
- Kopili Formation
- Shella Formation
- Langpar Formation
- Mahadek Formation
- Jadukata Formation
- Sylhet Trap
- Gondwana (Lower)
- Granite
- Pyroxenite
- Dolerite Basic Dykes
- Shillong Group
- Amphibolite Dolerite/Ultrabasic intrusives
- Sillimanite Quartz schist
- Gneissic complex

Garo Gr. Jaintia Gr. Khasi Gr.

Lithological Contact — Fault

Road — District boundary

State boundary — International boundary

C	Coal	PY	Pyrite Pyrrhotite	P	Phosphorite
CY	Clay	CU	Copper	OL	Oil & Gas
Fe	Iron ore	F	Feldster, Beryl, etc.	Si	Sillimonite

G.S.I. N.E.R. D.O. NO. 369/84

Drawn by: U. Mangi Singh. D/man.

FIG :-23

Prepared by: A. C. Bhattacharyya.

GEOLOGICAL MAP OF EAST KHASI HILLS AND JAINTIA HILLS (MEGHALAYA) IN PARTS SHOWING BAPUNG COAL-FIELD AND SUNG VALLEY.

KM. 10 0 10 KM.

SCALE :

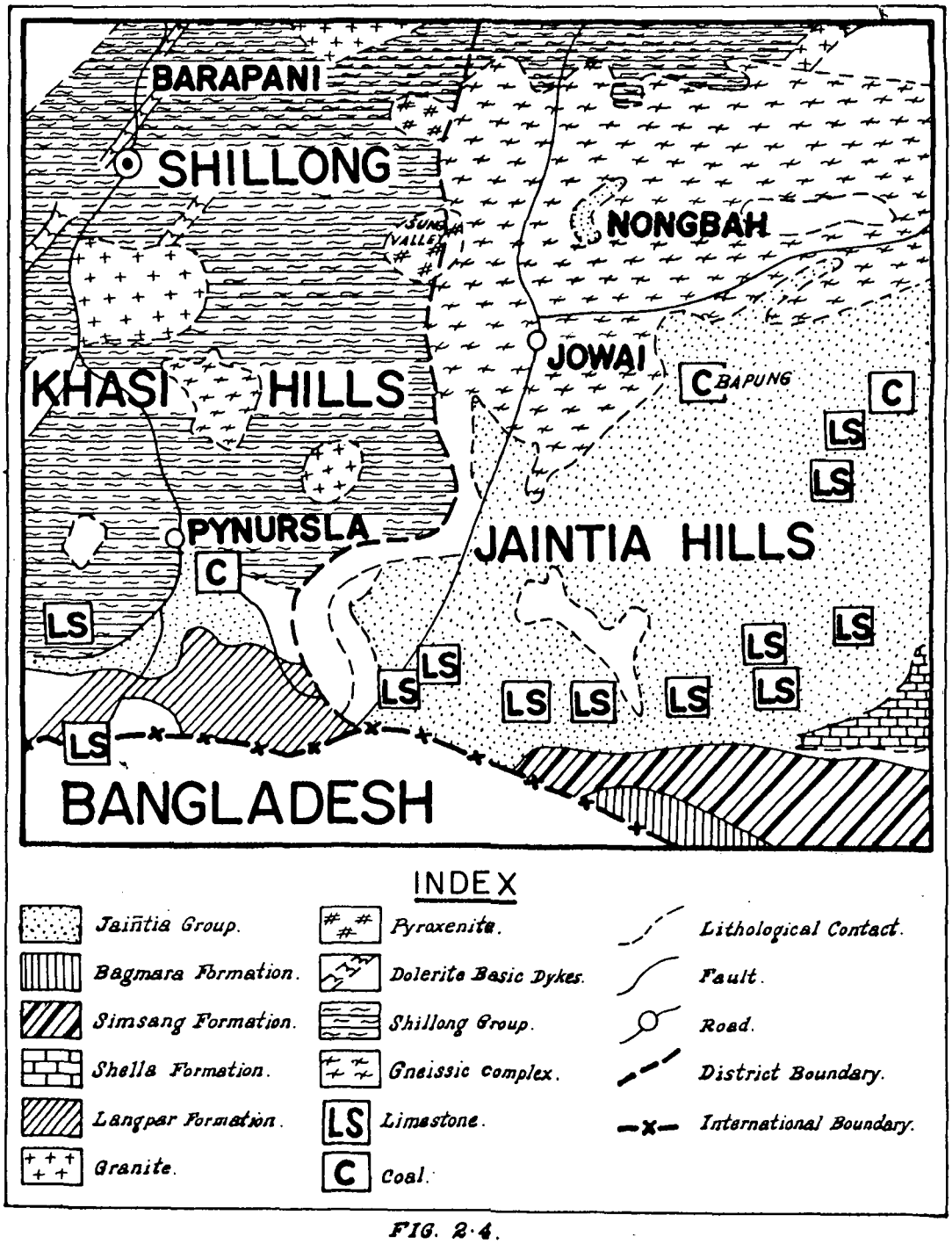


FIG. 2·4.

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CHAPTER--3

ANALYSIS OF THE X-RAY DIFFRACTION DATA OF THE SUBSTITUTED APATITES.

3.0 Introduction

Apatites are essentially phosphates of calcium with chloride, hydroxyl, flouride or carbonate acting also as anions and therefore placed just before the phosphate in the formulae. A wide range of substitutions is possible among these anions and cations resulting in a broad variety of species. The series contains flourapatite, chlorapatite, hydroxyl apatite, etc.

Substituted apatites are important because of their biological significance and have been investigated by many workers(3.1). Human bones and teeth contain calcium phosphate apatite, $Ca_{10}(PO_4)_6(OH)_2$ which is also called Hydroxyl apatite as the principal inorganic constituent(3.2). This belongs to the isomorphous series of apatites. Isomorphous substitution may be defined as the replacement of one ion by a similar ion in a crystal lattice without disrupting its geometry violently. The members of apatites group can also enter into a wide range of substitutional solid solutions. The study of the Solid State Chemistry of

substituted apatites is important in understanding the process of decay and growth of bones as well as that of teeth. The substituted apatites are exepected to be hexagonal in structure.

In isomorphous substitution, it is generally observed that the unit cell parameters (and hence the unit cell volume) change smoothly with the degree of substitution. Vegard's Law, in fact, implies a linear relationship between the unit cell parameters and the precentage of substitution. The linear dependence was illustrated by means of two examples.

In the substitution of Ca^{++} by Ba^{++} on Calcium Hydroxyl apatite, (3.3), the variations of the unit cell parameters 'a' and 'c' of which were shown in Figures 3.0-3.1. Figures 3.2-3.4 gave the variation of the unit cell parameters 'a' and 'c' and unit cell volume of hydroxyl apatite of Arsenic(3.4), $Ca_{10}(AsO_4)_6(OH)_2$ when OH^- is replaced by Cl^-. On the basis of these figures, it was concluded that Vegard's law was satisfied qualitatively. Same conclusions were reached in an extended study of similar substituted apatites.

A closer look at Figures 3.0-3.4 suggested that the unit cell parameters 'a' and 'c' had two different linear behaviours in the range 0-50% and in the range 50%-100% as represented by dashed lines. A cursory glance at a few

more substituted apatites supported the feeling of the deviation of'a' and'c' from Vegard's Law. As the substitution level and the unit cell parameters were not reported to sufficient accuracy,it was difficult to arrive at definite conclusion.The remaining part of the chapter deals with the careful analysis of the powder X-Ray spectra involving a series of substituted apatites in one particular case,where the level of substitution was known accurately.

Calcium Hydroxyl apatite (in which Phosphate was substituted by Vanadate) was selected for the through study. The procedure for the preparation of these samples was given in Appendix D (3.5). Substituted apatites could be represented as

$$Ca_{10}^{++}(PO_4)_{6(1-x)}^{---}(VO_4)_{6x}^{---}(OH^-)_2$$

Where x denoted the molar fraction of Vanadate

3.1.1 X-Ray Diffraction

Crystals are substances which have definite structures. They are made up by the identical structural units which repeat regularly in space. When X-Ray radiation is incident on a series of parallel lattice planes of atoms in the crystal,diffracted beams are found when

the reflections interfere constructively. The condition for constructive reflection is given by Bragg's Law:

$$2d \sin\theta = n\lambda \quad ----- (3.1)$$

Where d is the perpendicular distance between two adjacent planes.

λ is the wavelength of the incident radiation.

θ is the angle made by the incident radiation with the plane (or by the diffracted ray with the plane)

n is an integer.

The method of synthesis of the substituted apatites yields the substance in the form of powdered microcrystalline structure. The incident X-Ray radiation would find at least some microcrystals, properly oriented so as to satisfy Bragg's Law for a given set of parallel lattice planes. The Powder Method is also known as Debye-Scherrer Method.

The apatites are believed to belong to hexagonal system in structure. In the hexagonal system, the conventional unit cell chosen is a right prism based on a rhombus with an angle 60°. The axes and angles of a conventional unit of a hexagonal crystal are restricted as follows :-

$$a = b \neq c \;, \quad \alpha = \beta = 90^\circ \;, \quad \gamma = 120^\circ \quad ---- (3.2)$$

The interplanar spacing 'd' is related to the Miller Indices(hkl) for the hexagonal system by the following equations:

$$\frac{1}{d^2} = \frac{4}{3}\,\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \qquad \text{------(3.3)}$$

using Bragg's Law

$$\left.\begin{aligned} \sin^2\theta &= \frac{\lambda^2}{3a^2}\left(h^2 + hk + k^2\right) + \frac{\lambda}{4c^2}\,l^2 \\ &= \alpha\left(h^2 + hk + k^2\right) + \beta l^2 \end{aligned}\right\} \text{---(3.4)}$$

Where $\alpha = \frac{\lambda}{3a^2}$ and $\beta = \frac{\lambda}{4c^2}$ ----(3.5)

3.1.2 Instrumentation

The X-Ray diffraction patterns of the powdered samples of substituted apatites were recorded on a film with the help of a Debye-Scherrer Camera of diameter 114.6 m.m. The target used was copper, Cu K_α radiation of wavelength 1.5424 A^0 was then emitted under 40 Kv of voltage and 25mA of current. The X-Ray beam coming from the target was first collimated. The sample is introduced in the path of X-Ray beam. A photographic film is then placed normal to the X-Ray beam in a circular path such that the distance represents the diffraction angle.

The powder grains which are so oriented that their planes satisfy Bragg's law are in a position to reflect X-Rays. The reflection occurs in a direction making an angle 2θ (θ = glancing angle for a particular plane) with the direction of X-Ray beam. The locus of directions making an angle 2θ with a given direction is a cone of half opening angles 2θ . The angle θ is determined by measuring the distance between the similar arcs which correspond to 4θ .

3.2 Previous Work on Substituted Apatites.

Previous workers (3.3, 3.4) assigned the Miller Indices to the spectral lines by solving the linear equation in α and β.

For hexagonal crystal, the measured glancing angle θ the Miller Indices (hkl) and the lattice constants 'a' and 'c' are governed by the relationship given in Eqns. 3.4 & 3.5. Knowing the values of 'a' and 'c' for compounds from the literature and with the known values of θ as recorded by the instrument, the values of hkl were assigned by the previous workers within tolerable error. This was done for a few lines having lower values of θ. It was obvious that lines with high values of θ would have multiple assignments.

The smooth dependence of the unit cell parameters with respect to the levels of substitution gave an idea of assigning hkl values. This was done to the spectral lines of a compound of next higher substitution by comparing the spectrum with that of the pure compound. All the lines belonging to a lowest nonzero degree of substitution which had the θ values very close to those lines of pure compound were given the same values of hkl. Three or four pairs of these lines then were chosen for solving

α and β by using Eqn. 3.4. If the values of α and β obtained from the different pairs were found to agree, the corresponding values of 'a' and 'c' were accepted as valid.

In the same way, the assignment was done for the next higher substituted compound which came in the series. The lines were assigned the same values of hkl of the immediate previous compound. The values of α and β were then estimated as before. This procedure was repeated for successive higher degree of substitutions.

The foregoing method dealt with the low values of θ and did not use all the diffraction data. We adopted a procedure using all the available data in evaluating the values of 'a' and 'c' and obtaining error estimates using the Least-Square-Technique.

3.3 Indexing Procedure

On looking carefully at the low values of the measured θ, attempts were made to identify (5 or 6) lines which have a reasonable Greatest Common Factor for $\sin^2\theta$ such that the ratio of the $\sin^2\theta$ to the Common Factor is an integer of the form $h^2 + hk + k^2$ where h and k are integers. This common factor was identified with α.

This was achieved usually with an accuracy better than 2% . Using Eqn. 3.4, the value of $Sin^2\theta$ were calculated for different h and k (with l=0).

The lines corresponding to the calculated values of $Sin^2\theta$ with fixed values of h and k were drawn parallel to X-axis,(Fig. 3.5). These lines were associated with the values of h and k as assigned to them while 'l' was zero. Using the same scale,the lines which represent the observed values of $Sin^2\theta$ were graphically drawn in a separate sheet (Fig.3.6). The two graph sheets were placed side by side and compared thoroughly.These lines which agreed in the values of $Sin^2\theta$ were assigned values of h and k (with l=0). The remaining lines were considered to be associated with non-zero values of 'l'. The graph which contained the calculated values of $Sin^2\theta$ (with l=0) was raised up by such a distance that there was an agreement between a few lines in both the graphs (Compare Figures 3.6 and 3.7). The distance by which the graph sheet was moved up is taken to be β tentatively.These lines were alloted with proper h and k and l=1.Then the graph sheet was moved up further by 3β (i.e.the total distance moved was 4β) and noted if there were some more lines agreeing with observed spectrum (Compare 3.6 and 3.8). These lines were assigned the respective h and k values

(with l=2.) Same procedure were tried by shifting the graph sheet with a distance of 9 β , 16 β and so on for assigning the rest of the lines of the observed spectrum. The lines which agreed with the measured diffraction data were given the same h and k values and the corresponding l value was put depending on the distance shifted.

The lines of higher values of θ were found to have multiple assignments. With the accepted values of α and β , some lines could not be assigned within tolerable error. This will be discussed later.

3.4 Refinement in the values of 'a' and 'c'

The graphical method used was quite successful. The values of 'a' and 'c' were quite acceptable as most of the lines could be assigned within allowable limits (of ½%).

Using the above mentioned method, it was noted that lines of the observed spectrum with higher values of θ had multiple assignments. A standard technique was adopted for refinement the values of 'a' and 'c' determined graphically. This had improved the assignment and also the best values of hkl could be selected for those lines having multiple assignments. The technique could be briefly described.

The principle of the technique was that the best values of 'a' and 'c' were those which made the sum of the squares of the residuals a minimum. Now, from Eqn. 3.4.

$$y = \alpha x_1 + \beta x_2 \qquad \text{-----} \quad (3.4)$$

Where, $y = \sin^2\theta$, $x_1 = h^2 + hk + k^2$ & $x_2 = l^2$

$$R^2 = \frac{1}{N}\sum \left| y - (\alpha x_1 + \beta x_2) \right|^2 \qquad \text{----} \quad (3.6)$$

where N is the number of lines observed. R was minimised which gave the best values (α_o and β_o) of α and β as follows in terms of x_1, x_2, and y.

$$\left.\begin{aligned} \alpha_o &= \frac{\sum x_2^2 \sum x_1 y - \sum x_1 x_2 \sum x_2 y}{\sum x_1^2 \sum x_2^2 - \left(\sum x_1 x_2\right)^2} \\ \beta_o &= \frac{\sum x_1^2 \sum x_2 y - \sum x_1 x_2 \sum x_1 y}{\sum x_2^2 \sum x_1^2 - \left(\sum x_1 x_2\right)^2} \end{aligned}\right\} \text{---} (3.7)$$

Once α_o and β_o were determined, best values (a_o and c_o) could be found.

3.5 Estimating the Errors in a_o and c_o

A typical $\theta_{observed}$ and $\theta_{calculated}$ is given in Table 3.1.

The best values of a_o and c_o were then obtained after refinement. The errors in them were also calculated.

The ranges of α_o and β_o were determined by multiplying R^2 of Eqn. 3.6 by 2. Table 3.2 gave the best values of a_o and c_o obtained for different compounds at different degrees of substitution together with the estimated errors in them.

3.6 Relation between the Lattice Constants and the Degree of Substitution.

The best values a_o and c_o obtained at different levels of substitution were examined to see their relation with the degrees of substitution. To test this, the entire series of substituted compounds were grouped into two parts i.e. 0% -50% and 50%-100%. For the sake of comparison, the slopes and intercepts of the two lines at 50% were determined.

The method of Least Squares (3.6) was adopted to obtain the values of the slope, intercept and the errors in them.

The intercept (b), the slope (m) and the errors r_b and r_m in the intercept and slope respectively were given by the following equations :-

$$b = \frac{\Sigma y(\Sigma x^2) - \Sigma x \Sigma xy}{D}$$

$$\text{where } D = n(\Sigma x^2) - (\Sigma x)^2 \qquad \text{----(3.9)}$$

$$r_b = r_e \left(\frac{\Sigma x^2}{D} \right)^{1/2}$$

$$m = \frac{n(\Sigma xy) - (\Sigma x)(\Sigma y)}{D}$$

$$r_m = r_e \left(\frac{n}{D} \right)^{1/2} \qquad \text{---(3.10)}$$

$x \rightarrow$ (degree of substitution -50%

$y \rightarrow$ Lattice constant (a)

$r_e \rightarrow$ is the probable error of the point as calculated by external consistency.

$$r_e = 0.6745 \left(\frac{\sum v^2}{n-2} \right)^{1/2} \qquad \ldots\ldots (3.11)$$

where $\sum V^2$ = sum of the squares of the $| y_{obs} - y_{exp} |^2$

n = number of substituted compounds.

similarly, the method was applied for the lattice constant (c_o) and the unit cell volume (v).

The analysis of the X-Ray diffraction data of the substituted apatites showed that the lattice constants (a and c) followed different behaviours in the two regions. The variation between the lattice constants obtained from our analysis with respect to the degree of substitution was presented in Figures 3.9 and 3.10 . As seen from Table 3.3, there was a marked differences in the slopes of the two lines for both the constants. The differences between the two intercepts were not significantly larger than the uncertainties (for both a and c) in them.

As a consequence of the above, it easily followed that unit cell volume also behaved in the same way i.e. intercepts are the same but slopes are different. In short, it meant that unit cell parameters change continously but not strictly linear.

Table 3.4 supported the conclusion drawn from the above analysis. It presented the number of lines observed and the number which could be assigned within an error of 1% using the calculated values of the lattice constants (a and c).

As can be seen from the Table 3.4 the number of lines observed was more than 20 in the higher substituted compounds i.e. 50% - 100% . In the case of lower substituted compounds (i.e. 0% - 50%), the number of lines observed was less than 20 except in one case (i.e. at 18,3% of substitution). The accuracy of the assignment with calculated values of a and c was found to be better for lower (0% - 50%) substituted compounds compared to the higher substituted compounds (50% - 100%).

The above analysis clearly showed the inadequacy of the Vegard's law for the whole range of substitution but separately valid in the two different ranges i.e. 0% - 50% , 50% - 100% . The implication of this would be discussed in a later chapter in detail.

CAPTIONS FOR THE TABLES

TABLE 3.1 gives the values of $\theta_{observed}$ and $\theta_{calculated}$ of a pure compound.

TABLE 3.2 gives the best values of the lattice constants 'a' and 'c' as determined, together with the estimated errors in them.

TABLE 3.3 gives the slopes and intercepts of the calculated lattice constants 'a' and 'c' in two different regions i.e. 0% - 50% and 50% - 100% degree of substitution of Vanadate.

TABLE 3.4 gives the number of lines as observed in the spectrum for different levels of substitutions of Vanadate and the number of lines that can be fitted to an accuracy of 1%.

TABLE 3.1 Pure Compound $Ca_{10}(PO_4)_6(OH)_2$

Observed values of θ in degree	Observed Values of $Sin^2\theta$ ($X\ 10^{-2}$)	Calculated Values of $Sin^2\theta$ ($X\ 10^{-2}$)	% difference between observed and calculated Values of $Sin^2\theta$	Assigned Values of (h k l)
10.91	3.582	3.549	0.920	2 0 0
12.89	4.977	4.988	0.230	0 0 2
15.85	7.460	7.458	0.02J	2 1 1
16.41	7.981	7.986	0.056	3 0 0
17.13	8.675	8.537	1.590	2 0 2
17.71	9.254	9.233	0.230	3 0 1
19.92	11.608	11.535	0.630	3 1 0
23.29	15.633	15.635	0.015	2 2 2
23.95	16.479	16.523	0.260	3 1 2
24.71	17.474	17.434	0.230	2 1 3
25.16	18.075	18.105	0.170	3 2 1
27.83	21.795	21.870	0.340	2 2 3

TABLE 3.2

Sample No.	% of substitution of Vanadate	a_o (A^o)	a_o (A^o) (error in)	c_o (A^o)	c_o (A^o) (error in)
1	0.00	9.464	0.628	6.913	0.036
2	5.70	9.419	0.009	6.886	0.008
3	10.00	9.343	0.112	6.956	0.0622
4	18.30	9.463	0.065	6.993	0.0749
5	36.67	9.498	0.039	6.920	0.0333
6	37.50	9.488	0.043	6.903	0.034
7	49.16	9.790	0.104	7.240	0.055
8	61.33	9.632	0.0744	7.080	0.052
9	74.17	9.780	0.075	7.023	0.070
10	86.66	9.731	0.056	7.037	0.060
11	100.00	9.8059	0.033	6.969	0.066

TABLE 3.3

	LATTICE CONSTANTS				UNIT CELL VOLUME	
	$a_o (A^o)$	Error	$c_o (A^o)$	Error	$V_o (A^o)^3$	Error
Intercept (<50%)	9.651	0.0480	7.0820	0.052	571.600	9.400
Intercept (>50%)	9.720	0.0400	7.1803	0.0279	588.000	6.200
Difference	0.069	0.062	0.0980	0.059	16.400	11.300
Slope (<50%)	0.0057	0.0015	0.0040	0.0016	0.974	0.288
Slope (>50%)	0.0011	0.0013	-0.0046	0.0010	-0.255	0.206
Difference	0.0046	0.0020	0.0086	0.0018	1.229	0.354

TABLE 3.4

Sample No.	Molar % of substitution by Vanadate	No of lines observed	No. of lines filted within an error of 1%
1	0.00	12	11
2	5.70	15	15
3	10.00	17	9
4	18.30	23	17
5	36.67	13	11
6	37.50	13	9
7	49.16	17	8
8	61.33	20	9
9	74.17	28	14
10	86.66	29	19
11	100.00	25	18

CAPTIONS FOR THE FIGURES

FIG : 3.0 Shows the behavior of the lattice constant 'a' versus the molar % of Ba^{++} (adapted from Ref. 3.3)

FIG : 3.1 Shows the behavior of the lattice constant 'c' versus the molar % of Ba^{++} (adapted from Ref. 3.3)

FIG : 3.2 Shows the behavior of the lattice constant 'a' versus the molar % of Cl^- in hydroxyl apatite of Arsenic (Adapted from Ref. 3.4)

FIG : 3.3 Shows the behavior of the lattice constant 'c' versus the molar % of Cl^- in hydroxyl apatite of Arsenic (adapted from Ref. 3.4).

FIG : 3.4 Shows the behavior of the unit cell volume (V' versus the molar % of Cl^- in hydroxyl apatite of Arsenic (adapted from Ref. 3.4)

FIG : 3.5 Shows the lines which are drawn parallel to X-axis corresponding to the calculated values of $Sin^2\theta$ for different values of h and k(with l=0). Here the value of α is assumed to be 0.009(Figs. 3.5-3.8 refer to pure Calcium Hydroxyl apatite)

FIG : 3.6 Shows the lines drawn parallel to X-axis correspond to the observed values of $\sin^2\theta$ for a pure compound $Ca_{10}(PO_4)_6(OH)_2$

FIG : 3.7 Shows the figure: 3.5 when raised by a certain distance. It is raised by a distance 0.012 units and hence $\beta = 0.012$ and l=1 while the values of h and k are same as in FIG : 3.5.

FIG : 3.8 Shows the FIG : 3.5 raised by a distance 4β where $\beta = 0.012$ units. Here l=2 and h and k are as in FIG : 3.5

FIG : 3.9 Shows the behavior of the lattice constant 'a' obtained from our analysis versus the molar % of VO_4^{---} together with the best fit straight line.

FIG : 3.10 Shows the behavior of the lattice constant 'c' obtained from our analysis versus the molar % of VO_4^{---} together with the best fit straight line.

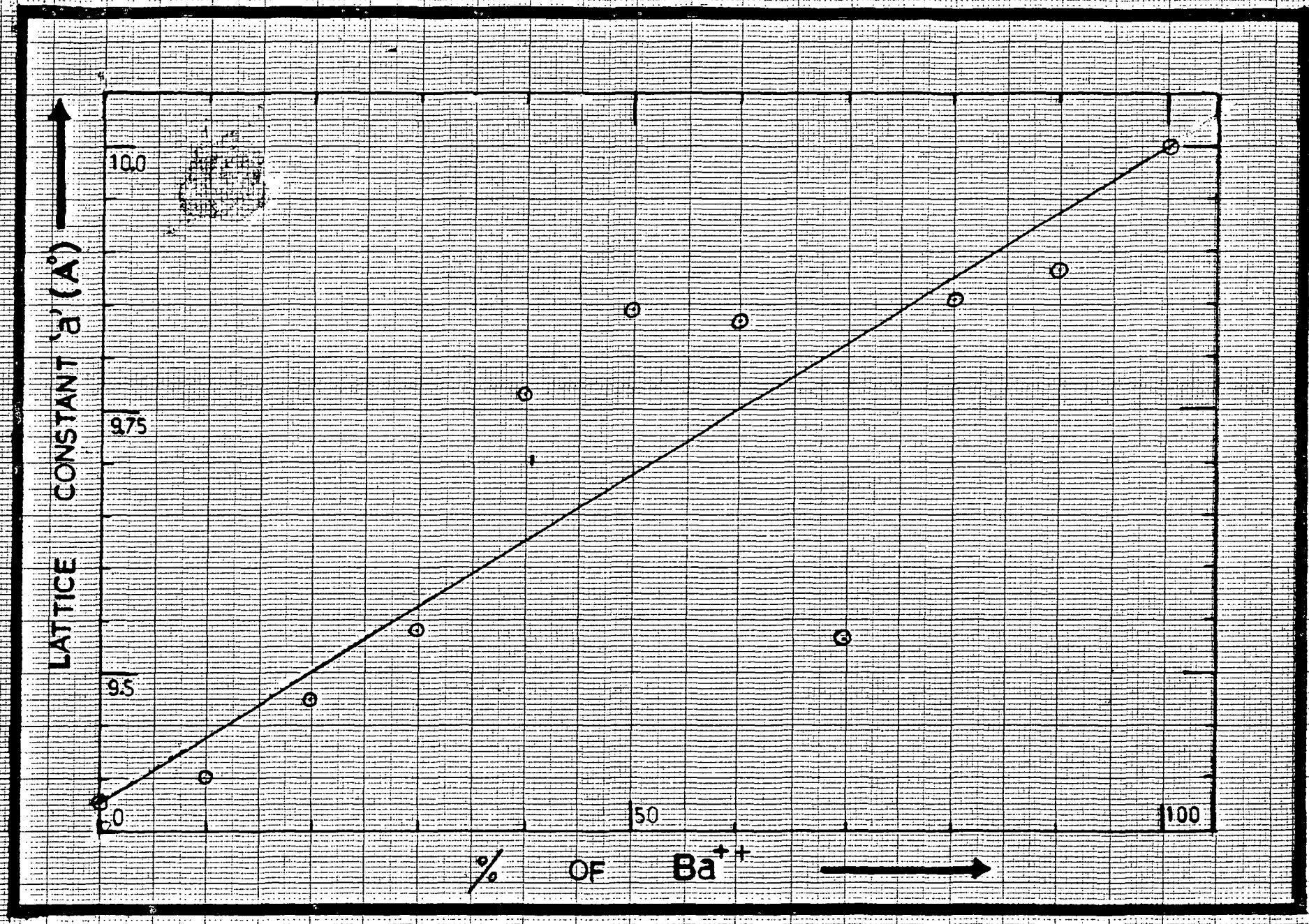

FIG :- 30

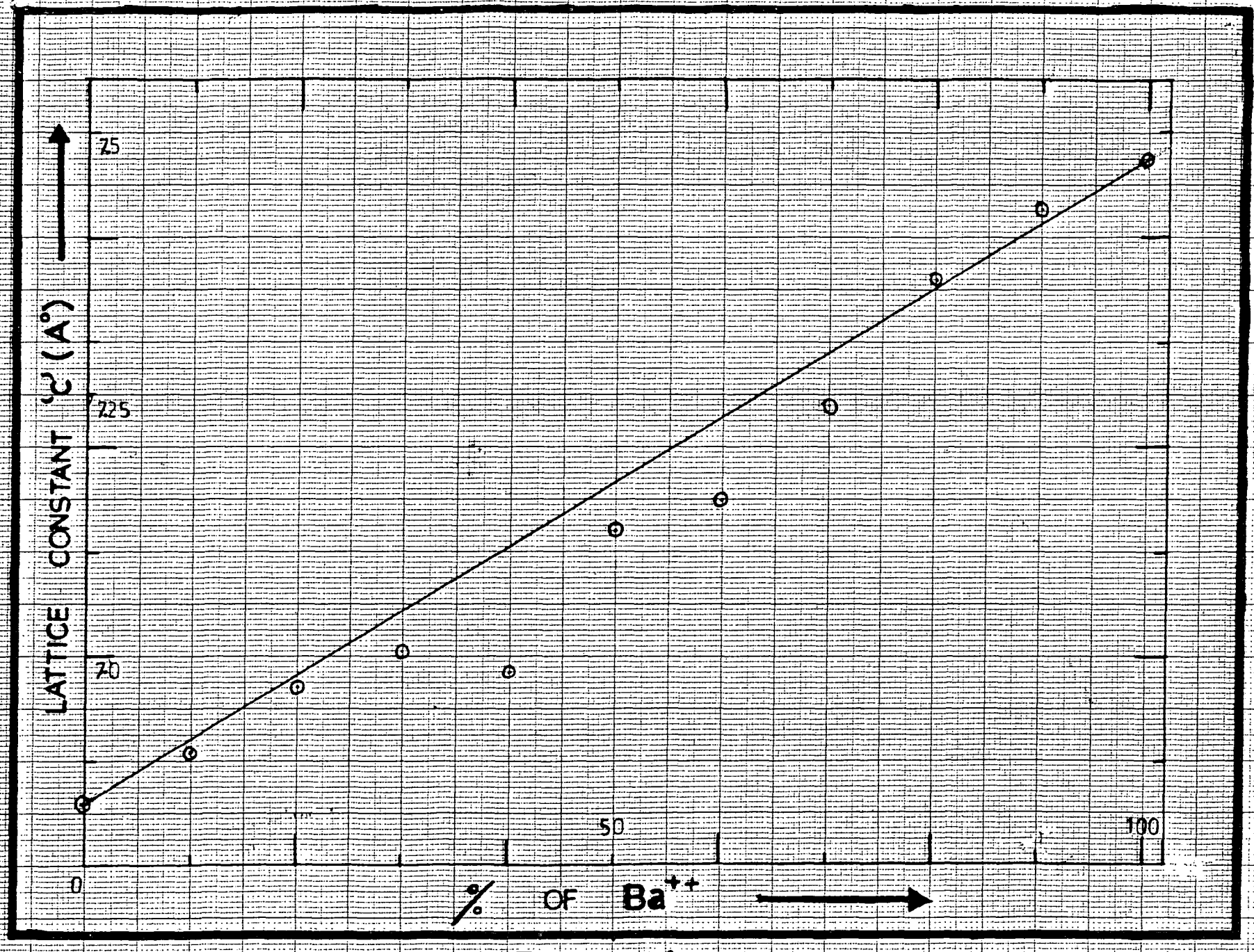

FIG :- 3.1

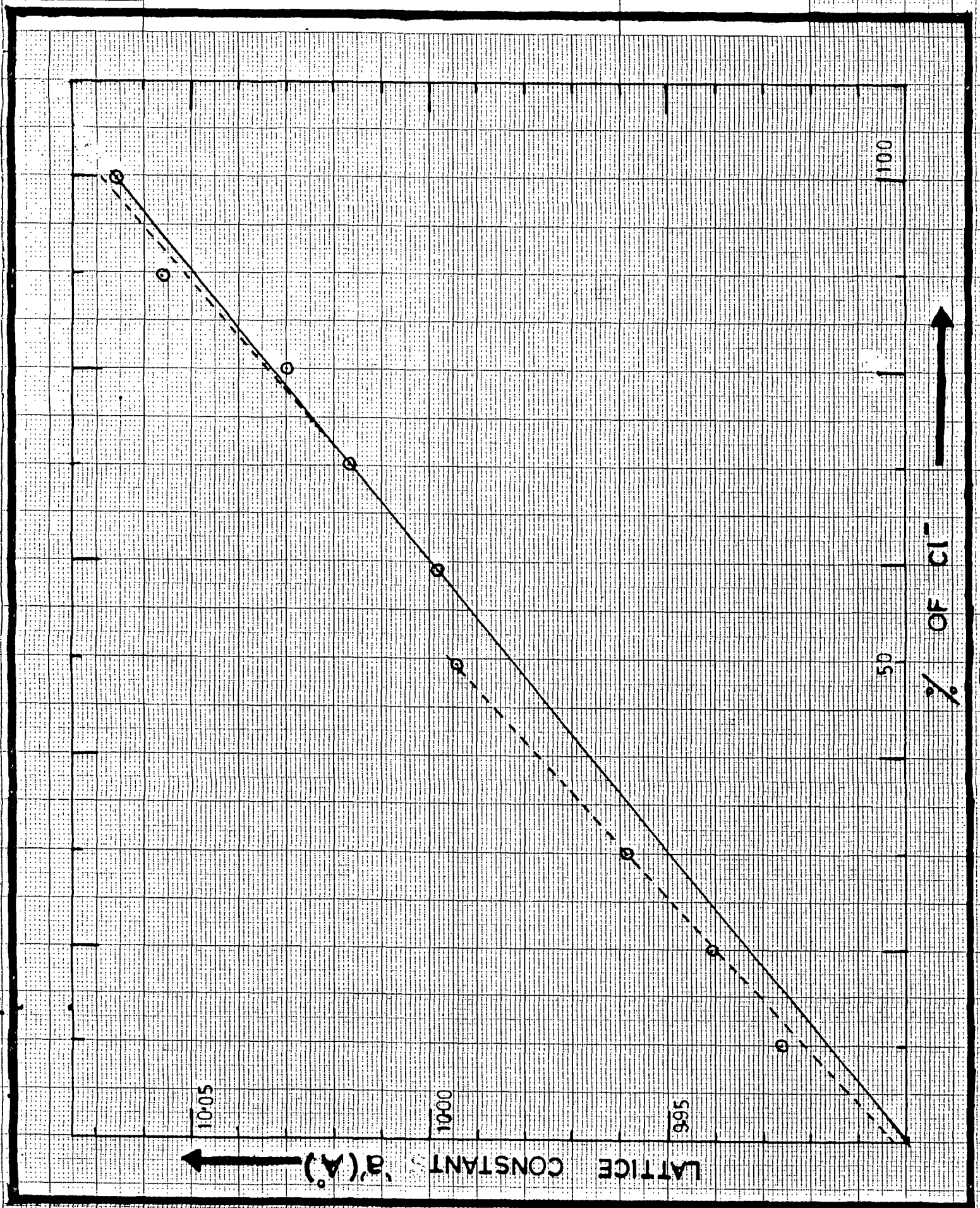

FIG:- 3.2

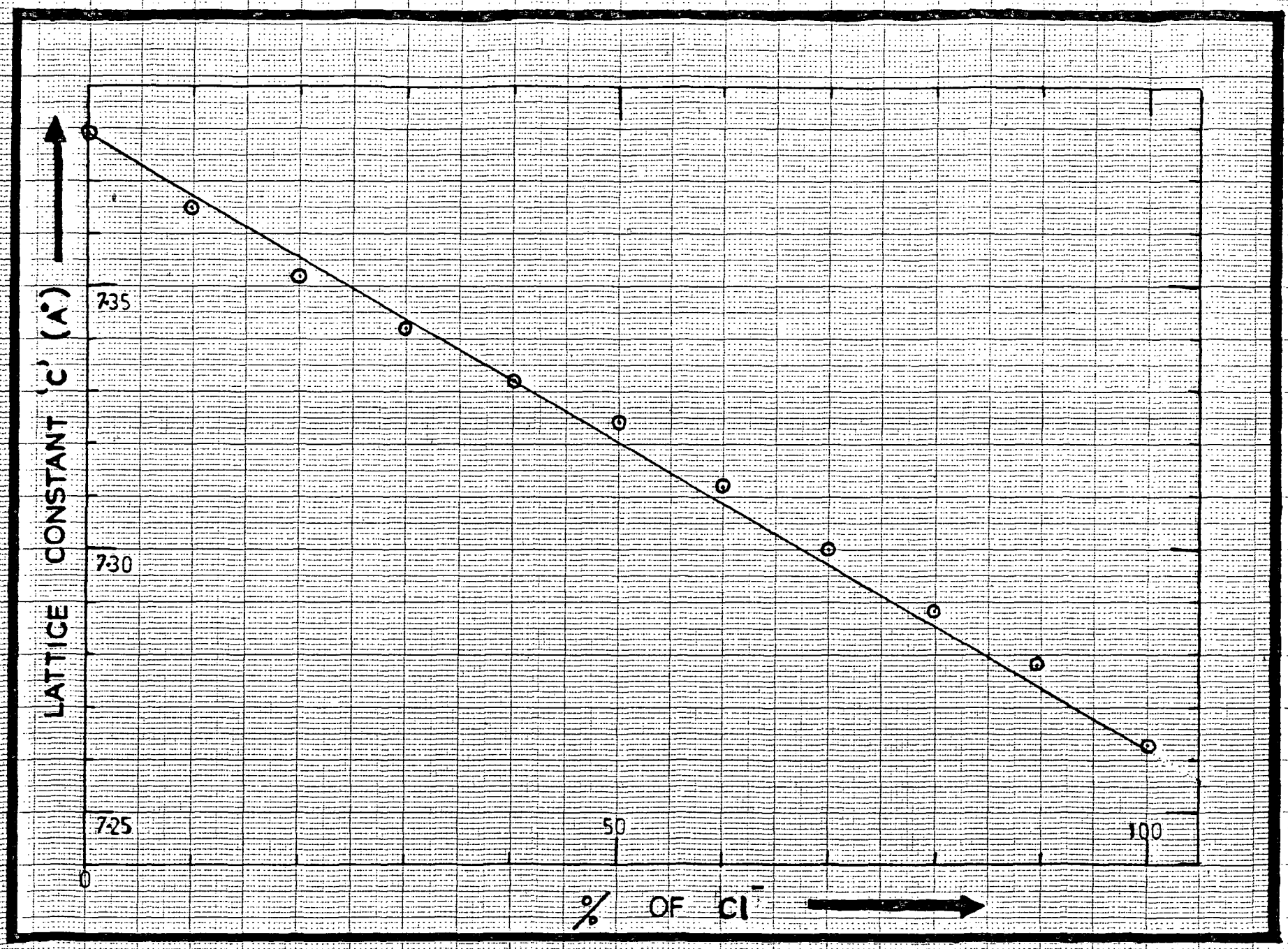

FIG :- 3·3

FIG :- 34

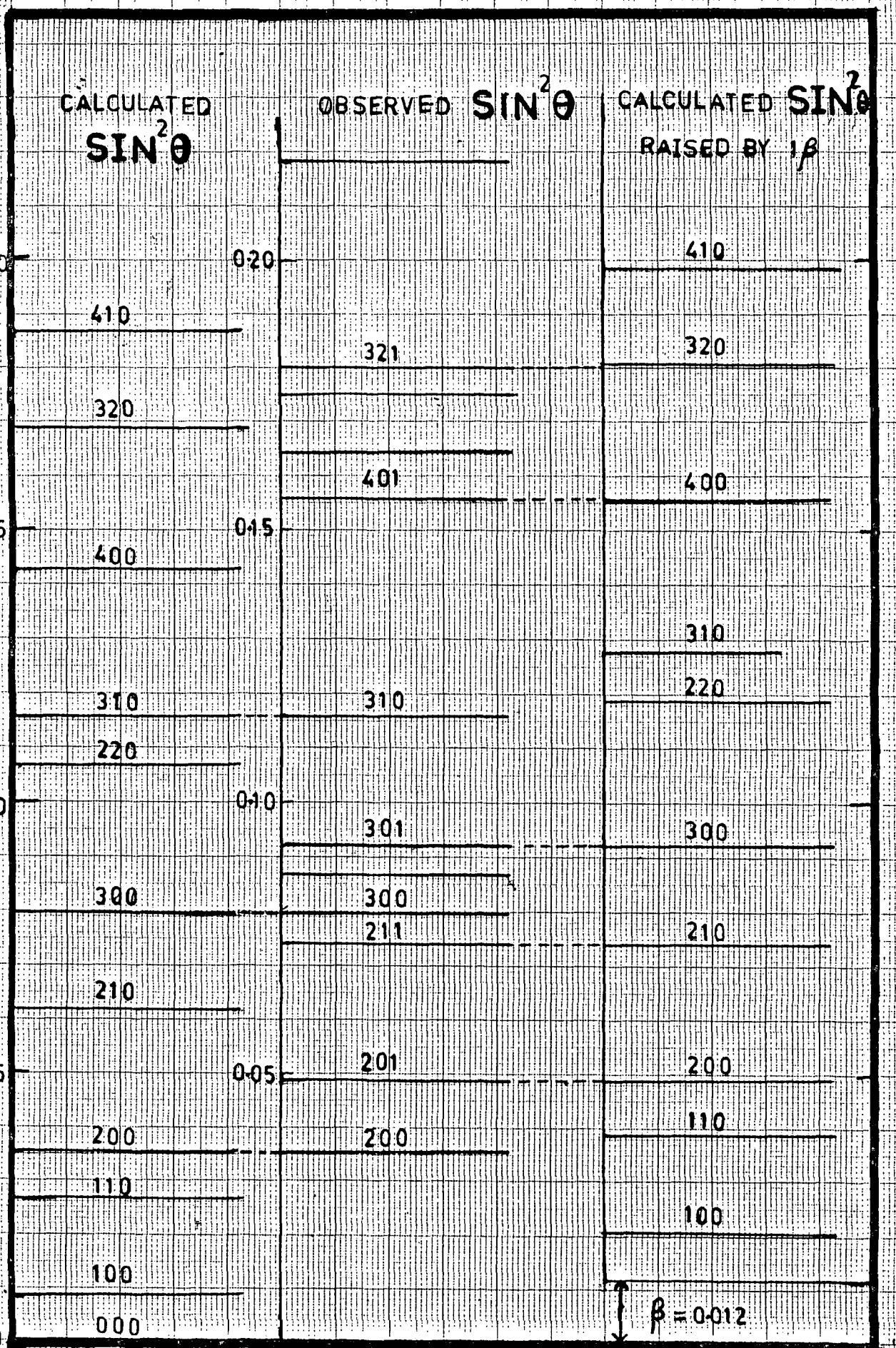

FIG:-3·5 FIG 3·6 FIG 3·7

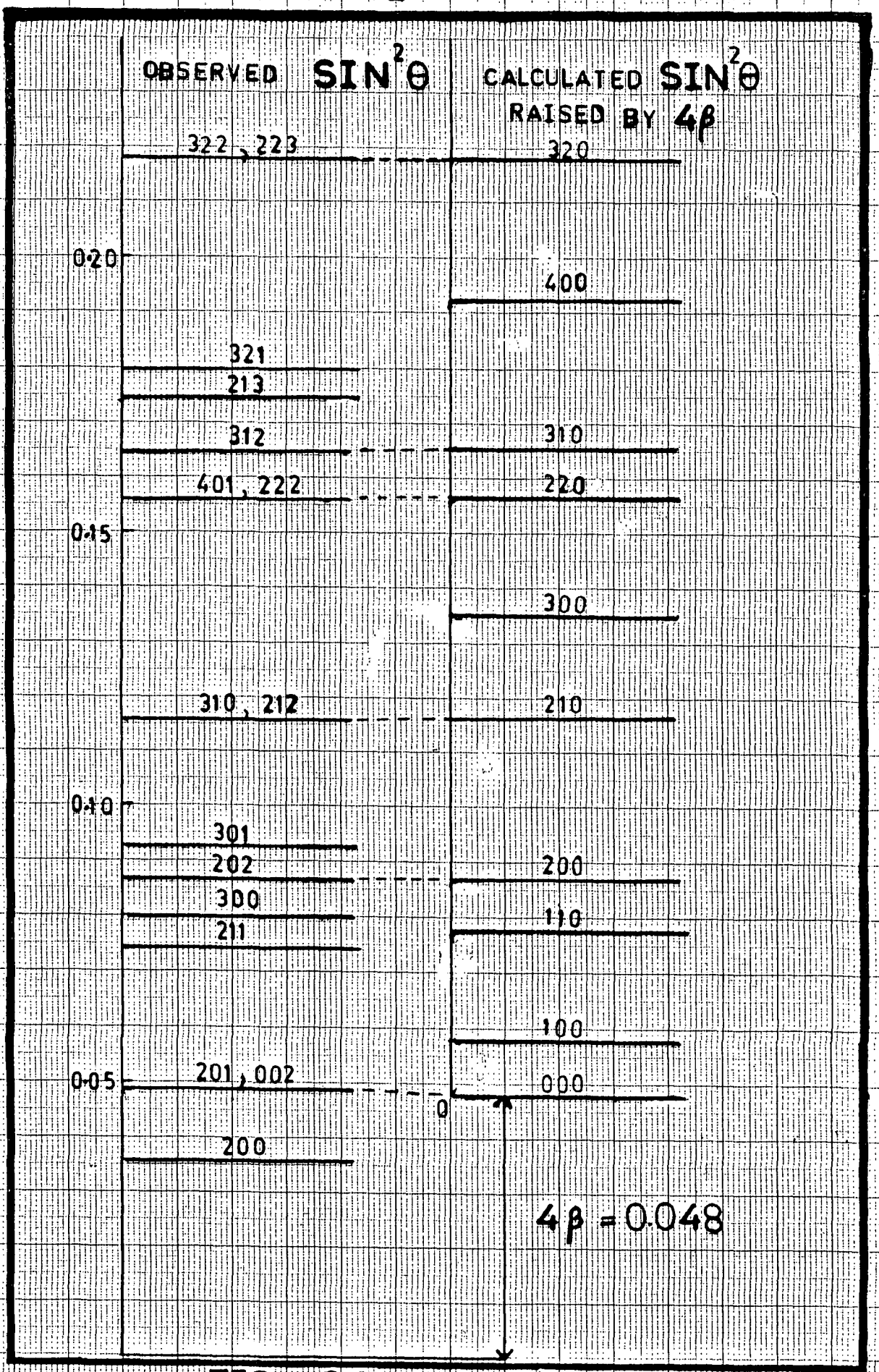
OBSERVED $SIN^2\theta$
CALCULATED $SIN^2\theta$
RAISED BY 4β
322, 223
320
0·20
400
321
213
312
310
401, 222
220
0·15
300
310, 212
210
0·10
301
202
200
300
110
211
100
0·05
201, 002
000
0
200
$4\beta = 0.048$

FIG :- 3·6 FIG 3·8

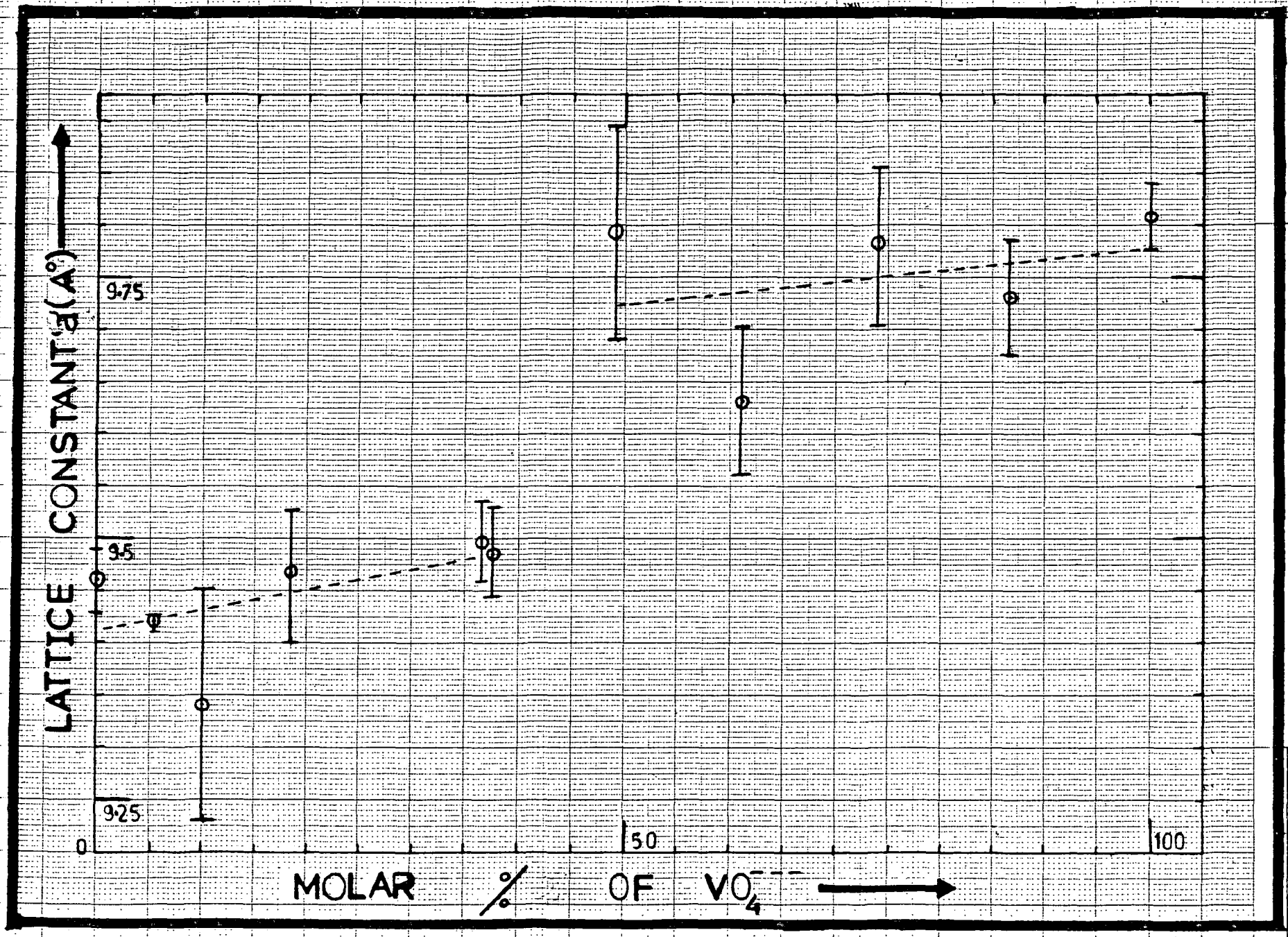

FIG :- 3.9

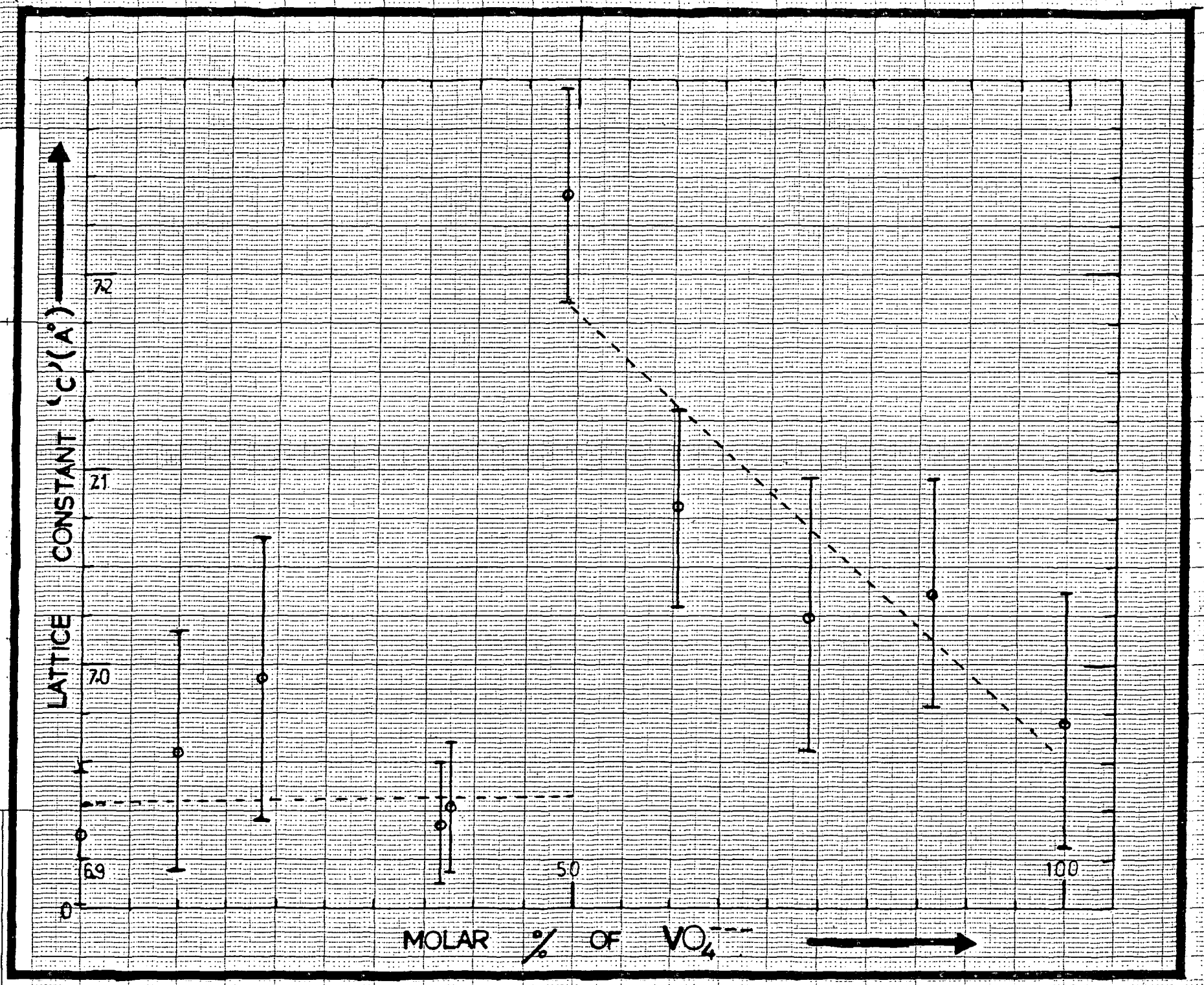

FIG:-3.10

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CHAPTER - 4.

ANALYSIS OF THE I.R SPECTRA OF THE SUBSTITUTED APATITES

4.0 Introduction :

The thorough analysis of the X-Ray diffraction data of the substituted apatites clearly showed that the lattice constants 'a' and 'c' did not vary smoothly with the degree of substitution. In fact, a break was observed around 50% degree of substitution.

To support the result obtained from the previous analysis, Infrared absorption Spectroscopy has been applied to the analysis of a different series of substituted apatites. The Infrared spectra originated in transitions between two vibrational levels of the molecules in the electronic ground state and are usually observed as absorption spectra in the near Infrared region.

The Infrared Spectra of these substituted apatites were recorded by the Perkin - Elmer Infrared Spectrometer, Model 983. The Substituted apatites chosen could be presented as

$$\left[Pb_5(PO_4)_{3(1-x)} (VO_4)_{3x} (OH) \right]_2$$

Where 'X' denoted the fraction of Vanadate (The preparation of this series of substituted apatites was given in Appendix C (and did not form part of the thesis)

4.1 Vibrational Modes of the Molecules.

The substituted apatites under study were powdered crystalline solids in which the crystallographic unit cell contained several polyatomic ions. The internal modes of vibration of the VO_4^{---}, PO_4^{---} occured in the region 700 - 1200 cm^{-1}.

4.2 I.R Spectroscopy

4.2.1 Instrumentation :

The Spectra of the substituted apatites were recorded by using the Perkin - Elmer Model 983 Spectrophotometer with a dedicated data processor. The instrument can record the transmittance or absorbance of infrared radiation through a sample during a selected time period in either the single or double beam mode. Our spectra had been taken in the double beam mode. After the radiation passes through the sample, a monochromator is used to produce a spectrum or a fixed frequency (expressed in wave number units) during the recording period. The range of frequency is 180 - 4000 cm^{-1}

The samples were prepared by applying Nujol technique. The technique (4.1) is preferable compared to Potassium bromide pellet technique in the sense that there might be a possibility of cation exchange reaction with KBr. Moreover the material under investigation may also undergo changes in crystalline form as a result of the high mechanical pressure (10,000 p s i) used in the pelleting process.

4.2.2 Procedure :

The spectra which gave the positions of Nujol peaks were recorded. Fig : 4.1 was a typical spectrum taken for the pure Nujol. Fig : 4.2 was another typical spectrum of a pure compound. The Vanadate peaks were found at 724 cm^{-1} and 808 cm^{-1} . At 724 cm^{-1} , there was an overlapping with the Nujol peak and hence correction was done when the area under the Vanadate peaks was estimated.

The location of the Phosphate peaks in the spectra was also noted down for the whole series of the substituted apatites. The peaks occured around 972 cm^{-1} and 1154 cm^{-1}. The areas under the peaks were measured. Besides measuring the areas under the Phosphate and Vanadate peaks, their heights from the background were determined.

4.3 Influence of the Crystallographic Environment on the Vibrational Modes of Molecules and Ions.

The location of the radicals (VO_4^{---} or PO_4^{---}) in the I.R Spectra differ considerably as compared to when they are in a crystalline environment. The changes in I.R behaviour may throw some light on the crystal structure. The crystal structure affects the Vibrational modes in two ways.Unlike the free radical which had the tetragonal

symmetry in free space, the crystal fields either hexagonal or monoclinic may split the natural vibrational modes of the radicals, or change their frequencies. Secondly, if there are two molecules (as in the case of apatites) in the Unit cell, there could be interaction between them to modify the frequencies.

However, these influences are rather difficult to observed as at room temparatures, the lattice excitation and other impurity modes spread the absorption spectra. Broadly speaking one expects apart from slight drift in the peak frequencies, the height of the peak to reflect the changes in the crystal structure. The relevant characteristics of the peaks in substituted apatites is given in Table 4.1 . Measurements for the whole series of substituted apatites had been repeated so that the results obtained after analysis became more reliable. Regarding the areas under the peaks (Table 4.2), it is expected that there should not be any change. In the case of isomorphous substitution, one expects that the area under the phosphate (or Vanadate) peak to represent the fraction of phosphate (or Vanadate).

A graph of $y = (A_v - A_p)/(A_v + A_p)$

Where A_v = Area under Vanadate peak

and A_p = Area under Phosphate peak.

versus the degree of substitution clearly supports the linear behaviour as shown in Fig : 4.1 .

On the other hand, a similar analysis of the heights of the peaks rather than the areas shows some clear cut systematic changes in crystal structure, the plot of

$$z = (h_v - h_p)/(h_v + h_p)$$

Where h_v = Peak height at VO_4^{---} frequency

h_p = Peak height at PO_4^{---} frequency.

versus the degree of substitution shows marked deviation from the linear behaviour. This shows two distinct linear behaviours on the two regions 100% - 50% and 50% - 0%. The Least-Square-Fit estimates of the intercepts at 50% and the slopes along with their error estimates are shown in the Table 4.3 .

4.4 Conclusions from I. R Spectra

The analysis of the I. R Spectra showed that the areas and heights when plotted versus the level of substitution (Figs : 4.3 - 4.4) supported our expectation. This comfirmed that when PO_4^{---} was substituted by VO_4^{---} in the apatites, the behaviour of the I.R Spectra in the regions 100% - 50% and 50% - 0% were observed to be distinctly different.

As seen from Table 4.3 of the previous section, there was no clear cut difference between the intercepts of the two lines in the two regions (100% - 50% and 50% - 0%) obtained by plotting the peak heights versus the degree of substitution. But there was the difference in the slopes which was much more than the estimated errors in them, the areas under the peaks as expected showed a linear behaviour with the degree of substitution (Fig : 4.3). The best fit is presented by the dashed line.

4.5 Crystal Structure of Substituted Apatites.

4.5.1 Summary from X-Ray and I.R data.

The analysis of the X-Ray and I.R data of the synthesized apatites $\{ Ca_{10}(PO_4)_6(OH)_2$ and $Pb_{10}(PO_4)_6(OH)_2 \}$

at different degree/of substitution of PO_4^{---} by VO_4^{---} (in both cases)clearly suggested a Phase Transition around 50% degree of substitution. The results obtained from the analysis of the two different data were very consistent as both showed that there was a different linear behavior in the two regions 0%-50% and 50%-100% separately. In both the cases,there was a marked deviation in the slopes when the best fit was done in two regions. Hence this is a direct contradiction with Vegard's Law.

4.5.2 Previous Work on Mineral and Synthesized Apatites.

The study on Crystal Structure of apatites is considered an important that International Union for Crystallography (I.U.Cr.) (4.2) had formed a Commission on Crystallographic Apparatus in the year 1966 to analyse thoroughly the crystal structure of apatites both mineral and synthesized. Young (4.3) had shown marked deviation from hexagonal structure for the substituted apatites and established a mono-clinic phase. This was shown to be the case for both the synthesized and mineral apatites. A particular study on chloro-apatite showed the establishment of the Hexa-mono transition in substituted apatites at 37% degree of substitution.

The failure in assigning some lines in the X-Ray Diffraction data within tolerable error as mentioned in section 3.3 may be presumably explained as due to change in crystal structure.

4.5.3 Techniques for Studying Crystal Structures.

The techniques used for studying crystal structure are broadly classified (4.3) into Diffraction techniques and Spectroscopic techniques. The Diffraction techniques which include the X-Ray Diffraction (XRD), Neutron Diffraction (ND) and Electron Diffraction (ED) are primarily sensitive to spatial Relative Positions and Vibration of atoms. On the other hand, the departure of some atoms or atom groups from the average structural behavior has been studied by using Spectroscopic techniques rather than Diffraction techniques. The Spectroscopic techniques include the Infrared (IR), Laser Raman (LR), Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR), Optical Emission and Fluorescence. The Diffraction and Spectroscopic techniques are highly complementary in nature. It is reported that the application of both techniques to the same problem and same specimens often can be particularly fruitful.

CAPTIONS FOR THE TABLES

TABLE 4.1 gives the areas under the Vanadate and Phosphate peaks and the ratios between them for different degrees of substitution of Phosphate by Vanadate.

TABLE 4.2 gives the Peak heights of the Vanadate and Phosphate from the background and the ratios between them for different levels of substitution.

TABLE 4.3 gives the slopes and intercepts of the ratios of the Peak heights of Vanadate and Phosphates in two different regions that is 100% - 50% and 50% - 0% degrees of substitution of Phosphate by Vanadate.

TABLE 4.1

Molar % of VO_4 ---	Area (in cm^2) under VO_4 --- Peak (A_V)	Area (in cm^2) under PO_4 --- Peak (A_p)	$A_V - A_p$ (in cm)	$A_V + A_p$ (in cm)	$\frac{A_V - A_p}{A_V + A_p}$
100	9.647	0.000	9.647	9.647	1.000
100	3.667	0.000	3.667	3.667	1.000
94	5.413	0.000	5.413	5.413	1.000
94	11.297	1.010	10.287	12.307	0.836
80	2.706	0.400	2.312	3.112	0.743
80	5.181	0.906	4.275	6.087	0.702
70	3.835	2.053	1.702	5.888	0.303
70	4.228	2.106	2.122	6.334	0.335
57	3.828	1.888	1.940	5.716	0.339
57	5.296	3.067	2.229	8.363	0.266
50	9.348	7.973	1.375	17.321	0.079
50	5.730	3.733	1.997	9.463	0.211
50	6.575	4.240	2.335	10.815	0.216
40	5.261	6.720	-1.459	11.981	-0.122
40	3.181	6.160	-2.979	9.341	-0.319
25	2.187	5.040	-2.854	7.226	-0.395
25	3.163	6.750	-3.587	9.913	-0.362
25	3.903	7.760	-3.857	11.663	-0.331
10	2.464	5.120	-2.656	7.584	-0.350
10	1.129	3.547	-2.418	4.676	-0.517
10	0.966	5.520	-4.554	6.486	-0.702
0	0.611	7.070	-6.549	7.681	-0.841
0	0.221	9.947	-10.167	9.726	-1.045
00	0.544	4.240	-3.696	4.784	-0.773
0	1.167	6.264	-5.097	7.431	-0.686

TABLE 4.2

Molar % of VO_4	Peak height (in cm) of VO_4	Peak height (in cm) of PO_4	$h_v - h_p$ (in cm)	$h_v + h_p$ (in cm)	$\frac{h_v - h_p}{h_v + h_p}$
100	4.00	0.00	4.00	4.00	1.00
100	0.00	0.00	2.00	2.00	1.00
94	0.70	0.70	4.00	5.40	0.74
94	2.50	0.00	2.50	2.50	1.00
80	2.55	0.60	1.95	3.15	0.62
80	1.70	0.35	1.35	2.05	0.66
70	2.40	1.10	1.30	3.50	0.37
70	2.05	0.90	1.15	2.95	0.39
57	1.85	1.20	0.65	3.05	0.21
57	2.40	1.80	0.60	4.20	0.14
50	4.40	4.20	0.20	8.60	0.023
50	2.95	1.80	1.15	4.75	0.24
50	3.15	1.90	1.25	5.05	0.25
40	2.70	3.05	-0.35	5.75	-0.06
40	2.20	2.20	0.00	4.40	0.00
40	2.40	2.90	-0.50	5.30	-0.094
25	2.50	3.15	-0.65	5.65	-0.12
25	2.40	2.70	-0.30	5.10	-0.06
25	1.55	1.90	-0.35	3.45	-0.101
25	1.00	2.20	-1.20	3.20	-0.38
10	0.70	1.35	-0.65	2.70	-0.24
10	1.20	3.60	-1.40	3.80	-0.37
10	1.70	3.70	-2.00	5.40	-0.37
0	0.95	1.60	-0.65	2.70	-0.24

TABLE 4.3

Ranges of the regions relative to the degree of substitution of VO_4^{---}	Intercept ($X\ 10^{-2}$)	Error in intercept ($X\ 10^{-2}$)	Difference in Intercept ($X\ 10^{-2}$)	Error in the difference.
50% - 0%	9.023	1.538		
			2.144	1.729
100% - 50%	11.167	0.791		

Regions	Slope ($X\ 10^{-2}$)	Error in Slope ($X10^{-2}$)	Difference in slopes ($X\ 10^{-2}$)	Error in the difference. ($X\ 10^{-2}$)
50% - 0%	0.941	0.0502		
			0.778	.0568
100% - 50%	1.719	0.0265		

CAPTIONS FOR THE FIGURES

FIG : 4.1 shows the locations of the Nujol peaks.

FIG : 4.2 shows a typical I.R spectrum of a pure compound $Pb_{10}(VO_4)_6(OH)_2$

FIG : 4.3 shows the linear relationship between the areas under the Phosphate and Vanadate I.R peaks versus the degree of substitution by Vanadate.

FIG : 4.4 shows the behaviour of the Peak heights of Phosphate and Vanadate Versus the degree of substitution.

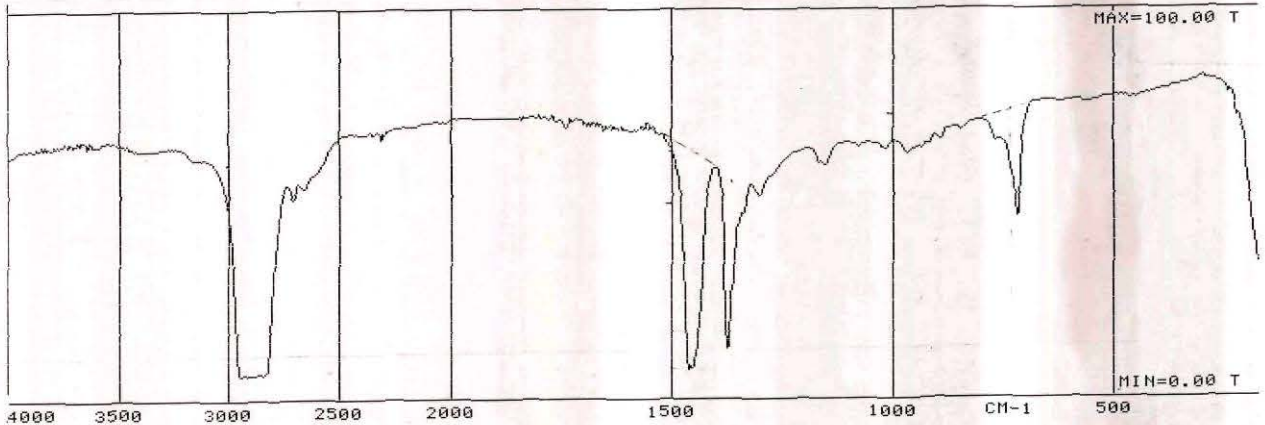

FIG :-4.1

X: 3821 4000- 180 1.00 6.26 82.73 T 4 10B

REF. VALUES : 4000 62.5 2000 71.8 PAGE 1

3888.	64.1	3840.	64.5	3826.	64.6	3808.	64.8	3788.	65.0
3770.	64.9	3729.	65.3	3707.	65.5	3678.	65.9	3658.	65.9
3647.	65.3	3626.	65.4	3618.	65.4	3602.	65.3	3556.	66.0
3547.	66.0	3377.	63.8	2920.	6.3	2841.	6.3	2717.	51.2
2663.	54.2	2354.	67.1	2344.	67.9	2333.	68.0	2314.	67.0
2059.	70.7	1892.	71.8	1845.	71.8	1777.	71.9	1762.	71.0
1741.	69.7	1728.	71.1	1702.	70.5	1694.	69.9	1686.	70.0
1674.	69.8	1665.	69.4	1654.	68.5	1646.	69.6	1635.	69.3
1628.	69.2	1624.	69.3	1618.	69.0	1578.	68.2	1567.	69.2
1553.	69.3	1548.	68.9	1528.	67.7	1510.	64.9	1463.	7.6
1377.	12.9	1307.	52.3	1170.	60.3	1156.	60.0	1079.	64.9
1019.	64.1	967.	63.1	891.	66.1	847.	69.0	722.	46.5
559.	75.9	462.	76.8	247.	78.1	225.	71.8	213.	66.3
207.	58.2	189.	39.3						

END 67 PEAKS FOUND

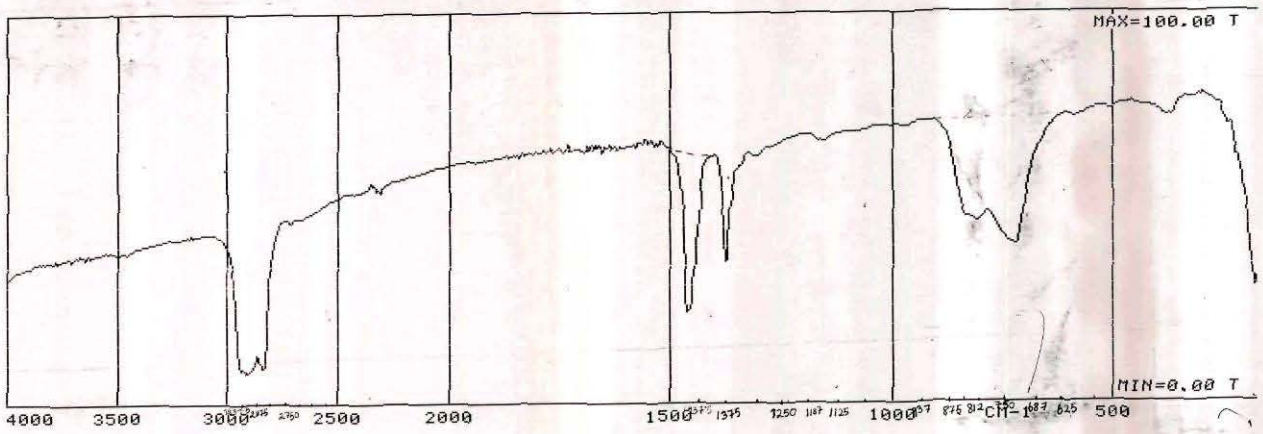

FIG :- 4.2

X: 3821 4000- 180 1.00 736 79.71 T 4 1DB

REF. VALUES : 4000 32.4 200 61.4 PAGE 1

3840.	35.8	3826.	35.9	3808.	36.1	3790.	36.2	3772.	36.3
3709.	36.8	3678.	37.5	3669.	37.7	3647.	37.1	3626.	37.5
3595.	38.1	3564.	38.2	3540.	38.4	3504.	38.3	3485.	38.5
3163.	42.8	2911.	7.2	2845.	8.9	2719.	46.2	2330.	54.0
2325.	55.6	2315.	54.	1941.	61.8	1866.	63.1	1844.	63.0
1781.	64.4	1766.	64.	1741.	64.1	1727.	64.6	1704.	64.7
1695.	64.2	1687.	64.	1674.	65.1	1665.	65.1	1654.	64.2
1646.	65.2	1635.	65.	1624.	64.9	1618.	64.9	1602.	65.3
1578.	65.3	1574.	661	1565.	66.3	1553.	66.3	1538.	65.8
1528.	65.8	1462.	231	1409.	63.0	1377.	36.2	1344.	60.4
1307.	63.2	1155.	671	808.	46.5	761.	43.8	724.	40.4
595.	73.2	372.	7.3	258.	72.9	199.	42.4	185.	29.8

END 60 PEAKS FOUND

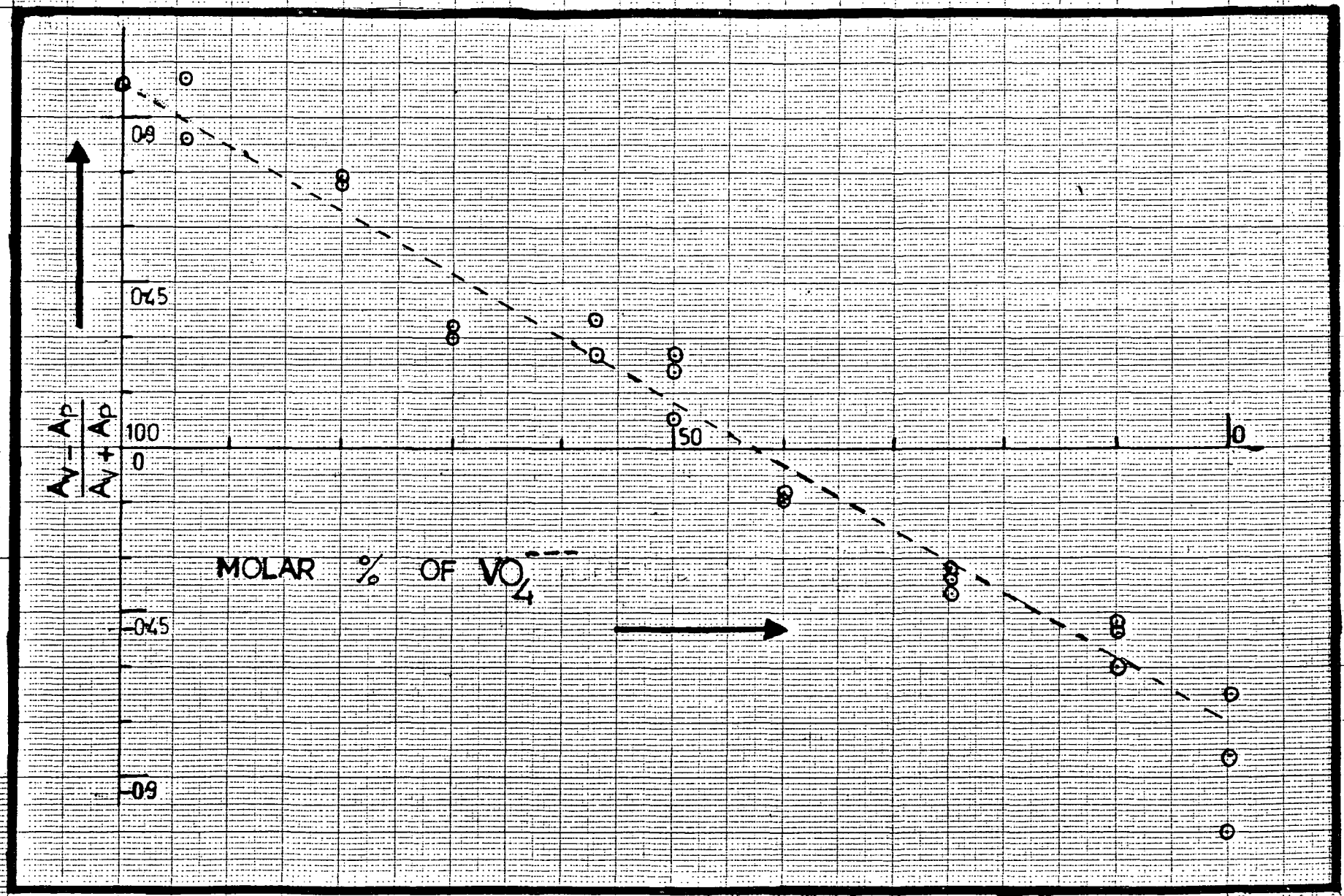

FIG:-4·3

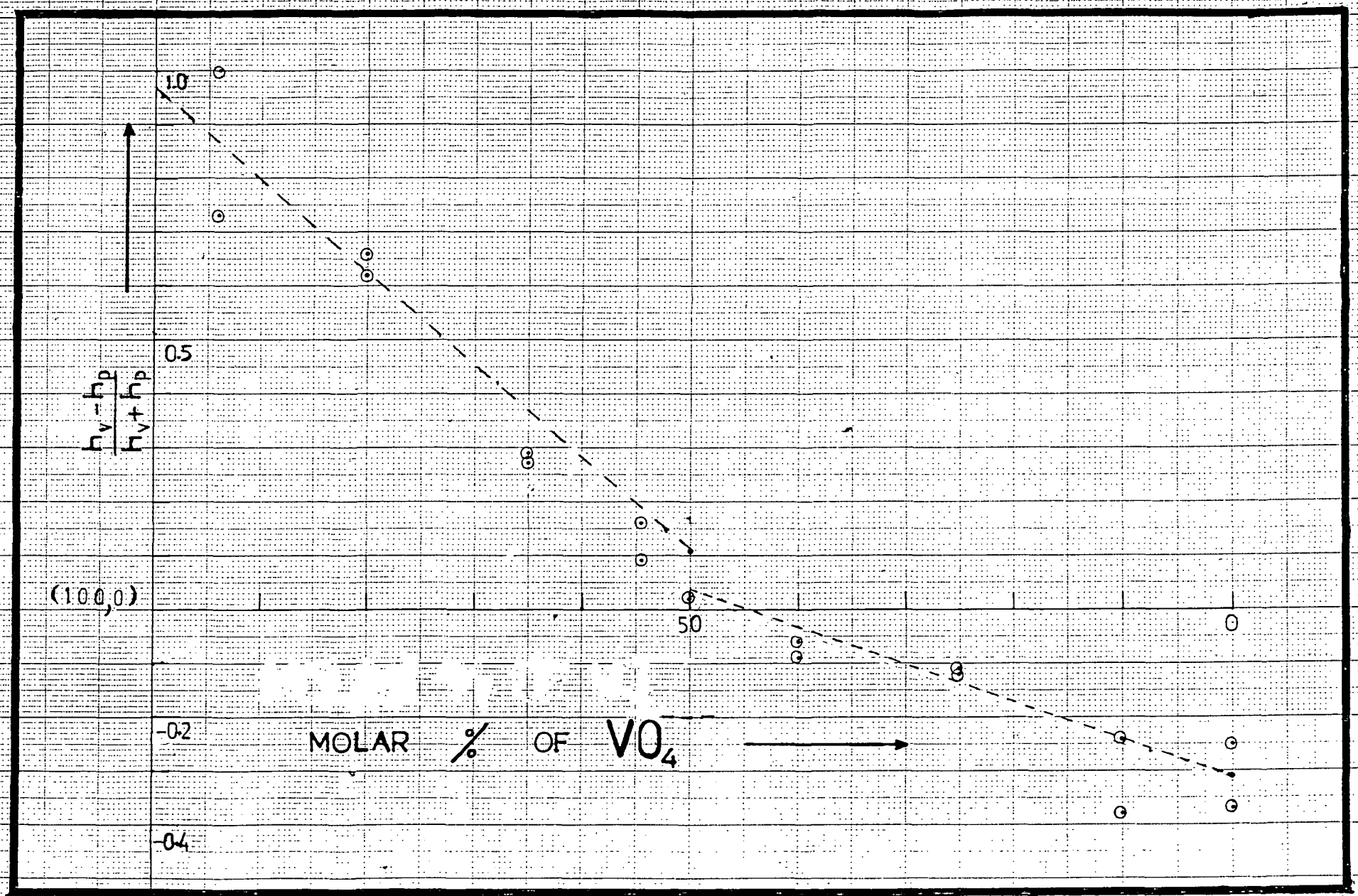

FIG :- 4.4

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CHAPTER - 5

CONCLUSION

Physics, the most basic science had influenced several other disciplines considerably. Several physical experimental techniques played important roles in researches in other disciplines - like C^{14} dating in Archeology History and Geology, Electron Spin Resonance, Spectroscopy, X-Ray diffraction, Electron Microscopy, Nuclear Tracer Technique, Ion Implantation, Atomic Absorption Spectroscopy, Mass Spectroscopy and several other have an impact on other branches of science which lead to the new findings; perhaps, the help rendered by the physicists in different fields is beyond comparison.

Physics involves mostly experimental work. In any experimental work, one measures specific physical parameters. Besides measuring, one should keep in mind that checking the accuracy, reliability and reproducibility of the measurement is to be done before interpreting the results. If necessary, one should even try to improve the accuracy, reliability and minimise the errors.

The theory of errors and Design on experiments both these subjects are unfortunately not studied widely and not used by most experimenters in other disciplines (sometimes in physics even). Consequently, full benefit can not be obtained just by using powerful physical techniques. Combining powerful statistical techniques with physical Analytical instruments can lead us to better understanding in Geology, Chemistry, Biology etc. This is true because the results obtained from the analysis have been examined by estimating the error in them in more detail.

Simple check like repetation of an experiment, multiple checking of several parts, using an alternative experiment for the same purpose make the results more reliable.

In the present thesis, two different problems have been studied. Trace elemental analysis of coal-fields in North-Eastern India, which is of importance to Geologists. Unusually large amounts of Titanium was identified in an area called Bapung in Jaintia Hills District, Meghalaya. This occurence of a fairly high amount of Titanium compared to other areas was somehow missed by several previous workers. The second problem dealt with structural changes in substituted apatites- a problem of importance to solid state Chemistry and medicine.

A definite deviation from Vegard's Law is established which suggests phase transition around 50% degree of substitution.

Finally, we hope that we have established the importance of using the statistical techniques for analysing the experimental data before any conclusion can be drawn. The findings presented in this thesis are the ones which have escaped from the sight of the previous workers.

APPENDIX A

Extract from

MEGHALAYA COMES ON THE BAUXITE MAP OF INDIA.

G.S.I., North Eastern Regional News Letter 2 (1), (1983), page 15.

Quaternary investigations by S/Shri B.C. Poddar and K.K. Sinha in Meghalaya have led to the discovery of a spectacular lateritic bauxitic weathering profile at Lumkynthang (25° 35' 15" N : 92° 06' 55" E) about 50 Km from Shillong. Initial scanning of the scarp sections reveals that a very thick (+ 30 m) residual, in situ laterite - bauxite cap has developed on a substrate of coarse crystalline pyroxenite which is a component of the Sung Valley Magmatic Complex of Cretaceous (? Ca 85 m.y) age. This complex is intrusive into a suite of Precambrian metamorphites. The weathered cap lies at an elevation of 1100 m above mean sea level. It persists essentially as a flat relict patch of "mesa" in the landscape of the Sung Valley which is dominated by polycyclic slopes. Megascopic identification of bauxite has been fully corroborated by chemical and X-Ray analysis. The dominant mineral phased are anatase, diaspore and hematite. Chemically, the bauxite appears to belong to "tiallitic" variety characterised by uncommonly high content of TiO_2 ,

The discovery marks a break-through in our geological knowledge of Meghalaya. Investigations are in progress to assess and evaluate the economic and scientific value of the occurrence.

APPENDIX B

Extract from

Petrology of the carbonatites and associated rocks of Sung Valley, Jaintia Hills District, Meghalaya, India.

By P. Krishnamurthy
Atomic Minerals Division, Begumpet, Hyderabad

Journal Geological Society of India 26 (1985), 361.

Sung Valley has a fairly easy access and is located between latitude 25°31' - 25°38' N and longitude 92°05' - 92°10' E in the Jaintia Hills district of Meghalaya. It is connected by road from Shillong (N.H. 44 between Shillong and Jowai) the nearest bus stop being Mookundur situated at a distance of about 49 Km from Shillong.

The country rocks are primarily Pyroxenites, Peridotites, Ijolites, Carbonatites, Syentites Feldspathic Veins, Fenites and Melilite bearing types. Fourteen chemical Analyses of major and minor element compositions of the different rock types and averages are given in Tables I, II, III and IV. Assuming a magmatic evolution among the different members of the silicate rocks, the Variation of Metallic oxides vs MgO shows

a) A steep increase of CaO reaching a maximum in pyroxinites followed by a steep decrease.

b) Steady decrease in Fe_2O_3 + FeO and MnO

c) Steady increase in Al_2O_3, Na_2O, K_2O, TiO_2

d) Initial increase of SiO_2 and P_2O_5 followed by a decrease.

TABLE I. Chemical analyses of carbonatites from Sung Valley, Meghalaya, India.

Wt %	1	2	3	4	5
SiO_2	<1.00	<1.00	<1.00	<1.00	<1.00
TiO_2	0.01	<0.05	0.04	0.02	0.62
Al_2O_3	<0.10	1.17	<0.10	<0.10	1.54
Fe_2O_3(T)	0.30	2.70	5.00	1.80	1.30
MnO	0.20	0.10	0.10	0.10	0.30
MgO	2.10	3.50	2.40	2.30	16.80
CaO	53.20	51.30	51.80	49.80	34.70
Na_2O	0.10	0.08	0.04	0.03	0.06
K_2O	0.01	0.01	0.02	0.01	0.01
P_2O_5	<0.01	9.70	6.30	2.70	4.10
H_2O^*	0.40	0.30	0.40	0.20	0.20
LOI*	2.10	1.7	2.3	1.3	0.5
CO_2	40.10	28.0	31.0	38.3	40.2
Total	99.32	98.29	99.50	96.56	100.33

TABLE I. Continued. (Trace Elements)

ppm	1	2	3	4	5
Ni			<4	<4	<4
Co	<4	<4	<4	<4	<4
Cr	13	13	20	19	2
V	BDL	57	83	39	56
Zr	<10	628	117	11	16
Nb	154	503	237	606	512
La	50-100	50-100	50-100	50-100	30-50
Y	50-100	50-100	50-100	50-100	10-50
U	29	0.3	0.5	<0.3	18
Th	7.8	6.5	5.2	<0.6	65.1
Cu	15	45	30	14	4
Ba^+	523	521	513	517	622
Sr^+	3909	3609	3396	3355	1399
Ce	467	244	471	308	149
Cation Norm (%) (Partial) :					
Calcite	94.62	70.26	76.44	80.52	7.38
Dolomite	-	-	-	12.12	80.80
Apatite	-	20.08	12.82	5.37	0.79
Hematite	0.20	1.87	3.40	1.20	0.79

Index to Numbers :

1. Sovite. 2. and 3. Apatite sovite. 4. Dolomitic sovite. 5. Beforsite.

*Excluding CO_2 (T) Total iron as Fe_2O_3

+Ba and Sr data on analogous samples from Verma et al (1977)

Major and minor oxides analysed by Tikoo et al 1978 - Rapid methods.

Trace elements by Patwardhan et al (1979) - Optical spectrograph.

U and Th data by Atal and Bhalla (1978)- Gamma-ray spectrometry.

Cation norms following the methods of Shaw (1969).

BDL - Below Detection Limit (<4 ppm).

Table II. Chemical analyses of silicate rocks from Sung Valley, Meghalaya, India.

Wt.%	6	7	8	9	10	11	12	13	14
SiO_2	48.80	45.50	42.50	44.50	67.30	67.30	42.80	33.10	39.10
TiO_2	0.53	0.76	0.55	0.38	0.89	0.11	0.42	1.08	0.09
Al_2O_3	2.12	3.70	17.40	20.20	15.00	16.90	2.10	<0.10	0.50
Fe_2O_3	4.60	4.20	3.90	5.70	5.1	2.70	2.20	15.20	9.10
FeO	3.33	3.40	4.10	3.30	1.2	0.50	2.50	2.90	1.50
MnO	0.10	0.10	0.13	0.20	0.10	0.20	0.40	0.30	0.20
MgO	17.50	13.70	4.70	3.50	0.4	0.50	0.30	32.20	34.30
CaO	21.00	23.80	15.30	9.40	1.50	0.90	42.00	0.30	0.30
Na_2O	1.18	1.05	5.05	5.39	4.97	3.96	0.97	0.05	0.08
K_2O	0.75	0.22	2.56	3.32	4.07	6.21	0.30	0.01	0.03
P_2O_5	<0.01	<0.01	1.24	0.09	0.10	<0.01	1.59	<0.01	<0.01
H_2O^+	0.20	0.30	0.60	0.30	0.4	0.3	0.3	2.30	2.90
LOI	0.20	1.10	2.10	2.30	0.4	0.9	0.6	12.11	12.52
Total	100.31	97.83	100.13	98.48	99.93	100.18	96.48	99.55	100.62

TABLE II. Continued

ppm	6	7	8	9	10	11	12	13	14
Ni	502	462	16	22	21	20		1115	
Co	41	25	10	14	<4	<4		141	
Cr	843	916	11	19	16	16		1635	
V	126	172	300	137	36	104		105	
Zr	55	139	457	267	1037	57		27	
Nb	66	57	198	56	370	145		45	
La	<30	<30	<30	<30	<30	<30		<30	
Y	<10	<10	10.50	<10	10.50	<10		<10	
U	0.3	0.3	0.6	0.4	2.3	0.8	0.8	0.2	0.2
Th	1.6	1.7	4.7	4.9	11.0	0.7	4.7	0.5	0.7
Cu	18	13	8	9	12	9		8	
Ba^+			540	481					
Sr^+			313	360					

Index to Sample Nos. :
6. Medium-grained pyroxenite. 7. Coarse-grained pyroxenite 8. and 9. Ijolite.
10. Syenite. 11. Fenite. 12. Wollastonite rock. 13. Peridotite (magnetite-rich type).
14. Peridotite.

These features seem to suggest a mineral controlled magmatic evolution for the parental liquid of the suite.

Evidences from the major, minor and trace elements variations among the different silicate rocks and their mineralogical compositions suggest that the different rock types encountered in Sung Valley could be derived from a parental alkali pricritic or melanephelinite magma, although there is no direct evidence on the surface for the availability of such a liquid.

TABLE III. Cation norm (%) of silicate rocks of Table II

	6	7	8	9	10	11	12	13	14
Q	-	-	-	-	16.98	16.00	-	-	-
Or	-	-	-	15.0	24.10	36.90	1.95	0.05	0.20
Lc	4.80	0.81	12.16	4.0	-	-	-	-	-
Ab	-	-	-	-	44.70	35.75	9.50	0.50	0.70
Ne	3.21	4.20	27.33	29.64	-	-	-		-
An	-	4.56	27.80	34.52	5.44	3.60	0.88	-	1.28
Acm	3.60	-	-	-	-	-	-	-	-
Di	65.80	75.40	12.48	3.08	2.28	2.07	7.00	1.32	-
Wo	-	-	-	-	-	-	47.57		-
Cs	5.95	6.15	5.34	-	-	-	26.37		
Hy	-	-	-	-	-	-	-	33.90	49.14
Ol	16.68	22.25	77.41	6.94	-	-	-	48.90	40.29
Il	0.74	1.10	0.78	0.54	1.24	0.16	0.64	1.68	-
Mt	3.36	4.54	4.09	6.09	0.93	1.41	2.52	5.01	3.78
Hm	-	-			2.94	0.95	-	8.48	4.36
Ap	-	-	2.61	0.19	0.21	-	3.62		
Cor	-	-	-	-	1.30	3.15	-	-	0.07

TABLE IV. Average compositions of some representative samples of Sung Valley along with averages of similar rock types.

Wt. %	1	2	3	4	5	6
SiO_2	42.40	47.55	43.50	67.30	41.55	38.12 - 47.26
Al_2O_3	0.59	2.91	18.80	15.95	7.25	11.99 - 20.82
TiO_2	0.69	0.64	0.46	0.50	3.31	0.32 - 3.90
Fe_2O_3	14.29	4.40	4.80	3.90	6.80	3.53- 7.08
FeO	2.58	3.36	3.70	0.63	7.77	2.16 - 6.46
MnO	2.29	0.10	0.16	0.15	0.20	0.11 - 0.35
MgO	39.06	15.50	4.10	0.45	13.02	3.30 - 5.70
CaO	0.35	22.40	12.35	0.95	16.93	6.45 - 22.56
Na_2O	0.07	0.96	5.22	4.46	1.38	4.65 - 11.69
K_2O	0.01	0 63	2.94	5.14	0.70	1.35 - 3.84
P_2O_5	<0.01	<0.01	0.66	0.10	0.59	0.16 - 1.87
CO_2	-	-	-	-	-	Nil - 1.66
H_2O_+	-	0.25	0.45	0.35	0.50	0.11 - 2.94
Total	100.33	98.30	97.14	99.88	100.00	

TABLE IV. Continued.

ppm	1	2	3
Ni	1115	482	19
Co	141	33	12
Cr	1635	879	15
V	105	149	218
Zr	27	97	362
Nb	45	61	127
La	<30	<30	<30
Y	<10	<10	
Ba			
Sr			
Rb			
U	0.3	0.4	0.6
Th	0.7	1.85	5.5
Cu	8	15	8

Index to numbers in Table IV :

1. Average of two peridotites 13 and 14 of Table II recalculated loss on ignition free.
2. Average of two pyroxenites (No. 6 and 7 Table II).
3. Average of two ijolites (No. 8 and 9 of Table II)
4. Average of syenitic types (No. 10 and 11 of Table II).
5. Average alkali pyroxenite (Nockolds, 1954).
6. Range of ijolite compositions. Samples included are from complexes such as Fen, Napak and Budeda (Tuttle and Gittins, 1966, p. 235, 212. 103 and 78 and East Africa Le Bas, 1977, p. 307).

APPENDIX - C

Extract from

Preparation and Characterization of Solid Solutions of Phosphate and Vanadate Apatites of Lead.

T.S.B. Narasaraju, S.K. Gupta and P.V.R. Rao
Department of Chemistry, School of Physical Sciences,
North - Eastern Hill University, Shillong - 793003,
India.

Current Science, 54, No. 2 (1985), 63

EXPERIMENTAL

The preparation of the samples was based on the following equations :

$$10\,Pb^{2+} + 6\,XO_4^{3-} + 2OH^- \Rightarrow Pb_{10}(XO_4)_6(OH)_2$$

Where X = P or V or (P + V). While stock solutions of Pb^{2+} and PO_4^{3-} were prepared from lead acetate and diammonium hydrogen phosphate in double distilled water, sodium orthovanadate solution was obtained by dissolving vanadium pentoxide in sodium hydroxide solution. All these solutions were preserved in polyethylene containers. The amounts of lead, phosphorus and vanadium present in the respective solutions were determined by complexometric[11], Washburn and Shear's[12] and iodometric[13] methods respectively. Aqueous solutions of the reactants containing stoichiometric quantities required for an yield of 30 g of the sample were used. An appropriate volume of lead acetate solution added to a required volume of ethylenediamine [10,14,15], to maintain a pH of 12 on dilution to 1000 ml was taken in a 3 litre round bottom flask.

Diammonium hydrogen phosphate and/or sodium orthovanadate solutions stoichiometric with that of Pb^{2+} solution taken were treated with ethylenediamine and diluted to 1000 ml such that the pH of the resulting solution was 12. This solution was added dropwise to that Pb^{2+}. The precipitation was done at 37 C to stimulate biological conditions. Air (free from CO_2) was bubbled through the medium to eliminate the formation of carbonate apatite. The precipitate was refluxed for about two hours in contact with the mother liquor, left overnight, filtered through a IG4 sintered glass crucible and washed with water till the washings were neutral. In order to eliminate extraneous phases[16] likely to get co-precipitated with the sample, the latter was equilibrated for about 6 hr with 2% EDTA solution maintained at a pH of 10. The sample was washed with acetone and air dried. A part of the sample was heated to 300 C for 6 hr[14] and cooled in a desiccated atmosphere. This was used for chemical, x-ray and IR analyses. The weight per cents of Pb, P and V of the samples were determined by methods[17] specially worked out by us for the purpose and reported in columns 3,4,5 of table 1. From these results the molecular formulae were calculated and given in column 7 of the table. The g atom ratio, Pb/(P + V) was calculated and included in column 6.

Table 1 Chemical Analyses of Solid solutions of Phosphate and Vanadate apatites of Lead.

Sl. No	Sample	Wt (%)			g atom ratio,	
		Pb	P	V	Pb/(P + V)	Molecular formula*
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	Lead Phosphate apatite (LPA)	77.86	6.97	-	1.67	$Pb_{10}(PO_4)_6(OH)_2$
2.	Solid Solution I	76.61	6.19	1.16	1.66	$Pb_{10}(PO_4)_{5.4}(VO_4)_{0.6}(OH)_2$
3	Solid solution II	77.36	5.13	2.74	1.70	$Pb_{10}(PO_4)_{4.5}(VO_4)_{1.5}(OH)_2$
4	Solid Solution III	76.69	4.15	4.22	1.71	$Pb_{10}(PO_4)_{3.69}(VO_4)_{2.31}(OH)_2$
5	Solid Solution IV	75.46	2.99	6.40	1.64	$Pb_{10}(PO_4)_{2.6}(VO_4)_{3.4}(OH)_2$
6	Solid Solution V	75.26	2.15	7.54	1.67	$Pb_{10}(PO_4)_{1.9}(VO_4)_{4.1}(OH)_2$
7	Solid Solution VI	75.69	1.32	8.81	1.69	$Pb_{10}(PO_4)_{1.2}(VO_4)_{4.8}(OH)_2$
8.	Lead Vanadate apatite (LVA)	74.37	-	10.80	1.69	$Pb_{10}(VO_4)_6(OH)_2$

* Based exclusively on Pb, PO_4 and VO_4 contents, (OH)) content being assumed to be stoichiometric.

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APPENDIX - D

Extract from

Preparation and Characterization of Solid Solutions of Phosphate and Vanadate Apatites of Calcium.

GUPTA, S.K., RAO, P.V.R. and NARASARAJU, T.S.B.

Indian Journal of Chemistry (in print)

Materials and Methods.

The sample were prepared based on the following equation :-

$$10\ Ca\ SO_4 + 6\ Na_3\ XO_4 + 2\ Na\ OH = Ca_{10}\ (XO_4)_6\ (OH)_2 + 10 Na_2\ SO_4$$

Where 'X' = P or V or (P+V) of desired proportion. Stock solutions of phosphate and vanadate were prepared by dissolving disodium hydrogen phosphate and vanadium pentoxide respectively in 0.5 M sodium hydroxide solution, preserved in polyethylene containers and analysed for phosphorus[10] and vanadium[11].

Appropriate volumes of the above solutions maintained at a pH of about 12 were mixed with a stoichiometric amount of calcium sulphate suspended in 0.5 M sodium hydroxide solution under CO_2- free atmosphere, the suspension being maintained at its boiling point. The product was aged for about 2 hrs.and left overnight to facilitate hydrolysis and to improve crystallinity. It was them filtered through a 1 G4 sintered glass funnel and washed till the washings were neutral. In order to eliminate extraneous phases likely to get co-precipitated with the sample, the latter was equilibrated for about 6 hours in a 2% EDTA[12] solution at a pH of about 10. Each sample was washed with acetone and air-dried. A part of each sample was heated to about 300° C for about 6 hrs.[13] and cooled in a desiccated atmosphere for use in chemical, x-ray and infrared analyses.

For the preparation of the samples, a preference for a co-precipitation technique to crystallization from fused mixtures was justified by the consideration that fusion needs different temperature for the end-members resulting in decomposition due to inequalities in individual thermal stabilities. Formation of tertiary phosphates of heavy metals through a conventional precipitation from aqueous media is complicated due to co-precipitation of their hydroxides and acid phosphates[23] . Mayer, et. al[24] . suggested a method for the preparation of apatite based on the use of a reaction between solid lead sulphate and a highly alkaline solution of sodium ortho-phosphate. It is claimed by them that the method is capable of application to prepare a wide-ranging series of apatites. With appropriate modifications of the method[24] , appreciable quantities of CPA,CVA and a series of their solid solutions over the entire compositional range could thus be prepared. It is evident that the mechanism of precipitation operative in the method adopted is based on a preferential precipation of CPA, CVA and their solid solutions controlled by a consideration of their solubility products.

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