CHAPTER- II

METHODS & TECHNIQUES

2.1 FIELD STUDIES

During the field studies, with the help of geological map and topographic sheet (53J/3) of the investigated area 65 fresh representative samples were collected from outcrops, adits and quarries at regular intervals.

2.2 LABORATORY TECHNIQUES

2.2.1 Microscopic Study

The thin sections of the representative samples of phosphorites were prepared in the lab and examined under the petrological microscope to study their optical properties, texture and structure of the mineral assemblages under plane polarised light and between crossed nicols. A systematic and careful mineralogical and petrographic study was carried out in order to make identification of essential minerals (phosphate minerals) and accessory ones.

2.2.2 X-Ray Diffractometer (XRD)

Few samples of phosphorites were analysed by X-ray Diffractometer (XRD) at National Institute of Oceanography (NIO), Goa for identification of various minerals on the basis of following principle.

2.2.2.1 Basic Principle of XRD

X-ray Diffractometer is an instrument used for analyzing the structure of crystalline materials from the scattering pattern produced when a beam of X rays interacts with it. The crystal structure is a unique parameter of a mineral. Regular arrangements of cations and anions in a crystal lattice make the basis of the most reliable method of identification. Each crystalline substance has a particular diffraction pattern which is like a finger print of its crystal structure. X-ray diffraction study provides an insight on the internal array of atoms. When a monochromatic X-ray beam falls on a crystal surface it is diffracted in a manner partly analogous to reflection of light from a surface. Atoms scatter incident X-rays in all directions and in some of these directions the scattered beams will be completely in phase and so reinforce each other to form diffracted beams. The Bragg’s law states that when the
angle θ between the incident X-ray beam and a planar array of atoms in a crystal satisfies the relation \( n\lambda = 2d \sin \theta \) (\( n \) is an integer, \( \lambda \) is the wave length, \( d \) is the Interplanar spacing and \( \theta \) is the diffraction angle), X-rays are diffracted by the array. For each (hkl) plane in the crystal, there is a discrete value of \( \theta \) at which diffraction occurs. This angle depends only on the interplanar spacing and on the characteristic wave length of the X-rays. This technique is, therefore, considered as an essential tool in the investigation of mineral components of a rock.

2.2.2.2 Sample Preparation

As the intensity of diffracted light very much depends upon the state and grain of size of the sample, the preparation of sample is very important. In order to obtain a good diffraction pattern of a mineral the sample must be ground to approximately <200 mesh size. The finer fraction of -200 mesh powder of few samples was taken and put into the glass slide holder and loaded on the sample of the machine. The diffraction data were obtained with a RIGAKU-ULTIMA IV X-ray diffractometer using nickel filtered Cu Ka radiation at National Institute of Oceanography (NIO), Goa. This incorporated a focusing monochromator from a tube separated at 40 kV and 20 mA. The divergence and scatter slits were 1° wide and the receiving silt 0.3 mm wide. The samples analyzed were from -200 mesh powder.

2.2.2.3 Method

Samples were run at 25°C i.e., room temperature and the line profiles were recorded at scanning rate of 0.02° 2θ/second. The scan was made over an angular range of 8° to 70° 2θ and the chart speed was 10 mm per minute. The range conditions chosen were 1×10³ CPS and 4×10² CPS to permit maximum resolution of the peaks and sufficient peak intensity for accurate measurements. Diffractograms so obtained were used for mineralogical characterization.

The X-Ray reflection (peaks) was carefully measured and the minerals were identified by conversion 20 values‘d’ using the table of National Bureau of Standards, series 10 of U.S. Department of Commerce. The mineralogical identification was done by measuring the intensity of each reflection against their respective‘d’ values. The maximum reflection then was taken as 100 and each reflection was converted to nearest whole number with respect to this 100 percentile maximum reflection. This
was done to obtain a definite intensity ratio. The mineral identification was done by following the X-ray identification charts of Match Software and International Centre for Diffraction Data (ICDD) or Joint Committee on Powder Diffraction File (JCPDF) cards.

2.2.3 Geochemical Analysis

On the basis of Microscopic and XRD investigations 40 representative samples of phosphorites were selected for their geochemical analysis. All of the samples were analysed at NGRI (National Geophysical Research Institute) Hyderabad. The sophisticated instruments used for geochemical analysis were the X-Ray fluorescence Spectrometry (XRF of the Philips Company) for major element analysis and Inductively Coupled Plasma (ICP) using Perkin Elmer, SCIEX, Model ELAN DRC- II for trace and rare earth elements.

2.2.3.1 Major Elements

2.2.3.1.1 Sample Preparation

Rock sample is a heterogeneous mixture of different minerals present and it is necessary to make the sample homogeneous to get accurate analytical data as it is essential that the surface layer should be representative of the bulk specimen. Rock samples are finely powdered to better than −200 mesh size with the help of jaw crusher and pulveriser. Pressed pellets were prepared by using collapsible aluminium cups (Govil, 1985). These cups were filled with boric acid and about 1gm of the finely powdered rock sample was kept on the top of the boric acid and pressed under a hydraulic press at 20 tons pressure to get a pellet.

The sample pellets were analyzed using a Philips MagiX PRO model PW–2440 wavelength dispersive X-ray fluorescence spectrometer (XRF) coupled with automatic sample changer PW 2540. The obtained data is presented in Table- 5.1 and 5.2.

2.2.3.1.2 Application

X-ray fluorescence spectrometry is one of the most powerful tools in the study of geological materials. It is almost an essential instrument in all the institutes where studies on geological samples are carried out. Most of the elements present in rock samples vary depending on the variation of silica concentration. Therefore, all the
rocks are divided into four types depending on the silica content - Acidic 66-90%, Intermediate 55-66%, Basic 45-55% and Ultra basic <45%. XRF spectrometry has been applied successfully to a number of geological problems requiring rapid answers such as identification of unknown rock types, geochemical prospecting and genesis of rocks in nature. All major (Si, Al, Fe, Mn, Mg, Ti, Ca, Na, P) and trace elements such as (Co, Cu, Cd, Ni, Rb, Sr, Se, Y, Zr, As, Nb, Ba, Zn, U, Th, Mo, V) can be determined.

2.2.3.1.3 Principles of Operation

A beam of X-rays is directed on to a sample of the substance causing secondary or fluorescent x-rays to be emitted. This secondary radiation contains wavelengths that are characteristic of each element present.

The basic sequence of an X-ray spectrometric analysis is as follows:

(a) The X-ray tube produces the X-ray primary beam.

(b) The primary X-ray beam irradiates the sample and excites each element to emit its characteristic x-ray spectrum. The wavelength of the emitted spectral line is characteristic of the emitting element (basis of qualitative analysis). The intensity of each line is related to the concentration of the emitting element (basis of qualitative analysis).

(c) The collimator renders the secondary X-rays from the sample parallel.

(d) The analyzer crystal specially disperses the secondary X-rays, causing each analyze line to go in a different direction. As per Bragg's law it works as a monochromator.

\[ n \lambda = 2d \sin \theta \]

\( n \) = order of diffraction  \( \lambda \) = wavelength  
\( d \) = inter planer spacing of the crystal  \( \theta \) = angle of deffracton

At one angle of the crystal only one wavelength will be diffracted. e.g. at 45.2° 2\( \theta \) only Cu K\( \alpha \) line is diffracted.
The detector receives each wavelength diffracted by the crystal and for each X-ray photon absorbed produces an output pulse of electric current having an amplitude proportional to the incident X-ray photon energy.

The pre amplifier and amplifier amplify these pulses linearly i.e. without changing their relative amplitudes.

The pulse height selector passes all pulses having a preset range of amplitudes.

Scaler counts these pulses digitally.

Timer measures the counting time.

2.2.3.2 REE and Trace Elements

Analyses of about 40 samples for the quantitative determination of trace as well as rare earth elements were carried out on an Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using Perkin-Elmer, SCIEX, Model ELAN DRC-II system at National Geophysical Research Institute (NGRI), Hyderabad. The elements determined include Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th and U.

2.2.3.2.1 Preparation of Solution

Solution of the samples was prepared by Open acid digestion technique (Roy, et al, 2007) using PTFE Teflon beakers. First of all clean and dried Teflon Beakers were taken with a cover lid then 50mg (0.0500gm) sample powders each after weighted on an electronic weighing machine were taken and then 10 ml of Acid mixture (HF : HNO₃ : HClO₄) in the proportion of 7 : 3 :1 were added to it and was swirl until it get completely moist. After this process beakers were covered with lids and kept for overnight digestion and next day it was heated on a hot plate with a temperature of about 150°C, after an hour the lids were removed and the samples were allowed to dry to form a crystalline paste but for a complete digestion again 5 ml of acid mixture were added to them and again they were dried up. After completion of this process 20 ml of 1:1 HNO₃ were added and kept on a hot plate of about 70°C temperature for dissolving the precipitate then 5 ml of 1 ppm $^{103}$Rh used as an internal standard were added and volume was made upto 250 ml with doubled
distilled water and the prepared solution was stored in a 60 ml HDPE sample bottle and labelled with sample code and serial number.

The instrumental and data acquisition parameters are same as given by Roy et al. (2007). The precision of ICP-MS data is better than ± 6% RSD for all the trace and REEs and was obtained in all cases with comparable accuracy. All the available data were standardized against the international reference rock standard NIST-120C for phosphorites. The obtained trace and rare earth element (REE) data is presented in Table- 6.1, 6.2, 7.1 and 7.2.

2.2.3.2 Application

The precise and accurate determination of trace and rare earth elements (REE) in geological samples are important to understand the evolution of the rock and to quantify the processes, which have taken place in the rock history. Accurate estimation of platinum group of elements (PGE) and gold in certain rocks are essential for understanding the processes, which concentrate these elements in the crust, mantle and in ore deposits. ICP-MS has proved to be extremely sensitive for the accurate and precise estimation of these elements in geological samples. The isotopic ratio determination in geological samples is useful to date a rock and to understand the process during evolution. Though ICP-MS permit accurate determination of isotope ratios, it cannot attain the precision of thermal ionization mass spectrometry (TIMS). However, the latest advancements in this field have lead to the development of high resolution –ICP-MS (HR-ICP-MS) which can provide extremely precise and accurate isotope ratio analysis (better than 0.001% RSD) which are comparable to those obtained by TIMS (3).

2.2.3.2.3 Principles of ICP-MS

The ICP-MS is the most simple and direct method of chemical analysis. The sample to be analysed is introduced into argon based high temperature plasma by a nebulizer spray chamber system. The sample stream causes desolvation, vaporization, atomisation and ionisation of target elements. Ions thus generated are extracted from the plasma into a low-pressure region through a sampler and skimmer cones and are allowed to pass through an electrostatic lens system, which extracts positively charged ions. These ions are separated on the basis of their mass–to-charge ratio by
quadrapole mass analyser. A detector counts the filtered ions and a computer processes the resulting information.

2.2.3.2.4 Technique

The raw data in the form of counts per second are obtained either by continuous scanning or by peak-hopping mode. The spectra generated by continuous scanning are used for qualitative identification of elements present in the sample. The peak-hopping mode is used for quantitative analysis.

2.2.3.2.5 System Optimisation

The important optimisation criteria include adjustment of nebulizer gas flow, setting of detector and lens voltages, radio-frequency forward power settings and performance of mass calibration. Optimize the instrument by adjusting all the above settings to obtain maximum counts for an analyte with minimum oxide and doubly charged species.

2.2.3.2.6 Internal Standardization

The various instrumental and sample induced variations such as instrumental drift, physical interferences in the sample introduction system due to differences in total dissolved solids (TDS), plasma effects due to relatively high concentrations of easily ionisable elements (EIEs) and acid concentrations, can be compensated by using internal standardization. The different elements like Rh, In, Bi, Cd, Ti etc., may be used as internal standards.

2.2.3.2.7 Quantitative Measurement

The instrument may be calibrated using an appropriate range of calibration standards, preferably with matching of matrix. The required analyte isotopes may be measured and calibration curves may be prepared between intensity and concentration after applying necessary corrections using computer software. The curves obtained may be used for characterizing unknown samples.

2.2.4 Loss on Ignition

Loss on ignition (LOI) was determined by fusing the sample powder in the muffle furnace upto 1000°C temperature and loss in weight due to water vapours and other gases was calculated in percent. LOI of the samples were determined at the geochemistry lab, department of geology, Aligarh Muslim University, Aligarh.
The empty silica crucibles were weighed exactly, using the mass balance and the noted mass was $n_1$. The 1.00 gm sample powder was added to the crucible with the spatula and the total mass noted was $n_2$. The crucibles were placed into the muffle furnace at $1000^\circ$C temperature and were left in it for 8 hours after that the crucibles were taken out and put into the desiccators after cooling at room temperature. Then each crucible was re-weighed immediately and the total mass noted down was $n_3$. Then the LOI was calculated using the formula:

$$\text{LOI (weight \%)} = 100 \times \frac{(n_2 - n_3)}{(n_2 - n_1)}$$