CHAPTER I

INTRODUCTION

Phosphorus (At. No. 15) ranks eleventh in crustal abundance (0.23% P₂O₅), and is present in most rocks in minor to trace quantities ranging from an average of 0.04% P₂O₅ in sandstones to 0.40% P₂O₅ in intermediate igneous rocks (McKelvey, 1973). However rocks containing more than 18-20% of P₂O₅ have been named as phosphorites (Cook and Shergold, 1986a). Phosphorus is one of the indispensable element to all forms of life and plant growth, without which agricultural productivity and hence, food production cannot be maintained or increased. Thus phosphate becomes the only source of raw material in manufacture of phosphate fertilizers.
Although nearly 300 mineral species (Nriagu, 1984) of natural phosphates containing $\text{PO}_4^{3-}$ radical have been reported. However of these the most widespread mineral species belongs to the apatite family known as fluorapatite $\text{Ca}_5(\text{PO}_4)_3F$, or carbonate fluorapatite (francolite) represented by approximate formula $\text{Ca}_{10-x-y}\text{Na}_x\text{Mg}_y(\text{PO}_4)_6 \text{CO}_3(\text{CO}_3)_2 F_{0.4} F_2$ (McClellan, 1980).

The phosphate resources of the world ranging from Precambrian to Recent have been reported from all the continents except Antarctica. In India as well, several phosphorite occurrences have been reported from various localities belonging to different geologic periods (Table-I). The Proterozoic phosphorites of India are either associated with stromatolites, such as those of Udaipur (Rajasthan), Jhabua (M.P.) and Pithoragarh (U.P.), or nonstromatolitic such as found in Hirapur-Bassia area of Sagar district M.P. and Sonrai, Lalitpur district of U.P. All these Proterozoic phosphorites were identified as shallow marine deposits characterized by the presence of carbonate fluorapatite as main apatite mineral species (Banerjee et al. 1980, Banerjee et al., 1982).

The phosphorite occurrences have earlier been reported from the Upper Proterozoic sedimentary sequences belonging to Chhattisgarh Supergroup, the present thesis embodies detailed studies of the phosphorites of Lohara area, Durg district, M.P., where it is well developed.
<table>
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<th>Age</th>
<th>Locality (Formation/Group)</th>
<th>Nature and associated lithofacies</th>
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<tr>
<td>Miocene</td>
<td>Mandai</td>
<td>Phosphatic shell fragments in sandstones.</td>
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<tr>
<td>Cretaceous</td>
<td>Fatehgarh</td>
<td>Pelletal, phosphatic shell fragments in sandstones.</td>
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<td>- Eocene</td>
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<tr>
<td>Cambrian</td>
<td>Birmania</td>
<td>Pelletal, grainstones, bedded in siliceous limestones and sandstones.</td>
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<tr>
<td>Lower</td>
<td>Musqori</td>
<td>Laminated, mudstone phosphorites in black shales and carbonates.</td>
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<tr>
<td>Cambrian</td>
<td>(Krol-Tal)</td>
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<td>Stromatolitic in dolomitic limestones.</td>
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<td>Chelima-Pachcherla</td>
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<td>Chandi, Argarh, Dala</td>
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<td>Proterozoic</td>
<td>Susnai (Lr. Vindhyan)</td>
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<td>Pithoragarh</td>
<td>Stromatolitic phosphorites in dolomitic limestones.</td>
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<td>(Calc-zone)</td>
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<td>Jhabua</td>
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<tr>
<td>Lower</td>
<td>Hirapur-Bassia (MP)</td>
<td>Nonstromatolitic bedded phosphorites in sandstones.</td>
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<td>Proterozoic</td>
<td>Sonrai (UP)</td>
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<td>(Bijawars)</td>
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Source: Chauhan & Sisodia, 1989
The present area of investigation (Fig.1) i.e. Lohara, Durg district, Madhya Pradesh lies in the toposheet number 64 H/1 and 64 H/2 of Survey of India, bounded by Lat. 20°40' and 20°55' N, and Long. 81°0' and 81°10' E in the southwestern part of Chhattisgarh basin and is situated about 77 Kms. south west of district headquarters Durg. The area is also approachable from Rajnandgaon by State highway number 09. The nearest railway station Balod is 19 Kms. east of Lohara.

PREVIOUS WORK

The rocks of Chhattisgarh basin were first studied by H.B. Medlicott during 1866-67, from that time these rocks have been attracting geologists to study the various aspects of so vast Chhattisgarh basin (~ 33000 Sq. Kms.). Medlicott (1866-67) found these rocks similar with the rocks of Son and Bundelkhand area and so he proposed these rocks as equivalents of lower Vindhyans. Later Ball (1877) and King (1885) grouped them under Purana Formations, while Bose (1899) named these rocks as 'Chhattisgarh plain series (Lower Vindhyan)'. Bose (op. cit.) also suggested a two fold classification of these sediments, the Chandarpur sandstones as lower and Raipur shales and limestones as belonging to the upper series. Bhattacharjee, (1936-37, 1937-38) mapped the western part of Durg district and correlated them with Cuddapah rocks. He (op. cit.) classified them as (a) Chandarpur sandstones (b) shales and phyllites (c) Raipur limestones often with autolith concretions and (d) Kharagpur sandstones, whereas...
Fig. 1 Location map of study area
eastern part of the basin, Pascoe (1963) found only two series i.e. basal Chandarpur (1600 m.) and upper Raipur series (300 m.). Dutt (1964) gave a somewhat better nomenclature to the Purana sediments of Chhattisgarh region. He considered them as equivalents of Kurnools. Schnitzer (1971) took several traverses throughout the area and proposed a detailed classification scheme for these sediments of Chhattisgarh basin. Schnitzer (op. cit.) gave a Supergroup status to the Chhattisgarh sediments and identified five cycles beginning with limestones or light coloured sandstones, extending into "Red beds" i.e. claystones and red shales, developed in shallow intracratonic basin. Murti (1980, 1987) carried out significant work in the central part of the basin. Murti (1987) introduced many new units and modified the stratigraphic schemes proposed earlier by Dutt (1964) and Schnitzer (1971, 1977).

The stromatolitic limestones of the Raipur Group bear a great significance for regional correlation and proper age dating. Thus a number of workers such as Ghosh and Shah (1965), Sen (1966), Chanda and Bhattacharjee (1973), Jairaman and Banerjee (1978) attempted to describe the stromatolite assemblages, however yet no complete biostratigraphic scheme has so far been proposed.

Phosphorites of the Chhattisgarh basin have received little attention. Workers like Adyalkar et al.
Vishwanathan and Sastri (1973), Bhaté and Jha (1971-72) have made passing reference to their occurrences in the limestones of Charmuria Formation and Raipur Formation. Khan and Mukherjee (1988) and Mukherjee and Khan (1989) carried out preliminary investigations on mineralogy and petrography of the phosphorites of Charmuria Limestone Formation around Lohara, Durg district M.P.

**SCOPE OF THE PRESENT INVESTIGATION**

The Upper Proterozoic Chhattisgarh sedimentary sequence has not yet been investigated in detail for phosphorites, in spite of the fact that phosphorite occurrences have earlier been reported from Charmuria and Raipur Formations.

This project bears great significance for the reasons, that Phosphogenic Provinces are well defined within Proterozoic sequences in Indian subcontinent, and secondly the Chhattisgarh sedimentaries belonging to Upper Proterozoics were laid down under shallow marine conditions—the most conducive for the phosphorite development.

This investigation was initiated to generate a new set of data on the mineralogy, petrography, geochemistry and sedimentology of the phosphorites and the associated carbonates, occurring around Lohara, Durg district, M.P.
attempt has also been made to correlate these mineralogical, chemical and petrographical data to the sedimentologic, stratigraphic framework of Chhattisgarh basin.

On the basis of these studies, the author has proposed a new phosphogenic model. Such a model has also been evaluated in the context of Proterozoic Phosphogenesis in the Indian subcontinent.

**METHODOLOGY AND INSTRUMENTATION**

**Field Studies**

About two months intensive field work was carried out during the field seasons 1986-89, in the area of present investigation around Lohara. An updated geological map of the area covered 445 Km\(^2\) was prepared with the help of available base map of the southern part of Chhattisgarh basin. Fresh and unweathered samples from each lithounit were selectively collected for laboratory work. Channel sampling of the exposed sections in Kharkhara canal was also carried out for study of mineralogical and chemical variations. Field photographs were also taken wherever found necessary, for displaying field relations and structures etc. Representative samples of investigated area are catalogued and preserved in geochemistry laboratory of the Geology Department, Ravishanker University, Raipur.
Laboratory Techniques

Various standard techniques have been used during the course of present investigation, in order to determine and describe the petrological, mineralogical and geochemical characters of these phosphorites and other lithofacies. These are briefly summarized as under.

Staining Test: Staining tests have been applied on polished slabs, thin sections, following the method of Dickson (1965). The samples were first etched with 1.5% HCl for 10-15 seconds. The etched samples were then dipped for 30-40 seconds in a solution of Alizarin red-S and Potassium ferricyanide (Alizarin red-S and Potassium ferricyanide were dissolved separately in 1.5% HCl, and mixed in the ratio of 3:2).

The calcite stains with pale pink to red, ferroan calcite with pale blue to dark blue and dolomite takes no colour. It was observed that all the limestones of the area are free from mineral dolomite.

Insoluble residue analysis: For insoluble residue analysis, 50 g. of limestone samples were crushed into 0.5 to 1 cm. pieces and were treated with 500 ml. of 10% HCl for a day, if the digestion is incomplete the spent acid was poured off, and with new acid the above step was repeated till the completion of digestion. The insoluble fractions were washed several
times with distilled water and then dried at temperature below
100°C, cooled and the percentage of insoluble was calculated
by taking weight.

Separation of clay fraction: The clay fractions were
separated from limestones and phosphorites of the area. The
insoluble residue fraction obtained by above methods were
further treated for identification of clay fraction by
settling method in a one litre cylinder. The cylinder then
kept at room temperature (25°C) for settling the silt
fractions. After 9 hours and 58 minutes an aliquot of 20 cc
was taken out from a depth of 7 cm and collected in a
separate beaker. The above steps were repeated several times
to collect nearly 100 cc of aliquot. The fraction so
collected was washed with distilled water and then centrifuged
in a mechanical centrifuge to collect the clay size fraction
separately.

The clay fraction was then smeared over a glass slide
to obtain a uniformly oriented slide of clay minerals. The
oriented slides thus obtained were scanned under X-ray
diffractometer through 3°-70° 2θ for identification of clay
minerals.

Preparation of powdered Samples: For mineralogical and
geochemical work, samples were crushed to -200 mesh following
coning and quartering to obtain proper and homogeneous sample.
Special care was taken to prevent any contamination. Whenever felt necessary the samples were washed before crushing. Fine powder was used for analysis and coarse powders were kept as reference material. For infrared analysis, samples were further powdered up to -300 mesh.

**Extraction of powdered samples** : For X-ray and infrared analysis, few samples of phosphorites and phosphatic siliceous clays were extracted to remove the free but mechanically inseparable calcium carbonate, with ammonium citrate solution following Silverman et al. (1952) and Srivastava (1982). About 4 g. of powdered sample (-200 mesh) was suspended in 500 ml of 0.5 M triammonium citrate solution (pH 8.1) and digested at 65°C for about 8 hours on a magnetic stirrer ensuring constant agitation after which the mixture was allowed to stand at room temperature for 24 hours. The mixture then was filtered and the extracted sample was washed and dried at 105°C. The sample so obtained were referred as concentrates.

**X-ray diffraction studies** : X-ray diffraction studies were carried out for limestones and clay fractions separated from insoluble residues of limestones and from disaggregated phosphatic siliceous clays, and bulk and concentrated samples of phosphorites and phosphatic siliceous clays, with the objective (a) to identify the mineral phases present in them, (b) to determine the unit cell parameters and crystallite size measurements in bulk and concentrated samples of phosphorites and phosphatic siliceous clays.
X-ray diffraction data for powdered samples (-200 mesh) were obtained with a Philips (PW 1130/00) X-ray diffractometer in Cu Kα radiation fitted with nickel filter. This incorporated a focusing monochromator from a tube operated at 40 KV and 20 mA. The divergence and scatter slits were 1° wide and the receiving slit was 0.1 mm wide. The chart speed was 10 mm per minute. The range condition chosen was $4 \times 10^2$ to $10 \times 10^2$ counts per second (c.p.s.). The angular range for phosphatic samples were selected between $20°$ to $55°$. For oriented samples of clays the scan was made over an angular range of $3°$ to $70°$.

(1) Identification of mineral phase: The X-ray reflections (peaks) were carefully measured and minerals were identified by conversion of 2θ values to 'd' Å values using the standard tables. The maximum reflection was taken as hundred and each reflection was converted to a nearest whole number with respect to this hundred percentile maximum reflection peak. This was done to obtain a definite intensity ratio. The mineral identification was subsequently done following the X-ray diffraction chart of J.C.P.D.S. data book (1980).

(2) Determination of unit cell dimensions: The unit cell dimensions for apatite mineral phase were calculated using equations:
a = \sqrt{1.333 \times d^2 \left( h^2 + k^2 + h k \right)} \qquad (i)

with (210), (310), (320), and (410) planes and

\[ c = 1 \times d \qquad (ii) \]

with (004) and (002) planes.

The cell parameters so obtained, are used for mineralogical characterization of different mineral phases of apatite.

(3) Determination of CO₂: The percent CO₂ in apatites has been calculated following the method of Gulbrandsen (1970), using the equation,

\[ y = 23.6341 - 14.7361 \times \qquad (iii) \]

where \( y \) is CO₂ weight percent and \( x = 2\theta(004) - (410) \). The uncertainty factor of \( Y \) value for this formula is 0.5569.

An other formula proposed by Gulbrandsen (1970)

\[ y = 185 - 25.57 \times \qquad (iv) \]

in which \( x \) represents the 2\( \theta \) (002) - (300) peaks, for this formula the uncertainty factor of \( Y \) = 0.5295. Since this peak of pair is not good as the (004) and (410) pair for measurement of CO₂ content, it is not preferred. However, Chaabani (c.f. Slansky, 1986) is of the opinion that in less crystalline apatites the (002) - (300) peaks are more clearly distinguished, and more intense, and give better results.

The author has followed the equation (iii) for calculation of % CO₂, as these apatites give sharp X-ray diffraction peaks indicating good crystallinity.
Crystallite size measurement by X-ray line broadening:

The crystallite size of these apatites were obtained for eight samples according to the procedures described by Rau (1962), which is based on broadening of the line profiles of (002) and (300) reflection and measuring the peak widths at half height.

The goniometer settings were 0.125° 2θ with a time constant of 4 seconds and chart speed of 20 mm/minute. The crystallite sizes were obtained from curves of Rau (1962) applying Debyesherer equation.

\[
dhk = \frac{(k\lambda 57.3)}{\left(\beta_1 / 2 \cos \theta\right)}
\]

where, shape constant \( k = 0.9 \)

\[
\lambda = 1.54 \text{ Å for Cu Kα radiations}
\]
\[
\theta = \text{diffraction angle}
\]
\[
\beta = \text{line broadening in degrees}
\]

During the present investigation it is observed that crystallite size measured by this method gives average values, as the SEM studies reveal that apatite crystallites are bimodal and vary in size considerably. Thus it is inferred that Rau's (op. cit.) method is applicable to only homogeneously crystalline substances and not for those having bimodal size distributions.
Scanning Electron Microscopy:

Eight polished and fresh fractured samples of phosphorites and phosphatic siliceous clays were studied under Scanning Electron Microscope at R.S.I.C. Nagpur.

Before scanning under SEM, the samples were coated by gold under vacuum under an autocoating unit E 5200 (Poloron Equipment Ltd.). Instrument settings were in between 20-21 KV accelerating voltage with variable beam current (80-100 nA). Photomicrographs were also taken to display the mutual relationship of nannograins and their sizes.

The elemental distribution patterns were also obtained of one polished sample of phosphorites at Regional Research Laboratory, Bhubaneshwar. Before analysis the sample was gold coated under Coat Ion Sputter JFC-1000 and was exposed under SEM (JSM 35 CF) and analysed at accelerating voltage of 25 KV with variable beam current (80-100 nA), and X-ray image mapping of elements (P, Ca, Si, Fe and Al) was also carried out.

Infrared Spectroscopy:

For 15 representative bulk and concentrate samples of phosphorites and phosphatic siliceous clays, infrared spectra were taken using the solid phase KBr pellet technique in an infrared spectrophotometer (Perkin-Elmer) at R.S.I.C. Nagpur.
A powdered sample (2 mg) of -300 mesh was mixed with 200 to 300 mg of KBr to prepare pellets under vacuum following the procedures described by Rao (1966) and Bellamy (1966). The spectra was recorded from 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) with a scanning speed set to cover whole range in about 4.4 minutes.

**Geochemical Analysis:**

Major element analyses have been carried in duplicate by conventional wet method following Shapiro (1975) in the Geochemistry laboratory of Department of Geology R.S.U., Raipur. BCR-32 and NBS-120b were run simultaneously as standard samples, alongwith these samples. The results obtained are accurate to ± 0.5%.

For estimation of various oxides and trace element concentrations, two solutions A and B were prepared.

Solution A was made by digesting 0.05 g. of silicates and 0.2 g of carbonate and phosphate rock powder in NaOH, diluting to one litre. This solution was used for determination of SiO\(_2\) and Al\(_2\)O\(_3\) concentrations.

Solution B was prepared by digesting 0.5 g of sample powder in 15 ml acid mixture (HF : H\(_2\)SO\(_4\) : HNO\(_3\) = 12:4:1) using Sapiro's (op.cit.) method and diluting to 250 ml. This solution was used for determination of CaO, MgO, MnO, Fe\(_2\)O\(_3\), Na\(_2\)O, K\(_2\)O and trace element concentrations (Cr, Cu, Sr, Pb, Zn). Blank solutions A and B were also prepared by the same method without taking the sample powder.
All major elements except CaO, MgO, Na₂O and K₂O were determined colorimetrically employing Varian UV-VIS Spectrophotometer, Model DMS 100S. Na₂O and K₂O were determined by Flame photometer (Systronics, Model 121). CaO and MgO were determined titrimetrically.

**Determination of various oxides:**

P₂O₅ was determined using molybdovanadate solution (for carbonate and silicate rocks 1.2 g. sodium metavanadate in 400 ml of 1:1 HNO₃ + 75 g of ammonium molybdate in 400 ml. distilled water were mixed and made to two litres with distilled water. For phosphates 5 g of sodium metavanadate in 400 ml of 1:1 HNO₃ + 66 g of ammonium molybdate in 400 ml of water mixed and diluted to two litres). Absorbance was measured at 430 nm.

For CaO determination 25 ml of solution B was taken in a conical flask in which 2 ml. HCl + 5 ml triethanolamine + 2 drops of polyvinyl alcohol + screen calcine indicator + 200 ml. of water and 15 ml of 30% KOH were added. It was titrated against E D TA till purple colour appeared.

For MgO, to an aliquot of solution B, 5 ml HCl + 20 ml triethanolamine + 50 ml ammonia solution were added, using O-cresolphthalein complexone and napthol green-B as indicator. It was titrated against E D TA which gives us
CaO+MgO concentration. After calculations, CaO concentration as detected earlier were subtracted to obtain MgO concentrations.

Selected number of samples were analysed for determination of F following Rund et al. (1975) using zirconyl chloride octahydrate and alizarin red S.

L.O.I. (Loss on ignition) was determined by the weight difference after igniting the sample powder in an oven upto 1000°C.

For SiO₂ determinations, 8 ml of solution A was taken in a 100-ml flask in which 10 ml of ammonium molybdate solution (1.5 g ammonium molybdate + 2 ml of 1:1 H₂SO₄ diluted to 200 ml ) + 10 ml of stannous chloride solution (40 g SnCl₂. 2H₂O + 50 ml HCl diluted to 100 ml, 2 ml of this solution further diluted to 200 ml ) + 50 ml of H₂SO₄ (25 ml of 1:1 H₂SO₄ is diluted to 1 litre) were added and diluted to 100 ml. The absorbance was measured at 640 nm after one hour.

Concentration of Al₂O₃ was detected using 15 ml of solution in a 100-ml volumetric flask in which 2 ml calcium chloride solution (7.0 g of CaCO₃ dissolved in 15 ml HCl, and diluted to 500 ml ), 1 ml of 10% hydroxylamine hydrochloride solution + 1 ml of 0.75% potassium ferricyanide solution + 2 ml of 4% thioglycollic acid + 10 ml of Buffer solution (100g of sodium acetate + 30ml of glacial acetic
acid, diluted to 500 ml; + 10 ml of 0.05% Alizarin red-S solution, were added and diluted to 100 ml. The absorption was measured at 475 nm after 75 minutes.

Trace elements Pb, Zn, Cr, Sr, Cd, Co and Ni, were determined at Geology Department, Delhi University, Delhi, and at Regional Sophisticated Instrumentation Centre, NEHU, Shillong by Perkin-Elmer (Model 603) Atomic Absorption Spectrophotometer.

As, Mo, Se, U, and Th, were determined by Philips-XRF at Regional Research Laboratory, Bhubaneshwar.