Chapter V
PETROMINERALOGY

The petromineralogic description and characteristics of the phosphorites and the rocks associated with them are mainly based on thin section study of the representative samples, collected from Matoon and Dakan Kotra. The x-ray powder pattern was also studied for some identified minerals. The compositional characters of the phosphate minerals were determined by infrared absorption spectroscopy. Radioluxographic techniques were applied for locating radioactive minerals in uncovered thin sections. The heavy minerals in the insoluble residues of phosphatic rocks and dolomitic marble were also determined.

Phosphorites

It is well known that phosphorite contains more than one apatite like minerals and the following names have been used to indicate the subspecies; pedolite, dahllite, francolite, staffelite, kurskite, grodnolite, wilkeite, ellestadite and morinite. Since such wide compositional variations are common, hence it is convenient to use collophane as a generic term in phosphorite. The minerals identified in these phosphorites are described in detail.
Collophane

Collophane happens to be the dominant mineral of phosphates. It occurs in the form of fine granules, sub-angular to angular, elongated to wedge-shaped fragments of stromatolitic phosphorites and also as an interstitial material between the gangue minerals. Collophane in Matoon phosphorites generally appears light to dark grey in colour and faintly anisotropic. The thin sections of the Matoon phosphorite show extremely fine and irregular granules of collophane and phosphoritic algal stromatolite cemented by calcareous and cherty material (Pl. VIII, Figs. 1 and 2). The average size of phosphatic granules ranges from 0.03 to 0.06 mm. Irregular fragments of phosphoritic algal stromatolite of varying sizes occur in association with cherty brecciated quartzite (Pl. VIII, Figs. 3 and 4). The algal structures show yellowish brown and light to dark grey colour. Collophane chiefly occurs either in the form of random rounded grains or arranged in linear bands. The carbonates occur either in discontinuous clusters or as disseminated individuals interlocked in collophane. This is a common feature of the phosphorites. Occasionally the clusters of carbonates follow a linear arrangement and are found in association with quartz. Apatite, a later generation of crystallization is rather rare. The presence of francolite and collophane projecting outwardly from a geode of quartz (Pl. IX, Fig. 1) indicates incomplete cementation during reworking of Matoon phosphorites.

Most of the phosphatic minerals from Jakan Kotra, which
occur between the gangues are spherical, oval and pelletal in shape (Pl. IX, Figs. 2, 3 and 4) and range in size from 0.03 to 0.08 mm in diameter. These pellets and ovules appear isotropic. The stromatolitic phosphorite, which is composed of elongated to wedge-shaped fragments of stromatolite and varies in size from 0.1 to 2.0 mm is partially replaced by collophane, francolite and dahllite, which occur in a matrix of crystalline carbonate with minor amounts of subangular to subrounded fine grained quartz (Pl. X, Fig. 1). In a few cases the collophane ovules and pellets are rimmed by light grey coloured dahllite (Pl.X, Fig. 2). The phosphatic ovules are made up either of extremely fine grained francolite (light colour) or of collophane (dark colour). Often numerous veinlets of calcite cut across the phosphatic band (Pl. X, Fig. 3). Granular apatite frequently occurs along the contact of larger calcite veins and collophane bands. Complete algal structures namely *Collenia symmetrica* and *Minjaria* species were identified from Matoon and Dakan Kotra phosphorites (Pl. X, Fig. 4 and Pl. XI, Fig. 1).

**Quartz**

Quartz is the dominant gangue mineral of the fragmental phosphorites. In grain size it varies from 0.009 to 0.29 mm in diameter and in shape subangular to subrounded. The mineral shows oblique to slightly undulose extinction and occurs in two forms associated with collophane, viz., (i) as tiny inclusions in collophane measurable in micron scale, and (ii) as coarse grained recrystallised quartz and chert forming the matrix of phosphate
minerals (Pl. XI, Figs. 2 and 3). Dusty quartz grain also found in association with dolomite (Pl. XI, Fig. 4). Often the carbonates, collophane and quartz are coated with ferruginous material. The possible fragmentation and brecciation of the original columnar stromatolites owing to wave action is indicated by the presence of the fragmental phosphoritic stromatolites in a cement of chert and quartzose material (Pl. VIII, Figs. 3 and 4).

Calcite and Dolomite

Calcite and dolomite are the predominant gangue minerals of the stromatolitic phosphorites. Aphanitic to finely crystalline grains of dolomicrite are also present in these phosphorites. Calcite is generally colourless to light grey in colour and varies in size from 0.30 to 1.18 mm. Dolomite also shows almost the same optical characteristics and varies in size from 0.38 to 1.76 mm. Calcite and dolomite in the Matoon phosphorites occur as very fine grained ground mass and rarely they are coarse grained. In Jakan Kotra phosphorites they are fine to coarse grained. Cleavages are well-developed in the coarse grained calcite forming the ground mass (Pl. IX, Fig. 3). Fine to medium grained calcite and dolomite envelope the collophane found in the intercolumnar spaces of stromatolites. The light to dark greyish cryptocrystalline laminae of collophane generally have gradational boundaries with adjacent laminae of fine grained calcite and dolomite (Pl. XII, Fig. 1). Penetration of the grain boundaries of collophane in to that of calcite provides an evidence in
support of the replacement of calcite by collophane, grain by grain.

Accessory Minerals

The carbonate mosaic is constituted mainly of carbonate minerals together with minor amounts of chert, feldspar, mica and sericite. Replacement of calcium-phosphate by chert which is a common feature, indicates partial silicification of Matoon phosphorites. Chert along with some calcite and dolomite has invaded the fractures in collophane. Under microscope chert looks fine grained, cryptocrystalline and colourless to faintly brownish in colour (Pl. XII, Fig. 2).

The other minerals identified, viz., feldspar, mica, sericite and glauconite occur as shapeless plates and elongated laths (Pl. XII, Fig. 3). Sericite and muscovite are generally colourless to yellowish in colour. Glauconite which is olive-green to dark green in colour occur as laths or flakes in Dakan Kotra phosphorites. Secondary limonite and limonitised pyrite occur sporadically.

Heavy Minerals

Heavy minerals in phosphorites, dolomitic marble and phyllites consist mainly of rounded grains of tourmaline, zircon, rutile, anatase, garnet, zoisite and some opaques in order of abundance. The abundance and distribution of these heavy
minerals are variable in different samples. In the most of the samples, their amount hardly exceeds 0.2 per cent by number of the total grains in any individual samples.

Tourmaline mostly occurs as small rounded to subrounded grains in these phosphorites. Most of the grains are coloured brown but black varieties are also common. The zircon grains are smaller in size as compared to tourmaline. They occur as rounded to completely unabraded grains whose original crystal faces can be marked out. Garnet occurs as rounded to subrounded grains of deep red colour in the Jakan Kotra phyllites.

Rutile occurs in tabular form in the phyllites of Jakan Kotra (Pl. XII, Fig. 4). Anatase which is commonly identified from all these rocks of area studied occurs in various forms. Pseudo-octahedral and tabular crystals of blue colour are very common (Pl. XIII, Fig. 1). Zoisite occurs in the form of euhedral small tabular crystal (Pl. XIII, Fig. 2) of light grey colour. Small quantities of opaque minerals namely magnetite and ilmenite are commonly seen in these phosphorites as well as in other associated rocks.

Radioactive Minerals

Forty samples (26 from Matoon and 14 from Jakan Kotra) were selected from these phosphorite horizons for radiolucoxographic and radiometric analysis. Radiolucoxographic techniques were applied following Mohammad H. (1975) procedure.

The intensity of radioactivity in these phosphorite is very
low and mostly the samples show the absence of any radioactive mineral. The \( \text{U}_3\text{O}_8 \) values represent the total radioactivity. Because total radioactivity is low, the radioluxograph naturally shows negative results. The result of radiometric analysis shows the \( \text{U}_3\text{O}_8 \) and \( \text{ThO}_2 \) below 0.008 % in most of the samples.

**X-ray Diffraction Mineralogical Analysis**

X-ray diffraction studies were carried out on a Phillips PW 1010 X-ray diffractometer with a sealed proportional detector using nickel filtered CuK\( \alpha \) radiation. Powdered phosphate samples less than 250 mesh were pressed into CuK tube operated at 32 kv and 19 ma, which were scanned from 6 to 60° 2θ at 2° 2θ/minute to assess the general mineralogy of the rocks. The unit cell dimension \( a_0 \) and \( c_0 \) determined from \((300)\) and \((002)\) reflection respectively using silicon as an internal standard.

The X-ray pattern (Fig. 7) exhibits well defined diffraction lines at d-spacings for the minerals francolite and dahllite. Mineral composition and axial parameters of Matoon and Dakan Kotra phosphorite samples are given in Table IV. The bulk of these phosphorites are composed of well crystallized apatite mineral that gave strong diffraction peaks at 2.79 Å, 2.77 Å and numerous other spacings which correspond closely with d-spacing data for carbonate apatite given by McConnell, D. (1938 and 1952). The d-spacing data of samples X-rayed are presented in Table V. Dolomite with 211 strong refraction peak occurs at 2.88 Å as well developed clear rhomb, whereas its weak
FIG. 7 X-RAY DIFFRACTOGRAMS OF PHOSPHORITES
A, B & C - MATOON, D & E - DAKANKOTRA.
intensity peak appears at 2.18 Å and 2.14 Å. Quartz show the
diffraction peaks at 4.30, 4.26, 4.23 and 1.6 Å. The d-spacing
at 3.42, 1.87 and 1.85 Å indicates the presence of calcite in
these phosphorites. The diffraction data show the presence of
goethite at 4.30 Å in many of the samples. The diffraction
d-spacings at 9.90 Å and 9.80 Å correspond to the presence of
illite whereas peaks at 8.17 Å and 8.03 Å indicate the presence
of kaolinite.

The unit cell dimensions of apatite have been calculated
with an accuracy of ± 0.002 Å. It can be seen from the unit cell
dimension data that ao varies from 9.358 to 9.366 and Co from
6.882 to 6.883. The axial ratio (Co/ao) varies from 0.7349 to
0.7354. Thus it indicates that there is a larger variation in
the cell dimension of 'a' rather than in 'C'. It suggests the
substitution effect on the length of 'a' axis.

Considering the axial parameter of apatite studied
(corresponding more to the parameters of the end member of
carbonate fluorapatite than to those of ideal fluorapatite) with
excess of CO₂, the formula of this mineral may be calculated as
Ca₁₀ (PO₄, CO₃OH)₆(F,OH)₂ assuming the probable replacement of
PO₄ by CO₃OH or CO₃F or CO₃ (see Deer, H.A., Howie, R.A. and

Infra-red Absorption Spectral Study

The infra-red spectra of Matoon and Dakan Kotra phosphorites
have been recorded in the 2.5 μ to 15 μ wavelength region using
Table IV: Mineral composition and axial parameter of Matoon and Dakan Kotra Phosphorites.

<table>
<thead>
<tr>
<th>Area</th>
<th>Description of sample</th>
<th>Constituents Major</th>
<th>Minor</th>
<th>Axial parameter</th>
<th>Axial ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matoon</td>
<td>Dark grey phosphorite with cherty brecciated quartzite</td>
<td>A Q,C,G</td>
<td></td>
<td>9.364</td>
<td>6.883</td>
</tr>
<tr>
<td></td>
<td>Granular grey phosphorite with dolomitic limestone</td>
<td>A Q,C,D,I</td>
<td></td>
<td>9.362</td>
<td>6.882</td>
</tr>
<tr>
<td></td>
<td>Brownish grey phosphorite with calcareous phyllite</td>
<td>A Q,C,G</td>
<td></td>
<td>9.358</td>
<td>6.882</td>
</tr>
<tr>
<td>Dakan Kotra</td>
<td>Dark grey phosphorites with dolomitic marole</td>
<td>A Q,C,D,I</td>
<td></td>
<td>9.366</td>
<td>6.883</td>
</tr>
<tr>
<td></td>
<td>Light greyish phosphorite with dolomitic marble</td>
<td>A Q,C,D,I</td>
<td></td>
<td>9.362</td>
<td>6.882</td>
</tr>
</tbody>
</table>

A = Apatite  
G = Goethite  
Q = Quartz  
D = Dolomite  
C = Calcite  
I = Illite
K Br pellet on a Perkin-Elmer infra-red spectrophotometer. The I-R spectra of these phosphorites are illustrated in Fig. 8 and the frequencies along with a classification of their \((\text{PO}_4)^{3-}\) and \((\text{CO}_3)^{2-}\) ions are tabulated in tables VI and VII. The vibration frequencies corresponding to major absorption bands at approximately 7, 11 and 13 \(\mu\) wave lengths are primarily related to the vibration energies of \((\text{CO}_3)^{2-}\) ions, which has more or less fixed structural configuration. The non-carbonate varieties of apatite, give a broad absorption band at 5.60 \(\mu\) (1040\(^{\text{cm}^{-1}}\)) with two satellite peaks at about 9.15 \(\mu\) (1100\(^{\text{cm}^{-1}}\)) and 1040 \(\mu\) (960\(^{\text{cm}^{-1}}\)) wavelength. The carbonate stretching mode \(V_3\) and \(V_1\) found near 7 and 9 \(\mu\) and the banding modes \(V_2\) and \(V_4\) occur at about 11 and 14 \(\mu\) wavelength as suggested by Adler, H.H. and Kerr, P.F. (1963). According to Adler (1964) the peaks at 9.15 \(\mu\) and 9.60 \(\mu\) represent the \(V_3\) mode (P-O-asymmetric mode) while the peaks at 10.40 \(\mu\) corresponds to \(V_1\) mode (P-O-symmetric stretch) of PO\(_4\) ions. The broad absorption band at 2.78 \(\mu\) to 2.86 \(\mu\) (3500-3600\(^{\text{cm}^{-1}}\)) shows the presence of (OH) in apatite structure (Romo, L.A., 1954) while the occasional presence of bands at 6.25 \(\mu\) (1600\(^{\text{cm}^{-1}}\)) is attributed to the presence of adsorbed water molecules (Adrievaskaya et al., 1967).

Out of all these peaks the doublet in the 1450\(^{\text{cm}^{-1}}\) and 870\(^{\text{cm}^{-1}}\) frequency region, appears in carbonate apatites. Two hypothesis have been put forward to explain these peaks, viz., 1) the bands are caused by the presence of some carbonate minerals like calcite or magnesite mixed with apatite (Posner, A.S., and Duyckaerts, G., 1954) and 2) the bands are formed by a
molecular species forming an integral part of the apatite structure. McConnell, D. (1952, 1960) and Altschuler et al. (1952) have demonstrated the existence of carbonate apatite as a distinct variety of apatite rather than a mixture of carbonate mineral and fluor-apatite. This has been substantiated by 1) infra-red spectral study of pure as well as apatite-carbonate mixture which can show the presence of even 0.03 % CaCO₃; 2) leaching studies and 3) heating experiments (Tuddenham, W.K.; and Lyon, R.J.P., 1960; Rooney, T.P. and Kerr, P.F., 1967; Brophy, G.P., and Nash, T.J., 1968).

The infra-red spectral studies of Matoon phosphorite samples (A, B and C) show the characteristic doublet absorption in the 1445 cm⁻¹ frequency region. This coupled with the absence of the V₄ vibration of (CO₃)⁻² in the 14.8 μ (710 cm⁻¹) frequency region, a characteristic of all carbonate mineral, indicates that the CO₂ content of these sample is structural instead of any discrete carbonate mineral admixture. The infra-red spectra of Dakan Kotra samples (D and E) which show the doublet absorption in 870 cm⁻¹ frequency region and presence of V₄ vibration of (CO₃)⁻² in the 710 cm⁻¹ frequency region, indicates that the CO₂ is in a state of discrete phase. The presence of a weak absorption peak in the 3600 cm⁻¹ region in these sample indicates the presence of (OH) in the apatite structure. In Dakan Kotra sample (E) a hump at 1625 cm⁻¹ was noticed and which could be due to the presence of hydroxylapatite or due to moisture absorption during Kbr pellet preparation. However, the
Dakan Kotra variety shows a band at $650\text{cm}^{-1}$ frequency region, which may be interpreted as due to the definite presence of hydroxylapatite.

Most of the samples contain quartz, which is characterised by the appearance of the bands at $780\text{cm}^{-1}$ and $795\text{cm}^{-1}$ frequency region. Infra-red spectra of the samples D and E, which show additional weak bands at 6.95 $\mu$ and 11.40 $\mu$ wave lengths, indicate the presence of calcite while at 6.90 and 11.30 $\mu$, the presence of dolomite. The weak absorption band of illite appears at 7.75 $\mu$ region. Some of the Matoon samples show the characteristic absorption band of ilmenite at 10.4 $\mu$, hematite at 7.05 $\mu$ and kaolinite at 9.65 $\mu$ and 10.68 $\mu$ regions.

**Dolomitic Marble**

In general, the rock is fine to medium grained. The major mineral assemblage in these rocks include mainly calcite and dolomite with quartz and rarely opaque of iron. Calcite and dolomite were distinguished by staining with alizarin red-S (Friedman, G.M., 1959). Calcite grains generally range in size upto 1.18 mm or more in diameter. The grains are generally colourless in appearance but also show greyish colour with two sets of intersecting cleavages (Pl. XIII, Fig. 3). The grains are so arranged as to give the appearance of mosaic. Dolomite crystals vary in size between 0.38 and 1.71 mm in diameter. Recrystallization produced a medium to coarsely
crystalline mosaic in which many of the dolomite crystals show euhedral form (Pl. XIII, Fig. 4). The unaltered calcite matrix shows patchy distribution of fine grained dolomite.

The quartz, which is occasionally associated with the rocks occur in several forms. Many samples have rounded clastic grains of quartz. Authigenic euhedral crystal of quartz replacing calcite and dolomite could be seen in some samples of Dakan Kotra area (Pl. XIV, Fig. 1). There are also veins of quartz (Pl. XIV, Fig. 2) with ferruginous chert.

Quartzites

The quartzites are mainly composed of quartz with minor amounts of carbonate and micaceous minerals. The cementing material is fine grained quartz with some chert and iron oxides. The texture is typically granoblastic with medium to coarse grained quartz having angular to subangular and subrounded shape. Fine inclusions of minerals like tourmaline, apatite, zoisite and zircon are commonly seen in quartz (Pl. XIV, Fig. 3).

Several varieties of quartz have been identified according to the terminology given by Folk, R.L. (1958). Common quartz (Pl. XIV, Fig. 3) occurs as monocrystalline grain and generally shows clear appearance except a few minerals with dusty inclusions. The stretched metamorphic quartz occurs in the form of polycrystalline grains with sutured boundaries along with the occasional development of muscovite (Pl. XIV, Fig. 4). The
reworked quartz (Pl. XV, Fig. 1) grains show abraded overgrowth. They are clear in appearance and often show inclusion of tourmaline, zircon, zoisite, mica and apatite (Pl. XV, Fig. 2).

**Phyllites**

Microscopic examination of phyllites reveals that quartz, mica, biotite, feldspars and chlorite are the principal constituents with appreciable amounts of carbonate materials. The other minor minerals identified include graphite, pyrite, tourmaline, apatite, garnet, rutile and iron oxides.

There are a few prophyroblasts of medium to coarse grained quartz having subangular and subrounded shapes. The smaller quartz grains are frequently intermixed with muscovite and biotite, while the large quartz grains often show eye-shaped pressure shadow (Pl. XV, Fig. 3) filled up with carbonate, chlorite and muscovite. Some porphyroblasts of quartz show a halo of muscovite and chlorite around them (Pl. XV, Fig. 4).

Generally the phyllites along their foliation direction show parallelism of micaceous minerals and quartz (Pl. XVI, Fig. 1) as well as microfolds (Pl. XVI, Fig. 2).

The greenish yellow coloured chlorite, appears almost isotropic and often shows inclusions of quartz and tourmaline (Pl. XVI, Fig. 3). The subhedral grains of plagioclase feldspar (Pl. XVI, Fig. 4) occur in association with quartz and micaceous minerals.