CHAPTER 3

MOLYBDENITE MINERALIZATION & ORE PETROGRAPHY
3.1 Introduction

Molybdenum is a metallic, silvery-white element, with an atomic number 42. Chemically, it is very stable, but will react with acids. One of the unique physical properties of molybdenum is its very high melting point about 2,600 °C. This is 1,000 °C higher than the melting point of steel and 500 °C higher than the melting temperature of most rocks. It has the fifth highest melting point of all of the elements. Molybdenite (MoS₂, molybdenum sulphide) is the major ore mineral of molybdenum. It is rarely found as crystals, but is commonly found as what the mineralogists describe as foliated masses. This means the mineral forms folia or layers, like the mineral mica. It is metallic gray, has a greasy feel, and very soft only 1 on Moh’s hardness scale. Its softness, metallic luster and gray colour led scientists to mistakenly believe it as a lead mineral. Geologically, molybdenite forms in high-temperature environments particularly in igneous rocks. The high-grade ores contain over 0.5% Mo, whereas an ordinary contain 0.5-0.2%, low-grade ores 0.2 – 0.1% and very low-grade ores 0.1 – 0.02% Mo.

A number of Molybdenite occurrences are reported in Raichur district in Karnataka, where, the study area is incidentally being situated. Molybdenite deposits at Ashapura occur as disseminations and along fracture fillings within granites, situated around Ashapura village (Fig 3.1). The molybdenum bearing area forms the western periphery of an oval shaped pink granite pluton (Map 4), which forms a part of fine to medium grained pink granite (Prakash, 1996). The granites of the mineralised zone vary in composition from adamellite to granodiorite due to varying degrees of microclinization. Ubiquitous saussuritisatized plagioclase, fresh K feldspar replacing plagioclase megacrysts, clots of epidote + Biotite + Chlorite ± hbl ± opaque as break down product of hornblende and isolated occurrence of deformed biotite flakes (mostly chloritized)
are some of the characteristic features. The granites are grey in colour and are intruded by pink granites, which carry Mo-mineralization. Chalcopyrite and other sulphide minerals like bismuth, pyrite, sphalerite are associated along with molybdenite mineralisation.

![Image of mineralization in pink granites](image_url)  
Fig 3.1 Photograph showing nature of mineralization in pink granites of Ashapura

### 3.2 Mode of Occurrence

The molybdenite occurrence in the Ashapura area is associated with the medium to fine-grained pink granites as disseminations. Marked concentration of molybdenite is also noticed in 0.5 m thick leucogranite dyke trending E-W direction. This dyke is lensoid in shape and has a sharp contact with the enclosing pink granite. The estimate of molybdenite in leucogranite is 5-6% by volume (Prakash, 1996). The mineralised zone is intensely fractured with complex crosscutting fracturing and movement occurred both during and after mineralization. A majority of these fractures are filled with sulphide mineralization. The molybdenite flakes varying from 1 mm to 3 mm is observed smeared along the fractures filled with sericite, kaoline, epidote, chlorite and Muscovite mica. Some of these fractures are altered and comprise of muscovite+quartz+k-feldspar+molybdenite. Pyrite occurs in major quantities in most molybdenite-bearing granites and is weakly disseminated in the altered rocks. Good concentration of Molybdenite is also seen around the biotite
segregation in the eastern part of the Ashapura quarry and also in pegmatite veins between Ashapura and Jalibenchi quarries (Prakash, 1996)

Map 4: Geological map of Ashapura showing sample location
(after Prakash 1996)

3.3 Ore Minerals

Ore petrographic studies reveal a fairly consistent mineral assemblage of ore minerals like Molybdenite, Pyrite, Chalcopyrite, Bismuth, Sphalerite and Magnetite. The physical properties of the minerals as determined by polished surfaces assist substantially in the mineral identification. The most important physical properties are crystal form and habit, cleavage and parting, twinning, zoned structure, intergrowths, hardness, and resistance to abrasion, tenacity and colour of powder.
Molybdenite is a very soft metallic mineral. It can be easily confused with graphite. **Graphite** has a darker black-silver colour and a black-grey to brown-grey streak, whereas molybdenite has a bluish-silver colour and streak. Unfortunately, the difference is so slight that it is recommended that the two minerals be seen side by side. Their respective streaks should also be observed side by side to appreciate the differences. If larger samples, free of host rock, are available, then the greater density of molybdenite can be used for identification.

Molybdenite's structure is composed of molybdenum ions sandwiched between layers of sulphur ions. The sulphur layers are strongly bonded to the molybdenum, but are not strongly bonded to other sulphur layers, hence the softness and perfect cleavage. It is soft enough to leave a mark on paper and fingers. Its greasy feel is due to its extreme softness. It is sometimes called a very high lustre mineral and can be an interesting mineral to add to a collection.

### 3.3.1 Magnetite

Magnetite is present in the ores in rather variable quantities as euhedral rounded and even skeletal crystals dispersed within chalcopyrite, pyrite and sphalerite (Fig 3.2). It shows brownish grey colour and isotropic with no bireflectance, cleavages are absent. The early formed magnetite crystallized as euhedral to subhedral, skeletal grains that appear to have exsolution of titanium as oriented blades of ilmenite and is almost entirely martitised.

![Photomicrograph of pyrite, magnetite and chalcopyrite association](image-url)
3.3.2 Pyrite

Pyrite is the dominant sulphide and is present as anhedral to euhedral grains surrounded by chalcopyrite or is replaced by chalcopyrite (Fig.3.2). It is shows yellowish white colour, no bireflectance, isotropic. Being one of the first minerals to crystallize, it is replaced by many other minerals like chalcopyrite, sphalerite, magnetite, covellite and molybdenite. Twinning lamellae is very rarely observed and zoning is not uncommon. At some places it shows some replacement relics of chalcopyrite, sphalerite and magnetite. The chalcopyrite/pyrite ratios vary strongly but, if the entire deposit is considered, pyrite is more abundant.

3.3.3 Chalcopyrite

Chalcopyrite is the dominant copper mineral occupying as anhedral interstitial grains and as fracture fillings in pink feldspar, pyrite and replacing molybdenite along its cleavages (Fig 3.3). Substantial amount of chalcopyrite is also noticed along the fracture fillings within granites leading to the alterations and mineral assemblages of chlorite, epidote and biotite. Under microscope, it shows yellow colour, no bireflectance, no internal reflection. It replaces pyrite, molybdenite at places, and contains some inclusions of sphalerite showing the characteristic exsolution lamellae.
3.3.4 Molybdenite

Molybdenite is mainly confined to the periphery of the granite pluton, where it is locally the predominant ore. It is dispersed in granites forming plates as irregular rosettes (Fig. 3.1) and disseminated grains. The molybdenite dissemination is generally observed as sub-parallel to crumpled blades in small veinlets.

Under microscope, it shows white colour, very strong internal reflection white with pinkish tint with marked variable extinction. It veins with chalcopyrite, bismuth and wolframite. It shows characteristic extremely strong bireflectance, parallel displacement is very common, often produce twinning like texture. The polysynthetic twinning is indicated by marked variation in polarisation effects in sections. It contains some inclusions of Bismuthinite, Chalcopyrite and wolframite (Fig 3.4).

![Fig 3.4: Photomicrographs showing the typical Molybdenite with lamellar twinning (B) and associated minerals like chalcopyrite, bismuth and wolframite(A)](image)

3.3.5 Bismuth

Bismuthinite and native bismuth are the important minerals associated with molybdenite in the Ashapura area, but occur in minor quantities. It is shows white creamy colour, showing weak but distinct bireflectance, anisotrophism is distinct. Twinning is common and may be induced by grinding or scratching, stresses created within the bismuth on crystallization are apparently to produce twinning. Occur as anhedral inclusion within molybdenite specks (Fig 3.4A).
3.3.6 Covellite

It shows indigo-blue colour, extraordinarily high bireflectance, high anisotrophism and absence of internal reflection. It occurs as idiomorphic crystals and it replaces chalcopyrite along grain boundaries (Fig 3.5A).

![Photomicrograph showing covellite replacing chalcopyrite](image)

3.3.7 Sphalerite

It shows grey colour, no bireflectance, slightly anisotropic from light to dark grey, no visible internal reflection has been seen. Occur as inclusion with in chalcopyrite as exsolution lamellae (Fig 3.5 B).

3.3.8 Wolframite

It occurs as the tabular idiomorphic crystals and as masses of interpenetrating laths with in the molybdenite flakes, shows the characteristic grey colour, weak bireflectance property and slightly anisotropic. Associated with chalcopyrite and bismuth.

3.5 Ore Mineral Texture

The ore microscopy involves not only identification of individual mineral grains but also the interpretation of the relationship between grains or ore mineral textures. These textures may provide evidence of the nature of such processes as initial ore deposition, post-depositional re-equilibration or metamorphism,
deformation, annealing and weathering. The recognition and identification of texture is important step in understanding the origin and post depositional history of an ore. The textures observed in many polymetallic ore reflect the stages, sometimes numerous in their development and post depositional history.

3.5.1 Replacement texture

Replacement of one ore mineral by another mineral during mineralization is common in many type of ores. A major problem in textural interpretation is the recognition of replacement when no vestige of the replaced phase remains. In the Ashapura Molybdenite mineralization, replacement textures are common in many associations, the most common and important replacement textures noticed are between Molybdenite-Chalcopyrite, Molybdenite-Wulfenite, Chalcopyrite-Covellite, Molybdenite-Bismuthinite, Pyrite-Chalcopyrite, Magnetite-Chalcopyrite. The replacement may result from one or more of the following processes; dissolution and subsequent reprecipitation, oxidation and solid-state diffusion. The resulting boundary between the replacing and the replaced minerals is commonly either sharp or irregular or diffused. Replacement of Chalcopyrite by Covellite along the grain boundary appears in the form of thin laths the replacing phase projecting in to the host (Fig 3.5A). It also appear as thin concentric coatings developed roughly parallel to the advancing front of replacement. The chemical composition of the primary phase may control the composition of the phase that replaces it, replacement may also selectively remove one cation while leaving another, this is frequently seen in the replacement of chalcopyrite by Covellite.

Very small blebs of chalcopyrite distributed through sphalerite (Fig 3.5B), this texture has usually be referred by ore microscopists as emulsion texture, and it has been interpreted to have formed by solid state exsolution of a solid solution during declining temperatures. The fact that such textures are confined to higher temperature ores is seemed to support this interpretation. However, recently it has been clearly demonstrated that some (or most) emulsion-like textures have developed by replacement in which copper has been introduced in later ore fluids.
and combined with the iron in iron-rich bands of the host sphalerite to form chalcopyrite blebs.

3.5.2 Exsolution texture

Ore minerals undergo compositional or structural readjustments in the form of exsolution or inversion as they cool from the temperatures of initial crystallization or the maximum temperature of metamorphic recrystallization. The forms of the exsolved phases vary with the minerals involved, their relative proportions, and the post-depositional cooling history of the ore. The exsolution process results from diffusion, the nucleation of crystallites and the growth of crystallites or crystals. Similarities of crystal structure and chemical bonding between host and exsolved phase, particularly the matching of atomic arrangements in specific layers resulting in a shared plane of atoms, frequently dictate that exsolution is crystallographically controlled. If parent and exsolved phases have completely different structures or if there is no crystallographic continuity across the interface between phases, noncoherent exsolution occurs. Here the exsolution between sphalerite-chalcopyrite intergrowths is observed. The sphalerite in this type of ore contains chalcopyrite in the form of crystallographically oriented rows of blebs and rods (Fig 3.5 B). This form of chalcopyrite, appropriately termed "chalcopyrite disease" has commonly been ascribed to exsolution on the cooling of the ores after emplacement.

3.6 Twinning

Twinning may occur in mineral during initial growth, during structural inversion on cooling or as a result of deformation. This type of feature occur in ores subjected to any type of deformation and can even be artificially introduced into some of the soft minerals by rough treatment of specimens. Breaking of specimens by hammering, or damage caused during grinding or even in careless polishing can induce local pressure twinning in very soft phases such as native bismuth, argentite and molybdenite.
3.7 Paragenitic position

Mineral identification and the textural characterization are two major objectives in ore microscopy. These include the determination of the order of formation of associated minerals in succession or paragenesis and the estimation of the conditions under which the minerals formed. Paragenetic determination requires the detailed examination of the polished section to identify phases, recognize diagnostic textures, and decipher "time diagnostic" features.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
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<tbody>
<tr>
<td>Pyrite</td>
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<td>Magnetite</td>
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<td>Molybdenite</td>
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<td>Chalcopyrite</td>
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<td>Sphalerite</td>
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<td>Covellite</td>
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<tr>
<td>Bismuth</td>
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Fig. 3.6: Paragenetic sequence of ore minerals of the Ashapura area.

Molybdenite occurs generally as pegmatitic-pneumatolytic formation of the intrusive sequence, and consequently can be considered as a characteristic mineral for it. It has its widest extent in very quartz-rich pegmatites and similar pneumatolytic to high temperature hydrothermal veins. The Paragenesis is consequently variable, it also occurs always in contact pneumatolytic replacements, especially those in silicate rocks, although in minor amounts.

Ore petrographic studies reveal a fairly consistent mineral assemblage in all the ore-types, indicating an overall similarity in the environment of mineralization in spite of the diverse modes of occurrence. The primary minerals in order of decreasing abundance in all the ore-types are: molybdenite, chalcopyrite, pyrite, magnetite, sphalerite, covellite, and bismuth.
Quartz and microcline are the major silicate phases associated with ore minerals in all ore-types. A variable amount of biotite, epidote and chlorite is present. Epidote and chlorite here are conspicuous breakdown/alteration products of biotite and are quite coarse in nature. Since the alteration products in the pink granitoid predate quartz, microcline precipitation that broadly overlapped with precipitation of ore minerals, the alteration assemblage in the pink granitoid (saussuritized plagioclase, epidote, chlorite and biotite) is assigned a 'pre-ore' stage. The following discussion deals with the mineralogical and textural features of the different identifiable stages of ore-mineralization. Magnetite and pyrite constitute the early phase of mineralization. In all instances, euhedral magnetite occurs as inclusions with sharp outline within pyrite. These early generations of magnetite and pyrite (magnetite I and pyrite I) are fractured and have undergone fracture filling and replacement by chalcopyrite. Tiny euhedral unfractured pyrite grains dispersed in chalcopyrite mosaic represent a later generation of pyrite precipitation (pyrite-II). A younger generation of magnetite (magnetite-II) is found as minor phases that co-precipitated along with chalcopyrite. Chalcopyrite constitutes the major ore mineral. Medium grained equigranular aggregates with unequigranular grains forming and coarse-grained are common. Chalcopyrite commonly displays various types of twins; thick lamellar uniformly spaced twins assigned to a growth/annealing origin; thin, tapering and unequally spaced bent lamellae (deformation twins) and lensatic twins (thermal relaxation) Kelly and Clark (1973); Clark and Kelly (1973) were revealed on etching.

3.8 Alterations

K-silicate alteration (K-feldspar, biotite and quartz) is established in the granites, K-feldspar and biotite replace the primary K-feldspar and plagioclase, biotite is partly replaced by chlorite.

Phyllic alteration: Consist of quartz + molybdenite + K-feldspar, sericite with sporadic pyrite, chalcopyrite, bornite, magnetite, and bismuthinite and are concentrated in the potassically altered core of the deposit in which plagioclase and mafic minerals have been replaced pervasively by K-feldspar and Mg-rich
biotite, respectively. Sericitic alteration is developed in the upper levels of the deposit and is represented by a quartz-pyrite assemblage and to coarse-grained, euhedral pyrite and minor carbonate. The term 'sericitic' is used in this work in the sense of alteration consisting of a mica-type mineral quartz + pyrite, (Hayba et al. 1985). These assemblages were formed during the sericitisation as a reaction of the fluid with K-silicate altered rocks. The transitional zone (K-silicate-sericitic) between the K-silicate alteration and sericitic alteration is characterised by the presence of chlorite, sericite, quartz, pyrite and chalcopyrite. The propylitic alteration includes chloritisation, epidotisation, sericitisation of the granite as described by Bogdanov (1987). Local epidote-chlorite-quartz-carbonate alteration is contemporary with the magnetite-chalcopyrite assemblage (Dragov and Petrunov 1996), and is grouped with the propylitic alteration. The Ashapura mineralization comprising early potassic (core) and propylitic (periphery) alteration. Based on fluid inclusion data presented in Hezarkhani and Williams-Jones (1998), the hydrothermal fluids responsible for potassic alteration at high temperature (420 °C, and 360 °C, respectively), high salinity (up to 60 wt.% NaCl equiv.) aqueous liquids and were accompanied by a low salinity vapor. These fluids are interpreted to represent an orthomagmatic fluid, which boiled episodically. Locally the proportion of quartz is sufficiently high that this alteration is better described as silicification.