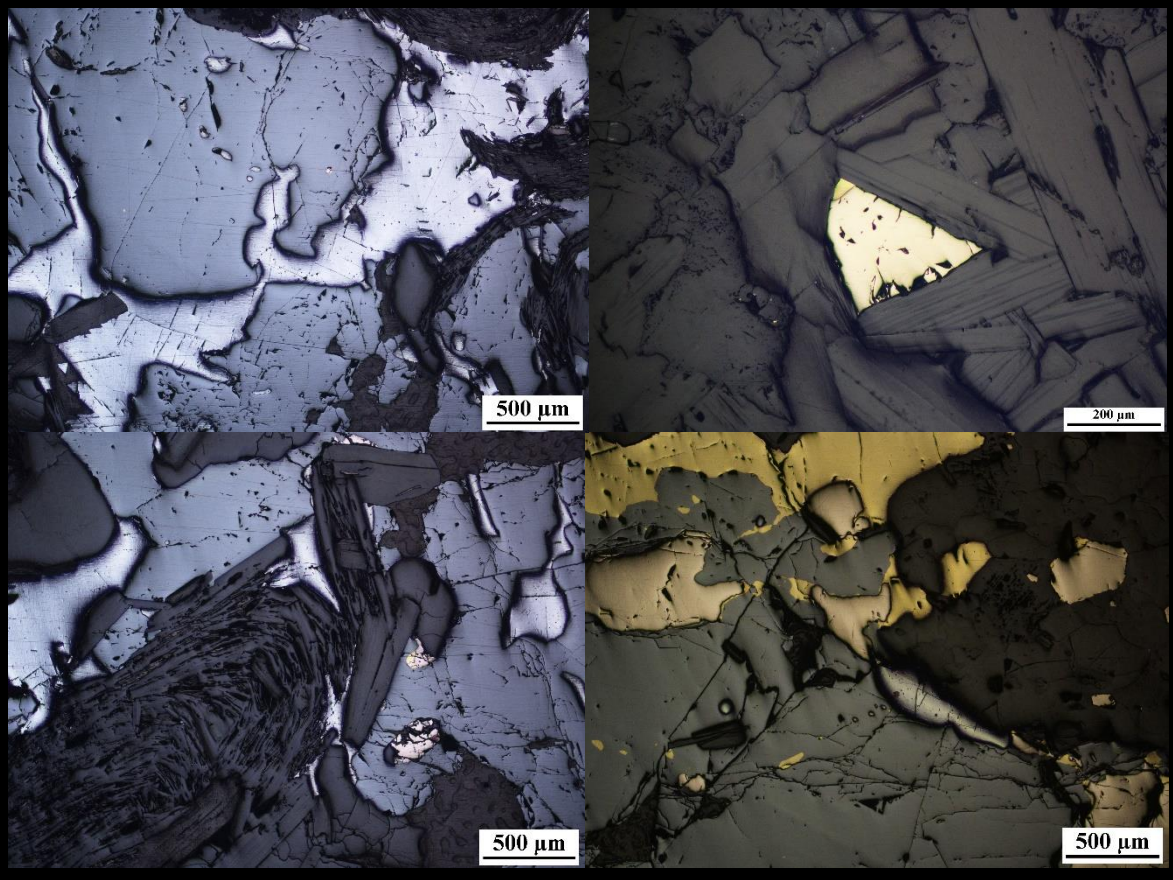
MODE OF OCCURRENCES , TEXTURE AND GEOCHEMISTRY OF SPHALERITE AND GALENA IN Zn-Pb ORES FROM KAYAD DEPOSIT



Sohini Chatterjee
Exam roll. MGEO194010
Department of Geological Sciences
Jadavpur University

MODE OF OCCURRENCES , TEXTURE AND GEOCHEMISTRY OF SPHALERITE & GALENA IN ZN - PB ORES FROM KAYAD DEPOSIT

Thesis submitted

For the partial fulfilment of Master of Science in Applied Geology , 2019

Submitted by

SOHINI CHATTERJEE

PG II

EXAM ROLL NO : MGEO194010

REGISTRATION NO : 128250 0F 2014-15

Department of Geological Sciences

Jadavpur University

May , 2019

Under the supervision of

Dr. Dipak C. Pal

Professor

Department of Geological Sciences

Jadavpur University

যাদবপুর বিশ্ববিদ্যালয়
কলকাতা-৭০০০৩২, ভারত

JADAVPUR UNIVERSITY
KOLKATA-700032, INDIA

FACULTY OF SCIENCE : DEPARTMENT OF GEOLOGICAL SCIENCES

Certified that the dissertation entitled "***Mode of occurrence, texture and geochemistry of sphalerite and galena in Zn-Pb ores from Kayad deposit, Western India***" submitted by **Sohini Chatterjee** for the partial fulfilment of the M.Sc. Final Year, Final Semester Examination in Applied Geology, 2019, Jadavpur University embodies the results of studies carried out by her under my supervision and guidance. This work has not been submitted elsewhere for the award of any other degree.

31.5.2019

Dr. Dipak C Pal
Professor
Department of Geological Sciences
Jadavpur University
Kolkata 700 032

Forwarded by

Dr. Dipak C. Pal
Professor
Dept of Geological Sciences
Jadavpur University
Kolkata - 700 032, WB, INDIA

31-5-19

Dr. Sanjoy Sanyal
Professor and Head
Department of Geological Sciences
Jadavpur University
Kolkata 700 032

Head
Department of Geological Sciences
Jadavpur University
Kolkata-700032

দূরভাষ : ২৪১৪-৬৬৬৬/প্রসারণ : ২২৬৮
Website : www.jadavpur.edu
E-mail : hod_geological@jdvu.ac.in
Phone : 2414 6666/Extn. 2268

ACKNOWLEDGEMENT

I am extremely grateful to Professor Dipak C Pal as he gave me an opportunity to work in the HZl mines ,Vedanta on the sulphide ores present in that area .Without his guidance , valuable suggestion and criticism the work would never have been completed .Besides this I am also thankful to him for providing me the chance of working in the laboratory as well as getting the opportunity to work with different instruments

I would also like to thank Phd scholar Eileena Das for her persistant guidance and help.

I extend my sincere thanks to IIT-Kharagpur for conducting EPMA and LA-ICP-MS studies for our required samples

I thank my friend Koushik Das for helping me throughout .Besides my teachers and classmates who made life worth living and Jadavpur University for giving me a chance to spend five years of my life in this campus

ABSTRACT

The Aravalli mountain range trending NNE-SSW is one of the most prominent physiographic feature of the Western Indian Shield rich in different mineralization. This geological region is characterized by several metallogenic provinces. Kayad is a mineralized belt in Ajmer that extends over a strike length of 60 km from Kharwa (37 km southwest of Ajmer) in the southwest to Hoshiara in the northeast (13 km northwest of Kishangarh).It is famous for Pb-Zn mineralisation . Hzl under Vedanta had started mining in this area five years ago due to its richness with respect to lead-zinc deposits and also extracted silver and cadmium as by-products, however there has not been any extensive study with respect to the different types of ore deposits , the rock types and mode of occurrences of sulphides as well as ore genesis and hence lack of any publication .

Thus the study claims at understanding the different types of ore deposit , mode of occurences of sulphides as well geochemical analysis of Zn-Pb to get an idea about the possible causes of ore mineralisation through field and handspecimen study of the rocks followed by thin section analysis and finally EPMA and LA-ICP-MS study of the minerals

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CHAPTER 1

INTRODUCTION

1.1: *Introduction*

The Western Indian Shield is one of the most important metallogenic provinces in India and serves as a voluminous contributor of economically important minerals in India. This geological region is characterized by several metallogenic provinces representing several epochs containing various economically important metals. One of such economically important ore deposit is the lead-zinc ore deposit and it is distributed in the south-eastern Rajasthan. Pb-Zn deposits occur within the Bhilwara Supergroup of Archaean to Lower Proterozoic age (e.g. Agucha, Dariba-Rajpura, Pur-Banera), Lower Proterozoic Aravalli Supergroup (e.g.Zawar) and Lower to Upper Proterozoic Delhi Supergroup (e.g. Kayad-Ghugra). In terms of tonnage and grade the deposits occurring within the Archaean basement rocks far exceed those occurring in the main Aravalli and Delhi basins. Amongst all these, the Ajmer Pb-Zn belt extends over a strike length of 60 km from Kharwa (37 km southwest of Ajmer) in the southwest to Hoshiara in the northeast (13 km northwest of Kishangarh).

1.2*: Origin of the problem*

The extensive metallic mineralisation in terms of lead and zinc is well known in the Kayad area however there is no considerable amount of work in terms of different types of ore deposits and rock associated, mode of occurrences of sulphides and ore genesis in the Kayad belt. The primary mineralisation appears to be a remobilization phase in the wake of granitic intrusions in the area that has resulted in the setting up of thermal and chemical gradients resulting in the formation of Zn-rich sulphide deposit (Vashistha et al., 2018). However the question still remains whether the ore genesis actually occurred through the above mentioned phenomenon and whether the deposits in the ductile shear zone belong to a single deposit or superimposition of multiple deposit types.Our present study is centred around the kayad mines which is located about nine kilometres NNE of Ajmer city and about three kilometres of North of village Ghughra.

1.3: *Objective of the study*

Due to the unavaibility of detailed work in terms of research papaers and documentation on the ore minerology of the kayad area in Rajasthan, our objective for the present study summarizes as follows ;

- Identification of different types of Zn-Pb ores in the Kayad area
- Detailed investigation of different lithologies hosting the suphide ores and their textural relations with other sulphide phases

- Investigation of geochemistry of sphalerite and galena including major, minor and trace element composition
- Understanding the possible causes of ore formation

1.4: *Methodology of the present study*

In course of our present study firstly systematic sampling has been done in and around kayad and at different levels of the kayad mines .Additional samples were collected from the dump area and were sorted out according to different levels.The rock samples were collected from various levels like N330 mrl,N169 mrl,S150 mrl etc.The rocks within the mines dip around 50-72 degrees and are associated with complicated structural attributes and superposition of various folds. After systematic sampling several handspecimens representative of various rock lithology were studied in details in the laboratory. Selected hanspecimens were prepared for thin section analysis under petrographic microscope both in both transmitted and reflected light for identification of different ore and host rock minerals alongwith their textures and mineral associations.

For obtaining the geochemical data, the selected thin sections were analysed by Scanning Electron Microscope (SEM) and Electronprobe microanalyzer (EPMA) for their major and minor element compositions.

Trace element composition using LA-ICPMS of sphalerite and galena has also been done to understand variation in composition of the ore minerals in various rock types

CHAPTER 2

GEOLOGICAL BACKGROUND

2.1*: Regional geology*

The Rajasthan State is bounded on the west and northwest by Pakistan, on the north and northeast by Haryana and Uttar Pradesh and on the south-southeast and southwest by Madhya Pradesh and Gujarat States respectively. The Aravalli hill range extending from Delhi in the northeast to the plains of north Gujarat in the southwest, divides the State into two unequal parts. The area to the east of the hills is covered by the eastern plains and the Vindhyan plateau. Rajasthan forms north-western part of the Indian Shield. The rock sequences of the region cover a timespan of about 3500 to 0.5 Ma. The State exposes a variety of lithological and tectonic units ranging in age from Achaean to Recent times. The basement rocks, Sandmata Complex, Mangalwar Complex and Hindoli Group of Bhilwara Supergroup, occupy central and south-eastern plains. They are Achaean in age and comprise in general, granulite-gneiss, amphibolite, metapelite, paragneiss, calc-silicate rocks, greywacke (the older granite-greenstone belt) and metavolcanic, metagreywacke (the younger granite greenstone belt) respectively. The Lower Proterozoic supracrustal rocks of the Jahazpur, Rajpura-Dariba, Pur-Banera and Sawar Groups of Bhilwara Supergroup rest on the basement rocks of the Mangalwar Complex and host a number of lead, zinc and copper deposits.

The Bhilwara Supergroup of rocks is intruded by the Untala-Gingla Granite, Berach Granite, basic and ultramafic bodies.

The Proterozoic fold belts, viz., the Aravalli fold belt (the Aravalli Supergroup) and the Delhi fold belt (the Delhi Supergroup) occupy the southern and south-eastern, and south-western and north-eastern Rajasthan respectively. The Aravalli Supergroup is represented by metamorphosed and complexly folded clastic sediments with minor chemogenic and organogenic assemblages with interlayered basic whereas the Delhi Supergroup comprises mainly carbonates, metavolcanics, meta pssammites an metapelites, intruded by magmatic rock of Phulad Ophiolite Suite and syn-orogenic granites of Sendra-Ambaji, Bairath, Dadikar, Harsora, etc. A number of base metal deposits are located in these belts as also other minerals.The isolated hillocks of western Rajasthan constitute the Upper Proterozoic Malani Igneous Suite and the Erinpura Granite pluton.The northern and north-western parts of the State exhibit Upper Proterozoic-Early Cambrian rocks of the Marwar Supergroup which are overlain by sedimentary rocks of different ages of Palaeozoic and Mesozoic Era. Many industrial mineral deposits are found in these rocks. The Deccan Traps are restricted to the south-eastern part of the State in Chittaurgarh-Banswara area. The Cenozoic rocks are manifested Barmer and Jaisalmer basins in the west and Ganganagar-Palana shelf in the north. The Quaternary sediments of aeolian and fluvial origin constitute the Thar Desert of Rajasthan. The lead-zinc deposits of Agucha and Pur-Banera in Bhilwara district, Kayar-Ghughra deposit in Ajmer district, Dariba-Rajpura-

Bethumbi deposit in Rajsamand district; gold in Jagpura-Bhukia belt in Banswara district; limestone in Jaisalmer and Chittaurgarh districts; potash in Ganganagar-Nagaur basin etc are some of the important mineralised belts.

Physiographically, Rajasthan is divided into four regions,(fig 2.1) bearing a close relationship with the geological history of the State, viz., (i) Western desert plains, (ii) Aravalli mountain range, (iii) Eastern plains and (iv) Vindhyan plateau. The Aravalli hills of Rajasthan traverse the State in a NNE-SSW direction exposing rocks of the Delhi Supergroup comprising alternating hill ranges . The Western Indian Shield can be conveniently sub-divided into provinces on the basis of distinct lithological, structural, metamorphic, geochemical characteristics and geochronology. Shears/fault zones mark the boundaries and join the Provinces. The different provinces of the Western Indian Shield from east to west are the BGC Province, the Aravalli-Delhi Province and the Trans-Aravalli Province. The oldest cratonic nucleus of the Western Indian Shield, familiarly known as the Banded Gneissic Complex (BGC), occupies a large tract in the Mewar plains of south and east Rajasthan and forms a major component of the BGC Province. It is skirted on the west and southwest by Proterozoic fold belts of the Aravalli and the Delhi Supergroups (forming theAravalli-Delhi Province), and an arcuate belt of low grade metamorphosed volcano-sedimentaries (erstwhile Gwalior Series of Heron, 1953; Eastern Aravalli Belt of Gupta, 1934; and Hindoli-Jahazpur Groups of Gupta et al. 1980)

and Vindhyan platformal sediments (Upper Proterozoic) demarcate the eastern boundary of this craton. Besides, a Deccan Trap cover delimits the southern boundary of its outcrop area. The Delhi Supergroup occurs in the form of two distinct fold belts, i.e., the North Delhi Fold Belt (NDFB) in Alwar, Dausa, Jaipur, Bharatpur, Sikar and Jhunjhunu districts and the South Delhi Fold Belt (SDFB) in Ajmer, Pali, Rajsamand , Udaipur and Sirohi distrcits. The Trans-Aravalli Province encompasses the area west of the Aravalli Mountains. Late Proterozoic igneous and sedimentary rock assemblages, grouped under the Malani Igneous Suite alongwith crystalline of Achaean age (equivalent of the BGC) and the Marwar Supergroup occupy a large part of the Trans-Aravalli Province. The Malani and the Marwar rocks are not deformed and, therefore, the episodes of the Precambrian magmatism/sedimentation in this part of the Western Indian shield are post-tectonic (anorogenic phenomenon).The Late Proterozoic to Early Cambrain (?) MarwarSupergroup occupies the western most and northwestern parts of the State and comprises the Jodhpur Sandstone, Bilara dolomite-limestone, Hanseran evaporate sequence and the Nagaur sandstone, clay and Siltstone.These sequences overlie the basement constituted mainly by the Malani Igneous Suite. The rocks of the Marwar Supergroup are unconformably overlain by the Bap Boulder Bed which forms the basement for the Badhaura Sandstone, the youngest Palaeozoic formation. (Geology and Mineral resources of rajasthan , 2011)

2.2: *Local Geology*

Kayad is situated about nine kilometers NNE of Ajmer city which isDistrict Headquarters and about three kilometers N of Village Ghugra .TheGhugra Village is located on the Jaipur-Ajmer National Highway No.8. The nearest Railway Station is Ajmer, which is on the Udaipur-Jaipur meter-gauge of Western Railway.The Madarpura, Ghugra Kayar belt forms a part of the east Central ProterozoicDelhi Super Group (Heron, 1953). The litho-units in the area are co relatable with Ajmer formation of the Ajabgarh Group , which is a sub-basin of older age in comparision to others located in the central axis and west . It is comprised of pegmatitic and quartz veins cross cutting all the lithologies, quartzite, calc-silicate , garnetiferous mica schist and migmatites (fig 2.2)

The Kayar area is mostly soil covered except for an isolated domal hillock in the eastern part, exposing quartzites, quartz mica-schist, carbonate and calc-silicate rocks.The Annasagar granite in the vicinity of Kayar occur intrudes the migmatites . The Western flat area is occupied by granite gneiss and migmatites. The meta-psammopelitic rocks occur in the eastern part. These litho-units are crisscrossed extensively by tourmaline bearing Pegmatites and vein quartz. Few basic dykes/sills are also recorded in this area.The general trend of the formations in this area is NNE-SSW with steep dips of 75° or more due east or west. Rich Zinc mineralisation is noted in the graphitic quartz mica schist with intercalated carbonate and acid volcanic (?) layers. Carbonate and calc-silicate

rocks,Garnetiferous and graphitic mica-schists and variants. (Intercalated meta-acidvolcanics),Quartzites (meta-cherts), Amphibolites.Our investigated area in kayad lies between N latitude 26°31'00" to 26°32'30" and E longitude 74°41'00" to 74°42'00".Underground Mines has been set up in this area which is a decline is nature to excavate the ores. Qms is the major rock type encountered and the schistose layers are dominated by graphite.Exploration of Hzl under Vedanta has established mineral reserves(probable and possible) of 9.2 million tonnes with 12%Zn and 1.2% Pb and minor amount of copper. The associated metals include silver, cadmium and mercury. The sulphide mineralization is mainly associated with graphitic quartz-mica schist, although it also occurs in quartzite and calc-silicate rock. These rocks are profusely invaded by pegmatite and quartz veins. The calc-silicate rocks show typical contact metamorphic skarn assemblages, characterised by the presence of diopside. Sulphides occur as fracture-fillings along fissures, veins, cleavages and foliation planes. The dominant sulphide ore is sphalerite with galena in subordinate amounts. Other sulphides include chalcopyrite, pyrite, and pyrrhotite

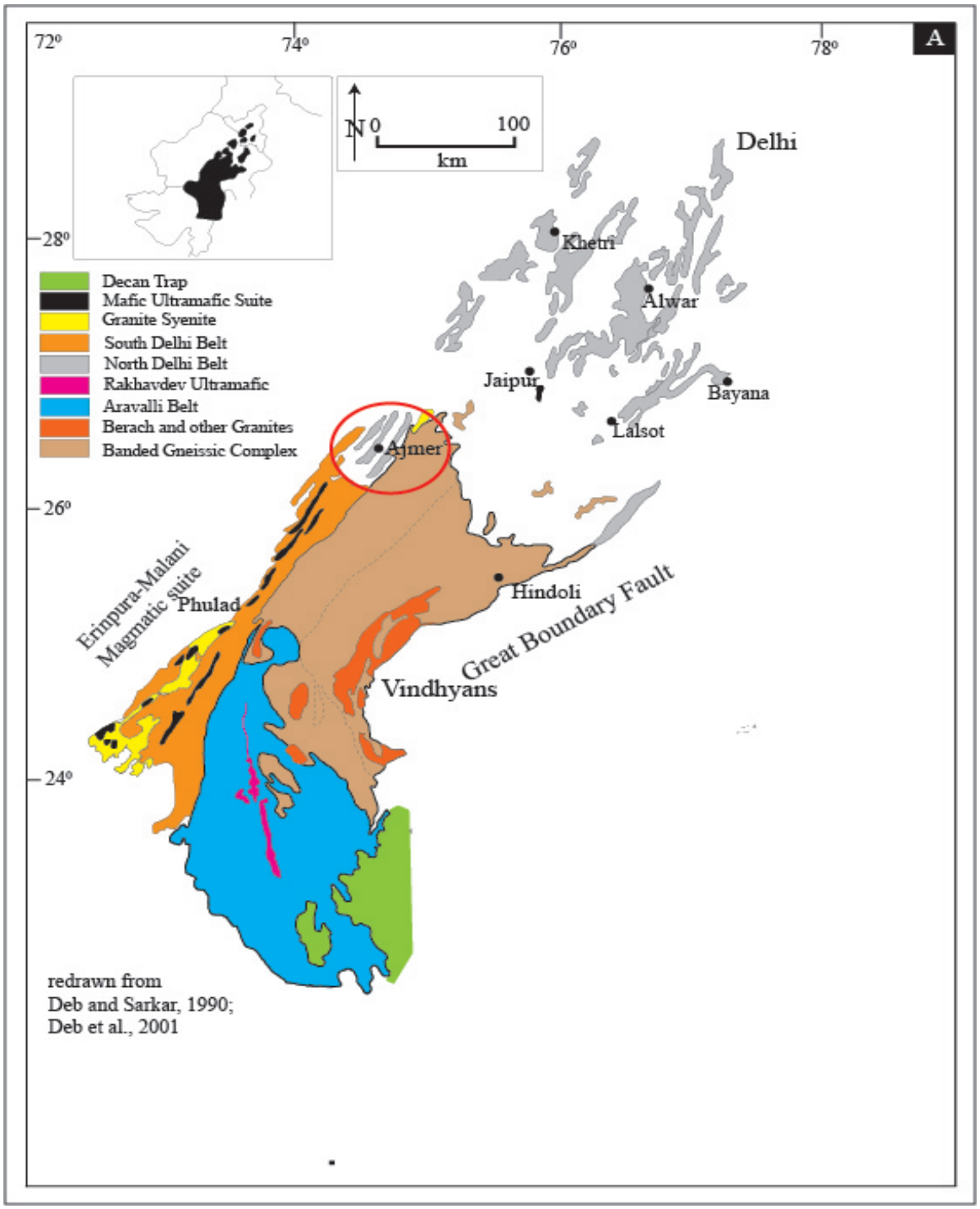


Fig 2.1 : Geological map of Western Indian Shield and location of Kayad circled . (Deb et al., 2001)

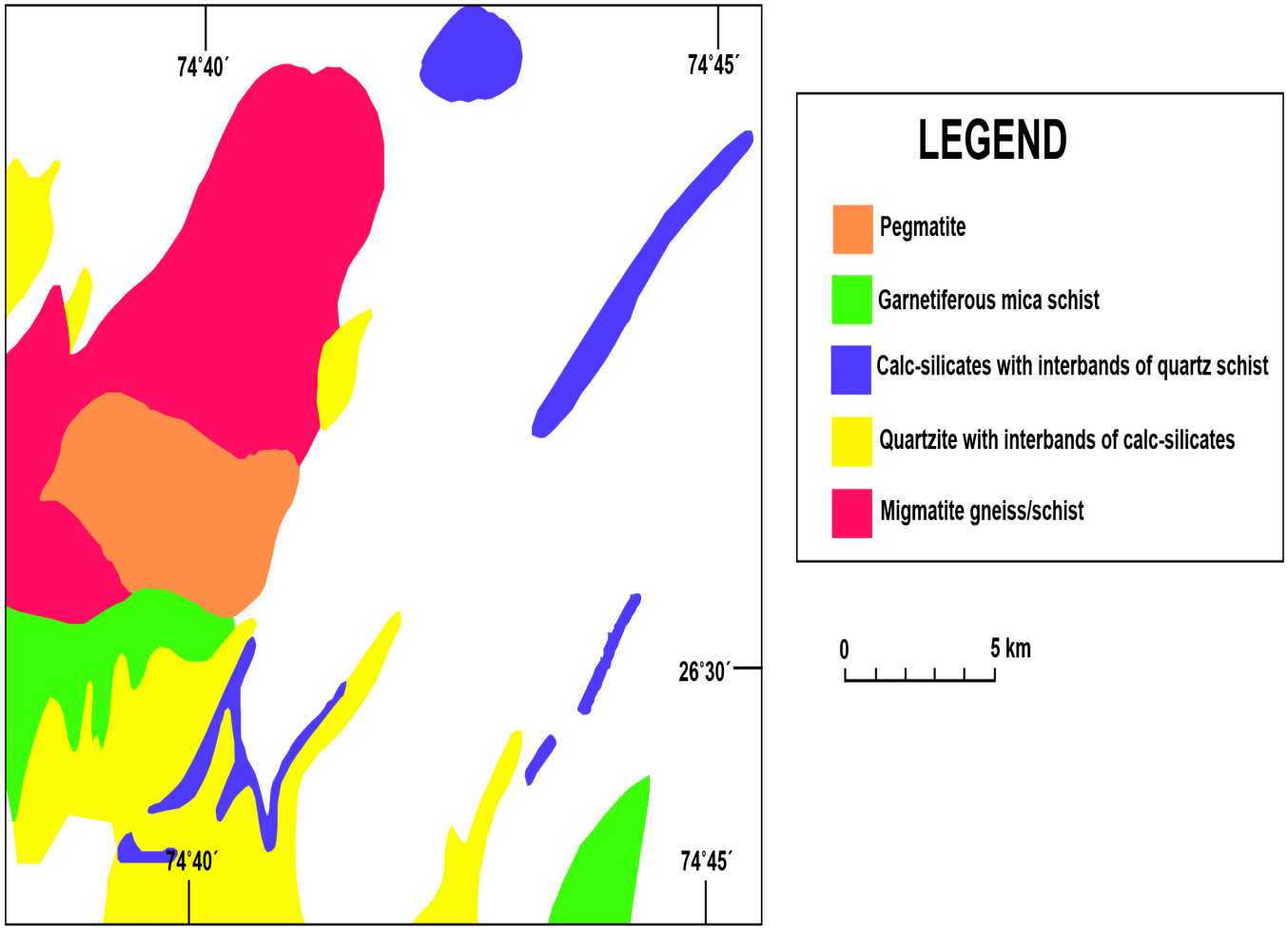


Fig 2.2 : Simplified geological map of Kayad area (After Sarkar and Deb,2012)

CHAPTER 3

HOST ROCK OF SULPHIDES vis-à-vis MODE OF OCCURENCES AND TEXTURES OF THE SULPHIDE ORES

In course of the investigation systematic rock samples were collected from multiple working levels in the mine. Additional samples were collected from the dump area and were arranged with respect to the different working levels. In this chapter we shall deal with the types of ore deposit, host rocks of the sulphides and mode of their occurrences

3.1*: Types of ore deposit in Kayad area*

There are two kinds of ore deposit present in Kayad area;

3.1.1: *Laminated ore*

The ore minerals that is sphalerite + galena + chalcopyrite + pyrrhotite and some pyrite occur layer parallel in the different rock types and in case of QMS parallel to the foliation planes. (Fig 3.1a, b & e)

3.2.2: *Massive ore*

The ore minerals are occupy most of the rock type, are extremely coarse grained and definitely are not concordant with the foliation. At some places the ore mineralisation is so intense that only relicts of foliation occur (fig 3.1c & d)

We will be concentrating on the massive ore and mode of occurrences of the sulphides falling under it

3.2: *Host rock of massive sulphides and mode of occurrences of the sulphides*

3.2.1: *Calc-silicates*:

The term calc-silicate is restricted to the coarse grained rock which is mineralogical composed of an assemblage of cpx + hornblende + calcite/dolomite + mica (Fig: 3.2.1a & c). It produces effervescence on using dil.HCl due to the presence of calcite. The massive rock has a uniform distribution of amphibole however the orientation is not in any particular direction rather haphazard. The cpx grains constitute the major portion of the rock. Quartz veins occur but in rare amount. These calc silicate assemblages of siliceous dolomitic limestone have without any doubt originated from the thermal metamorphism of siliceous dolomitic limestone by decarbonation reaction type and the representative skarn minerals are a proof of it

Calc-silicate rich zone chiefly hosts galena. The galena that occurs within the calc silicate rock is extremely coarse grained and occur in patches as well as disseminated(Fig 3.2.1.b) and is the dominant phase of sulphide besides which small amount of sphalerite occurs . Chalcopyrite and pyrrhotite is also present as minor patches in calc silicate rock. The sulphides are present in small amounts dispersed randomly in the rock matrix

3.2.2: *Graphitic Quartz Mica Schist (QMS)*

The rock type is a dark coloured mica schist where the schistose planes are defined by muscovite and quartz at some places.The normal mineral assemblage in these rocks is characterised by mica + quartz + graphite + sulphides. The rock overall is highly deformed, fractured and the foliation planes are folded gently (Fig 3.2.2a & b). Graphite is associated with the foliation planes. The vein quartz materials and pegmatite cut across the quartz-mica schist foliation planes and occur in multiple generations. Some are concordant with the foliation planes and are folded as such, hence are pre deformational events and some cut across the foliation at high angle thus are post deformational

The Qms majorly hosts Sphalerite+galena+chalcopyrite+pyrrhotite+pyrite (minor amount).The Sphalerite and galena rich zones vary in thickness and length

throughout the Qms body. These zones does not run along the entire body rather ends abruptly in between forming lumps. The Qms being highly deformed the Sphalerite does not have any specific localisation rather occurs both on the hinge and limb of the folded foliation planes. However the concentration in the hinge of the folds are maximum. They are coarse grained extensively. The Sphalerite grains are oxidised at most places however fresh surfaces do occur. Graphite within the Qms is mostly present in the Zn rich zones. The ore minerals are definitely not concordant with the foliation plane rather occur as lumps or discordant. At some places the ore mineralisation is so intense that only relicts of foliation are dispersed within the ore minerals(Fig 3.2.2c & d).Chalcopyrite and some pyrrhotite is also associated with massive sphalerite (Fig 3.2.2e)

3.2.3: *Quartzites*

Quartzites from kayad area have dense cherty appearance (Fig 3.2.3a) and shows transition to micaceous quartzites depending on the amounts of micaceous minerals namely muscovite and biotite .Some of them are pure Orthoquartzites with greater than 95% quartz. The cherty rock type has a dark coloured siliceous rock containing more than 90% fine to medium grained quartz . Some quartz veins containing occurs throughout the rock type. The veins as observed does not

follow any definite orientation and are of varying length and thickness. Their distribution is not uniform though. However the quartzite overall shows signature of deformation as well as fractures

The mineralogical assemblage comprises of Chalcopyrite+ Pyrrhotite + Sphalerite + Galena (minor amount) .Chalcopyrite is closely associated with the Quartzite rock type. Chalcopyrite is oxidised mostly and occurs as patches at some places too within the host rock (Fig 3.2.3a & b). At some places the chalcopyrite mineralisation has also concentrated around the quartz vein and the grains are much coarser, thus a variation of grain size. Pyrrhotite's major occurrence is within the quartzite rock. It is associated with chalcopyrite (Fig 3.2.3 b). Oxidation is least and occurs as disseminated without following any definite pattern and the distribution is not uniform too. Chalcopyrite occurs as discrete small inclusions within Sphalerite defining chalcopyrite disease as well as individual lumpy mass along the boundary of sphalerite and pyrrhotite .The sulphides also occur isolated in random orientation within the gangue. Galena occurs in extremely less amount associated with sphalerite mostly (Fig 3.2.3c)

3.2.4: *Pegmatite*

Numerous pegmatite are observed exposed in the Kayad area traversing all the other rock units in the area with varying dimensions. Quartz + plagioclase feldspar + tourmaline + muscovite are the chief constituents of the pegmatitic unit (fig 3.2.4a). Quartz is the leading phase present followed by feldspar and tourmaline.Feldsper grains are mostly weathered however fresh ones also prevail. Tourmaline grains are large enough and show a size variation. Some places have maximum concentration of tourmaline grains. Certain zones containing mica (muscovite) is observed within the pegmatitic unit.

With respect to ore mineralisation it is dominated by pyrrhotite + chalcopyrite and some sphalerite and galena, however the later occurrences are minimum (Fig 3.2.4 a).Fig 3.2.4b shows a thick pyrrhotite rich layer dispersed among the host rock. Fig 3.2.4c shows presence of galena in micro scale level

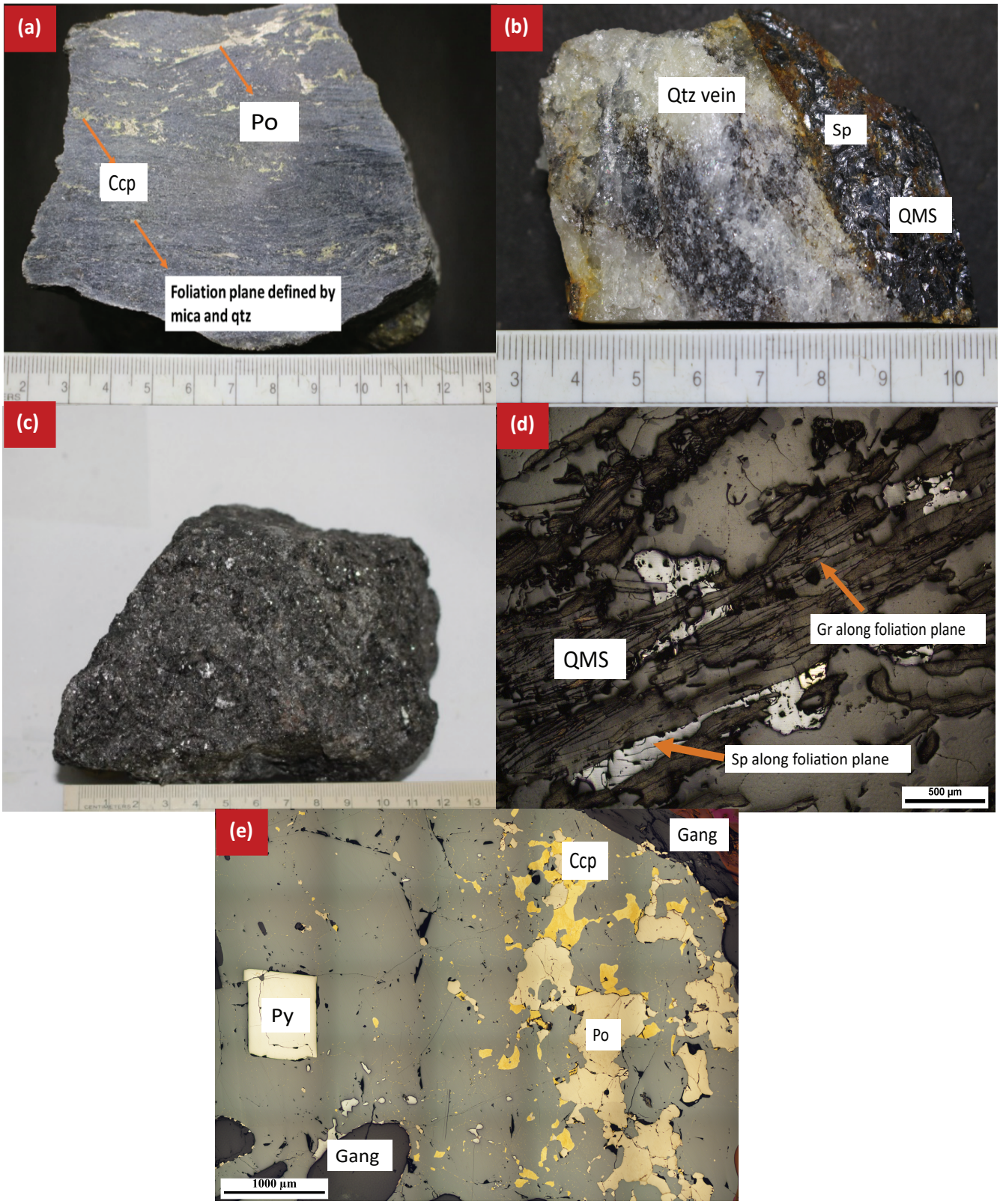


FIG 3.1. : Handspecimen and microphotographs of types of ore deposits a)handspecimen of laminated ore showing foliation parallel sulphides chalcopyrite and pyrrhotite b) laminated ore associated with quartzite c)massive sphalerite ore d)laminated ore in thin section comprising of sphalerite along foliation e)massive sphalerite ore comprising of different sulphide phases like pyrite , pyrrhotite, galena and chalcopyrite

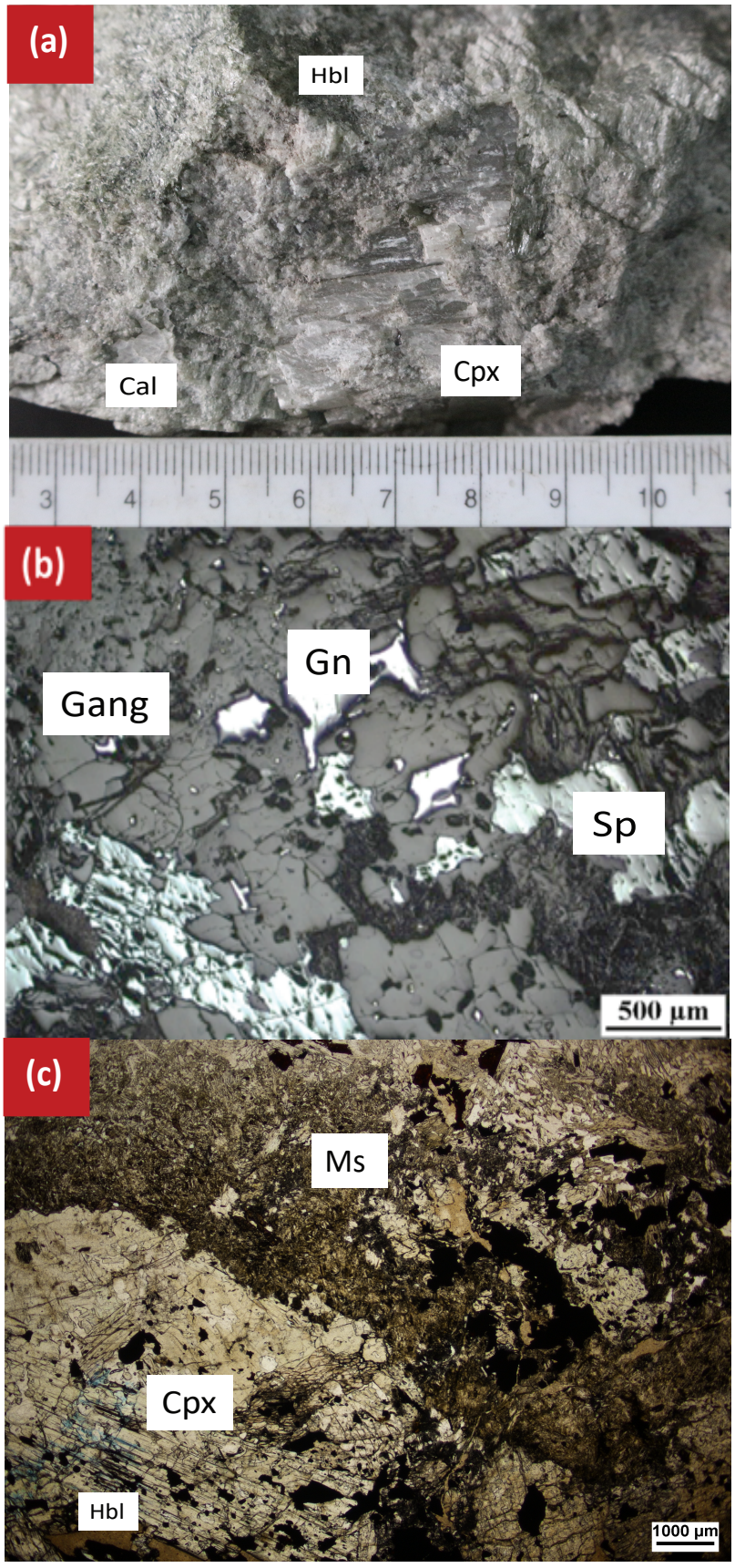


FIG 3.2.1 : Handspecimen and microphotographs of Calc-silicate a)mineralogical assemblage of calcite , quartz ,cpx and amphibole b) galena and sphalerite among gangue c)muscovite ,hornblende and cpx

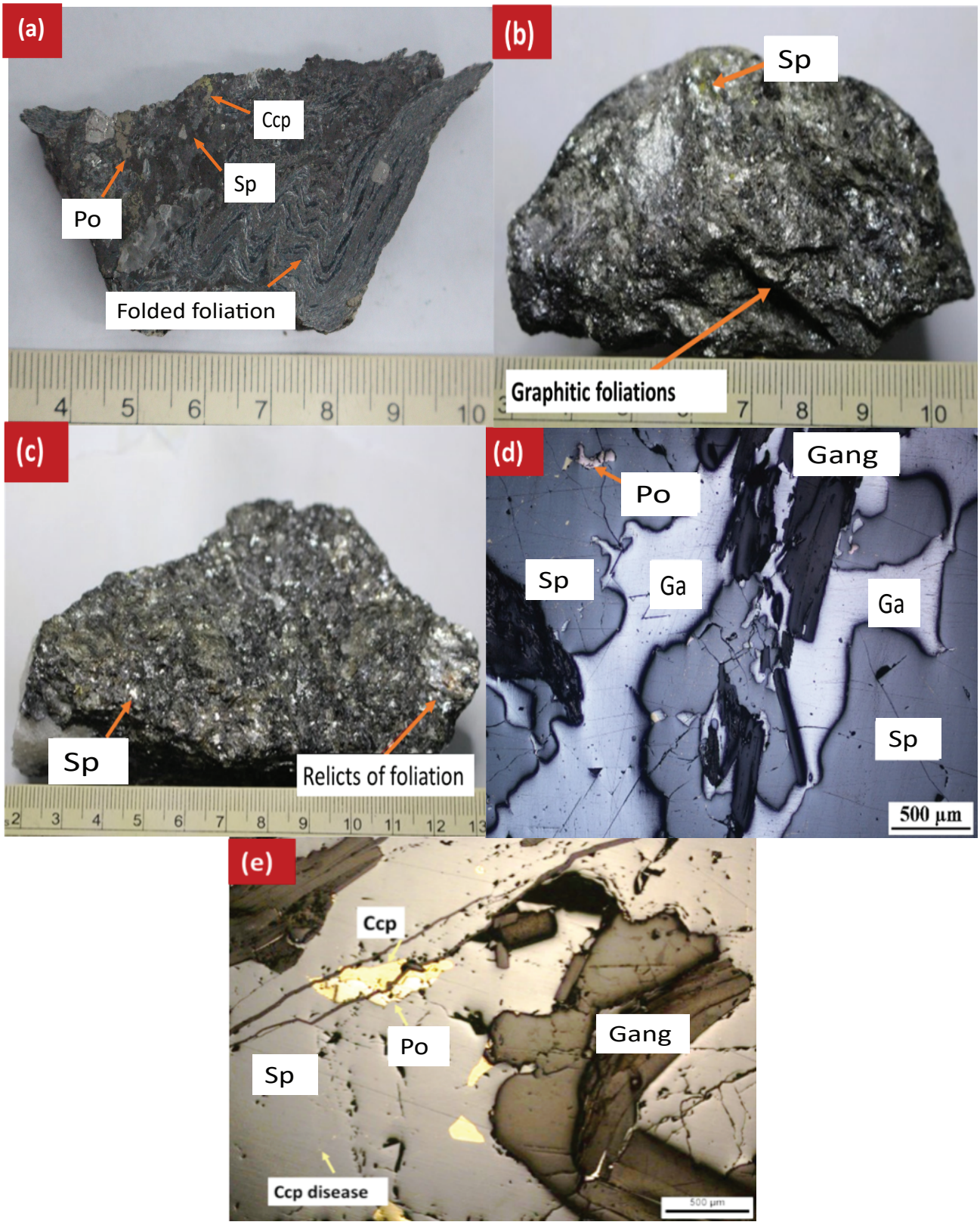


FIG 3.2.2 : Handspecimen and microphotographs of QMS a)foliated planes which are folded and defined by quartz, mica and graphite and having sulphide ores discordant to it b)foliated planes having good amount of graphite c) massive sphalerite having relicts of foliation d) massive sphalerite and galena having relict gangue e) massive sphalerite having chalcopyrite phase and some dispersed gangue

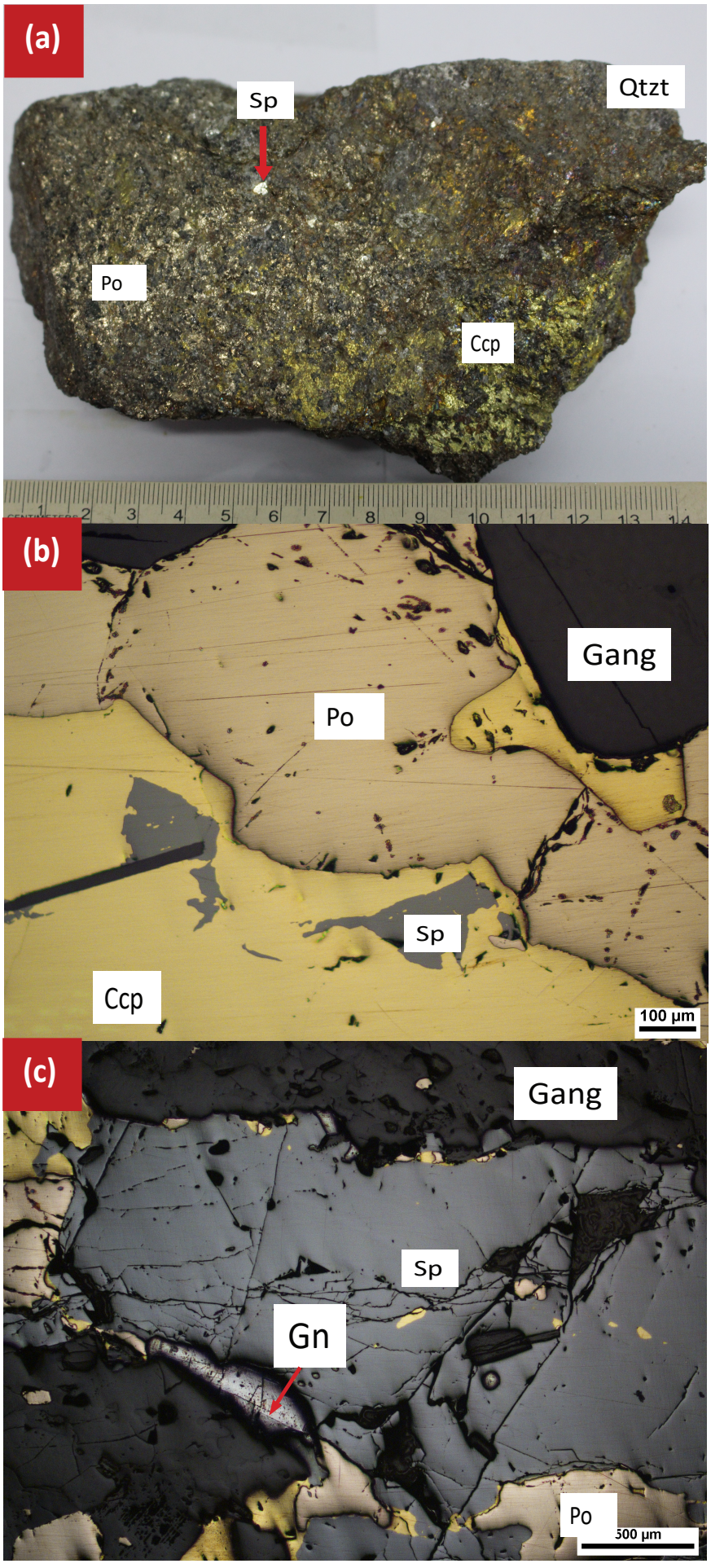


FIG 3.2.3 : Handspecimen and microphotographs of Quartzite a)quartzite having dense cherty appearance containing massive chalcopyrite an pyrrhotite b)pyrrhotite and chalcopyrite adjacent to each other and containing sphalerite which in turn has chalcopyrite disease c) small galena present along the boundary of sphalerite and gangue and also some pyrrhotite and chalcopyrite

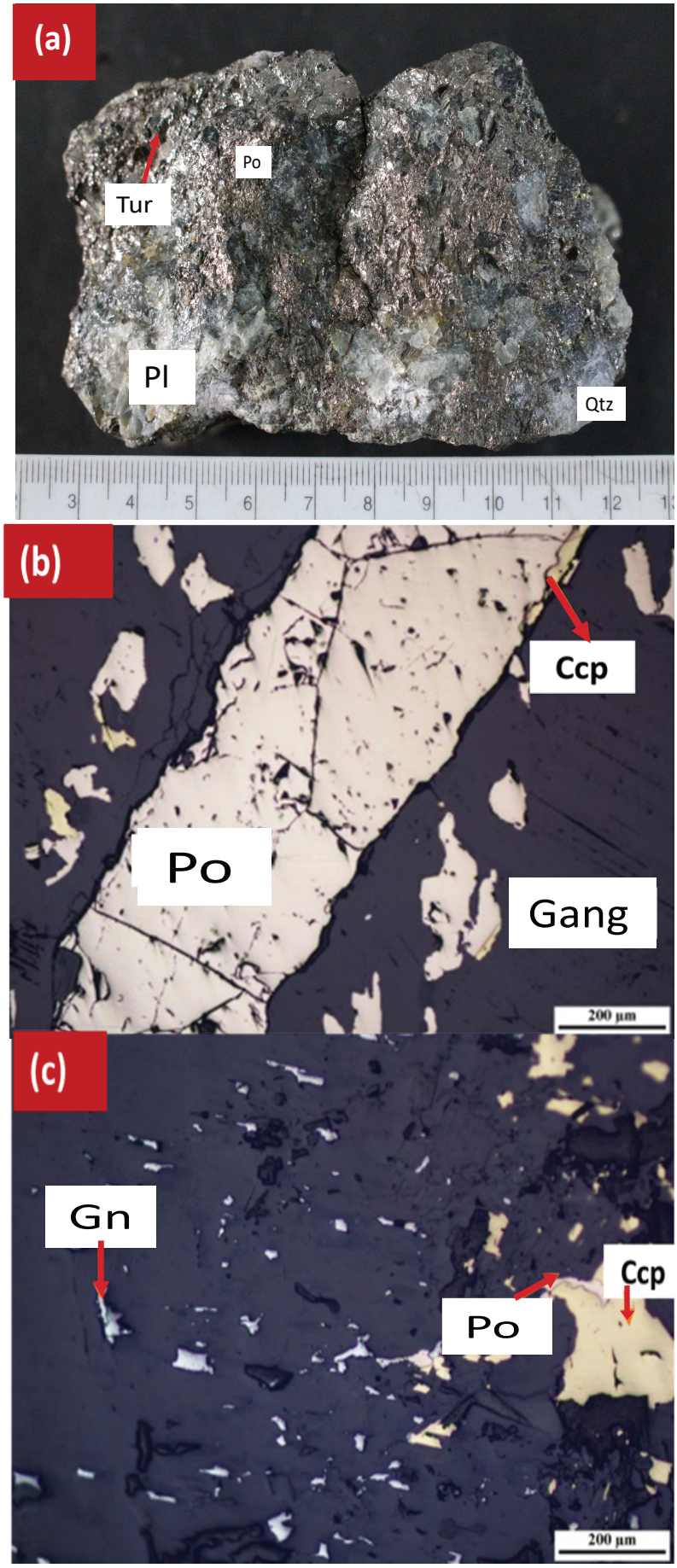


FIG 3.2.4 : Handspecimen and microphotographs of Pegmatite a)mineralogical assemblage plagioclase feldsper , cpx , tourmaline and hosying massive pyrrhotite b) a massive vein of pyrrhotite within gangue c) pyrrhotite and chalcopyrite associated with each other with minor galena in gangue

CHAPTER 4

GEOCHEMISTRY OF ORE MINERALS

The previous chapter describes the mode of occurrences, different mineralogical assemblages and textural variations in the sulphide ores. The compositional variation of the sulphide minerals have been emphasized in this chapter. It was analyzed using both EPMA (Electron Probe Micro Analyzer) and LA-ICPMS (Laser Ablation Inductively Coupled Plasma Mass Spectrometer).

4.1: *Methodology*

For our investigation certain thin sections were prepared to be analyzed. Electron probe micro analysis of the different sulphide minerals (sphalerite and galena) was conducted on a Cameca SX-100 equipped with four wavelength dispersive spectroscopy (WDS) spectrometers at Department of Geology and Geophysics, IITKharagpur. S, Fe, Co, Cu, Ag, Pb, As, Bi, Zn, Te, Se, Sb, Cd, were analyzed. For all analyses, a 20 kV accelerating potential was used.

4.2: *Compositional variation in sphalerite*

Investigation of composition of sphalerite has been done using major-minor element and trace element composition

4.2.1: *Major and minor element composition of sphalerite*

Major and minor element analysis in sphalerite has been performed on 47 points of 10 representative samples from the kayad mines. The two major elements Zn and S are detected in uniform amounts in all the sphalerite grains. Fe is also detected ubiquitously in all the grains and is most dominant besides the major elements. Among the minor elements Cu and Cd is detected in some of the sphalerite grains .The highest concentration of Cu and Cd goes up to 17580 ppm and 2800 ppm respectively. Consistent difference in the concentration of Cu and Cd and their homogeneity in particular zones makes the two element extremely useful. Fe and Cd are chalcophile elements which are similar to Zn in ionic radius. Therefore these element frequently isomorphously replace Zn in its structure. Conventionally, copper is not considered to be readily incorporated into the sphalerite structure in significant quantities, unless as part of a coupled substitution $(Cu)^{+}+(Bi,Sb)^{3+} \leftrightarrow 2Pb^{2+}$. However in our case high concentration of copper is due to good amount of chalcopyrite disease present in almost all sphalerite irrespective of rock type. The ‘‘chalcopyrite disease” is where chalcopyrite generally occurs as blebs in sphalerite, where Cu carries a single positive charge and appears as the host sphalerite cools (Govindarao et al. , 2018) . These excretions are typically observed along crystallographic axes or twin boundaries (fig 4.2.2)

4.2.2: Trace element composition in Sphalerite

The trace element composition of sphalerite has been performed on 21 points in the sphalerite grains from representative rock samples of QMS, calc-silicate and pegmatite. Different elements like ^{51}V,^{55}Mn,^{59}Co,^{60}Ni,^{63}Cu,^{71}Ga,^{73}Ge,^{75}As,^{82}Se,^{95}Mo,^{107}Ag,^{111}Cd,^{115}In,^{118}Sn,^{121}Sb,^{193}Ir,^{195}Pt,^{197}Au,^{202}Hg,^{205}Tl, ^{208} Pb . Absence of Bi, Au, Pt, Ir, Se and presence of Mn , Co , Cu , Ga, Ge, Ag, Cd, In, Sn , Sb , Pb , Hg is observed in all the grains irrespective of different lithology.

High concentration of Mn, Co, Cd and Cu has been detected in sphalerite. Cd-1631 ppm, Mn-1777 ppm, Co-66 ppm, Cu-2712 ppm.(Table 4.2.2) High concentration of copper is due to the presence of chalcopyrite disease in almost all sphalerite grains irrespective of the rock type (fig 4.2.2a). Cd, Mn and Co have similar ionic radii as iron and they show a positive correlation when concentration binary plots between Fe vs Cd (fig 4.2.2a), Fe vs Mn (fig 4.2.2b) and Fe vs Co (fig 4.2.2c) are plotted. So they might have replaced iron in the structure of sphalerite and resulted in their high concentration.

4.3: *Compositional variation in galena*

4.3.1: *Major and minor element composition of galena*

Major and minor element composition in galena was measured on 29 points across 10 samples for different grains of galena with respect to their association. The major elements Pb and S are present uniformly in all the grains and do not show any difference with respect to the association. Among the minor element Fe, Ag and Zn occur however neither their distribution nor their concentrations are uniform. The highest concentration of Fe, Ag and Zn were noted as 24480ppm, 3010ppm and 14650ppm respectively. However these values are not with respect to a single grain. The points on grains of galena which were taken on the rim and present only adjacent to the sphalerite grains along the foliation planes or within the gangue shows some concentration of Fe and Zn which can be due to diffusion of the cations along some crystallographic orientation .

4.3.2 : *Trace element composition in Galena*

Various elements in trace concentration have been detected in the the grains of galena representative of different rock lithology. ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn,^{71}Ga,^{73}Ge,^{75}As ,^{82}Se,^{95}Mo,^{107}Ag,^{111}Cd,^{115}In,^{118}Sn,^{121}Sb were studied. Absence of Ga, Ge and Mo and presence of Ag, Bi, Sb, As, Tl, Sn, Cd, As and Mn in trace amount in all the galena grains is noted. On an average High concentration of Zn , Fe , Ag (1886 ppm) , Bi (720 ppm) , Sb (520 ppm) and As (143 ppm) are seen

4.3.2.1: Silver, Antimony and Bismuth

Substitution of silver into galena represents a well characterised example of solid solution. Monovalent Ag is almost insoluble via the simple $2Ag^{+} \leftrightarrow Pb^{2+}$ substitution due to the requirement that one of the two silver atoms must be placed in a structurally unfavourable interstitial position in the galena lattice. In the absence of Bi, Sb or As, substitution of Ag into PbS in solid solution will not exceed 0.1 mol%.

When aided by the presence of Bi^{3+}, Sb^{3+}, As^{3+}, significant quantities of Ag can be added to the galena structure via the coupled substitution $Ag^{+} + (Bi,Sb,As)^{3+} \leftrightarrow 2Pb^{2+}$. This substitution results in the octahedral sites left by two Pb^{2+} ions being fully occupied by Ag^{+} and $(Bi, Sb, As)^{3+}$. In nature, galena commonly displays wide variations in Ag, Bi, and Sb concentrations. It has been demonstrated that Bi is preferred to Sb in the coupled substitution.

The presence of submicrometer-scale inclusions of Ag-minerals also contributes to high concentration of silver. Common Ag-bearing phases observed as inclusions in galena include acanthite (George et al., 2015).

In the samples which were analysed (table 4.3.2.1) , a very strong positive correlation between Ag and Sb (fig 4.3.2.1a) has been obtained however a very weak positive correlation between Ag and Bi (fig 4.3.2.1b) as well as Ag and As (fig 4.3.2.1c). The presence of Ag bearing inclusion mineral like Pyragyrite (Ag_3SbS_3) and Gudmundite (FeSbS) might be the cause of high Ag and Sb.

4.3.2.2: Zinc and Iron

In most of the rock types galena either occurs associated with sphalerite. So sphalerite might be the source of Zn and Fe in galena (Fig 4.3.2.2)

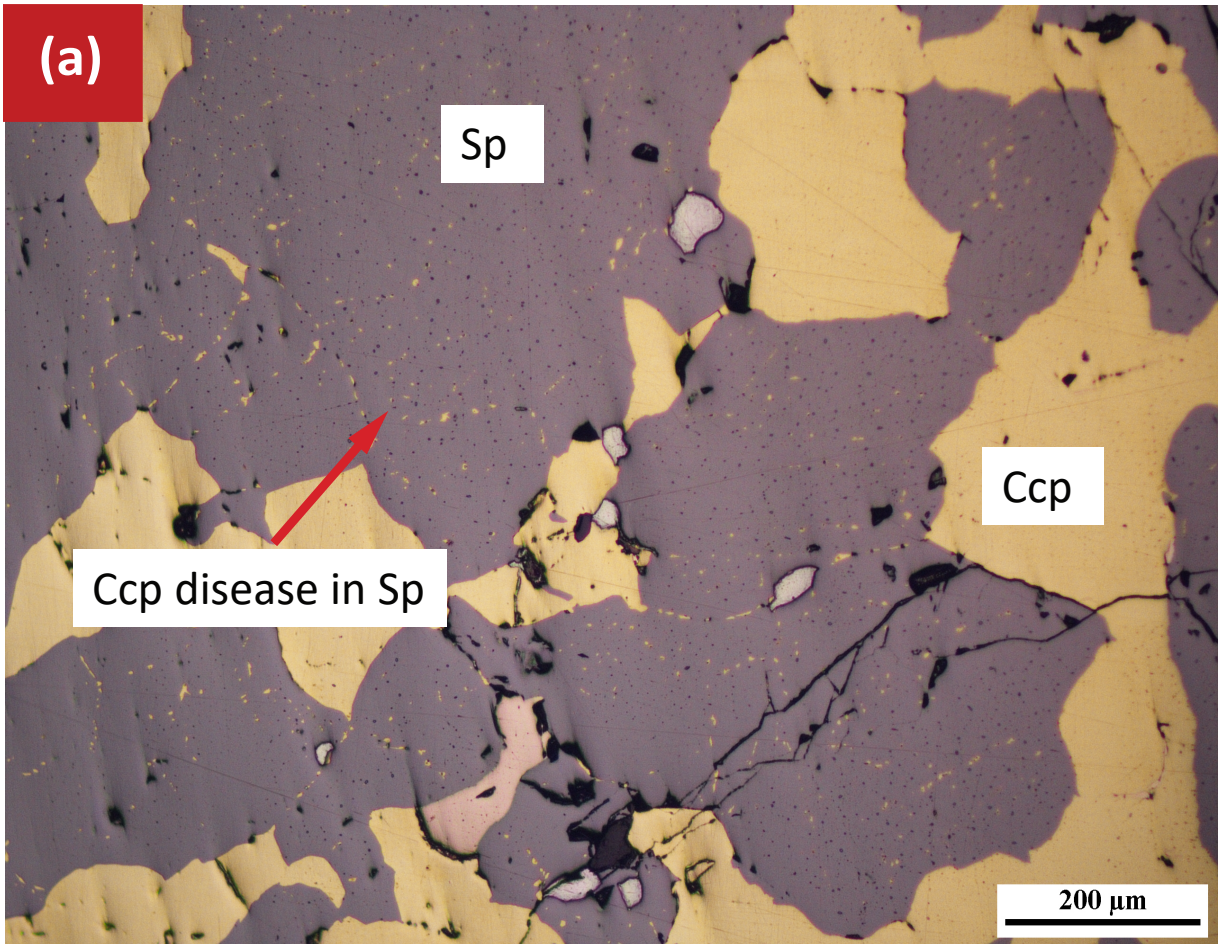


Fig 4.2.2 : Photomicrograph showing chalcopyrite disease in sphalerite

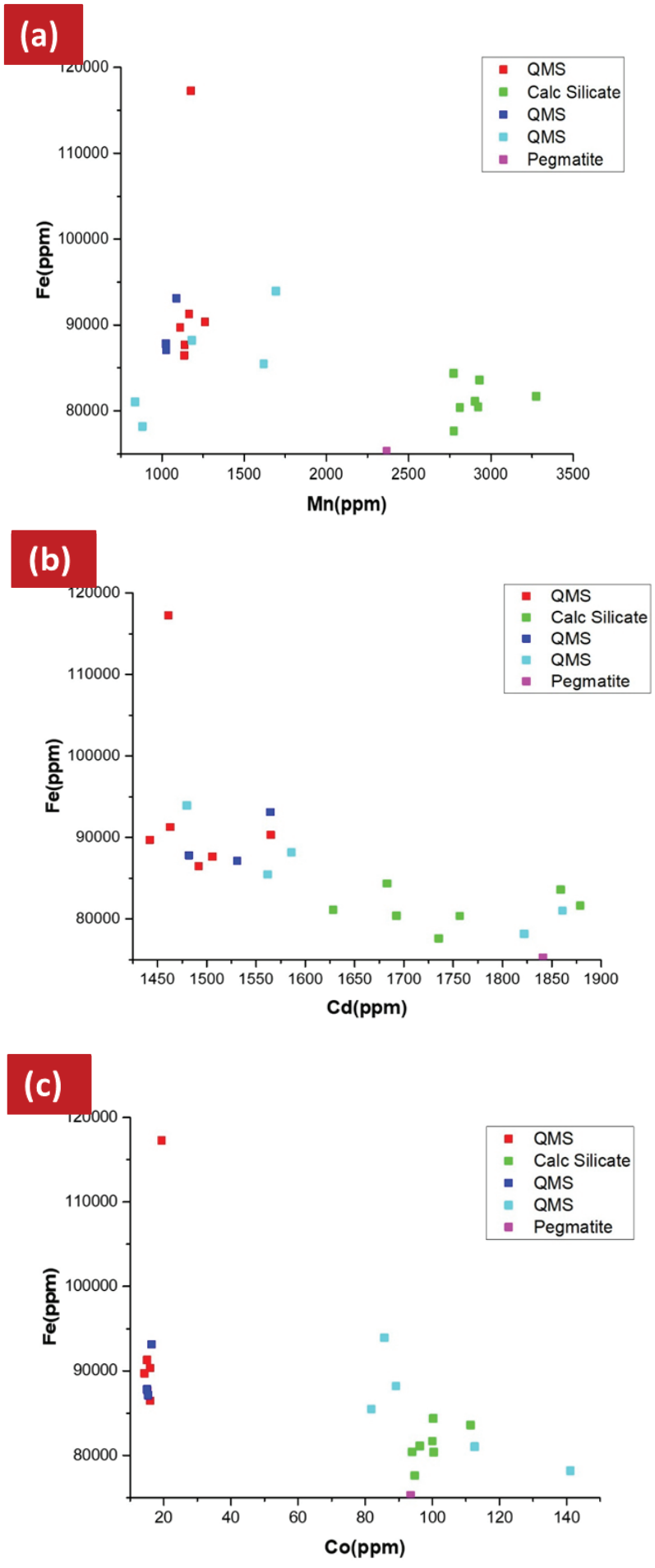


Fig 4.2.2 : Concentration binary plots in ppm for the trace elements in sphalerite showing negative correlation , a) Fe vs Mn b)Fe vs Cd c)Fe vs Co , for different sphalerite grains from different rock types

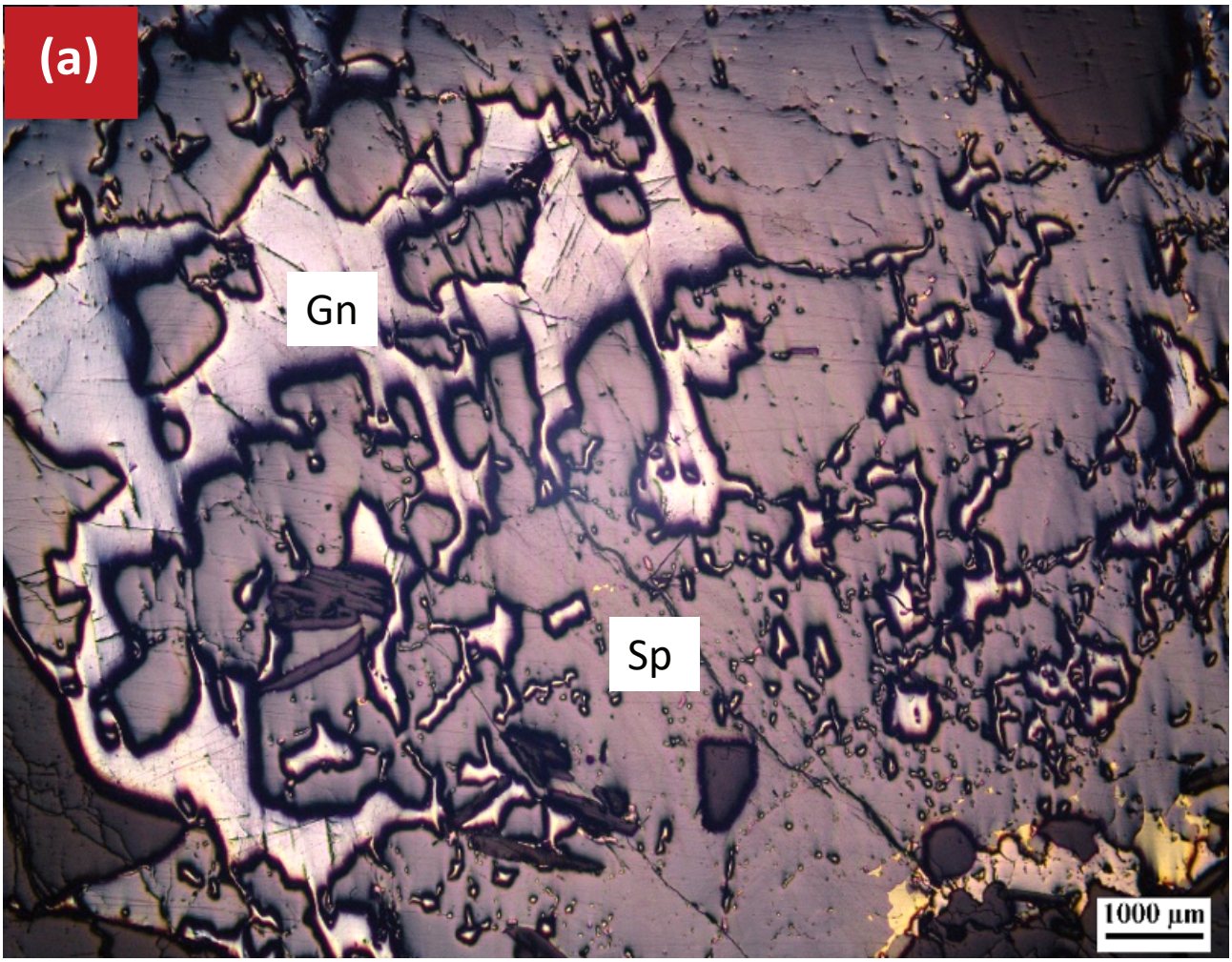


Fig 4.3.2.2 : Photomicrograph showing galena within sphalerite and having inclusions of the latter

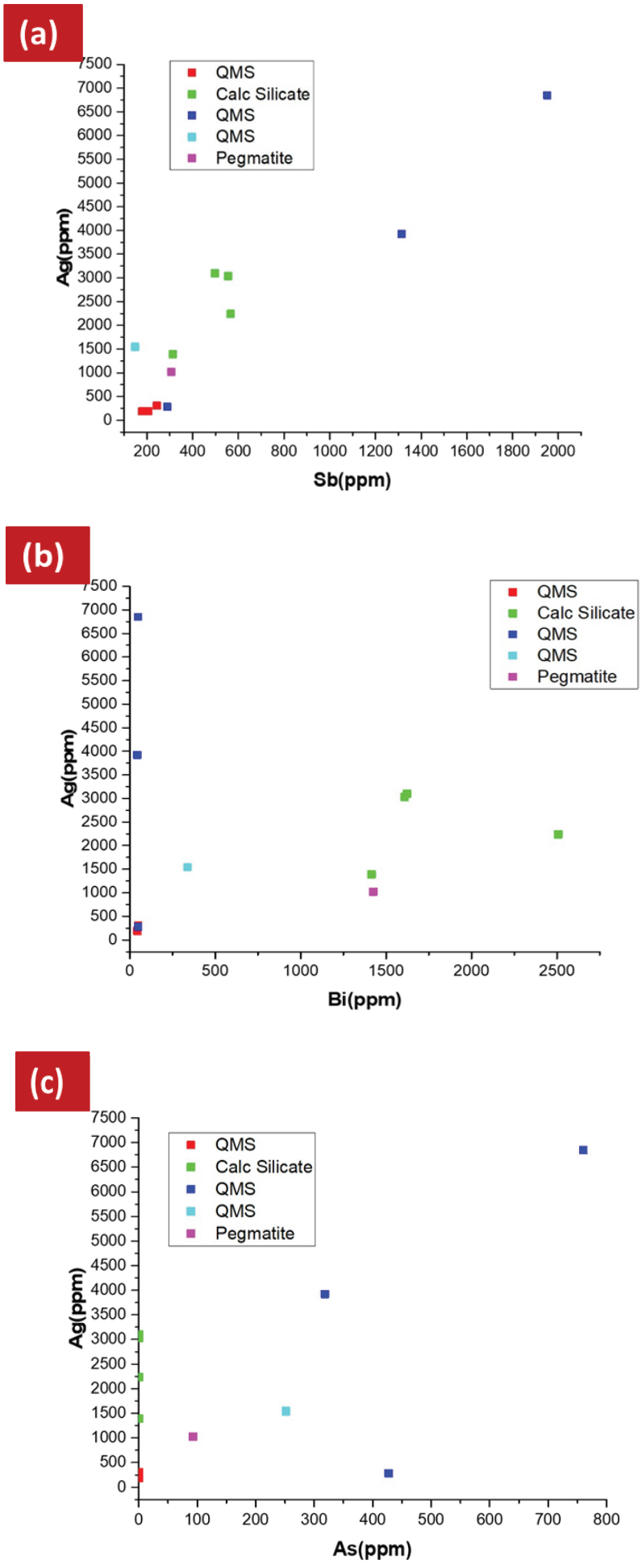


Fig 4.3.2.1 : Concentration binary plots in ppm for the trace elements in galena, a) Ag vs Sb b)Ag vs Bi c) Ag vs As , for different galena grains from different rock types

CHAPTER 5

DISCUSSION AND SUMMARY

In the previous chapters the host rocks and mode of occurrences of sulphide ores and texture and geochemistry of sulphide minerals have been discussed. This chapter highlights on whether the type of deposit associated with the ore minerals can be deciphered.

5.2: Type of Deposit of the massive sulphide mineralization?

The graphical plots of the trace elements of Lin Ye et al, 2011 were with respect to various base metal deposits that were already identified and categorized as Sedex, Skarn, Mississippi valley type (MVT). The trace elements determined from the LA-ICPMS of the sphalerite grains from all the three types of deposits were plotted as mentioned and the value range of the ppm concentration for individual deposits were deciphered for each binary plot. Our trace element concentration fell in similar region as that of the skarn deposit binary plots (fig 5.2) in all the cases thus giving us a hint of the sulphide deposits might be related to skarn. Thus this comparison collectively indicates that the sulphide mineralization is not constrained by the geochemistry of host rock or the mineralization is not heterogeneous with respect to the type of deposit and despite the difference in the individual trace element concentration in the

sphalerite grains associated with different host rocks, the binary plots reveals a similar type of deposit .

5.3: Possible explanation of the mineralisation history

The trace element content of the sulphide ores as well as presence of high concentration of tin and a positive correlation between In and Sn (fig 5.3) hint towards a possible influx of a granitic fluid. Presence of a huge granitic body in the vicinity of Kayad (Ana sagar granite) (fig 5.3) might be the source of the hydrothermal fluid and might have mobilized the ore to their present position today. Age of the granitic body is 2.5 Ga but age of the ore mineralization in Kayad area is unknown hence concluding that granite to be the ultimate source is a bit difficult and further research and field work is definitely needed

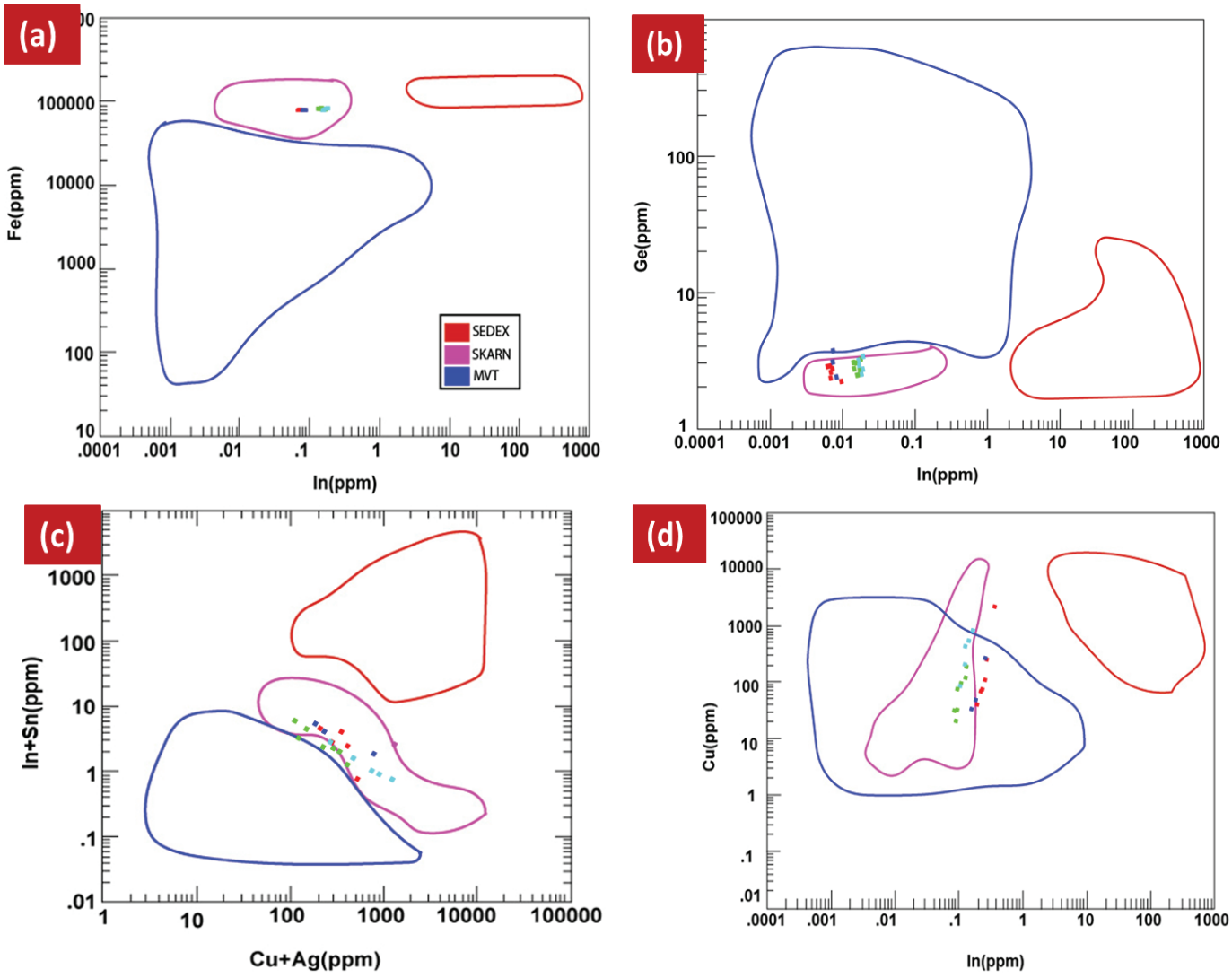


FIG 5.2 : Concentration binary plot of different trace elements in ppm where our data is superimposed on the plots created by Cook et al , 2011 a) Fe vs In b) Ge vs In c) In+Sn vs Cu+Ag d) Cu vs In

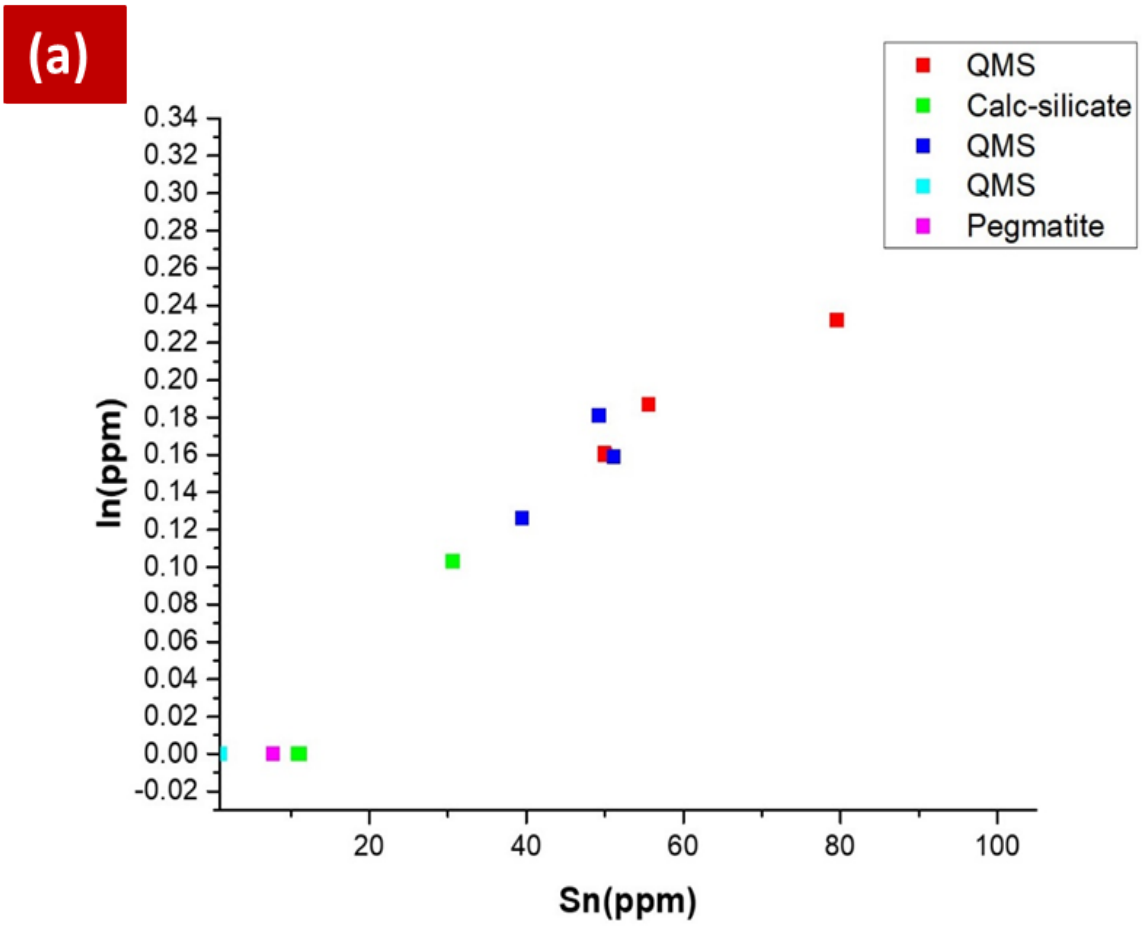


FIG 5.3 : Concentration binary plot of In vs Sn (in ppm) showing positive binary plot

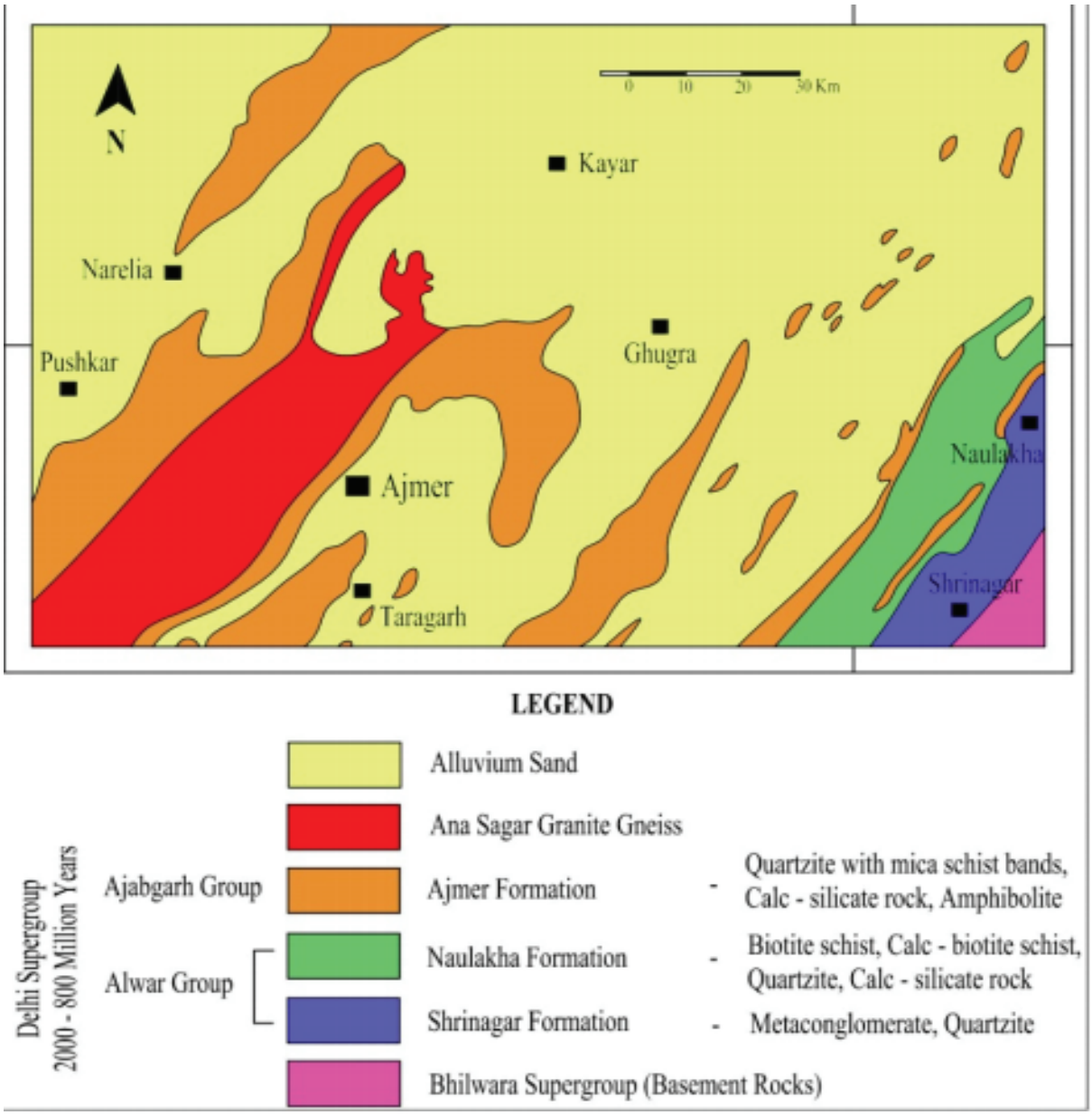


FIG 5.3 : Geological map of Delhi supergroup showing presence of Ana sagar granite in the vicinity of Kayad

Appendix

Table 4.3.2.1 : Concentration of trace elements in galena in ppm

Rock type	Sample no	Ag	As	Sb	Bi
QMS	KDY 21	194.4	1.1	195.6	43.6
		304.0	0.7	243.4	48.7
		187.59	0.74	179.28	44.85
		188.7	1.1	205.8	44.8
Calc-silicate	ML 13	1391.2	1.1	312.5	1414.7
		2238.7	1.0	566.8	2507.8
		3098.6	0.9	497.3	1622.5
		3036.6	1.0	555.9	1607.5
QMS	KYD 34	3923.0	318.5	1314.7	43.7
		6847.8	760.4	1951.9	48.4
		283.1	427.3	288.7	48.2
QMS	KYD14	1541.5	251.7	147.5	338.2
Pegmatite	STOCK3	1023.9	92.9	306.2	1425.0

Table 5.3 : Concentration of In and Sn in Galena in ppm

Rock type	Sample no	In	Sn
QMS	KDY 21	0.2	50.0
		0.2	50.0
		0.187	55.55
		0.2	79.6
Calc-silicate	ML 13	0.1	30.6
		0.3	96.7
		0.0	11.2
		0.0	10.9
QMS	KYD 34	0.1	39.5
		0.2	51.1
		0.2	49.2
QMS	KYD14	0.0	1.0
Pegmatite	STOCK3	0.0	7.7

Table 4.2 : Concentration of trace elements in ppm in sphalerite

Sample No	Mn	Fe	Co	Cd	Rock type
KYD21	1165.56	91296.23	15.04	1462.9	QMS
	1110.7	89717.23	14.29	1442.1	
	1135.27	86474.5	15.87	1491.7	
	1176.57	117256.8	19.35	1460.9	
	1137.78	87674.4	15.18	1505.6	
	1261.84	90344.73	15.87	1564.9	
ML13	2931.05	83596.35	111.4	1858.9	Calc-silicate
	2810.74	80383.86	100.39	1756.7	
	2774.9	77634.27	94.72	1735.2	
	2922.72	80428.89	93.93	1692.3	
	3275.84	81692.82	100.02	1878.8	
	2902.68	81132.07	96.28	1628.0	
	2773.08	84373.73	100.27	1682.8	
KYD34	1024.3	87831.16	15.04	1481.9	QMS
	1026.26	87131.24	15.36	1530.7	
	1089.08	93121.12	16.4	1564.3	
KYD 14	881.45	78185.71	141.1	1822.0	QMS
	1693.64	93941.45	85.73	1479.8	
	1619.12	85484.77	81.83	1561.8	
	1182.11	88209.6	89.18	1586.0	
	836.59	81037.67	112.6	1860.9	
STOCK 3	2366.6	75284.6	93.5	1841.0	Pegmatite

Table 5.2 : Concentration in ppm for various trace elements detected in sphalerite

Rock type	Sample no	Fe	In	Ge	In+Sn	Ag+Cu	Cu
QMS	KYD21	91296.2	0.1	0.2	0.804	280.95	276.6
		89717.2	0.1	0.2	0.722	48.14	46.4
		86474.5	0.1	0.3	0.957	123.39	118.0
		117256.8	0.2	0.5	24.151	42708.28	42681.5
		87674.4	0.1	0.4	0.538	142.5	139.8
		90344.7	0.1	0.3	2.262	1107.32	1101.9
Calc-silicate	ML 13	83596.4	0.8	0.2	1.368	91.57	85.9
		80383.9	0.5	0.2	1.171	226.75	215.0
		77634.3	0.6	0.3	1.629	471.13	454.8
		80428.9	0.5	0.3	0.898	12.05	10.1
		81692.8	0.7	0.3	1.582	22.88	19.5
		81132.1	0.5	0.4	0.974	25.85	21.7
		84373.7	0.7	0.4	1.161	155.12	136.1
QMS	KYD34	87831.2	0.2	0.1	0.669	33.66	30.4
		87131.2	0.1	0.4	0.641	1183.03	1172.9
		93121.1	0.1	0.2	0.747	63.29	60.4
QMS	KYD 14	78185.7	1.0	0.2	1.254	1719.14	1712.3
		93941.5	0.7	0.3	0.976	114.35	112.6
		85484.8	0.7	0.2	1.15	5668.87	5664.2
		88209.6	0.7	0.4	1.13	514.78	509.7
		81037.7	0.8	0.3	1.23	2687.39	2675.5
Pegmatite	STOCK 3	75284.6	0.0	0.2	0.3	2441.6	2419.4

Mineral Abbreviations

- Galena: Gn
- Pyrrhotite: Po
- Chalcopyrite: Ccp
- Sphalerite: Sp
- Muscovit: Ms
- Biotite: Bt
- Quartz: Qtz
- Calcite: Cal
- Tourmaline: Tur
- Gangue: Gang
- Graphite: Gr
- Clinopyroxene: Cpx
- Hornblende: Hbl
- Plagioclase: Pl

Pyrite: Py

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