Volume 67, Issue 2, 2023

Journal of Scientific Research

of

The Banaras Hindu University

Chalcopyrite-Pyrite-Pyrrhotite Mineralization from Thanagazi Formation in Alwar Group, North Delhi Fold Belt, India

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***Abstract:*The Thanagazi Formation of the North Delhi Fold Belt (NDFB) is extensively explored for copper mineralization. Copper occurs predominantly in quartz veins in volcanic rocks and quartz-carbonate veins hosted in dolomite of the Thanagazi Formation belonging to the Alwar basin. Sulphide mineralization in volcanic rocks includes sulphide ore minerals such as chalcopyrite, galena, sphalerite, and arsenopyrite. This study encompasses the ore mineralogy and textures of sulphide phases associated with quartz veins in the Thanagazi Formation. It is related to chalcopyrite, pyrite, and pyrrhotite mineral assemblages. Secondary alteration products such as malachite and iron oxides are also associated with copper mineralization considered as the surface indicators.**

***Index Terms:*Copper; Mineralization; Thanagazi; Alwar.**

I. Introduction

The AravalliSupergroupis considered to be a synclinorium with the core occupied by rocks of the Bhilwara, Aravalli, and Delhi Supergroups (Heron, 1953; Naha and Mohanty, 1990). It is a 700 km long mountain range that contains a record of two orogenic movements, an early Aravalli orogeny (Paleoproterozoic: ~2.5-1.9 Ga) and late Delhi orogeny (Mesoproterozoic: ~1.9-1.45 Ga) that evolved as ensialic fold belts through the development of a series of rift-basins, grabens and intervening horsts (Roy, 1990). Lithologies of the Aravalli, Delhi, Vindhyan and MarwarSupergroupsindicate their Proterozoic rocks. The AravalliSupergroupis the repository of a substantial quantity of major base metal and gold as well as phosphorite deposits (Sugden et al., 1990; Deb, 1990).In Indian Shield, the Aravalli-Delhi Mobile Belts and Central Indian Tectonic Zone (CITZ; Radhakrishan and Ramakrishnan, 1988) formed major Proterozoic mobile belts (Misra and Kumar, 2014) with adjoining cratons and contemporary basins (Fig. 1a). Records of geological events from the Paleoarchean (~3.5 Ga) to Neoproterozoic (~0.75 Ga) are preserved evidences for the base metal reserves along with a few occurrences of Sn-W and U mineralization's (Deb and Sarkar, 1990).

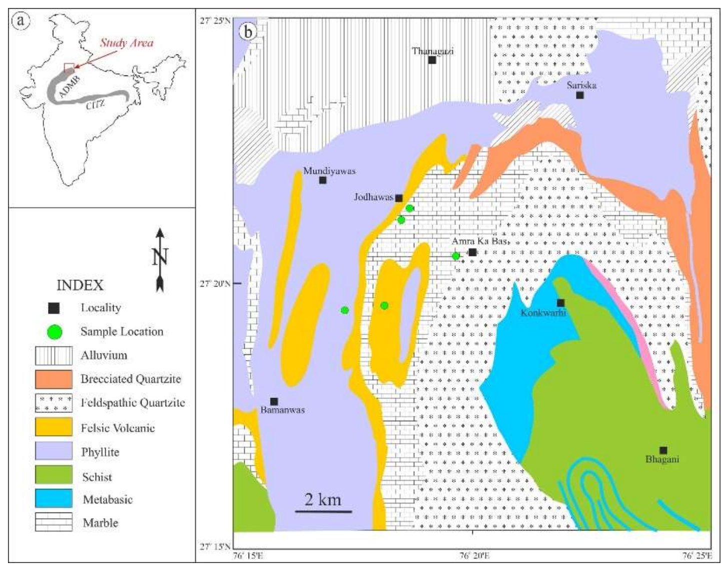

Fig. 1. (a) Location of the study area adjacent to the Aravalli Delhi Mobile Belt (ADMB) and Central Indian Tectonic Zone (CITZ) in the map of India; (b) Generalized local geological map of the Thanagazi Formation in the Alwar Group with sample locations (Courtesy: Geological Survey of India).

Extensive mineralization in the Proterozoic rocks of the ADMB occurs mainly in the form of base metals with minor occurrences of manganese, tungsten, and uranium recognized in northwest India (Deb, 1982). The geological attributes of major occurrences of world-class base metal deposits particularly described for copper in Khetri deposits and lead-zinc in Zawar deposits. Recent investigations in the Alwar basin of the North Delhi Fold Belt (NDFB) by the Geological Survey of India (GSI, 2019) suggest a large copper and associated gold deposits of economic significance (Khan et al., 2013). The copper mineralization in the Mundiyawas - Khera is hosted within the metavolcanic rocks and dolomites (Sajeev et al., 2019). Meanwhile, the mineralogical and geochemical aspects of these deposits are not yet fully understood. Information about the ore mineralogy of this deposit is limited. The present study focuses on the mineralogical characterization of copper sulphide ores associated with the volcanic rocks and dolomites of the Thanagazi Formation.

II. Regional Geology

The northwestern part of the Indian Peninsula represents a complex tectonic evolution that comprises three distinct Archaean to Neoproterozoicorogenies (Biswal et al., 2022). Proterozoic Delhi Supergroup occupies NE-SW trending linear belts in the northern part of the Aravalli Mountain range (Gupta et al., 1980), which is classified into three groups separated by unconformities, viz. the Raialo, the Alwar and the Ajabgarh(Singh, 1988). The Delhi Supergroup constitutes Delhi Fold Belt intruded by ~850 Ma old granites (Sharma, 2010). Delhi Fold Belt (DFB) referred as the North Delhi Fold Belt (NDFB) is evolved separately with a depositional age of ~1720 Ma for the uppermost unit and South Delhi Fold Belt (SDFB) represents initial sedimentation ages younger than ~1055 Ma (Fareeduddin and Banerjee, 2020).

The Alwar basin constitutes the central part of the North Delhi Fold Belt (NDFB), which occurs as a narrow linear belt in the south and central Rajasthan and fans out over a wider zone in north-eastern Rajasthan (Fig. 1b). This basin formed one such depocenter that was separated from Bayan in the east and Khetri basin in the west by pre-Delhi basement complex. The Alwar basin constitutes 6000m thick package of volcanic and sedimentary rocks that comprises three groups (Raialo, Alwar, and Ajabgarh). The Ajabgarh Group comprises five formations, (1) metamorphosed argillites with intercalated arenites and subordinate carbonates that have been included in the Kushalgarh and the (2) Sariska Formations, carbonaceous phyllite, an interlayered sequence of quartzite, phyllite and schists containing chlorites, garnet, staurolite and andalusite are included under the (3) Thanagazi Formation, (4) Bhakrol Formation, and (5) Arauli Formation (GSI, 2019). The exposed rock types in the Mundiyawas-Khera area belong to metavolcanic-sedimentary sequence, tremolite-bearing dolomitic marble and carbonaceous phyllite. The felsic volcanics are represented by felsic tuff, lapilli tuff and agglomeratic tuff which are rhyodacite in composition and occur as interlayered sequences within the fine-grained quartzites, carbonaceous phyllite and dolomitic marble of Ajabgarh Group (Khan et al., 2014). The base metal mineralization occurs over scanty outcrops belonging to the Thanagazi Formation of the Ajabgarh Group of the Delhi Supergroup (Fig. 1b).

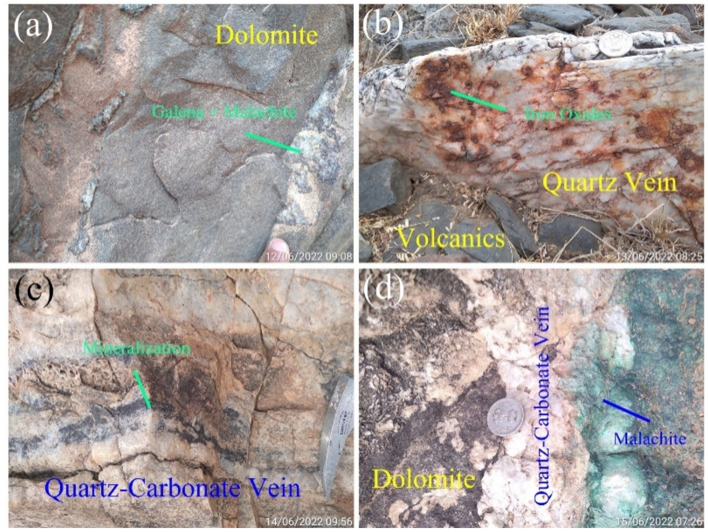

Fig. 2. Field photographs of exposed outcrops with indicators of mineralization from Thanagazi Formation in the Alwar Group, North Delhi Fold Belt: (a) specks of galena with malachite on the dolomite near Jodhawas village, (b) detrital iron oxides spots on quartz veins hosted in meta-volcanic rocks near Mejod village, (c) mineralized quartz veins with dolomite near Angari village, and (d) malachite stains with quartz-carbonate veins in crystalline dolomite with elephant skin texture near RoopuKa Bas village.

III. Local Geology

The studied area is located in the Alwar basin of the AravalliSupergroup. The rock types exposed in the area (AmraKa Bas, Jodhawas, Mundiyawas, Mejod and Biharisar) belong to Thanagazi Formation of the Ajabgarh Group of the Delhi Supergroup (Sajeev et al., 2019). Major rock types are represented by an interbedded sequence of bimodal volcanic rocks (mafic and felsic), quartzite, phyllite and dolomite. Mineralized dolomite is frequently associated with bimodal volcanic rocks near Jodhawas, Angari, and RoopuKa Bas villages. Dolomite is buff grey in colour, fine to medium grained with profuse development of a network of calcite veins that contain specks of galena, sphalerite and malachite (Fig. 2a). The dominance of sulphide mineralization is observed in the volcanic rock and the dolomite interface with the presence of chalcopyrite as the main ore minerals of copper, which is associated with sphalerite, galena, pyrrhotite, pyrite, and arsenopyrite (GSI, 2019). Striped patterns or rhythmic layers in dolomite characteristically appeared in the Jodhawas area. The volcanic rocks are light grey to dark grey and are bimodal in composition. The different varieties of volcanic rocks that have been observed in the area are massive, compact and hard, tuffaceous, foliated and immature vesicular types associated with meta-sediments viz. quartzites and carbonates. The rocks form small hillocks or mounds with lots of scree material at the gentler slopes and the presence of reddish-brown spots in quartz veins is indicative of gold mineralization near the Mejod village (Fig. 2b). Mineralized quartz-carbonate veins hosted in the dolomite near Angari village with discrete, subhedral grains constitute very fine to coarse(2-6 mm) size tourmaline (Fig. 2c). Rhythmic layers are curvilinear in nature with variable directional patterns at several sites. Accretionary structures in dolomitic limestone exhibit a variety of semi-circular to elliptical forms known as stromatolite intruded by quartz-carbonate veins with malachite stains observed at RoopKa Bas area (Fig. 2d). In the study area, most stromatolites are spongiostromate in texture, having no observed microstructure or cellular remains. Thin layers of dolomite occur at the Nala section of Sariska village in association with phyllite and felsic volcanics. The dolomite sequence is >1000 m in length and a few meters wide in the Sariska area.

IV. PETROGRAPHY

Investigations on ore association, geologic occurrence, country rock and its alteration, total mineral composition of the ore, the likely composition of the ore solution, etc. can be derived from the study of ore texture (Ramdohr, 1969). This is an important genetic interpretation that can possibly yield. A microcrystalline aggregate of silicate minerals in the groundmass of felsic extrusive rocks is known as felsitic textures which comprises microscopic crystalline grains, and finely dispersed vitreous material. Volcanic glass spontaneously devitrifies from the glassy to the crystalline state in due course of time. Volcanic rocks from the Alwar area consist of a mixture of glass and crystals and contain a higher ratio of glass and are described as hypohaline or holohyaline. Devitrification commonly begins along cracks in the glass or around large crystals and may spread outwards and results in a sub-microscopic mixture of various rock minerals and their alteration products along with ore minerals. In the studied samples, common ore mineral associations are observed with chalcopyrite inclusion in pyrite microphenocrysts embedded in silicate groundmass (Fig. 3a). Reflected light microscopy of mineralized rock samples from the studied area reveals three distinct pyrite morphologies and relationships to other features in the felsic rocks. These are illustrated in figures 3a to 3d. These textural types are designated as pyrite I, isolated grain in silicate ground mass; pyrite II, pyrite with the inclusions of chalcopyrite; and pyrite III, distinctive seeds of pyrite grains observed in quartz microphenocryts. All of these textural varieties are commonly present within mineralized volcanic rocks in the studied area.

Pyrite I correspond to isolated pyrite grains that occur within silicate groundmass without any association contact with sulphide or oxide minerals. The pyrite grains are anhedral in shape with corroded boundaries and the presence of inclusions of silicate matrix. Isolated pyrites are also irregular in shape. These pyrites are anhedralcoarse grained (>1000 µm) with tiny (mostly <50 µm) inclusions of silicate matrix that commonly occur as composite globular aggregates. Pyrite II comprises disseminated pyrite grains of variable size (200 µm to 1000 µm) with inclusions of chalcopyrite. Pyrite grains occur as a cluster of grains in the silicate matrix. These are homogenous withsubhedral-anhedral shapes and sharp grain boundaries in contact with silicate groundmass. These pyrite grains with tiny (mostly < 50 µm) inclusions of chalcopyrite shows straight contact grain boundaries. Pyrite III comprises distinctive seeds of pyrite grains in quartz microphenocryts with or without chalcopyrite inclusions. Pyrite seeds are occured as cluster of grains in the quartz microphenocryts. These pyrite grains are small sized (<50 µm) and subhedral-anhedral shape with sharp grain boundaries in contact with silicate groundmass. It has a relatively different shape with a large number of pyrite inclusions that occur in a single quartz microphenocryts.

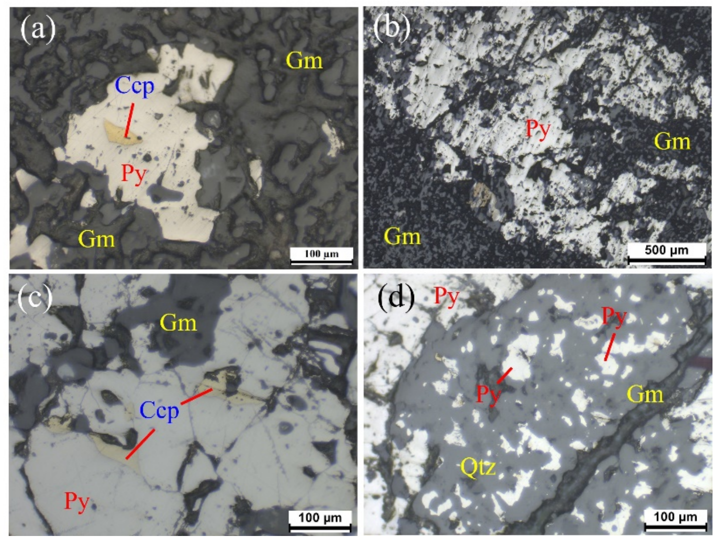

Fig. 3. Photomicrographs of felsic volcanic rock under plane polarized light (PPL) in reflected mode: (a) sulphide mineral assemblage of chalcopyrite inclusion in pyrite microphenocrysts embedded in silicate groundmass, (b) Pyrite I: microphenocryts of pyrite embedded within fine grain silicate groundmass, (c) chalcopyrite occurs as inclusions in the pyrite microphenocryts (Pyrite II), and (d) quartz microphenocrysts contain inclusion of pyrite grains (Pyrite III), which is embedded in the silicate matrix (grey). Mineral symbols: Gm – groundmass; Ccp – chalcopyrite; Py – pyrite; Qtz – quartz (after Warr, 2021).

Textural-microstructural features and ore petrography of diverse litho-units from the Mundiyawas-Khera copper deposit confirm the occurrence of chalcopyrite, pyrrhotite, arsenopyrite and pyrite as the main sulfide mineral phases (Srivastava and Prakash, 2020; Sahoo et al., 2022). Indications of hydrothermal alteration are testified by the presence of secondary mineral assemblages (sericite, epidote, scapolite, carbonates, etc.), which are invariably observed around the copper sulphides mineralization zone in the Thanagazi Formation (Sahoo et al., 2022).

V. SEM-BSE STUDIES

Polished sections of ore minerals were studied at the Petrological Laboratory of the Geological Survey of India (GSI), Bangaluru. Mineral chemistry of sulphides from the study area was obtained through electron probe micro analysis (EPMA), at the National Centre of Excellence in Geoscience Research (NCEGR) Laboratory, Geological Survey of India, Bangaluru. The instrument was operated at 15 kV acceleration voltage and 15 nA current for analyzing silicate and 20 kV acceleration voltage and 2 nA current for sulphides. SEM imaging was carried out using Carl Zeiss Scanning Electron Microscope (SEM) with model No. EVO40 and EDX studies using Oxford Instrument with Model No. INCA PENTA SET×3 at SEM-EDX Laboratory. In the study area, the sulphide disseminations are dominantly pyrite, pyrrhotite, chalcopyrite and oxide ore minerals (hematite, rutile, etc.). Sulphide mineral associations that comprise pyrite, chalcopyrite, pyrrhotite, and arsenopyrite were identified (Fig. 4).

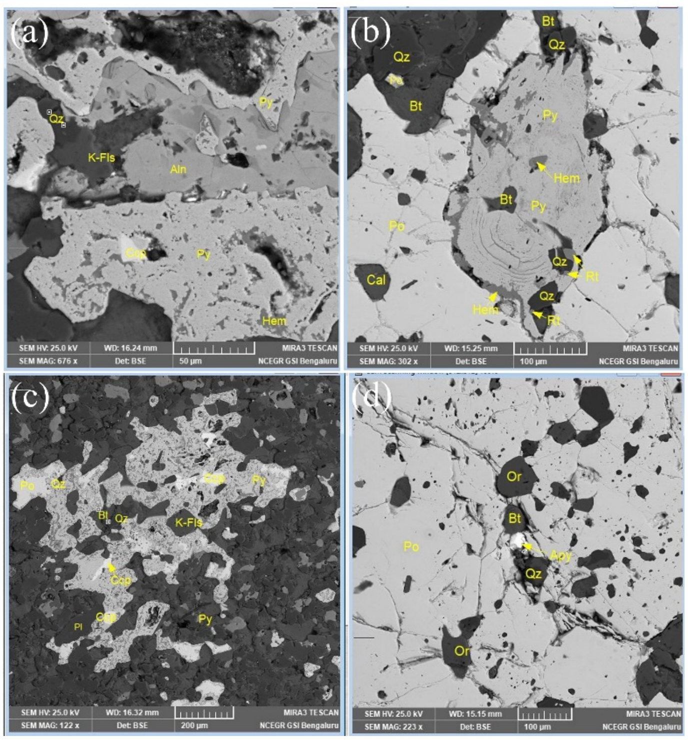

Fig. 4. Backscattered Electron (BSE) - Scanning Electron Microscopy (SEM) images of mineralized volcanic rock shows: (a) chalcopyrite inclusion in pyrite hosted with quartz veins, (b) pyrite inclusion in pyrrhotite with silicate minerals, (c) chalcopyrite occurs as inclusions in the pyrite microphenocryts embedded in silicate groundmass, and (d) arsenopyrite inclusion in pyrrhotite with silicate matrix. Mineral symbols: Gm – groundmass; Ccp – chalcopyrite; Py – pyrite; Po – pyrrhotite; Bt – biotite; Aln – allanite; Qtz – quartz; K-Fls – K-feldspar; Hem – hematite; Cal – calcite; Rt – rutile; Pl – plagioclase; Or – orthoclase; Apy - arsenopyrite.

The major sulphide mineral observed under the BSE mode is pyrite, having discrete small patches of chalcopyrite and pyrrhotite with inclusions of arsenopyrite. Small patches of pyrite grains also occur as fracture filling. Allanite and monazite occur as gangue minerals along the grain boundary of sulphide mineral phases (Fig. 4a). Pyrite inclusions in the pyrrhotitemicrophenocryts developed characteristic ore mineral assemblage associated with biotite, calcite, quartz, and hematite (Fig. 4b). Oxidized pyrite with inclusions of pyrrhotite and chalcopyrite form the characteristics alteration mineral assemblages with biotite, k-feldspar and quartz in the mineralized zone of the AmraKa Bas area (Fig. 4c). The studied section of ore minerals has the assemblage of arsenopyrite and pyrrhotite with inclusions of silicate minerals such as biotite, orthoclase and quartz (Fig. 4d).

The studied alteration mineral assemblage of biotite has Ag-Mo phases as small patches, besides K-feldspar (Fig. 5). The petrographic section of the quartz vein also contains pyrite with significant proportions of molybdenum telluride with traces of silver. The samples from the AmraKa Bas area contain chalcopyrite grains dominantly hosted in metavolcanic rock types. SEM-EDX studies have shown the presence of nano to micro inclusions of gold (Au) observed in a fracture within the chalcopyrite grain (Fig. 6).

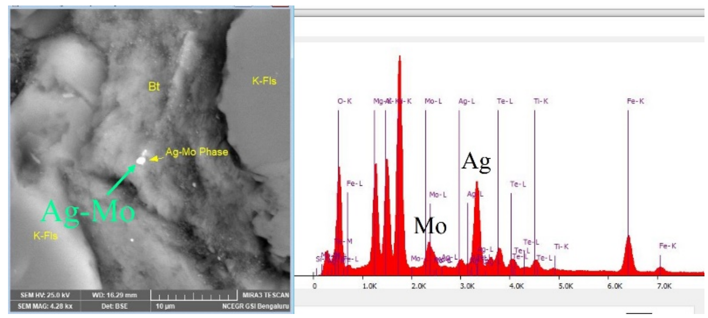

Fig. 5. BSE image under SEM shows Silver-Molybdenum-Tellurium in biotite grains, the EDX spectrum shows peaks of Ag-Mo-Te.

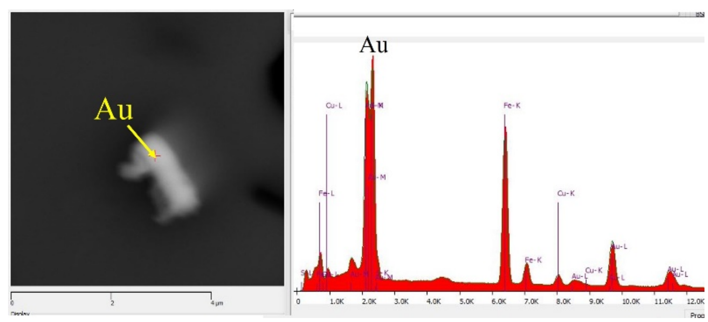

Fig. 6. BSE image under SEM shows gold (Au) in chalcopyrite grains, the EDX spectrum shows peaks of Au.

I. DISCUSSIONS

The occurrences of base metal-rich quartz and quartz-carbonate veins that traverse the volcanic rocks and dolomites of the Thanagazi Formation are reported from parts of the Alwar district, Rajasthan. The sulphide mineralization occurs in the quartz veins and along the contact of the quartz vein with volcanic rocks and also within the quartz-carbonate veins hosted in dolomite. The quartz veins and lumps of reddish-brown oxide ore minerals occur in the fractures of the milky white quartz vein from the RoopuKa Bas area. Channel samples from the studied area have yielded values up to 3900 ppm Cu, 35 ppm Zn, 40 ppm Pb, and <0.05 ppm Au (GSI, 2019).

In the Thanagazi Formation, the occurrences of base metal are generally associated with sulphide minerals phases. Copper behaves as an incompatible element and tends to concentrate in residual melts in which sulphide dissociates. Copper is primarily hosted in chalcopyrite which is related to pyrrhotite, pyrite and arsenopyrite ore mineral assemblages in most of the hydrothermal copper deposits, and its concentration in sulphide contrasts to an excessive amount (Fontbote et al., 2017). Experimental studies have demonstrated that copper is hosted in sulphide minerals with the following decreasing order of Cu concentration: chalcocite (79.85 wt%) >covellite (66.46 wt%) bornite (63.31 wt%) >enargite (48.41 wt%) >chalcopyrite (34.63 wt%) >pyrrhotite> pyrite (webmineral.com, Liu et al., 2018).

The SEM-EDXstudy of polished sections indicates that the Ag-Mo-Te phases are present as melt droplets in biotite grains and aligned within fractures. The local association of silver and Mo-Te-S phases suggest that Ag was likely scavenged from the hydrothermal fluids by Mo-Te-S liquids or melts (Paterson, 1990; Kouzmanov and Pokrovski, 2012).

Conclusion

In the Thanagazi Formation of the Alwar Group, base metal (Cu-Pb-Zn) mineralization is hosted in the quartz veins of volcanic rocks and quartz-carbonate veins of dolomites and acts as the prominent migration pathways and entrapment sites. The sulphides ore minerals occur in the form of disseminations, veins, stringers, and foliation parallel layers associated with volcanic rocks and dolomites. In volcanic rocks, sulphide minerals occur in dissemination form within the biotite segregates. The quartz veins which contain most of the chalcopyrite-pyrite-pyrrhotite ore mineral assemblages are characteristic indicators of copper deposits.

Massive sulphide ore deposits in the volcanic rocks and adjacent dolomite characterize the main stage of base metal mineralization in the Thanagazi Formation. Polished thin sections and SEM-EDS analyses indicate that base metals are associated with the most sulphide ores related to chalcopyrite, pyrite and pyrrhotite. Thus, chalcopyrite-pyrite-pyrrhotite ore mineral assemblage in quartz veins and quartz-carbonate veins with hydrothermal alteration envelopes, located near the contact of the volcanic rocks and dolomite, represent copper mineralization in the Thanagazi Formation of the Alwar Group. The physicochemical environment of ore deposition in the volcanic rock's association with chalcopyrite-pyrite-pyrrhotite suggests the existence of volcanogenic massive sulphide ore deposit (Einaudi, 1977; Brueckner et al., 2015). Hence, base metal deposits in the Alwar basin formed as a result of volcanic-associated hydrothermal events under submarine environments at or near the seafloor.

Acknowledgment

The authors are thankful to Dr Sanjay Das, Deputy Director General, State Unit: Rajasthan, Western Region, Geological Survey of India, for providing logistics and infrastructure to carry out the research work. SR is grateful to Smt. Swapnita Brahma, Geologist, NCEGR, GSI, Bangaluru for SEM studies. We thank the Head, Department of Geology for providing necessary facilities at Banaras Hindu University.

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