Characterization of Sulphide Ore Minerals Using Combined Laser Raman with Scanning Near-field Optical Microscopy (SNOM)

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Abstract: **The Laser Raman Micro Spectroscopy (LRMS) is a non-destructive material characterization technique. It is extensively used for the identification of minerals and gemstones. Raman spectra give crucial information on aspects of crystal structure, crystal chemistry, and chemical speciation in mineralogical and geochemical systems as specific compounds in a microsample. The Raman microprobe also permits Raman imaging and mapping of surfaces and inclusions. The LRMS study provides information that is sometimes difficult to obtain from Electron Probe Micro Analyzer (EPMA) and ion microprobes. The Raman microprobe offers an important method to the classification of minerals and associated gangue materials in the sulphide ores. Confocal Raman spectroscopy, in combination with Scanning Near-field Optical Microscopy (SNOM) has dramatically increased the applicability for mineralogical studies)**

Index Terms: **Raman, SNOM, Minerals, Alwar, Sulphide**

I. INTRODUCTION

The Laser Raman Micro Spectroscopy (LRMS) is a type of vibration spectroscopy technique. It is capable of in-situ molecular identification of solids, liquids, and gases. LRMS is serve as a finger print non-invasive, non-destructive, energy-shifted spectrum and back-scattered radiation serves as a fingerprint to the compositional and structural information (White, 2009). It is a useful analytical tool to study minerals in thin sections as a structural probe for analysis of micron-size mineral grains (Mao et al., 1987). The facility of LRMS to optically identify minerals makes it an ideal instrument for in-situ characterization of materials. The potential of using LRMS for identification and structural analysis of minerals is emerging as an important technique in mineralogical and petrographic research.

Specific Raman spectral bands represent the energies of definite vibration motions among bonded atoms within a molecule (Pasteris et al., 2001). The Raman spectrum identifies the compound structurally and permits its possible composition to be inferred. It is varied for the individual crystal structure and also reflects differences in the configuration among the atoms within the molecular structure (Ferraro et al., 2003). The Raman spectrum is plotted as intensity versus Raman shift in wave numbers (Δcm-1), which observed a shift from the absolute frequency (cm-1) of the excitation laser. This technique has been successful for mineral identification in the laboratory and is capable of depiction between mineral polymorphs (Haskin et al., 1997).
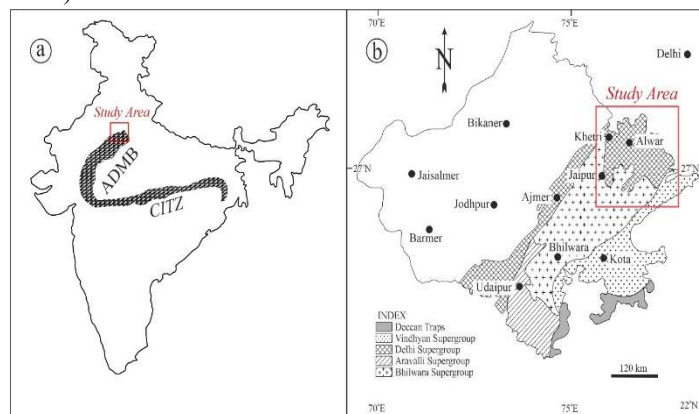

Fig. 1. (a) Map of India shows locations of the Aravalli-Delhi Mobile Belt (ADMB) and Central Indian Tectonic Zone (CITZ). (b) The geological map of the Delhi Fold Belt shows the location of the Alwar Basin (after the Geological Survey of India, Sajeev et al. 2022).

The LRMS is well suited to qualitative species identification of minerals and crystals, which depends on the band positions and relative band intensities. Raman band position may vary

slightly from one spectrum to another due to the orientation of the crystal lattice, optical properties of the crystal, the presence of local impurities, and distortion in the crystal structure (Hope et al., 2001). The intensity of the Raman band height in raw spectra cannot be used to directly related with concentration or abundance due to the fact that various species have different scattering efficiencies as well as heterogenous characteristics (Wopenka & Pasteris, 1987).

II. REGIONAL GEOLOGY

In the Alwar basin constitutes the central part of the Delhi Fold Belt (NFB), which occurs as a narrow linear belt in the south and central Rajasthan (Fig. 1). The Mundiyawas-Khera located in the Alwar basin reveals a felsic volcanic hosted thick copper and associated gold mineralization in the Thanagazi Formation of Ajabgarh Group within the DFB. Sulfide ore minerals are identified in this area as disseminations and stringers associated with pyrrhotite, pyrite, and chalcopyrite mineral phases, which indicates potential base metal mineralization (Sajeev et al., 2022). Sulphide mineralization in the volcanic rocks and dolomites includes ore minerals such as chalcopyrite, galena, sphalerite, and arsenopyrite (Sajeev et al., 2023). Stains of malachite and iron oxides are also associated with sulphide mineralization in the Alwar Basin, which is considered as the surface indicator (Fig. 2).

Fig. 2. Field photographs of exposed outcrop in the Alwar Basin: (a) galena with malachite in dolomite, (b) reddish-brown spot of iron oxides in volcanic rock, (c) sulphide ores in quartz-carbonate veins and (d) stains of malachite associated with quartz-carbonate veins in dolomite.

III. PETROGRAPHY

Polished thin sections of mineralized rock samples mounted on glass slides were studied using a petrological microscope under polarizing reflected light mode. A petrological study of mineralized rock samples from the Alwar Basin reveals characteristic colors and grain boundaries of sulfide ore minerals (Fig. 3). White color massive grain of pyrite contains inclusions of a yellow color grain of chalcopyrite. Pyrite is surrounded by grey colored quartz grains and silicate-rich groundmass. Pyrite grain occurs within silicate groundmass are anhedral in shape with corroded boundaries and the presence of inclusions of silicate matrix. These pyrite grain size >1000 μm with tiny inclusion (mostly <50 μm) of silicate matrix, which occurs as composite globular aggregates.
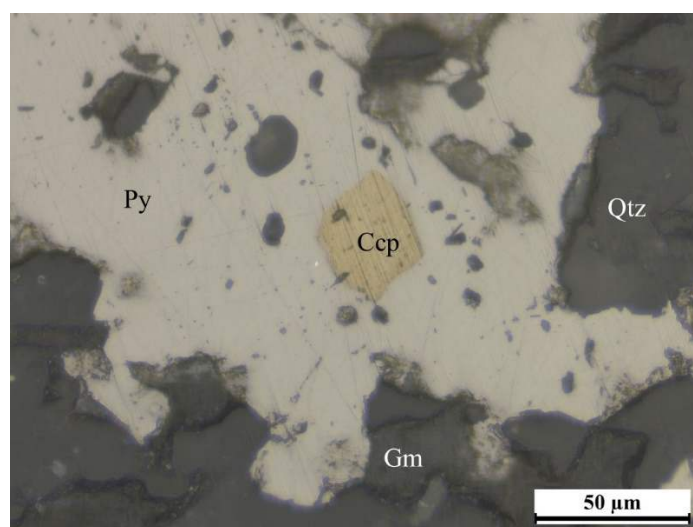

Fig. 3. Photomicrographs from Alwar Basin shows sulphide ore samples under polarized reflected light. Inclusion of chalcopyrite in pyrite associated quartz phenocryst and groundmass. Note: Ccp – chalcopyrite, Py – pyrite, Gm – groundmass, Qtz - quartz.

IV. THEORY AND METHODOLOGY

Polished thin sections of mineralized rock samples mounted on glass slides were studied using a petrological microscope under polarizing reflected light mode. Microtextural and microstructural characteristics of sulphide ore minerals confirms the presence of pyrite and chalcopyrite grain associated with quartz and silicate groundmass. However, tiny inclusions (<50 μm) are very difficult to identify using a petrological microscope. The broad scope and vast petrological, theoretical, and methodological background on the identification of ore minerals make it possible from a holistic perspective.

Polished thin sections of rock samples mounted on glass slides were studied at Raman-SNOM-AFM Microscope System, Central Discovery Centre (CDC), Banaras Hindu University, Varanasi, India. Raman spectra were acquired using Confocal Raman imaging in combination with Scanning Near-field Optical Microscopy (SNOM) Make WITec, GmbH, Model:

alpha300-RAS. The combined Raman-SNOM microscope is also very advantageous for high-resolution Raman imaging techniques. The Raman-SNOM instrument was operated at 1 mW output power with a solid-state YAG laser (532 nm) source. RRUFF database provides a standard Raman scattering spectral library for mineralogists, geoscientists, gemologists and the general public for the identification of minerals (Lafuente et al., 2015). In this study, Raman spectra from the RRUFF database are used to mark the characteristics of Raman frequencies (cm-1) of common oxide minerals such as quartz, hematite, and magnetite (Fig. 4). These Raman frequencies of common oxide minerals (Jayaraman et al., 1987; Schmidt & Ziemann, 2000; Sparavigna, 2023) are denoted by respective stretching, bending and torsional vibrational modes (Fig. 5).

Fig.4. Representative Raman spectra of quartz (Qtz), hematite (Hm), and magnetite (Mt) marked with characteristics observed Raman frequencies (cm-1) obtained from the RRUFF database (Lafuente et al., 2015).

Fig.5. Representative Raman spectra of quartz (Qtz), hematite (Hm), and magnetite (Mt) with characteristics vibrational modes obtained from the RRUFF database (Lafuente et al., 2015).

Raman spectra from the RRUFF database have a need for comparative databases used to mark the characteristics Raman frequencies (cm-1) of common sulphide minerals such as pyrite, chalcopyrite, arsenopyrite, pyrrhotite, galena, and sphalerite (Fig. 6). These Raman frequencies of common sulphide ore minerals (Mernagh & Trudu, 1993; White, 2009; Zheng et al., 2020) are represented by corresponding stretching, bending and torsional vibrational modes (Fig. 7).

Fig.6. Representative Raman spectra of pyrite (Py), chalcopyrite (Ccp), arsenopyrite (Asp), pyrrhotite (Po), galena (Gn), and sphalerite (Sph) marked with characteristics observed Raman frequencies (cm-1) obtained from RRUFF database (Lafuente et al., 2015).

Fig.7. Representative Raman spectra of pyrite (Py), chalcopyrite (Ccp), arsenopyrite (Asp), pyrrhotite (Po), galena (Gn), and sphalerite (Sph) marked with characteristics vibrational modes obtained from RRUFF database (Lafuente et al., 2015).

V. RESULTS

The Raman spectra were collected from sulphide ore minerals using solid state YAG laser (532 nm) attached with Raman-SNOM-AFM Microscope System operating between 0.3 to 1 mW output power. The acquisition region of spectra extended from 100 to 2500 cm-1, which have been normalized. The series of reference Raman spectra obtained for quartz, hematite, pyrite, and chalcopyrite from the RRUFF database (Lafuente et al., 2015; McGuire et al., 2001). Quartz is characterized by seven characteristic Raman peaks at 130, 206, 262, 355, 395, 462 and 806 cm-1. Hematite is characterized by seven characteristic Raman peaks at 225, 245, 292, 411, 496, 610 and 661 cm-1. Pyrite gives rise to six characteristic Raman peaks at 342, 353, 378, 387, 428, and 428 cm-1 (Mernagh & Trudu, 1993).

Chalcopyrite gives rise to seven characteristic Raman peaks at 265, 291, 320, 352, 378, 456, and 471 cm⁻¹ (White, 2009). Arsenopyrite is characterized by representative Raman peaks at 135, 171, 203, 212, 244, 274, 296, 334, 369, 388, 404, 481, 527, and 582 cm⁻¹ (Mernagh & Trudu, 1993; McGuire et al., 2001). Raman spectral linewidths, peak position, and band intensity are used to characterized stretching, bending, and torsional vibrational modes of in the natural minerals. However, Raman spectral features overlap, and extraction of linewidth, peak position, and band intensity becomes difficult to recognize, leading to large uncertainty in the Raman spectroscopy.
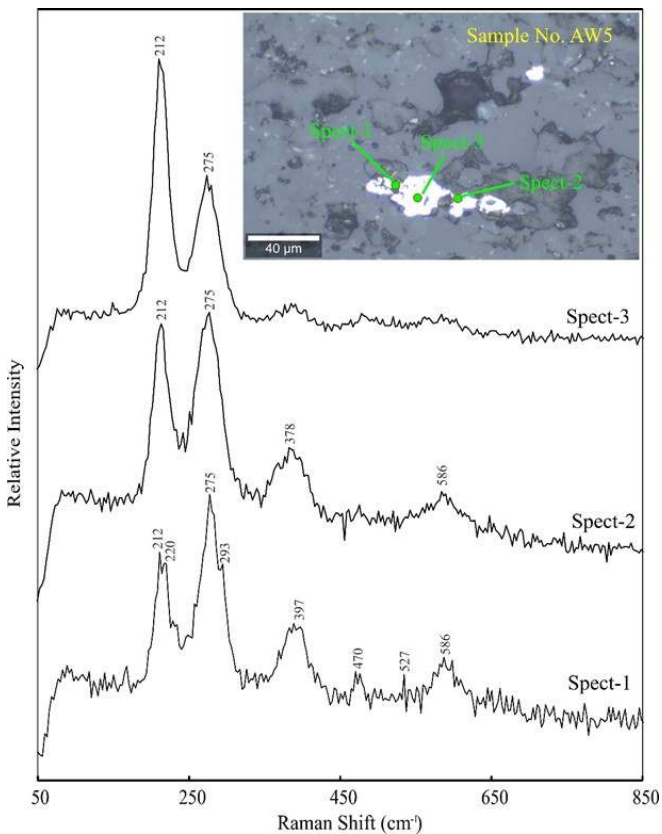
Fig.8. Scan of Raman spectra in the sulphide ores from Alwar Basin using SNOM: Spect-1 (Ccp), Spect-2 (Asp), and Spect-3 (Py) marked with characteristics observed Raman frequencies (cm⁻¹). Photomicrographs from Alwar Basin show sulphide ore samples under polarized reflected light.

Uncertainty is related to peak strength, noise, and spectral resolution, which relatively influences error in the Raman spectroscopy measurements (Ferraro et al., 2003; Saltonstall et al., 2019). A holistic approach is required to accomplish this by considering physical parameters such as the substitution of minor impurities in crystal lattice structure, which impact not only uncertainty but also the error-induced broadening distorts the spectral position. Taken together, the optical properties of the crystal and the presence of minor impurities that bring changes in the crystal chemistry of minerals highlight the relative option required when quantifying spectral linewidth compared to the Raman peak position.
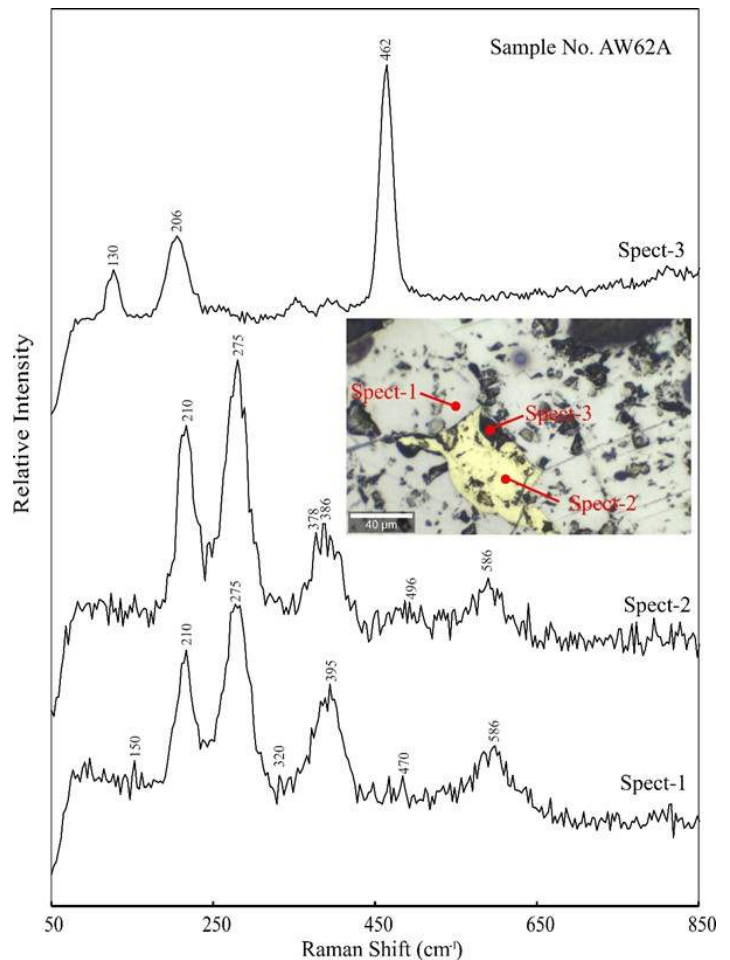

Fig.9. Scan of Raman spectra in the sulphide ores from Alwar Basin using SNOM: Spect-1 (Py), Spect-2 (Ccp) and Spect-3 (Qtz) marked with characteristics observed Raman frequencies (cm⁻¹). Photomicrographs from Alwar Basin shows sulphide ore samples under polarized reflected light.

VI. DISCUSSIONS

Theorems In the Alwar basin, the sulphide mineralization is observed as disseminations, stringers, and veins, mainly in the volcanic rocks and dolomites. The area shows very good exposure of fine-grained dark-colored metavolcanics in close association with dolomites and carbon-rich felsic tuffs. Ore and host rock petrographic studies can throw light into the mineral system, ore-forming processes, and their paragenetic sequences. Detailed ore petrographic studies have therefore been carried out on samples collected from the Alwar basin and adjoining areas to understand the control of mineralization and mineral assemblages. Under the microscope, the chalcopyrite occurs as golden yellow colored irregular grains of varying sizes within the interstices of the pyrite, where it has mutual straight boundary as well as embedded relationship indicating their coeval nature of origin (Fig. 3).

To identify the minor phases associated with the sulphide ore minerals, Raman-SNOM study has been carried out for selected samples from the Alwar basin and adjoining areas. The

occurrence of minor phases identified as arsenopyrite and quartz associated with sulphide ore minerals in the Alwar Basin. Copper mineralization is represented in the form of sulphide ore mineral assemblages of pyrite-chalcopyrite as major phases, whereas arsenopyrite is recognized as minor phases hosted in the silicate groundmass.

CONCLUSIONS

The study of copper mineralization from the volcanic rocks of the Alwar basin reveals that the primary mineralization is syngenetic as evidenced by the nature of occurrence of discrete grains of sulphide ore minerals as fine disseminations within the volcanic rocks. Identification and characterization of natural minerals are very fundamental aspects in the planning, development, and exploration of economic mineral deposits. The incorporation of Raman spectral signatures with available geological and geochemical data highlights the delineation of sulphide ore mineral phases that occurs in various areas of the Alwar basin for a further detailed investigation related to base metal exploration.

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