

**Spectral Characterization of Copiapite and Rozenite from Sulphide-rich Banded Iron Formations in Wayanad, Kerala, India and its implications.** Shubhonkar Paramanick<sup>1,2</sup>, V.J. Rajesh\*<sup>1</sup>, M.N. Praveen<sup>3</sup>, K.S. Sajinkumar<sup>4</sup> <sup>1</sup>Indian Institute of Space Science and Technology, Thiruvananthapuram-695547, India, <sup>2</sup>ISRO Satellite Centre, Bengaluru-560017, India, <sup>3</sup>Geological Survey of India, Bengaluru-560078, India, <sup>4</sup>Department of Geology, University of Kerala, Thiruvananthapuram-695581, India (\*Corresponding author: <rajeshvj@iist.ac.in>).

**Introduction:** Copiapite [ $\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ ] and rozenite [ $\text{Fe}^{2+}\text{SO}_4 \cdot 4\text{H}_2\text{O}$ ] are secondary hydrated sulphate minerals formed by weathering and oxidation of primary sulphides. These secondary sulphate minerals are significant in defining the environments of geological past, on Earth as well as on other rocky planets such as Mars. Copiapite is pale yellow in colour while rozenite is greyish to white in colour with vitreous lustre. Copiapite is found in diverse conditions on Earth: it is commonly found in acid mine drainages [1], intermixed with clay [2], in Greenland margin [3], with sulfotars [4] and in gossans as altered secondary sulphate. Rozenite forms under low temperature ( $\sim 30^\circ\text{C}$ ) and low humidity condition. It has been quarried from mines and has been found as surface seeps [8]. Apart from terrestrial occurrences, these secondary sulphates have also been detected in Mawrth Vallis [5] and in Gusev Crater [6] on Mars. Evidence of microbial activities has also been observed in these secondary sulphates in terrestrial environments [7]. These microorganisms can provide important clues to understand the geo-microbiological evolution of the past. Therefore, understanding its genesis is of great significance as copiapite is very rare on earth. We report here spectral analyses of copiapite and rozenite collected from sulphide-rich Banded Iron Formations (BIFs) in Wayanad in Southern India, which could be considered as potential chemical analogue mineral for the copiapite discovered in Mawrth Vallis on Mars [5]; though it requires more analyses to reckon it as analogue site. Our hyperspectral and Laser Raman analyses of copiapite and rozenite and its genesis on Earth will enhance understanding of similar mineral formation and aqueous processes on Mars and their correlation.

**Geological Setting:** The study area forms a part of Southern Granulite Terrain (SGT). The SGT constitutes high-grade metamorphic rocks mainly comprising of granulite facies. The study site (Fig. 1(A)) is a part of sulphide-rich BIF that consists of mid-Archaean supracrustals of the Dharwar Craton that extend upto Wayanad region in Kerala. BIF includes the following primary sulphides: pyrite ( $\text{FeS}_2$ ) and pyrrhotite ( $\text{FeS}$ ) with chalcopyrite ( $\text{CuFeS}_2$ ) and acanthite ( $\text{Ag}_2\text{S}$ ) in traces. Copiapite in Wayanad occurs as bloom while rozenite occurs as fine-grained coating (Fig. 1(B)). The occurrence of secondary sul-

phates as coatings on primary sulphide (pyrite) is indicative of direct alteration of primary sulphides to secondary sulphates by weathering and oxidation.

**Methodology:** In order to understand the occurrence and genesis of hydrated secondary sulphates and its association with primary minerals, systematic field investigation and sampling were carried out. Spectral and chemical analyses have been done to characterize the natural samples. The samples were analyzed using FieldSpec® Pro 3 spectroradiometer (ASD Inc.) by generating the reflectance spectra of the minerals. The spectroradiometer covers the spectral regime from 350 nm to 2500 nm covering visible to NIR part. The averaged spectrum over 20 scans was compared with the reflectance spectra of minerals from USGS and RELAB spectral database. For matching the continuum-removed spectra with the library spectra, different matching methods were used. Instead of taking the whole spectral range, a subset (2280 nm to 2600 nm) in the spectrum was taken. Different matching algorithms like Spectral Feature Fitting (SFF) (Fig. 3), Spectral Similarity Value (SSV) and Modified Spectral Angle Similarity (MSAS) were used for quantitative matching with the reference spectrum. Powdered and solid flakes of the samples have been analyzed to generate the reflectance spectra. The powdered samples have also been analyzed using Laser Raman spectroscopy and have been compared with the spectral data of copiapite and rozenite from RRUFF mineral database.

**Results:** The absorption features in visible-NIR reflectance spectroscopy are due to electronic transition of central metal ion and different bending and stretching vibration modes of anionic species ( $\text{SO}_4^{2-}$  and  $\text{OH}^-$ ) and water of crystallisation ( $\text{H}_2\text{O}$ ) and their combinations. The absorption feature around 432 nm in reflectance spectrum of copiapite is caused by  ${}^6\text{A}_{1g} \rightarrow ({}^4\text{A}_{1g}, {}^4\text{E}_g)$  transition and this transition imparts yellow color to copiapite. The broad absorption bands around 1450 nm and 1940 nm for copiapite (Fig. 3) and rozenite are attributed to bending vibration modes of water molecules. The continuum-removed spectra of copiapite exhibits the characteristic triple absorption feature around 2400 nm and is due to combinations of different vibration (stretching and bending) modes of  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$  and  $\text{OH}^-$ . For rozenite, unlike copiapite,

two absorption bands are observed in 2400 nm – 2600 nm range and thus enable spectral distinction between the two samples. The band width and shape depends upon the number of water molecules and extent of hydrogen bonding.

The strong doublet peak for copiapite around 1000  $\text{cm}^{-1}$  region in Laser Raman spectrum is attributed to stretching mode ( $\nu_1$ ) of sulphate (Fig. 4). The broad peak in 3000 – 3700  $\text{cm}^{-1}$  range is due to the stretching modes of  $\text{H}_2\text{O}$  ( $\nu_1$  and  $\nu_3$ ) and the first overtone of the bending vibration ( $\nu_2$ ). For rozenite, strong symmetric stretching vibration ( $\nu_1$ ) of sulphate is observed at 993  $\text{cm}^{-1}$ . As rozenite contains less water molecules, the band around 3000  $\text{cm}^{-1}$  is narrowed down. These results have been matched with the RRUFF database in-built in CrystalSuite software. On comparing the reflectance spectra of copiapite from Wayanad with the MRO CRISM spectral dataset of northern Mawrth Vallis region on Mars, identical trend in the absorption features in reflectance spectra were seen. Copiapite occurring on Mars was compared with the terrestrial analogue sites like the Iberian Pyrite Belt (Río Tinto, Spain), formed by microbial metabolic activities and provide knowledge about aqueous environment existed at the time of its formation [9]. Copiapite in Southern India was formed because of change in two important environmental factors viz. temperature and humidity. It can be associated with the diagenetic climate in the Meridiani Planum on Mars [10].

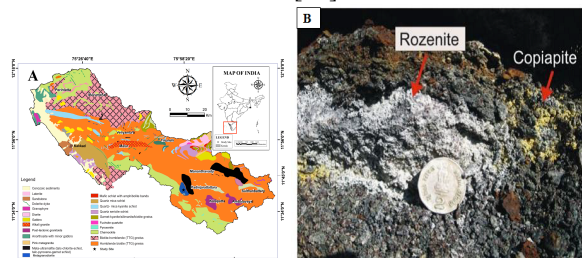


Figure 1(A). Location of the study site. 1(B). Occurrence of copiapite (yellow) in the field setting along with rozenite (white).

**Summary and Conclusions:** The occurrence of primary sulphides in association with volcanic rocks is widespread in terrestrial environment and are indicative of Volcanogenic Massive Sulphide (VMS) deposits. These volcanogenic deposits form under the sea where metallic solutions are released from marine volcanoes [11]. These hot discharge precipitate to form primary sulphides when it interacts with cold sea water. The primary sulphides transform to secondary sulphates by hydrothermal processes. Conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  involves oxidation. Water can be a possible oxidizing agent. However, low – humidity condition in Wayanad indicates that oxidation by microbial colonies (like *Leptospirillum* and

*Acidithiobacillus*) is also plausible. The northern Mawrth Vallis region on Mars hosts patchy occurrences of copiapite and has been posited as a result of acid leaching due to weathering and acid sulphate alteration. The spectral characterization of copiapite and rozenite from Wayanad region render reflectance data for mineral characterization for various space explorations and the spectral results can be confirmed. The spectral analyses, in response, are supposed to enhance the biogeochemical, mineral and geological information present today. This in return will assist in quantitative analyses and understanding of different biogeochemical cycles on other planetary bodies.

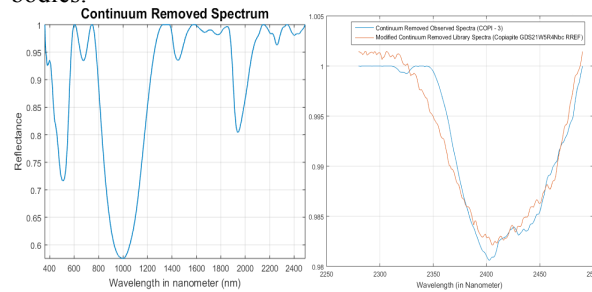


Figure 3. Continuum-removed reflectance spectrum of Copiapite (left). Spectral feature fitting of copiapite sample, COPI – 3, with the reference spectrum (right).

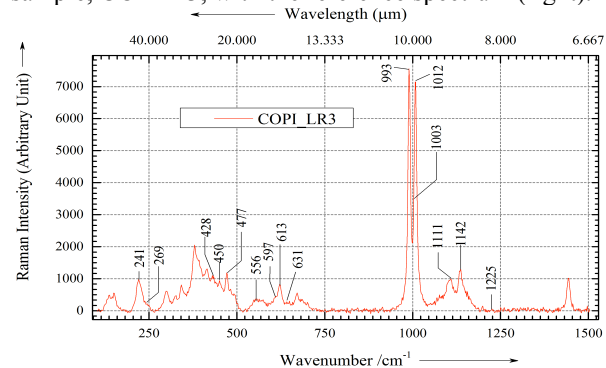


Figure 4. Laser Raman Spectrum of Copiapite with doublet peak around 1000  $\text{cm}^{-1}$ .

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