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RESEARCH ARTICLE

PETROGRAPHY, SEM-EDAX AND SPECTROSCOPIC IMPLICATIONS OF RUBY CORUNDUM OCCURRENCES, CLOSE TO THE CONTACT OF PERALIMALA PLUTON AND MOYAR SHEAR ZONE IN CHANAPPARA AREA OF KANNUR DISTRICT, KERALA, INDIA

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ABSTRACT

Corundum of semi precious gem variety occurs within the hydrothermally altered metaultramafites in the retrograde metamorphic terrain of kannur district along the north eastern part of kerala. Samples of semi-translucent to opaque nature with red to crimson red colour are studied through advanced spectroscopic techniques namely FTIR, Raman, Photoluminescence, UV-Visible and SEM-EDAX. Spectroscopic studies coupled with Geochemical perspective indicates the presence of considerable concentration of Cr^{2+} accompanied by more or less equal amounts of Ti^{2+}, V^{2+} and Ga^{2+}, along with other ions. A gemmological appraisal is carried out correlating the presence Cr^{2+} content and the absence of much OH associated impurities in them. Distinctive absorbance peaks of corundum corresponding to the Fe as well as Cr chromophores and typical emittance peaks with a greater magnitude indicating the prominence of Cr chromophores in the samples as evident from its colour is observed from the UV-Visible and the Photoluminescence spectrum respectively. The FT-IR spectrum shows the absence of much hydroxylated ions and the Raman spectrum substantiates it with the explicit presence of the peaks corresponding to the Raman active vibrational modes in corundum, which resulted in the diaphenity of the samples positively.

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INTRODUCTION

The occurrence of Ruby and other gemstones have been reported from various places in India localized within several gem tracts associated with tectonic events of the Geological past (Richard Hughes, 1997). Ruby variety of corundum is considered to be the most precious variety of gemstones, after Diamond (Sudheendra Rao *et al*, 2016). Indian contribution to the total supply of Ruby is mainly from the states of Orissa, Andhra Pradesh, Tamil Nadu and Kashmir among others (Atkinson and Kothavala, 1983; Shor and Weldon, 2009; Majumdar and Mathew, 2012; Giuliani, 2020). The possibilities of unraveling Ruby deposits from other probable places in Southern India are yet to be formulated. The present study is focused on characterizing the ruby corundum deposits from Chanappara village of Kannur district in Kerala, with an aim to know the possibility and nature of corundum crystallization in retrograde migmatised terrains (Vidhyadharan *et al*, 2008). As there is always a demand for natural gemstones, the necessity for carrying detailed geological as well as gemmological studies on their occurrences, to categorize them based on the economic potential is quite essential.

GEOLOGICAL SETTINGS

Chanappara village in Iritty taluk, Kannur district, geologically comprises the Wayanad Schist Belt, Peralimala Pluton and the Moyar Shear Zone (MSZ), and is within the latitude 11° 54' 42.9804" N and longitude 75° 44' 52.1304" E. The area is a part of the high grade granulite terrain of Southern India and is dominantly made up of hornblende-biotite gneisses, meta-ultramafites and metapelites along with the acidic intrusives. The MSZ which separates the Coorg block in the north from the Nilgiri block in the south (Ishwr Kumar *et al*, 2016), forms a part of the ancient suture zone (Krishna Brahmam, 1993), Moyar- Bhavani Shear Zone (MBSZ). The Peralimala pluton, termed by various authors as granite (Nair and Vidyadharan, 1982), alkali granite (Nair and Santosh, 1984) and syenite (Ravindrakumar and Sinha Roy, 1985), occupies a major portion of the study area. There are also views relating this pluton to be a deformed alkali rock and carbonatite (DARC) (Praveen *et al*, 2009) based on the observations that DARC occurrences are mainly confined to the suture zones or major terrane boundaries (Burke *et al*, 2003; Leelanandam *et al*, 2006) and it is also categorized to be anorogenic or post orogenic (Rajesh, 2000).

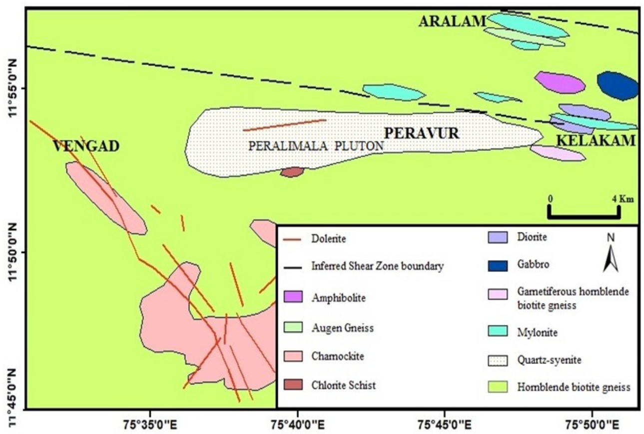


Fig.1. Geological map of the study area (modified after Pratheesh *et al*., 2013)

The Peralimala pluton covers an area of about 80 km^2 occurring from south-eastern part of Mattanur to Kanichar in the Iritty Taluk. It has a linear extension with a length of 20 km and an average width of 4 km (Ravindra Kumar and Sinha Roy, 1985) and is dated to be of 750Ma (Santosh *et al*, 1987) / 560Ma (Miller *et al*, 1996; Praveen *et al*, 2009), corresponding to the Pan African orogeny (Santosh and Drury, 1988; Rajesh *et al*., 1996). Similar alkaline rich granites were also reported from the Gundlupet area bordering moyar shear zone in Southern Karnataka (Shadakshara Swamy and Jayananda, 1989). Geochemical data of the Peralimala granite shows high content of alkalies suggesting possibly the existence of phlogopite - rich pockets in the mantle (Jakes and Smith, 1970; Forbes and Flower, 1974) from where the melt equilibrated. This may indicate that the granite pluton is a manifestation of rift related alkaline magmatism (Nair and Santosh, 1984). The Peralimala pluton is sporadically enveloped by high grade schists often rich in Chlorite. The area is marked by abundant fluid activities of a later stage, evident from migmatisation of the country rocks and the same can be inferred to be the reason for desilicification leading to the corundum mineralisation (Vidyadharan *et al*., 2008). The Metaultramafites hosting corundum occurs as well jointed conformable enclaves associated with other rock types of Wayanad schist complex in the study area. The faults and shears acted as weak zones for the movement of hydrothermal solutions and related interactions would have caused the formation of corundum in the metaultramafites (Vidyadharan *et al*., 2008). Semi precious varieties of corundum are seen to be occurring in lateritized gravels also (Vidhyadharan *et al*., 2008).

Fig. 2. Corundum bearing Chlorite and Steatite rich metaultramafites

The occurrence of corundum is understood to be a localized phenomenon which is triggered by the structural constraints of the Peralimala Pluton and the MSZ. Though the ruby corundum occurrences were reported from the study area (Vidyadharan *et al*., 2008), there are no reports pertaining to gemmological characterization.

Fig. 3. Fine quality corundum crystals collected from Peravoor, Kannur district, Kerala

Fig. 4. A sample after cabochon polishing

MATERIAL AND METHODS

Analyses carried out in this study are broadly classified under the headings Petrography and Spectroscopy. Spectroscopic studies namely Raman, FTIR, Photoluminescence, UV-Visible and EDXRF are carried out on the individual corundum specimens collected from the study area after acid treatment to remove the gangue impurities followed by slicing and polishing.

PETROGRAPHY: Thin section studies of the **c**orundum bearing chlorite rich meta- ultramafites indicate the presence of lamellar, subhedral to euhedral, porphyroblastic corundum, sillimanite, highly altered amphibole and plagioclase.

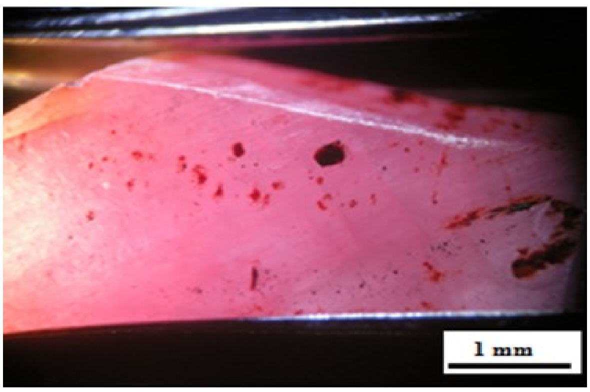
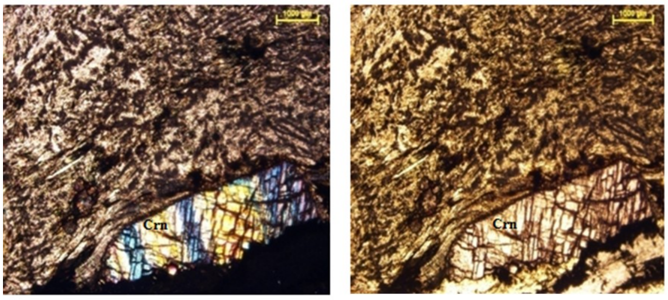


Fig. 5. Diaphaneity and Inclusions of Rutile seen in a semi precious variety Ruby Corundum from the study area

Spinel and titanite seen peppered throughout the rock, especially in the chloritized and sericitized portions. The textural studies indicate the formation of sillimanite at the expense of corundum. Some corundum grains exhibit a corona of a mafic mineral (possibly spinel) around it. Amphiboles are highly altered and chlorite is forming at the expense of amphiboles. Plagioclase is also seen being sericitized and lots of opaque grains are seen peppered throughout the rock, especially in the chloritized and sericitized portions.



(a) (b)

Fig. 6. Thin section photomicrograph of corundum (Crn) bearing rocks of Chanappara area, Kannur, Kerala, showing the presence of lamellar corundum in the Chlorite matrix (a) X Nicols (b) PPl

Gemmological properties: Individual crystals of corundum are washed with acid and cleaned in ultrasonic bath in order to remove the surface impurities. They are then cut into thin slabs which are further polished using conventional lapidary technique and subjected to the basic gemmological analyses to observe the desired properties namely Colour, Diaphaneity, Refractive Index (R.I), Birefringence, Dichroism, Specific Gravity (S.G) and Hardness.

Fig. 7. Showing average Gemological properties of the samples.

COLOUR	DIAPHANEITY	REFRACTIVE INDEX (R.I)	BIREFRINGENCE	DICHROISM	SPECIFIC GRAVITY (S.G)	HARDNESS
BROWNISH TO PINKISH RED	SEMI-TRANSLUCENT TO OPAQUE	1.761 –1.769	0.008	RED TO CRIMSON RED	3.9	9

SPECTROSCOPIC IMPLICATIONS

The Spectroscopic studies are employed for an advanced gemmological interpretation of gemstones with respect to their cause of colour and clarity.

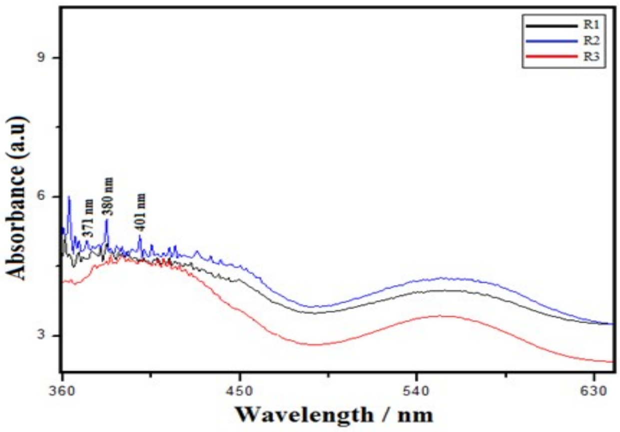


Fig. 8. UV-Visible spectrum of the Ruby corundum samples

It acts in a way to substantiate the preliminary gemmological assessment using the primitive techniques. Corundum in its native form is colourless and the colouration in corundum is mainly due to the presence of the desirable impurity elements Cr, V, Fe and Ti in considerable quantity (Nassau, 2003; Karantoni, V *et al*, 2021; Shyam Kumar and Shadakshara Swamy, 2022). Three samples collected from the area were subjected to different spectroscopic studies and the results are displayed in figures under each study. UV-Visible absorbance spectrum shows the prominent Fe and Cr related peaks in ruby at 371nm, 380 nm, 401nm, 461 nm, 467 nm, 475 nm, 491 nm and 535 nm. The peaks obtained in 371nm and 380 nm pertains to the Fe content and from 401 nm to 535 nm corresponds to the Cr ions present in them (Cartier 2009; Jathin and Pratima, 2013; Shyam Kumar and Shadakshara Swamy, 2017).

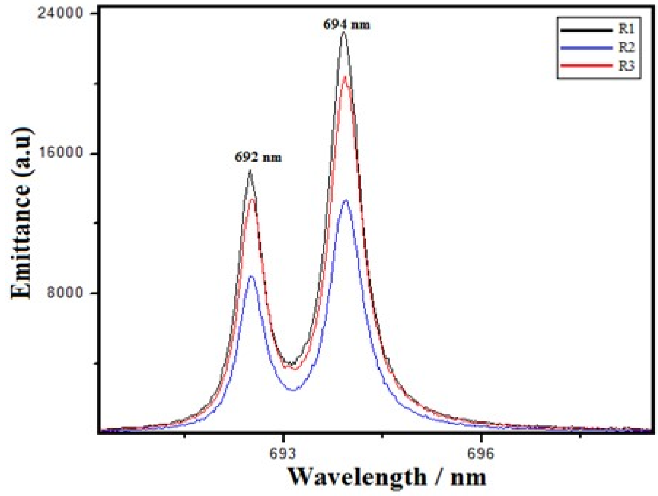


Fig. 9. Photoluminescence spectrum of the Ruby corundum samples

The emittance spectra obtained from Photoluminescence spectroscopy shows a greater prominence of chromium chromophore in them.

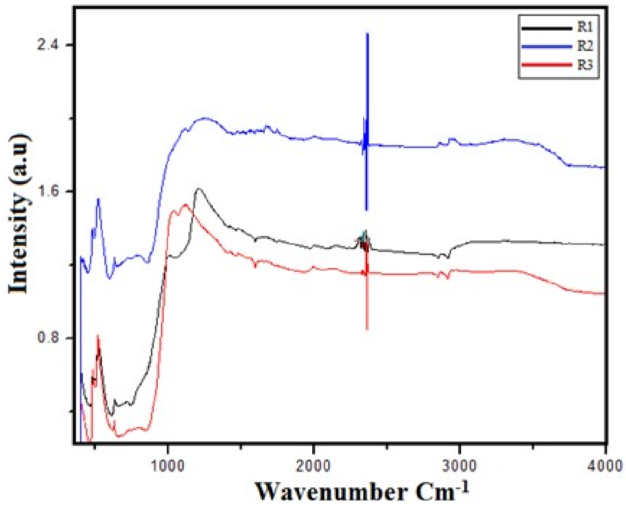


Fig. 10. FT-IR spectrum of the Ruby corundum samples

Emittance peaks at 692 nm and 694 nm are seen to be present in varying intensity among the samples, in Fig.9. The FT-IR Spectrum of the samples appears to be with infinitesimal spectroscopic implications. The typical absorption peaks seen in ruby are at 3086, 3240, 3324 and 3418 cm -1 (Cowley, 1969; Kloprogge *et al*, 2004; Abali *et al*, 2011; Beran et. al, 2006; Shyam Kumar and Shadakshara Swamy, 2017 a). In Fig.10, the spectrum is devoid of any significant peaks, implicating its crystal lattice to be devoid of much molecular inclusions, as the peaks corresponding to OH related molecules in these regions (Saikia *et al*. 2010) are either due to be 'Al' association or as an associate of 'Fe', 'Ti' and 'V' as surface impurities (Volynets *et al*. 1972) which would result in a consequent diminish in the colour and clarity. The Raman active vibrational modes in corundum observed at 378, 418, 432, 451, 578, 645 and 751 cm-1 (Richet *et al*. 1993; Xu *et al*. 1995; Shyam Kumar and Shadakshara Swamy, 2020) are seen to be depicted partially in the samples. The spectrum in Fig.11,is identified with considerable peaks at 378 cm^{-1}, 418 cm^{-1}, 451 cm^{-1}, 645 cm^{-1} and 751 cm^{-1}. Presence of maximum Raman active vibrational modes in the spectrum also suggests the absence of much OH associated impurities.

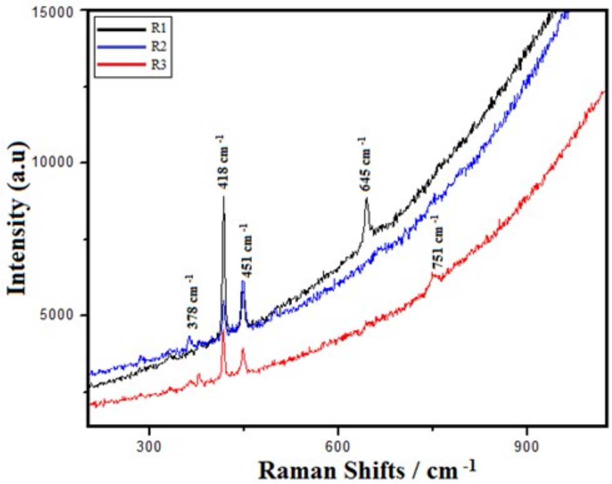


Fig. 11. Raman Spectrum of the Ruby corundum samples

SEM-EDAX and EDXRF Implications: The individual molecule with high calcium (5.64 Wt %), silica (7.70 Wt %) with probable wollastonite composition is depicted in Fig.12. The magnified view of a sample in Fig.15 implies it to be rich in silica (17.84 Wt %) and iron (23.37 Wt %) oxides. Micro surface cracks and distinct inclusions of zircon (51.98 Wt % and 41.30 Wt %) grains are present in Fig.14. Mg rich inclusions along with Al and O is seen to be present in the SEM photograph in Fig.13.

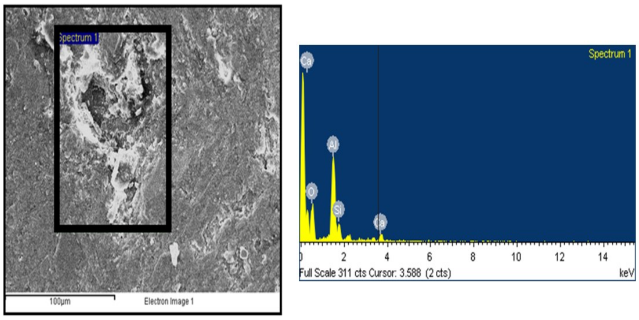


Fig. 12. SEM EDAX image showing Ca rich inclusions

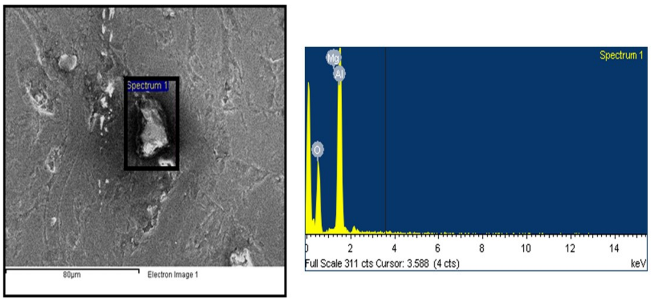


Fig.13. SEM EDAX image showing inclusions of Mg, Al and O

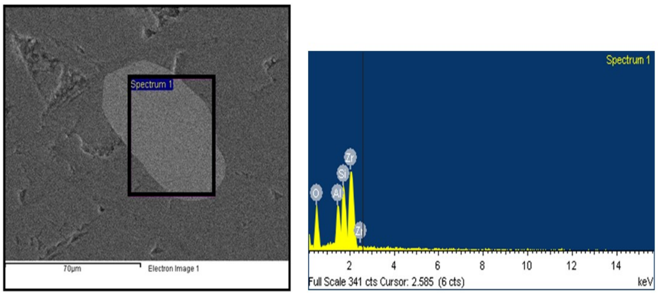


Fig.14. SEM EDAX image showing inclusions rich in Zr, Al, Si and O

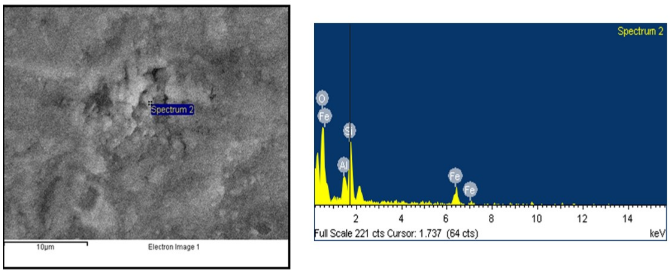


Fig. 15. SEM EDAX image showing inclusions of Fe, Al, Si and O

ED-XRF studies indicate the average concentration of different ions in the trend, Al_2O_3> Fe_2O_3> Cr_2O_3> ZrO_2> TiO_2> CaO> V_2O_5> Ga_2O_3.The chemistry generally shows a prominence of Al_2O_3 followed by Cr_2O_3.A greater content of Cr_2O_3 than Fe_2O_3 would have inherited more reddish colour to the samples, as 'Cr' content plays the pivotal in imparting colour in Ruby (Nassau, 1983; Lu, Q *et al*, 2022; Yang L, 2023).

DISCUSSIONS AND CONCLUSION

Thin section studies of the Chlorite rich Meta-Ultramafite shows corundum, sillimanite and the formation of sillimanite at the expense of Corundum, with coronary Spinel. The Primitive and conventional gemmological characterization of the selected samples classifies them to be of semi precious gem quality. Further survey is required to be carried out to know about the extent of its occurrence. The distinctive absorbance peaks of corundum corresponding to the Fe and Cr chromophores are well present in the UV-Visible spectrum. The typical emittance peaks in the Photoluminescence spectrum, with a greater magnitude indicates the prominence of Cr chromophores in the samples as evident from its colour. It is being understood that the FT-IR spectrum shows the absence of much hydroxylated ions, preventing the ubiquitous diminish in their clarity and transparency. Such a condition supplemented by an appreciable content of Cr has possibly brought to classify these samples under semi precious category. The Raman active vibrational modes are also explicitly present in samples, substantiating the possibility of less hydroxylated content. Point analysis of the inclusions are performed with the help of SEM-EDAX technique to understand the chemistry of the impurities present as incusions in the crystal lattice of corundum. SEM microphotographs depicts the lattice to be containing a very few inclusions alone, substantiating the results from spectroscopic study.

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