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# High incidence of vanadium and copper in the titanomagnetite and ilmenite samples off Ratnagiri, Maharashtra, India

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Samples of ilmenite and titanomagnetite collected off Ratnagiri and nearby bays exhibit elevated concentrations of vanadium and copper. In ilmenite, vanadium values range from 1429 to 1816 ppm, with an average of 1592 ppm. Titanomagnetite samples show vanadium concentrations ranging from 3392 to 4442 ppm (average = 4026 ppm). Copper values for ilmenite samples range from 345 to 1166 ppm, averaging 628 ppm, while titanomagnetite samples display copper values from 743 to 1030 ppm, averaging 943 ppm. The ternary diagram of $TiO_2$, FeO and $Fe_2O_3$ indicates that all the magnetite samples with a higher concentration of vanadium and copper fall in the titanomagnetite field. From the ternary diagram, it is interpreted that the higher concentration of vanadium in the samples is contributed by titanomagnetite in the survey area, which is reported from the Deccan basalt present in the hinterland. The strong positive correlation between Cu and V further supports the provenance of titanomagnetite from the Deccan basalt.

[**Keywords**: Copper, Deccan basalt, Ilmenite, Titanomagnetite, Vanadium]

## Introduction

The occurrences of onshore and offshore heavy minerals in the Ratnagiri area were reported by different workers[1-3]. These studies estimated 5.0 million-tonne onshore deposit of ilmenite between Jaigad and Vijaydurg. Surveys of 13 bays using advanced techniques uncovered offshore extensions of heavy mineral-rich sands, with ilmenite content of up to 64 % extending offshore to depths of 10 – 13 m over a 3 to 5 km lateral range. Surveys of Ratnagiri, Kalbadevi, and Mirya bays revealed that the seabed sediments contain significant amounts of heavy minerals, ranging from 1 to 91 %, with ilmenite comprising 1 to 52 % of the heavy mineral fraction. Besides ilmenite, magnetite and titanomagnetite are the dominant opaque minerals in the region. The other heavy minerals identified in the regions north of Ratnagiri, including Varvada Bay, Ambawah Bay, and Jaigad Bay, consist of zircon, monazite, tourmaline, pyroxene, hornblende, rutile, epidote, topaz, etc.[4].

A higher concentration of heavy minerals was reported from the dunes, berms, and foreshore areas of Ratnagiri and nearby beaches[5]. The Atomic Minerals Directorate explored 20 km in Ratnagiri district and identified eight heavy mineral concentration sites. The sites north of Ratnagiri are predominantly mono-mineralic, mainly of ilmenite (mode 74 microns), whereas in the south of Ratnagiri, ilmenite is admixed with magnetite and the reserves are estimated to be ~ 4.88 million tonnes, including 3.04 million tonnes of ilmenite[6]. The heavy mineral placers found along the Ratnagiri beaches and offshore areas are notably rich in ilmenite, which is almost free from monazite, zircon, sillimanite and rutile. Moreover, the ilmenite within these placers boasts a $TiO_2$ content very close to the theoretical values of the mineral. Despite being very fine in size (3.5 phi), they exhibit comparable trace element abundances to the ilmenites found at Kollam beach. This fine grain size may not be a significant drawback for their use in pigment manufacturing[7].

In India, imports of vanadium ores surged significantly to 2,658 tonnes in 2018 – 2019, up from 491 tonnes the previous year. Despite this increase, India lacks proven or probable reserves of vanadium ores. The reported ores mainly fall within the inferred resource category[8]. Onshore and offshore studies suggest the presence of vanadium within heavy minerals, particularly in opaque minerals. EPMA studies on titanomagnetite grains isolated from offshore sediments in the Gulf of Khambhat reveal $V_2O_3$ content ranging from 0.36 to 1.7 %. This suggests that vanadiferous titanomagnetites in the Gulf of Khambhat might originate from Deccan basalt, potentially transported by the Narmada and Tapti rivers[9]. Furthermore, chemical analysis of coastal sediment in the Gaonkhadi-Wada Vetye area of Ratnagiri district revealed significantly high vanadium concentrations of 3055 and 3358 ppm in the stabilised dunes of Gaonkhadi[5].

Dust accumulation poses a disposal challenge during titanium slag production from ilmenite, leading to environmental harm and loss of valuable components. Deep eutectic solvents, like choline chloride and carboxylic acids, offer promising solution for vanadium extraction from this dust. Compared to aqueous acid solutions, the oxaline system achieves the highest vanadium yield at 89 %. Ultrasound expedites the leaching process. The resulting vanadium-rich material can enhance vanadium pentoxide production, providing a sustainable solution to resource utilisation and waste management[10].

The present study focuses on the potential of ilmenite samples in the area as a source of vanadium and copper, in addition to their titanium content. It also examines the elevated levels of vanadium and copper found in the titanomagnetite samples.

## Materials and Methods

As part of the field season programme 2020 – 21, of the Geological Survey of India, Cruise SD-307 was undertaken Onboard R.V. Samudra Shaudhikama for the preliminary mineral exploration targeting vanadium-bearing magnetite and heavy minerals off the coast of Ratnagiri, Maharashtra (Fig. 1). The bathymetric survey indicates that the water depth in the area ranges from 5 to 25 m. Typically, the isobath runs parallel to the coastline. However, closer to cliffs and promontories, the isobath is closely spaced, suggesting steep terrain on the seabed.

Sediment cores collected beyond the 10-meter isobath consisted entirely of clay or silty clay fractions. Heavy mineral occurrences study was confined to eight bays fall in the survey area, namely Purnagad, Pawas in the south, Ratnagiri, Mirya, Kalbadevi in the central and Ganpathipule, Varvada in the northern part. Surface sediment distribution shows very fine sand predominating across various water depths. Medium sand prevails in shallower waters. Eight grab samples were collected from the bays, and the individual heavy minerals were separated from the sediments at Indian Rare Earths Limited (IREL), Kollam, India. The individually separated ilmenite and magnetite were further studied by X-ray fluorescence (XRF) analysis, Electron Probe Microanalysis (EPMA), and Scanning Electron Microscope (SEM) studies.

XRF analysis of 8 nos of magnetite and 8 nos of ilmenite grains was carried out at Chemical Division, SU: TN&P, GSI, Chennai. The XRF analysis of the separated heavy minerals proceeded as follows: Approximately 5 g of powdered sample (-200 mesh) was mixed with a few drops of Perspex binder. This mixture was then placed in an aluminium cup with the necessary amount of boric acid packing and compressed at a pressure of 20 tons using a hydraulic press machine. The resulting pressed pellet was then inserted into an XRF machine (Bruker S8 Tiger) and analysed for major and trace elements according to the manufacturer's recommendations, utilising appropriate standards.

EPMA facilitates the quick identification of mineral grains by analysing their chemical composition. EPMA was carried out on heavy

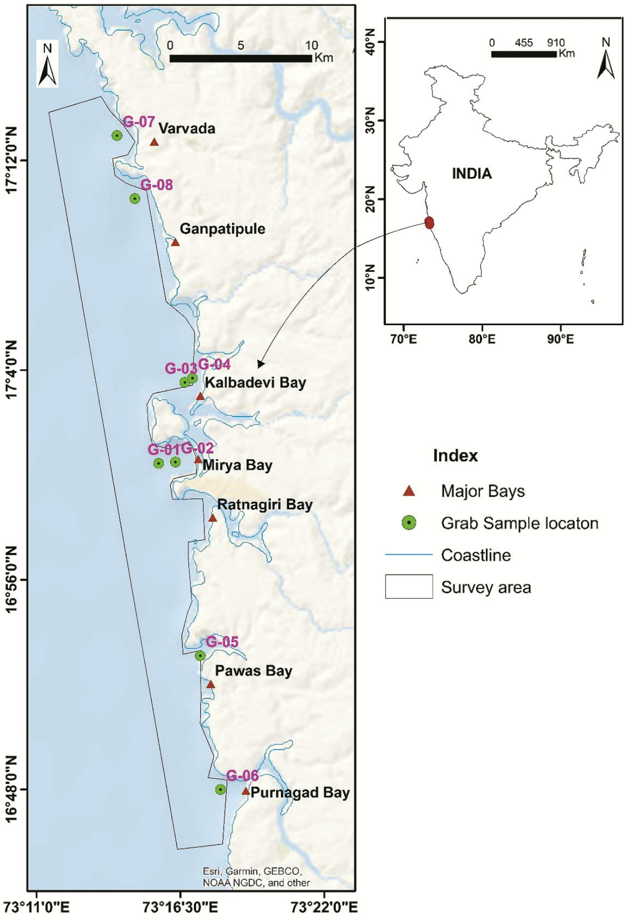


Fig. 1 — Location map of the study area

minerals at petrology lab, southern region, Hyderabad, using CAMECA SX 100. Accelerating voltage 15 keV and 15 nA beam current was used during the analysis with a beam size of 1 µm. The heavy minerals were identified under the binocular microscope, and then the sections were hand-picked and polished to determine the major oxides. EPMA studies were carried out in the separated grains of magnetite and ilmenite. The SEM studies were carried out at SEM lab, GSI, MCSD, Mangalore. The heavy minerals were identified under the binocular microscope, and then 5 – 10 grains of magnetite and ilmenite were hand-picked from the sediment samples collected from each bay off the Ratnagiri coast. The hand-picked grains were glued onto the stubs, coated with gold, and examined under VEGA3 (TSCAN make) scanning electron microscope. The magnetite and ilmenite were selected mainly for Energy-Dispersive X-ray spectroscopy (EDX). The SEM-EDX was used to determine the semi-quantitative variation of vanadium content in the sediment samples of bays from north to south.

## Results

The XRF analysis of major oxides and trace elements in ilmenite samples revealed varying concentrations: $Fe_2O_3$ ranged from 35.82 to 42.97 %, $TiO_2$ from 21.64 to 45.66 %, and vanadium from 1429 to 1816 ppm, averaging 1592 ppm (Fig. 2). In the magnetite samples, $Fe_2O_3$ ranged from 45.69 to 53.78 %, $TiO_2$ from 17.91 to 24.42 %, and vanadium from 3392 to 4442 ppm (Fig. 3). Notably, both ilmenite and magnetite samples exhibited higher concentrations of copper. Cu values for ilmenite samples ranged from 345 to 1166 ppm, averaging 628 ppm, while magnetite samples showed Cu values from 743 to 1030 ppm, averaging 943 ppm (Table 1).

Based on the Ti/(Ti+Fe) ratios, different stages of alteration are proposed to delineate the weathering mechanisms in ilmenite[11]. Values for different stages of alteration are as follows: ferrian ilmenite (< 0.5), hydrated ilmenite (0.5 – 0.6), pseudorutile (0.6 – 0.7) and leucoxene (> 0.7). This classification has been adopted and used for the chemical characterisation of ilmenite based on the major element chemistry. From the present study, it is observed that Ti/(Ti+Fe) values ranged from 0.34197 to 0.4768 with an average of 0.3637. The ilmenite in the investigation area fall under ferrian ilmenite, indicating less altered ilmenite.

EPMA analysis of ilmenite shows $TiO_2$ content range from 14.12 to 69.5 wt% with an average of 52.24 %. FeO ranges from 22.63 to 68.77 %, with an average of 41.01 %. MgO ranges from 0.81 to 3.81 %. MnO ranges up to 0.91 % (Table 2). Vanadium ranges from 0.06 to 0.73 % with an average of 0.20 % (Table 2). Ti/(Ti+Fe) ratios vary from 0.14 to 0.70 with an average of 0.49. Most of the values are less than 0.5, which indicates that it falls under ferrian ilmenite, a less altered ilmenite. Some of the grains fall in hydrated ilmenite and pseudorutile. EPMA studies show that FeO content in magnetite ranges from 47.058 to 86.845 %, with an average of 68.76 %. $TiO_2$ values range from 1.914 to 47.573 %, with an average of 20.654 %. $V_2O_3$ values range from 0.44 to 1.509 %, with an average of 0. 79 %. Vanadium values range from 0.3 to 1.026 %, with an average of 0.54 % (Table 3).

The EPMA study unveiled exsolution lamellae of ilmenite within titanomagnetite and vice versa (Fig. 4). The EDX spectrum, along with SEM images of minerals from each bay, shows the anomalous

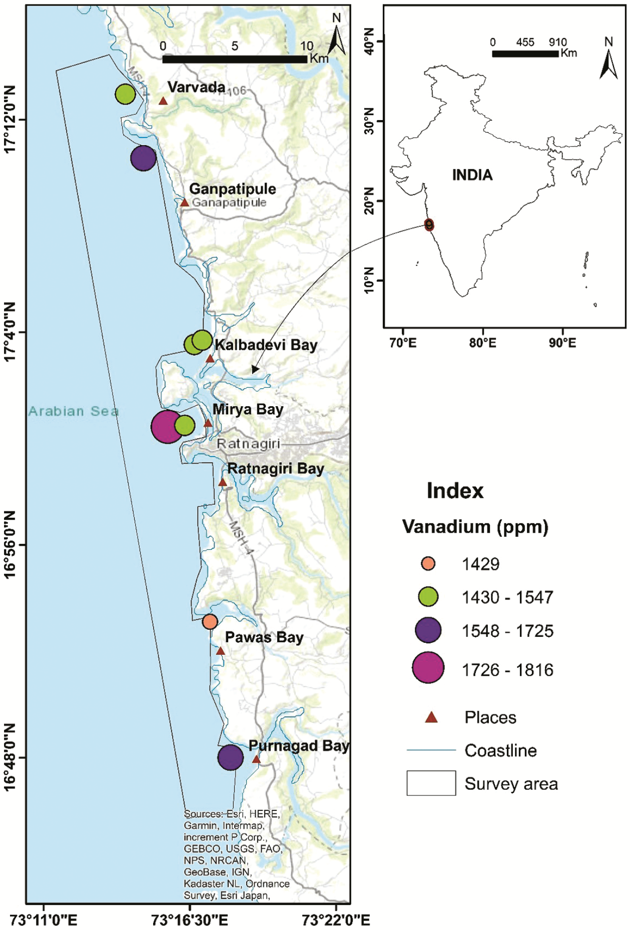


Fig. 2 — Concentration of vanadium in the ilmenite samples (Grab samples) off Ratnagiri, Maharashtra

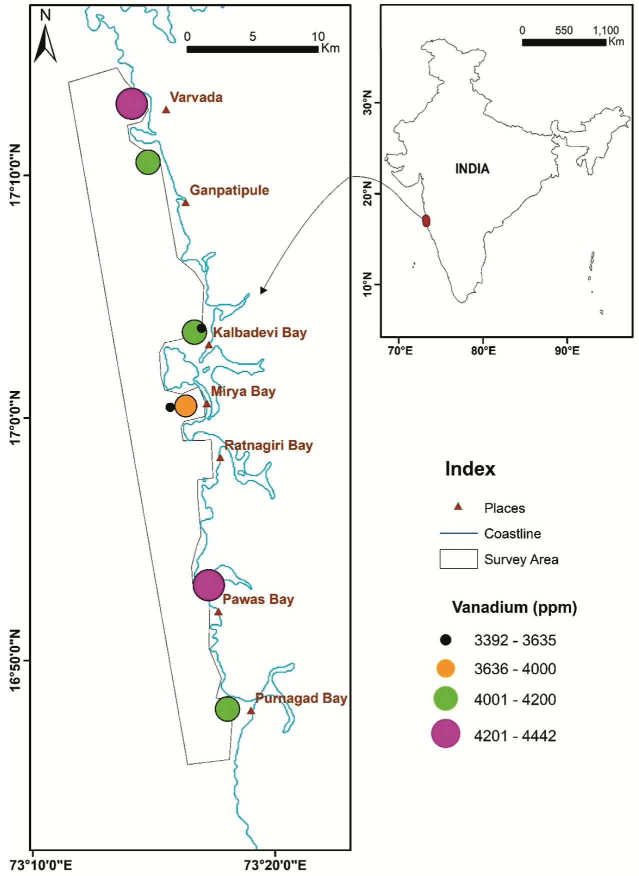


Fig. 3 — Concentration of vanadium in the magnetite samples (Grab samples) off Ratnagiri, Maharashtra

concentration of vanadium. The vanadium content in the ilmenite and magnetite from SEM-EDX varies from 0.31 to 1.39 %, with an average of 0.35 % in the study area (Fig. 5).

## Discussion

The Deccan basalts comprise titanomagnetite-rich magnetic minerals. Titanomagnetite is an intermediate member of the isomorphous series of solid solutions of magnetite ($FeFe_2O_4$, ferrimagnetic), ulvospinel ($Fe_2TiO_4$, paramagnetic), and magnesian ulvospinel ($Mg_2TiO_4$). Titanomagnetites occur as octahedral crystals and can contain substitutes like $Al^{3+}$, $V^{4+}$, $Gr^{3+}$ and $Mn_2^{+}$ and commonly occur as granular aggregates when observed under an ore microscope[12].

Correlation coefficients derived from the analytical data of major and trace elements (Table 4) in magnetically separated heavy minerals reveal a strong positive correlation between vanadium and $Fe_2O_3$ ($r$ = 0.90). Vanadium and Mn ($r$ = 0.91) indicate its source from titanomagnetite of Deccan basalt, the major lithounit in the hinterland. Titanomagnetite is a significant phase in the high titania basalts (average $TiO_2$ 2.55 %), and a portion of copper is bound with that phase[13]. A strong positive correlation between Cu and V ($r$ = 0.90), further indicates their provenance as titanomagnetite from Deccan basalt.

A ternary composition diagram showing a solid solution series of iron and titanium oxide minerals[14]

Table 1 — Analytical results of major and trace elements in magnetite and ilmenite samples off Ratnagiri, Maharashtra

| Sample No | $SiO_2$ | $Al_2O_3$ | Total Fe as $Fe_2O_3$ | Total Mn as MnO | MgO | CaO | $Na_2O$ | $K_2O$ | $TiO_2$ | $P_2O_5$ | LOI | Ba | Co | Cr | Cu | Ga | Nb | Ni | Pb | Rb | Sc | Sr | Th | V | Y | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | In % | | | | | | | | | | | In ppm | | | | | | | | | | | | | | |
| G1-/Mag | 14.87 | 7.47 | 48.55 | 0.427 | 2.79 | 1.61 | 0.17 | 0.16 | 20.06 | 0.11 | 3.09 | 132 | 328 | 726 | 968 | 42 | 37 | 158 | 21 | 8 | 37 | 33 | 41 | 3635 | 11 | 295 |
| G2-/Mag | 15.55 | 8.01 | 49.12 | 0.453 | 3.16 | 1.59 | 0.20 | 0.16 | 17.91 | 0.13 | 2.45 | 148 | 365 | 684 | 909 | 46 | 34 | 168 | 5 | 6 | 35 | 36 | <1 | 3908 | 11 | 328 |
| G3-/Mag | 12.99 | 6.35 | 51.52 | 0.464 | 2.93 | 1.13 | 0.16 | 0.14 | 20.73 | 0.11 | 2.23 | 155 | 358 | 820 | 948 | 47 | 38 | 157 | 8 | 6 | 33 | 21 | 3 | 4161 | 10 | 320 |
| G4-/Mag | 18.09 | 9.36 | 45.69 | 0.413 | 3.57 | 1.49 | 0.17 | 0.20 | 18.62 | 0.14 | 2.81 | 125 | 311 | 718 | 743 | 41 | 40 | 150 | 5 | 8 | 38 | 42 | <1 | 3392 | 11 | 282 |
| G5-/Mag | 11.42 | 5.57 | 53.78 | 0.487 | 2.40 | 1.19 | 0.15 | 0.11 | 20.15 | 0.10 | 1.73 | 171 | 428 | 751 | 1025 | 47 | 35 | 163 | 4 | 6 | 30 | 19 | <1 | 4442 | 9 | 341 |
| G6-/Mag | 13.29 | 7.33 | 50.99 | 0.473 | 2.31 | 1.31 | 0.18 | 0.12 | 19.69 | 0.11 | 3.48 | 153 | 379 | 689 | 1030 | 48 | 36 | 160 | 4 | 5 | 38 | 14 | <1 | 4143 | 11 | 324 |
| G7-/Mag | 9.53 | 4.37 | 52.67 | 0.462 | 3.00 | 0.88 | 0.12 | 0.10 | 24.42 | 0.10 | 1.21 | 149 | 332 | 987 | 935 | 43 | 45 | 147 | 6 | 5 | 34 | 14 | <1 | 4359 | 9 | 311 |
| G8-/Mag | 11.00 | 5.14 | 51.87 | 0.460 | 2.74 | 1.05 | 0.14 | 0.12 | 23.01 | 0.10 | 4.87 | 147 | 332 | 874 | 983 | 43 | 43 | 151 | 6 | 6 | 30 | 21 | <1 | 4171 | 9 | 310 |
| G1/Ilm | 10.70 | 3.73 | 42.97 | 0.329 | 3.13 | 1.63 | 0.14 | 0.09 | 34.84 | 0.08 | Nil | 10 | 154 | 533 | 1015 | 20 | 68 | 84 | 11 | 3 | 52 | 5 | 19 | 1816 | 11 | 110 |
| G2-/Ilm | 11.00 | 2.70 | 40.87 | 0.329 | 3.57 | 2.26 | 0.07 | 0.06 | 35.47 | 0.07 | 1.03 | <6 | 136 | 605 | 1166 | 16 | 70 | 80 | 25 | 5 | 61 | <5 | 51 | 1516 | 12 | 105 |
| G3/Ilm | 14.22 | 7.11 | 37.27 | 0.335 | 3.84 | 1.26 | 0.23 | 0.19 | 35.60 | 0.12 | 0.24 | <6 | 141 | 412 | 345 | 17 | 76 | 67 | 14 | 6 | 61 | 18 | 5 | 1511 | 11 | 88 |
| G4/Ilm | 11.93 | 5.64 | 38.05 | 0.343 | 3.38 | 1.27 | 0.16 | 0.14 | 38.91 | 0.10 | 0.59 | <6 | 116 | 504 | 441 | 15 | 78 | 64 | 18 | 5 | 63 | 19 | 2 | 1507 | 11 | 84 |
| G5/Ilm | 20.69 | 9.23 | 35.82 | 0.321 | 4.56 | 2.38 | 0.37 | 0.27 | 25.54 | 0.14 | 0.84 | 7 | 177 | 293 | 481 | 19 | 65 | 84 | 14 | 8 | 51 | 30 | 2 | 1429 | 13 | 103 |
| G6/Ilm | 22.72 | 9.74 | 36.28 | 0.313 | 4.01 | 2.92 | 0.36 | 0.24 | 21.64 | 0.12 | 1.87 | 46 | 189 | 317 | 493 | 24 | 55 | 100 | 7 | 8 | 49 | 27 | 2 | 1683 | 14 | 122 |
| G7/Ilm | 5.32 | 2.33 | 40.49 | 0.361 | 2.34 | 0.54 | 0.05 | 0.06 | 45.66 | 0.08 | Nil | <6 | 81 | 675 | 432 | 13 | 83 | 58 | 15 | 3 | 72 | 6 | <1 | 1547 | 11 | 78 |
| G8/Ilm | 6.94 | 2.77 | 40.90 | 0.361 | 2.56 | 0.79 | 0.06 | 0.07 | 42.59 | 0.08 | Nil | <6 | 97 | 724 | 649 | 16 | 79 | 65 | 18 | 4 | 71 | 9 | 8 | 1725 | 11 | 94 |

Table 2 — EPMA analytical results of oxides and vanadium in ilmenite grains off Ratnagiri, Maharashtra

| Sl No | Sample No | $Al_2O_3$ | $TiO_2$ | FeO | MgO | $V_2O_3$ | $Cr_2O_3$ | MnO | ZnO | Ti | V | Fe | Ti/Ti+Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | In % | | | | | | |
| 1 | G-01/I1 | 0.12 | 51.16 | 47.30 | 1.40 | 0.17 | 0.00 | 0.58 | 0.00 | 30.67 | 0.11 | 36.77 | 0.45 |
| 2 | G-01/I1 | 0.08 | 50.73 | 46.00 | 1.97 | 0.14 | 0.02 | 0.51 | 0.00 | 30.41 | 0.10 | 35.76 | 0.46 |
| 3 | G-01/I1 | 0.11 | 50.71 | 45.88 | 2.70 | 0.16 | 0.00 | 0.34 | 0.15 | 30.40 | 0.11 | 35.66 | 0.46 |
| 4 | G-01/I1 | 1.11 | 69.50 | 23.48 | 1.78 | 0.28 | 0.40 | 0.18 | 0.00 | 41.66 | 0.19 | 18.25 | 0.70 |
| 5 | G-02/I1 | 1.11 | 64.54 | 26.95 | 1.65 | 0.19 | 0.27 | 0.23 | 0.00 | 38.69 | 0.13 | 20.95 | 0.65 |
| 6 | G-02/I1 | 0.02 | 51.34 | 44.91 | 1.21 | 0.21 | 0.07 | 0.40 | 0.00 | 30.78 | 0.14 | 34.91 | 0.47 |
| 7 | G-02/I1 | 0.64 | 14.12 | 68.75 | 1.10 | 0.13 | 0.07 | 0.11 | 0.00 | 8.46 | 0.09 | 53.44 | 0.14 |
| 8 | G-02/I1 | 0.09 | 51.04 | 45.11 | 1.48 | 0.32 | 0.07 | 0.56 | 0.14 | 30.60 | 0.22 | 35.06 | 0.47 |
| 9 | G-03/I1 | 1.03 | 35.35 | 53.90 | 1.54 | 0.95 | 0.00 | 0.10 | 0.03 | 21.19 | 0.64 | 41.90 | 0.34 |
| 10 | G-03/I1 | 1.14 | 34.23 | 53.20 | 2.00 | 1.07 | 0.13 | 0.00 | 0.00 | 20.52 | 0.73 | 41.35 | 0.33 |
| 11 | G-03/I1 | 0.17 | 50.90 | 44.31 | 1.26 | 0.17 | 0.02 | 0.51 | 0.00 | 30.52 | 0.11 | 34.44 | 0.47 |
| 12 | G-03/I1 | 1.17 | 21.36 | 68.77 | 0.99 | 0.72 | 0.06 | 0.48 | 0.17 | 12.81 | 0.49 | 53.46 | 0.19 |
| 13 | G-03/I1 | 1.15 | 48.42 | 41.45 | 3.61 | 0.48 | 0.04 | 0.15 | 0.05 | 29.03 | 0.32 | 32.22 | 0.47 |
| 14 | G-03/I1 | 1.29 | 42.34 | 46.10 | 3.16 | 0.55 | 0.00 | 0.14 | 0.16 | 25.38 | 0.37 | 35.84 | 0.41 |
| 15 | G-03/I1 | 1.14 | 26.86 | 55.87 | 3.41 | 0.70 | 0.16 | 0.41 | 0.00 | 16.10 | 0.47 | 43.43 | 0.27 |
| 16 | G-04/I1 | 0.07 | 51.30 | 45.92 | 1.46 | 0.23 | 0.00 | 0.44 | 0.00 | 30.75 | 0.15 | 35.70 | 0.46 |
| 17 | G-04/I1 | 0.44 | 49.08 | 45.23 | 3.80 | 0.41 | 0.14 | 0.41 | 0.00 | 29.43 | 0.28 | 35.16 | 0.46 |
| 18 | G-04/I1 | 0.84 | 59.17 | 31.78 | 2.26 | 0.13 | 0.09 | 0.52 | 0.02 | 35.47 | 0.09 | 24.71 | 0.59 |
| 19 | G-05/I1 | 1.06 | 62.12 | 31.65 | 2.39 | 0.24 | 0.05 | 0.27 | 0.12 | 37.24 | 0.16 | 24.60 | 0.60 |
| 20 | G-05/I1 | 0.94 | 63.26 | 30.14 | 0.81 | 0.12 | 0.06 | 0.52 | 0.00 | 37.92 | 0.08 | 23.43 | 0.62 |
| 21 | G-05/I1 | 0.24 | 56.41 | 39.61 | 1.86 | 0.18 | 0.00 | 0.55 | 0.00 | 33.82 | 0.12 | 30.79 | 0.52 |
| 22 | G-05/I1 | 0.08 | 51.41 | 47.76 | 0.97 | 0.15 | 0.04 | 0.41 | 0.03 | 30.82 | 0.11 | 37.12 | 0.45 |
| 23 | G-05/I1 | 0.09 | 52.83 | 44.97 | 1.21 | 0.33 | 0.02 | 0.31 | 0.00 | 31.67 | 0.23 | 34.95 | 0.48 |
| 24 | G-05/I1 | 0.35 | 57.37 | 36.12 | 2.95 | 0.20 | 0.10 | 0.50 | 0.10 | 34.39 | 0.13 | 28.08 | 0.55 |
| 25 | G-05/I1 | 1.29 | 65.55 | 27.01 | 1.36 | 0.30 | 0.39 | 0.36 | 0.00 | 39.30 | 0.20 | 20.99 | 0.65 |
| 26 | G-05/I1 | 1.73 | 68.08 | 23.24 | 1.53 | 0.29 | 0.69 | 0.12 | 0.00 | 40.81 | 0.20 | 18.07 | 0.69 |
| 27 | G-05/I1 | 1.73 | 68.08 | 23.24 | 1.53 | 0.29 | 0.69 | 0.12 | 0.00 | 32.57 | 0.07 | 32.07 | 0.50 |
| 28 | G-05/I1 | 1.73 | 68.08 | 23.24 | 1.53 | 0.29 | 0.69 | 0.12 | 0.00 | 34.82 | 0.10 | 27.56 | 0.56 |
| 29 | G-06/I1 | 0.92 | 59.62 | 32.09 | 1.08 | 0.49 | 0.05 | 0.34 | 0.00 | 35.74 | 0.33 | 24.95 | 0.59 |
| 30 | G-06/I1 | 0.79 | 59.88 | 33.30 | 2.35 | 0.33 | 0.26 | 0.31 | 0.10 | 35.90 | 0.22 | 25.88 | 0.58 |
| 31 | G-06/I1 | 0.24 | 58.12 | 36.73 | 1.55 | 0.10 | 0.08 | 0.91 | 0.00 | 34.85 | 0.07 | 28.55 | 0.55 |
| 32 | G-06/I1 | 0.07 | 52.15 | 46.12 | 0.98 | 0.08 | 0.00 | 0.59 | 0.05 | 31.27 | 0.06 | 35.85 | 0.47 |
| 33 | G-06/I1 | 0.42 | 55.33 | 38.11 | 2.52 | 0.44 | 0.24 | 0.51 | 0.00 | 33.17 | 0.30 | 29.62 | 0.53 |
| 34 | G-07/I1 | 0.07 | 52.54 | 43.95 | 2.00 | 0.21 | 0.00 | 0.64 | 0.06 | 31.50 | 0.14 | 34.16 | 0.48 |
| 35 | G-07/I1 | 0.15 | 50.92 | 45.64 | 2.03 | 0.22 | 0.05 | 0.44 | 0.00 | 30.53 | 0.15 | 35.47 | 0.46 |
| 36 | G-07/I1 | 0.12 | 50.46 | 44.98 | 2.82 | 0.18 | 0.02 | 0.62 | 0.00 | 30.25 | 0.12 | 34.96 | 0.46 |
| 37 | G-07/I1 | 0.11 | 52.24 | 44.37 | 1.81 | 0.16 | 0.00 | 0.65 | 0.00 | 31.32 | 0.11 | 34.49 | 0.48 |
| 38 | G-07/I1 | 0.09 | 54.83 | 41.78 | 0.82 | 0.17 | 0.00 | 0.54 | 0.00 | 32.87 | 0.11 | 32.47 | 0.50 |
| 39 | G-07/I1 | 0.04 | 51.60 | 45.38 | 1.11 | 0.13 | 0.04 | 0.42 | 0.15 | 30.93 | 0.09 | 35.28 | 0.47 |
| 40 | G-07/I1 | 0.81 | 27.53 | 64.17 | 1.10 | 0.56 | 0.01 | 0.30 | 0.07 | 16.51 | 0.38 | 49.88 | 0.25 |
| 41 | G-08/I1 | 1.07 | 66.65 | 26.85 | 0.96 | 0.36 | 0.03 | 0.38 | 0.00 | 39.95 | 0.25 | 20.87 | 0.66 |
| 42 | G-08/I1 | 1.09 | 61.41 | 30.67 | 1.63 | 0.20 | 0.13 | 0.15 | 0.00 | 36.81 | 0.14 | 23.84 | 0.61 |
| 43 | G-08/I1 | 1.48 | 62.09 | 28.28 | 1.43 | 0.19 | 0.15 | 0.47 | 0.04 | 37.22 | 0.13 | 21.98 | 0.63 |
| 44 | G-08/I1 | 0.35 | 54.91 | 40.07 | 1.23 | 0.16 | 0.05 | 0.33 | 0.06 | 32.92 | 0.11 | 31.14 | 0.51 |
| 45 | G-08/I1 | 1.18 | 68.41 | 22.63 | 0.87 | 0.31 | 1.07 | 0.08 | 0.05 | 41.01 | 0.21 | 17.59 | 0.70 |
| 46 | G-08/I1 | 0.50 | 60.20 | 34.33 | 1.45 | 0.16 | 0.09 | 0.40 | 0.00 | 36.09 | 0.11 | 26.68 | 0.57 |
| 47 | G-08/I1 | 2.90 | 20.82 | 66.18 | 1.44 | 0.25 | 0.13 | 0.18 | 0.32 | 12.48 | 0.17 | 51.44 | 0.20 |

Table 3 — EPMA analytical results of oxides and vanadium in magnetite grains off Ratnagiri, Maharashtra

| Sl No | Sample No | $Al_2O_3$ | MgO | $TiO_2$ | $V_2O_3$ | $Cr_2O_3$ | MnO | ZnO | FeO | Ti | V | Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | G-05-M1 | 0.32 | 0.596 | 47.573 | 0.801 | 0.096 | 0.009 | 0.064 | 47.058 | 28.52 | 0.545 | 36.578 |
| 2 | G-05-M1 | 2.117 | 0.024 | 28.066 | 0.97 | 0.051 | 1.564 | 0.213 | 59.369 | 16.826 | 0.66 | 46.148 |
| 3 | G-05-M1 | 2.095 | 0.449 | 26.212 | 0.797 | 0.078 | 1.451 | 0.029 | 61.998 | 15.714 | 0.541 | 48.192 |
| 4 | G-06_M1 | 1.278 | 0.938 | 24.493 | 0.577 | 0.053 | 0.212 | 0.086 | 68.487 | 14.684 | 0.392 | 53.235 |
| 5 | G-06_M1 | 1.773 | 0.498 | 27.75 | 0.653 | 0.152 | 1.422 | 0.076 | 60.223 | 16.636 | 0.444 | 46.812 |
| 6 | G-06_M1 | 1.475 | 0.387 | 15.81 | 0.808 | 0.113 | 0.125 | 0.042 | 72.822 | 9.478 | 0.549 | 56.605 |
| 7 | G-06_M1 | 1.493 | 0.538 | 6.95 | 0.686 | 0.022 | 0.01 | 0.035 | 77.392 | 4.167 | 0.466 | 60.157 |
| 8 | G-06_M1 | 2.935 | 1.258 | 2.918 | 0.946 | 0.062 | 0.204 | 0.204 | 82.127 | 1.749 | 0.643 | 63.838 |
| 9 | G-08-M1 | 2.314 | 1.504 | 13.977 | 0.881 | 0.286 | 0.375 | 0 | 73.82 | 8.379 | 0.599 | 57.38 |
| 10 | G-08-M1 | 4.062 | 1.24 | 13.221 | 1.017 | 0.222 | 0.012 | 0.013 | 73.033 | 7.926 | 0.691 | 56.769 |
| 11 | G-08-M1 | 0.775 | 0.515 | 22.418 | 0.674 | 0.02 | 0.093 | 0 | 69.177 | 13.44 | 0.458 | 53.771 |
| 12 | G-08-M1 | 1.525 | 0.074 | 26.212 | 0.914 | 0.035 | 1.067 | 0.297 | 63.125 | 15.714 | 0.621 | 49.067 |
| 13 | G-07-M1 | 1.385 | 0.185 | 24.147 | 0.824 | 0 | 2.474 | 0.662 | 61.749 | 14.476 | 0.56 | 47.998 |
| 14 | G-07-M1 | 1.403 | 0.889 | 20.784 | 1.075 | 0.023 | 0.348 | 0.06 | 67.382 | 12.46 | 0.73 | 52.376 |
| 15 | G-07-M1 | 4.032 | 0.662 | 13.297 | 0.999 | 0.197 | 0.382 | 0 | 74.748 | 7.971 | 0.679 | 58.102 |
| 16 | G-07-M1 | 1.995 | 0.964 | 27.008 | 0.854 | 0.025 | 0.355 | 0.191 | 64.134 | 16.192 | 0.58 | 49.852 |
| 17 | G-07-M1 | 1.219 | 0.724 | 18.256 | 0.9 | 0.163 | 0.274 | 0.09 | 73.647 | 10.945 | 0.612 | 57.246 |
| 18 | G-01-M1 | 0.74 | 1.332 | 33.959 | 0.513 | 0.023 | 0.759 | 0 | 56.158 | 20.359 | 0.348 | 43.652 |
| 19 | G-01-M1 | 1.31 | 1.815 | 28.419 | 0.761 | 0.267 | 0.278 | 0.179 | 63.479 | 17.037 | 0.518 | 49.342 |
| 20 | G-01-M1 | 1.512 | 0.06 | 12.239 | 0.811 | 0.107 | 0.362 | 0.153 | 77.459 | 7.337 | 0.551 | 60.21 |
| 21 | G-01-M1 | 2.656 | 1.742 | 19.482 | 0.882 | 0.045 | 0.514 | 0.181 | 70.507 | 11.679 | 0.6 | 54.806 |
| 22 | G-02_M1 | 1.424 | 1.233 | 23.369 | 0.552 | 0.015 | 0.309 | 0 | 67.395 | 14.01 | 0.375 | 52.387 |
| 23 | G-02_M1 | 2.833 | 1.657 | 1.914 | 1.509 | 0.151 | 0.249 | 0.114 | 86.845 | 1.147 | 1.026 | 67.505 |
| 24 | G-02_M1 | 2.009 | 1.489 | 16.359 | 0.883 | 0.146 | 0.299 | 0 | 73.105 | 9.807 | 0.6 | 56.825 |
| 25 | G-02_M1 | 0.759 | 1.819 | 39.52 | 0.442 | 0 | 0.312 | 0.14 | 51.329 | 23.692 | 0.3 | 39.898 |
| 26 | G-02_M1 | 1.651 | 0.943 | 22.686 | 0.906 | 0.053 | 0.312 | 0.186 | 68.143 | 13.601 | 0.616 | 52.968 |
| 27 | G-02_M1 | 1.105 | 0.322 | 15.251 | 0.672 | 0.065 | 0.509 | 0.052 | 75.751 | 9.143 | 0.457 | 58.882 |
| 28 | G-04-M1 | 2.057 | 0.931 | 15.737 | 0.69 | 0.045 | 0.293 | 0.196 | 75.213 | 9.434 | 0.469 | 58.463 |
| 29 | G-04-M1 | 1.786 | 1.77 | 26.623 | 0.917 | 0.014 | 0.441 | 0 | 64.26 | 15.96 | 0.623 | 49.949 |
| 30 | G-04-M1 | 1.511 | 1.105 | 28.178 | 0.607 | 0.203 | 0.2 | 0.103 | 63.23 | 16.893 | 0.412 | 49.149 |
| 31 | G-04-M1 | 1.568 | 1.227 | 16.42 | 0.573 | 0.04 | 0.612 | 0 | 71.44 | 9.844 | 0.389 | 55.531 |
| 32 | G-03-M1 | 1.88 | 0.748 | 19.797 | 0.636 | 0.128 | 0.234 | 0.043 | 71.64 | 11.868 | 0.432 | 55.686 |
| 33 | G-03-M1 | 2.088 | 0.704 | 13.787 | 0.628 | 0.288 | 0.266 | 0.044 | 71.84 | 8.265 | 0.427 | 55.841 |
| 34 | G-03-M1 | 1.582 | 0.646 | 23.991 | 0.745 | 0.016 | 1.358 | 0.204 | 66.216 | 14.383 | 0.506 | 51.47 |
| 35 | G-03-M1 | 1.72 | 1.251 | 17.462 | 0.776 | 0.187 | 0.34 | 0.205 | 72.981 | 10.469 | 0.528 | 56.729 |
| 36 | G-03-M1 | 4.098 | 0.8 | 9.272 | 0.681 | 0.073 | 0.148 | 0.136 | 78.215 | 5.559 | 0.463 | 60.797 |

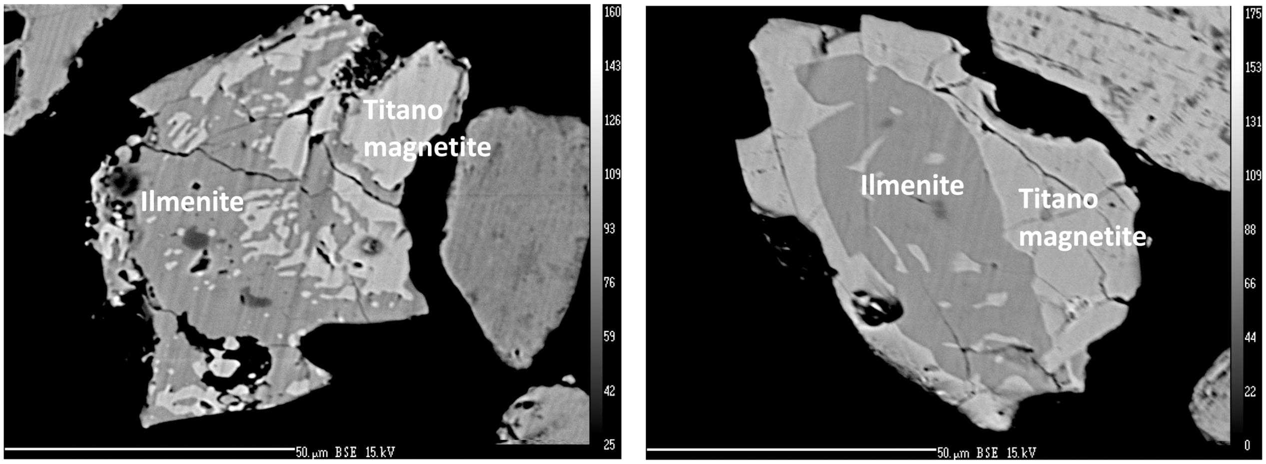
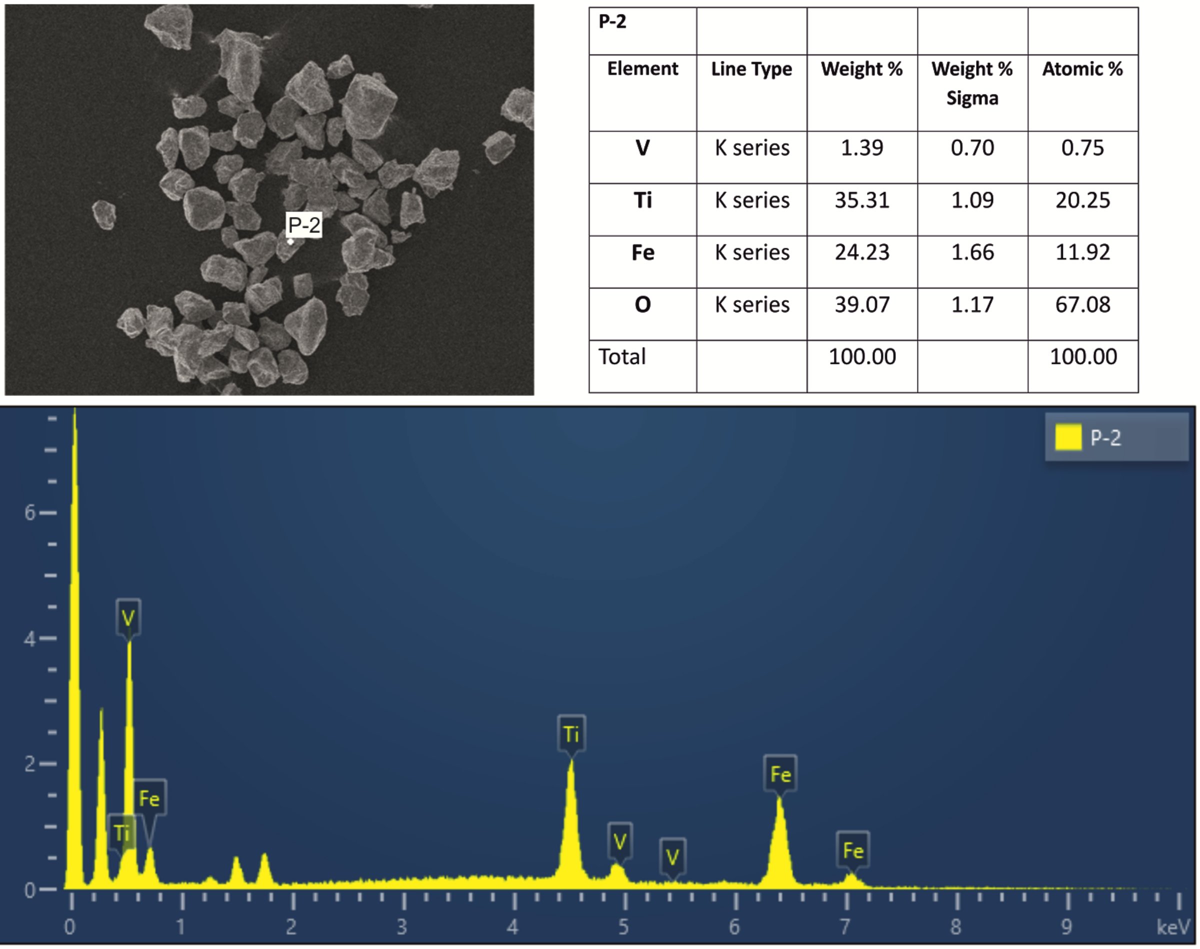


Fig. 4 — Back scatter images of titanomagnetite and ilmenite grains, showing exsolution lamellae EPMA studies



| P-2 | | | | |
|---|---|---|---|---|
| **Element** | **Line Type** | **Weight %** | **Weight % Sigma** | **Atomic %** |
| **V** | K series | 1.39 | 0.70 | 0.75 |
| **Ti** | K series | 35.31 | 1.09 | 20.25 |
| **Fe** | K series | 24.23 | 1.66 | 11.92 |
| **O** | K series | 39.07 | 1.17 | 67.08 |
| Total | | 100.00 | | 100.00 |

Fig. 5 — SEM images, EDX graph and tables of magnetite grains selected from G-02

Table 4 — Correlation coefficient of major and trace elements in magnetic heavy mineral samples off Ratnagiri, Maharashtra

| | **$SiO_2$** | **$Al_2O_3$** | **$Fe_2O_3$** | **$TiO_2$** | **$Na_2O$** | **$K_2O$** | **CaO** | **MgO** | **$P_2O_5$** | **Cu** | **Zn** | **Ni** | **Co** | **Cr** | **Mn** | **Sr** | **V** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | **1.00** | | | | | | | | | | | | | | | | |
| $Al_2O_3$ | **0.71** | 1.00 | | | | | | | | | | | | | | | |
| $Fe_2O_3$ | **-0.93** | -0.50 | 1.00 | | | | | | | | | | | | | | |
| $TiO_2$ | -0.61 | **-0.88** | 0.31 | 1.00 | | | | | | | | | | | | | |
| $Na_2O$ | 0.89 | **0.80** | **-0.78** | **-0.72** | 1.00 | | | | | | | | | | | | |
| $K_2O$ | **0.90** | **0.78** | **-0.81** | -0.64 | **0.92** | 1.00 | | | | | | | | | | | |
| CaO | **0.87** | 0.59 | **-0.84** | -0.59 | **0.81** | **0.73** | 1.00 | | | | | | | | | | |
| MgO | **0.82** | 0.53 | **-0.86** | -0.41 | **0.81** | **0.77** | **0.84** | 1.00 | | | | | | | | | |
| $P_2O_5$ | **0.80** | 0.67 | **-0.74** | -0.59 | **0.78** | **0.79** | **0.76** | **0.78** | 1.00 | | | | | | | | |
| Cu | -0.68 | -0.16 | **0.85** | 0.00 | -0.58 | -0.62 | -0.62 | **-0.79** | -0.55 | 1.00 | | | | | | | |
| Zn | **-0.81** | -0.37 | **0.93** | 0.21 | **-0.71** | **-0.75** | **-0.74** | **-0.79** | -0.65 | **0.94** | 1.00 | | | | | | |
| Ni | **-0.76** | -0.25 | **0.88** | 0.15 | -0.64 | -0.64 | **-0.78** | **-0.77** | -0.58 | **0.92** | **0.95** | 1.00 | | | | | |
| Co | -0.70 | -0.34 | **0.72** | 0.39 | -0.67 | -0.66 | **-0.76** | -0.65 | -0.57 | **0.74** | **0.81** | **0.86** | 1.00 | | | | |
| Cr | -0.65 | **-0.86** | 0.44 | **0.86** | **-0.74** | -0.66 | -0.64 | -0.44 | -0.60 | 0.16 | 0.41 | 0.38 | 0.50 | 1.00 | | | |
| Mn | **-0.90** | -0.51 | **0.98** | 0.31 | **-0.79** | **-0.80** | **-0.84** | **-0.89** | **-0.74** | **0.86** | **0.92** | **0.87** | **0.73** | 0.42 | 1.00 | | |
| Sr | **0.91** | 0.60 | -0.89 | -0.56 | **0.88** | **0.83** | **0.94** | **0.85** | **0.79** | **-0.72** | **-0.82** | **-0.81** | **-0.82** | -0.58 | -0.89 | 1.00 | |
| V | **-0.86** | -0.45 | **0.93** | 0.32 | **-0.76** | **-0.79** | **-0.78** | **-0.79** | -0.70 | **0.90** | **0.98** | **0.94** | **0.85** | 0.48 | **0.91** | **-0.87** | 1.00 |

> 0.9: Strong positive, 0.7-0.9: Positive correlation, < -0.9: Strong negative correlation, -0.7-to -0.9: Negative correlation

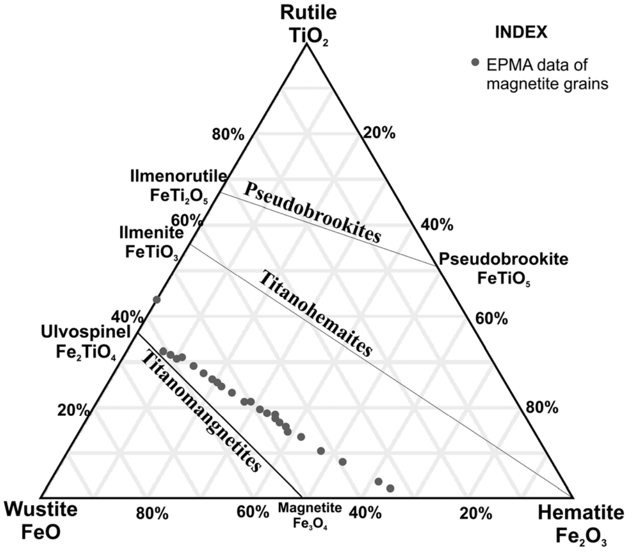


Fig. 6 — A ternary composition diagram showing a solid solution series of iron and titanium oxide minerals (After Deer *et al*. 1992). EPMA data of magnetite grains falls in titanomagnetite field

was prepared by using EPMA data of magnetite grains. The ternary diagram of $TiO_2$, FeO and $Fe_2O_3$ indicates that all the magnetite samples having higher concentrations of vanadium and copper fall in the titanomagnetite field (Fig. 6). From the ternary diagram, it is interpreted that the higher concentration of vanadium in the samples are contributed by titanomagnetite in the survey area, which is reported from the Deccan basalt present in the hinterland.

Ilmenite and magnetite sourced from Igatpuri and Mahabaleshwar are not composed solely of ilmenite or magnetite phases. The ilmenite samples contain varying amounts of hematite molecules, ranging from 3.03 to 12.59 %. Similarly, the magnetite specimens exhibit compositions with ulvospinel molecules, ranging from 36.06 % to as high as 90.53 %(ref. 15). Abrupt changes in FeO, $TiO_2$ and V in both ilmenite and titanomagnetite grains may be contributed by exsolution lamellae.

A key geochemical principle regarding vanadium suggests that magnetites collectively exhibit higher vanadium contents compared to either hematites or ilmenites. This relationship holds under most conditions wherein magnetite and/or ilmenite remain stable at elevated temperatures. Specifically, vanadium tends to be predominantly trivalent when substituting for $Fe^{3+}$ in magnetite and shifts to a tetravalent state when the oxygen fugacity approximates that defined by the magnetite-hematite equilibrium. In this latter scenario, vanadium primarily substitutes for $Ti^{4+}$ in minerals such as hemo-ilmenites, ilmenohematites, or rutile[16]. Vanadium mineralisation at the Sinarsuk deposit in West Greenland occurs in oxide-rich horizons within layered metagabbro zones, with vanadiferous magnetite and ilmenite. Electron microprobe analyses reveal that magnetite contains vanadium concentrations ranging from 1.93 to 2.68 wt% $V_2O_5$, while ilmenite has vanadium contents between 0.32 and 0.59 wt% $V_2O_5$(ref. 17).

From the present study, it is observed that the concentration of vanadium in titanomagnetite is higher compared to ilmenite. Geochemical analysis of heavy mineral grains indicates an encouraging concentration of vanadium in ilmenite and magnetite. The EPMA studies show that the vanadium concentration in the pure ilmenite grains is restricted to 0.2 %. Vanadium in titanomagneties ranges up to 1.2 %, with an average of 0.57 %.

## Conclusion

Vanadium holds a pivotal status as a critical raw material, particularly in strategic domains like defence and aerospace. These findings offer valuable insights into vanadium's presence and distribution in the studied mineral samples, providing crucial data for further research and resource assessment in the region. The ilmenite and magnetite/titanomagnetite are the major constituents of the heavy mineral suite in the area. These minerals can be separated together as magnetic heavy minerals and can be targeted for the exploitation of titanium, vanadium, and copper.

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## Conflict of Interest

The authors declare no competing or conflict of interest.

## Ethical Statement

The material is the authors original work which has not been published elsewhere. All authors have been personally and actively involved in substantial work leading to the paper and will take the public responsibility for its content.

## Author Contributions

PVS: Investigation, conceptualisation, formal analysis, interpretation and writing original manuscript; LGS: Investigation, EPMA analysis, and SEM studies; BG & AKY: Investigation and analysis; and BKJ: Investigation and SEM studies.

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