International Journal for Multidisciplinary Research (IJFMR)
E-ISSN: 2582-2160 ● Website: www.ijfmr.com ● Email: editor@ijfmr.com

Presence of Ecandrewsite and Zincian-Ilmenite in Auriferous Quartz Veins of North Singhbhum Mobile Belt, Jharkhand

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ABSTRACT
Ecandrewsite ($ZnTiO_3$), which is the zinc analog of ilemnite, has been found as an accessory phase in the metamorphosed hydrothermally altered rocks associated with gold mineralization in Lawa area, Jharkhand. We report the first description of zincian ilmenite-ecandrewsite from the auriferous mineralized zones of the area. The Palaeo to Mesoproterozoic North Singhbhum Mobile belt (NSMB), comprises low to medium grade meta-sedimentary and meta-igneous rocks along with auriferous quartz veins. The close resemblance of the NSMB to other Proterozoic gold deposits, with all the requisites for the formation of gold deposits, makes it potential auriferous deposit. The volcano sedimentary units comprise the dominant rock units at NSMB. The rock has undergone polyphase deformation and subsequent metamorphism, leading to extensive shearing of all the rock units. The gold in the northern part of the NSMB is associated with sheared grey quartz veins, trending E-W mostly showing parallel to sub parallel trends, with the South Purulia shear zone. Compositionally two distinct populations belonging to the (Zn-poor and Zn-rich) Ilmenite-Ecandrewsite solid solution series have been found from the auriferous mineralized zones in the Lawa mines. Petrographically also the distinction between both the end members of the ilmenite series have been observed, where the ilmenite is pure ilmenite along with zincian ilemnite along with ecandrewsite. Most of the grains of ecandrewsite donot show any zoning. Thermodynamically, at higher metamorphic grades the solubility of ZnTiO3 in ilmenite is primarily governed by temperature and pressure conditions, with the Zn atomic percent (apfu) rarely surpassing 4. Nevertheless, occurrences of zincian ilmenite containing 8 mol% ZnTiO3, accompanied by nearly pure ZnAl2O4 components, have been documented in areas subjected to nearly granulite grade metamorphic conditions.

INTRODUCTION

The Palaeo to Mesoproterozoic North Singhbhum Mobile belt (NSMB), comprises low to medium grade meta-sedimentary and meta-igneous rocks along with auriferous quartz veins, lying between the Archaean Singhbhum Craton (ASC>2.4 Ga) in the south, and the Meso to Neo Proterozoic (0.9–1.7 Ga) Chotanagpur Gneissic Complex (CGC) in the north. In the north the NSMB is separated from CGGC by SPSZ (also known as Tamar-Poraphar-Khatra shear zone) whereas to its south its separated from Singhbhum craton by Singhbhum shear zone.

The area comprises of three major rock types- phyllites, quartzites and mica schists. Ecandrewsite ($ZnTiO_3$), which is zinc analog of ilmenite, has been found as an accessory phase in the metamorphosed hydrothermally altered rocks associated with gold mineralization in Lawa area, Jharkhand. Ecandrewsite (ZnTiO3) from the Broken Hill, New South Wales, Australia, was first reported by Brown et al. (1970), where it coexists with almandine-spersartine garnet varieties, ferroan gahnite and rutile. The research paper provides first description of the presence of ecandrewsite and its relationship with ilmenite present along with sulphides within the auriferous quartz veins in the metasediementaries of lawa area. Two compositionally and petrographically distinct populations (Zn-poor and Zn-rich) of illmenite-ecandrewsite solid solutions are recorded. The compositions of coexisting zincian-illmenite and gahnite suggest that these two minerals did not form in equilibrium over the range of metamorphic conditions. Mineral chemistry reveals that the mineral forms a part of the discontinuous soild-solution, whose composition ranges from manganoan-ferroan ecandrewsite toward ilmenite *s.s*., passing through intermediate members such as ferroan-manganoan ecandrewsite, zincian-manganoan-illmenite, and manganoan-illmenite. Thermodynamically, even at Amphibolite and above grade of metamorphism, where T approximates 550-600^{0}C and P equivalent 2 kb, at high- metamorphic grade conditions the solubility of $ZnTiO_3$ in ilmenite is constrained by temperature and pressure, but zincian ilmenite with greater than a few mol% ZnTiO3 along with nearly pure ZnAl2O4 component have been reported from regions with significantly higher temperatures than are typically attained during regional metamorphism (> 800 °C). As there is no zonation or regular compositional difference in the mineral, thus this best explains the presence within the metamorphosed, later hydrothermally altered auriferous zones at the Lawa mines, North Singhbhum mobile belt.

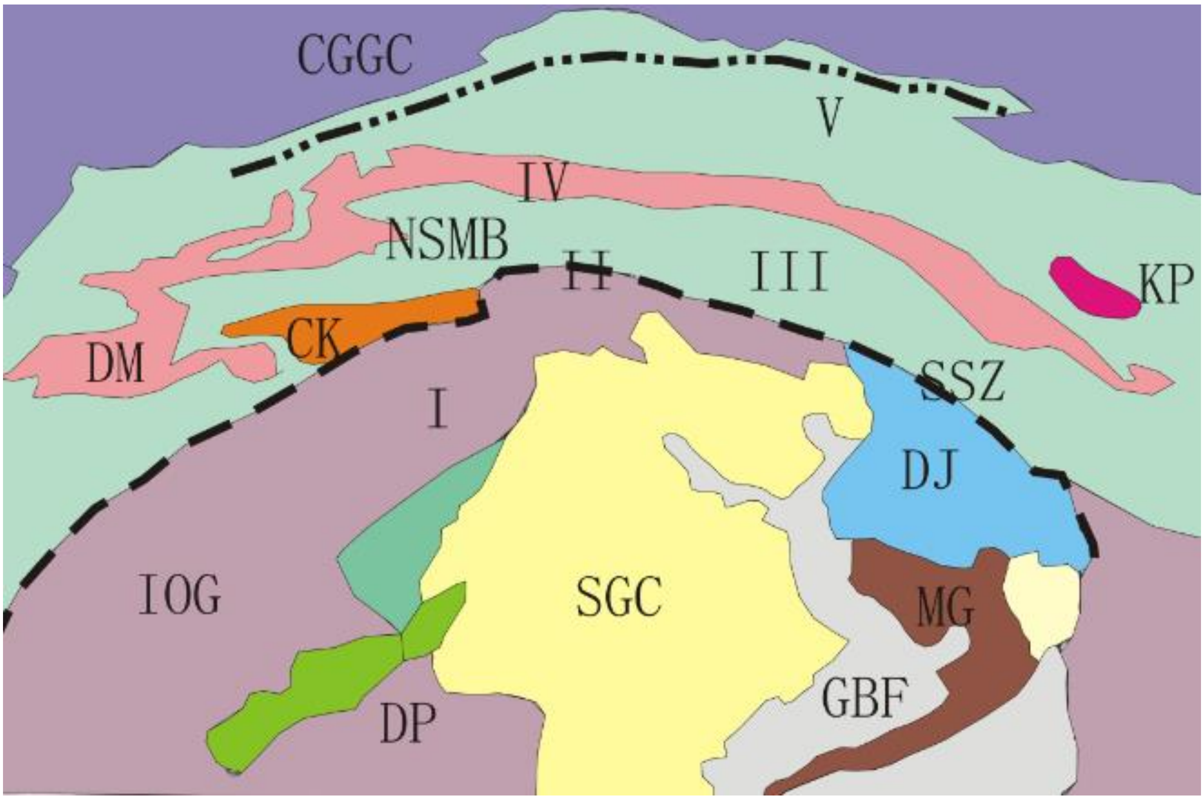
GEOLOGICAL SETTING

Paleo-Mesoproterozoic North Singhbhum Mobile Belt (NSMB) is a curvilinear belt of volcano-sedimentary sequence of Palaeo-proterozoic to Meso-proterozoic age. (Sarkar and Saha, 1962; Bose and Chakraborti, 1981; Gupta el al., 1980; Mukhopadhyay, 1988). The northern margin of the NSMB is bounded by the Tamar-Porapahar shear zone/South Purulia Shear Zone that separates the NSMB from the Chhotanagpur Gneissic complex. The NSMB is about 200 km long and it is characterized by a central volcanic range with Dalma lavas and tuffs which are flanked by the Singhbhum Group sediments and some ultramafic-mafic plutons both on the north and on the south. The sediments are generally metamorphosed to green schist facies forming different types of phyllites, mica-schists and quartzites. The ultramafic-mafic plutons are now transformed to chlorite-schists, chlorite-actinolite-schists, talc-tremolite-schists. Dalma lava varies from komatitic to tholeiitic types. Though the general trend of this mobile belt is east-west but it bears the evidences of at least three phases of tectonic deformation.

Regionally, NSMB is categorized into 5 domains (Sarkar et al. 1992; Gupta and Basu, 2000) (Fig. 1). The domain I comprising the Archaean Cratonic Core Region (ACCR) and bounded by Singhbhum Shear Zone (SSZ) in north. The domain II includes the rocks of Singhbhum Shear Zone (SSZ). Chaibasa and Dhalbhum formations between the SSZ and Dalma volcanics form the part of domain III. The domain IV consists of Dalma volcano-sedimentary belt. The domain V comprises low to medium grade volcano-sedimentary belt between the Dalma range and the CGGC in the north. The study area falls in domain V of NSMB, which falls in Saraikela-Kharsawan District of Jharkhand.

The region is well known for the numerous old gold working and abandoned gold mines apart from a long history of the gold panning activities within the Subarnarekha River and its tributaries. As many as

20 occurrences of gold are reported from these axes of NSMB. Gold mineralization in Lawa area reported in three old workings i.e. Tamapahar, Bhalukkhad east and Bhalukkhad west. Gold mineralization in the area is established along four prominent axes, one is well-known Tamar Lungtu-Parasi-Sindauri axis, second is Babaikundi-Birgaon-Lawa-Maysara axis, third one is Siadih-Chatuhasa auriferous axis and fourth is along northern and southern contacts of Dalma Volcanic Belt. The country rocks may be broadly divided into three major types: phyllites, quartzites and mica schists. Quartz veins of varied dimesions are extensively developed and have different orientations indicating multiple generations of the veins. Mineralization is confined within smoky quartz veins intruded in quartzite.



Major geological domains in North Singhbhum Mobile belt. **CGGC**- Chhotanagpur Granite Gneissic Complex; **CK**- Chakradharpur Granite; **DJ**- Dhanjhori Group; **DM**- Dalma Group; **DP**- Dangoaposi Volcanics; **GBF**- Gorumahisani Badampahar Formation; **IOG**- Iron Ore Group; **KP**- Kuilapal Granite; **MG**- Mayurbhanj Granite; **NSMB**- North Singhbhum Mobile Belt; **OV**- Ongarbira Volcanics; **SGC**- Singhbhum Granite Complex; **SSZ**- Singhbhum Shear Zone.

Fig.1: Regional Geological Map of North Singhbhum Mobile Belt (modified after Mahadevan, T. M., 2002)

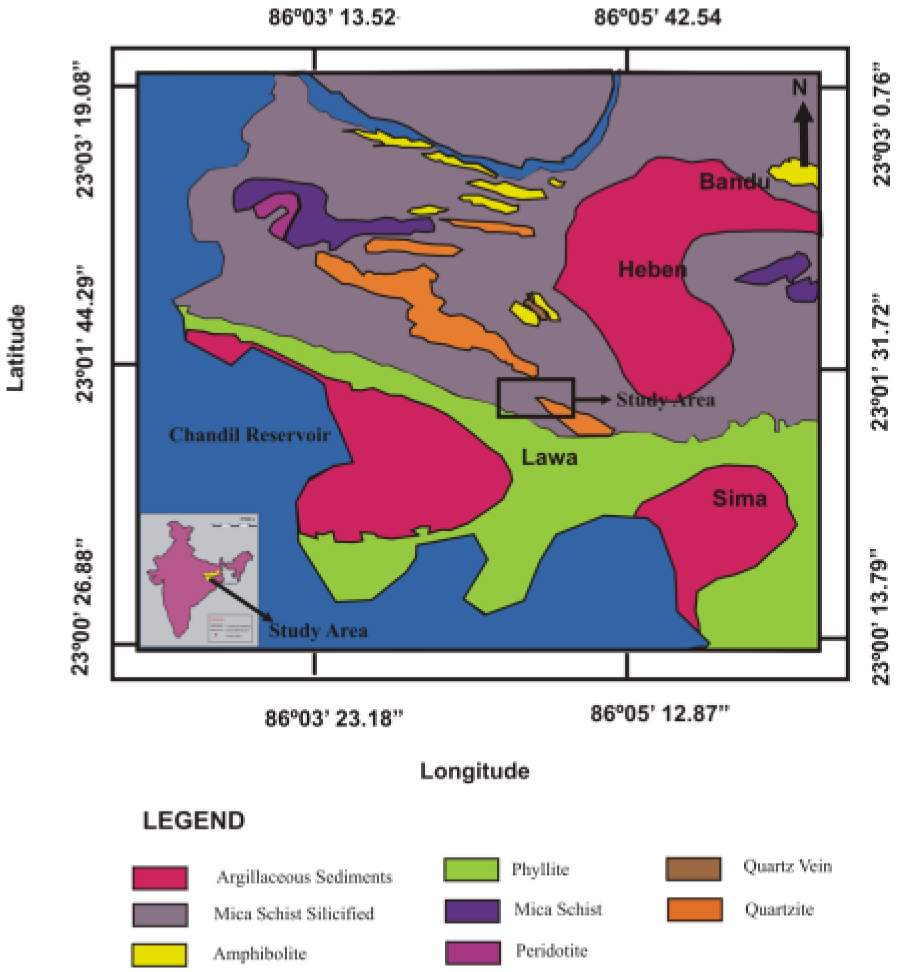


Fig:2 Geological Map of the study area in and around Lawa village (Cahndan et.al., 2013)

METHODOLOGY

Detailed field work has been carried out in and around Lawa mines, and its further west in the Sindauri and Parasi areas. Section study of Adit no-2, level-220m, in the Lawa mines has been carried out, to study the subsurface occurrence of the gold bearing quartz veins and the quartz mica schist country rock. At Lawa Gold Mine, the samples were collected from Adit-2, level-220m. From the entrance at Tamapahar to Lal Khadan, total 10 no. of samples were collected at regular interval along the East to West trend. At the entrance in the adit, the country rock, quartz-mica schist is observed which is highly deformed. Following this unit in the easterly direction is highly deformed and altered quartz veins within the quartz-mica-schists with extensive iron and malachite staining. At the central part of the Adit, profuse development of azurite was seen. Presence of ecandrewsite was noted in the country rock-quartz-mica-schist, as well as the associated quartz veins. Detailed study of the adit section has been done from east to west and representative samples have been collected with the aim to have lateral control of mineralization along with its characteristic mineralization.

The petrographic studies of the samples were carried out with the help of Nikon polarizing microscope E-600, in thin polished sections as well as stubs. The whole rock geochemistry of the samples collected from the lawa mine has been studied and the major as well as trace element data were collected using the XRF as well as the ICPMS instrument. Mineral chemistry with the help of Electron Probe Micro Analyzer instrument (EPMA) was attempted to understand the distribution and control of various elements within these studied silicates and oxide phases. Of the studied oxides, Ilmenite group was studied in detail to know about the redox conditions of the associated auriferous quartz veins. Mineral analysis of the ilmenite group of minerals were carried out in carbon coated samples using CAMECA SX 100 Electron Probe Micro Analyzer (EPMA) fitted with four spectrometers at EPMA Laboratory, Geological Survey of India, Faridabad. The EPMA analytical conditions included- 15kV accelerating voltage, 15nA beam current and 1 micron beam diameter with LaB_6 electron gun source. The natural mineral standards - rhodonite (Mn), rutile (Ti) and hematite (Fe) and sphalerite (for Zn) were used for calibration and quantification. The X-ray lines used are- Fe-Kα, Zn-Kα, Ti-Kα, Mn-Kα. Microprobe analysis shows compositional variability within individual grains- Zn-poor and Zn-rich varieties of ilmenite-ecandrewsite solid solutions series.

PETROGRAPHY AND MINERAL CHEMISTRY

The detailed petrographic study of the samples collected from Lawa mines, was done to study the lithounits and alteration characteristics. The petrological study indicates that the rock is highly sheared, composed dominantly of quartz, muscovite and chlorite as major mineral constituent with pseudomorphs of garnet. The garnet pseudomorphs varying in size from 0.5 to 2.0 mm, have been replaced by chlorite, muscovite and quartz along with magnetite and minor sulphides. The garnet pseudomorph is likely a pre to syn tectonic one, although it forms a part of the retrograde assemblage. The opaque phases found are gahnite, malachite, hematite and illmenite group of minerals.

Due to intense shearing and metamorphism, the microstructural features observed in the rock indicate that these have undergone intense ductile deformation, which is evident with the development of mylonitic fabric. The mylonitic foliation with zones with further grain size refinement has been observed at places, depending on the intensity of deformation. The development of S-C-C'fabric along with swerving of the mylonitic foliation around porphyroblasts is observed. The section shows formation of microlithons, the quartzose rich as well as mica rich domains. Both these are transected by the veinlets of carbonate at places. The quartz rich domains show grain size refinement. The coarser grains show undulose extinction and grain boundary migration. In the mica rich domain, modally muscovite is more abundant than chlorite, showing preferred orientation along S, C and C' fabric. The porphyroblasts consist of fine chlorite flakes, formed at the expense of garnet, retaining it's euhedral shape. Both delta and sigma type porphyroclasts are noted, mostly showing dextral sense of shearing. The pseudosection is prepared, which indicates that the assemblage was stable at ~ 620°C within a medium temperature metamorphic region.

Occurrences of ecandrewsite is noted in the quartz-mica-schist samples in the assemblage quartz+muscovite+chlorite+garnet(pseudomorph)+opaques. The oxides are the dominant opaque phases developed in the rocks of the area. Among the oxides the primary oxides as per abundance are: magnetite, hematite and ilmenite; whereas the secondary oxides are dominated by limonite, goethite etc. The presences of these oxides mark the high oxidation state of the sulphidised auriferous melt. Ilmenite occurs as disseminated, elongated, euhedral grains measuring approximately 0.5-1 mm, showing exsolved phases of ecandrewsite and other zincian ilmenite. The grains are mostly found to occur parallel to the C-plane, though a few grains are found oblique to it within the quartz rich domains. The oxide phases found are malachite (dominant), zincian ilmenite, and hematite. Very few grains of sphalerite (dominant) and chalcopyrite are observed. Presence of malachite, Cu-hydroxide, iron-oxide and carbonate grains are noted along veins. Under reflected light, ecandrewsite is greyish white with a pinkish tinge. Reflection pleochroism is weak in air but the mineral is strongly anisotropic between crossed polars, with colours changing from greenish grey to dark brownish grey. Neither cleavage nor twinning is observed in polished section. Genetically at least 2 generations have been identified for dominant primary oxides like the Magnetite as well as the ilmenite. Ilmenite mostly is of second generation which have no zoning and almost uniform composition throughout and are grown randomly across foliation (Fig 3e), whereas the early ilmenite with irregular grain boundaries and patchy/ bleb like composite exsolution are aligned parallel to dominant foliation (Fig 3f). This bleb like patchy exsolution is attributed to fluctuation in oxidation condition of the system, at the time of formation.

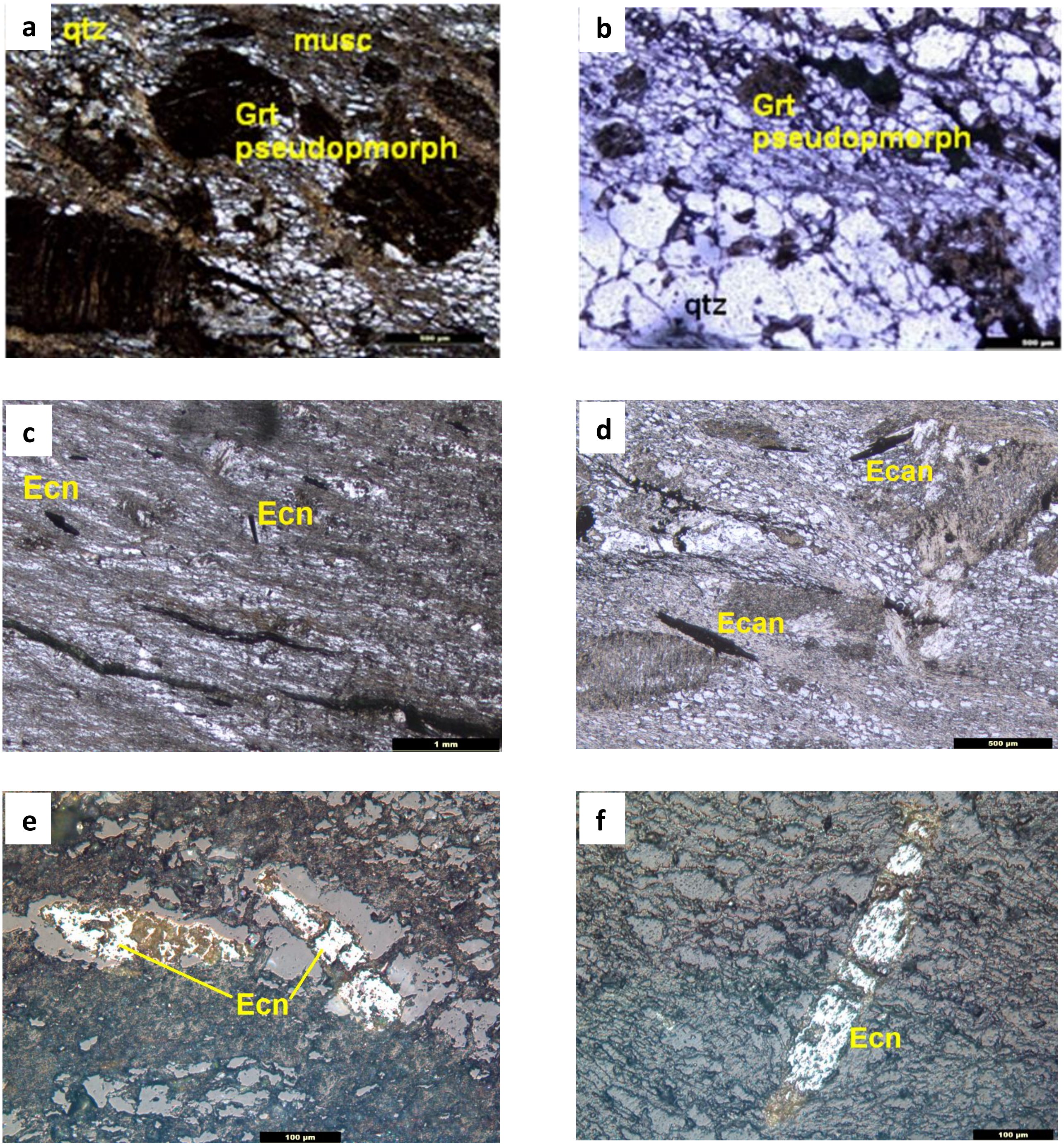


Fig. 3: Photomicrograph showing (a) & (b) the host rock quartz-mica-schist with pseudomorph of

garnet porphyroblasts. (c) & (d) elongated ecandrewsite grains showing preferred orientation. (e) & (f) discrete, euhedral grains showing exsolved phases of ecandrewsite and other zincian ilmenite group of mineral. Abbreviations: Ecn=Ecandrewsite, Grt= garnet, qtz= quartz, musc=muscovite.

Electron Microprobe analysis of the ilmenite group of elements gave ZnO3.16-37.89wt%, FeO5.34-

Ref. no.	1	2	3	4	5	6	7	8	9	10	11	12	13
TiO2	56.78	55.37	54.35	64.51	51.97	57.73	52.68	50.74	56.27	61.08	46.72	46.50	48.00
FeO	18.30	16.37	15.26	17.28	5.34	26.07	6.87	4.57	19.65	24.00	13.37	9.92	7.56
MnO	3.09	3.30	3.03	1.15	2.71	2.33	2.23	2.41	0.77	0.87	2.80	2.09	2.66
ZnO	15.61	20.57	22.83	7.42	37.89	5.34	29.70	36.03	3.16	3.77	22.29	26.59	26.98
TOTAL	95.16	96.50	96.35	91.23	98.93	91.98	92.42	97.27	90.85	91.05	86.51	86.05	86.02
Cations calculated on the basis of 3 oxygen atoms													
Ti	1.094	1.077	1.067	1.220	1.029	1.130	1.082	0.996	1.022	1.172	1.034	1.042	1.067
Fe	0.392	0.354	0.333	0.363	0.118	0.567	0.157	0.100	0.397	0.512	0.329	0.247	0.187
Mn	0.067	0.072	0.067	0.024	0.060	0.051	0.052	0.053	0.016	0.019	0.070	0.053	0.067
Zn	0.295	0.393	0.440	0.138	0.736	0.103	0.599	0.694	0.056	0.071	0.485	0.585	0.589

26.07wt%, TiO2 46.50-61.08wt%, MnO0.77-3.30wt%, yielding empirical formula ranging from $(Zn_{0.056}Fe_{0.397}Mn_{0.016})Ti_{1.022}O_3$to $(Zn_{0.694}Fe_{0.100}Mn_{0.053})Ti_{0.996}O_3$ and is classified as Ferroan-Ecandrewsite to Zincian-Ilmenite and Ecandrewsite. The compositions of the ecandrewsite and other zincian ilmenites are presented in table 1.

Table 1. Mineral chemistry of ilmenite from the studied samples.

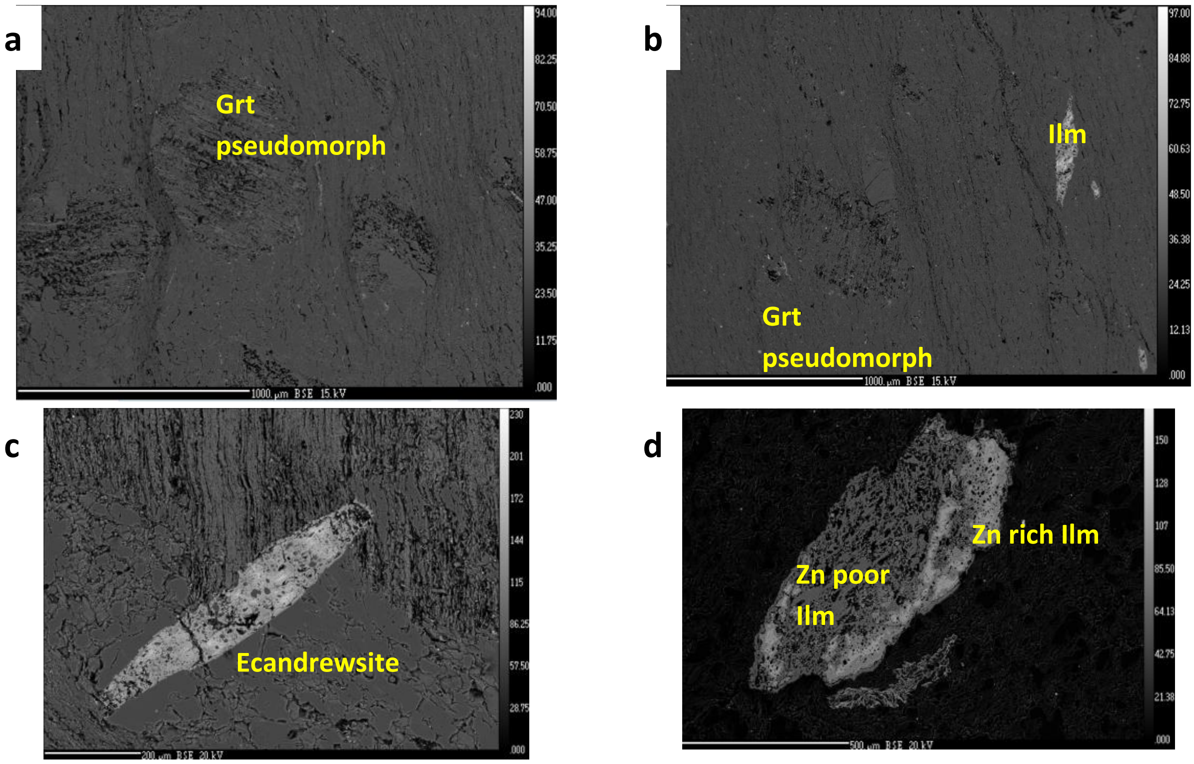
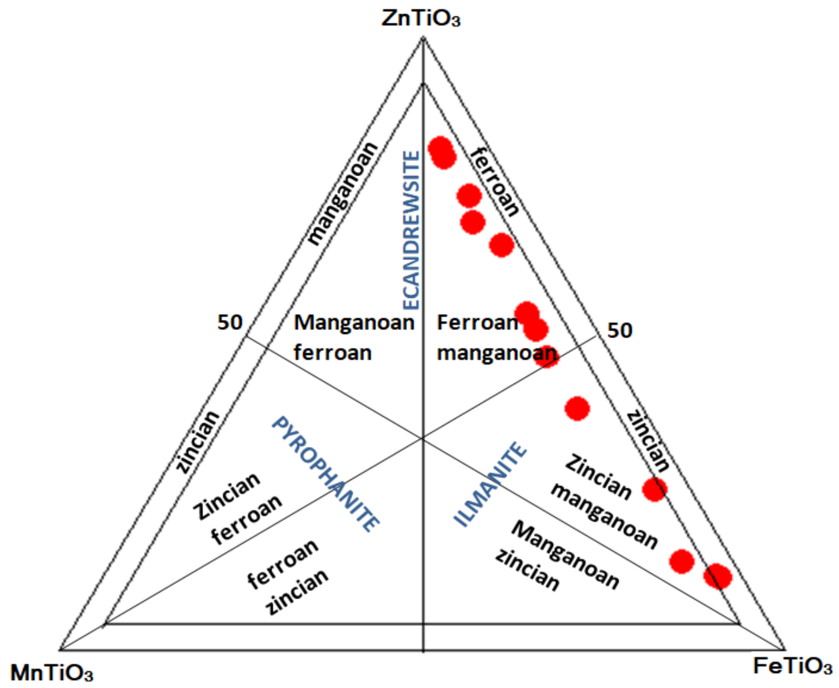


Fig.4: BSE images showing (a) & (b) garnet pseudomorph composed of chlorite, muscovite in association with zincian ilmenite (c) & (d) euhedral grains showing exsolution between

candrewsite and zincian ilmenite.

Formula on the basis of 3 oxygen atoms is as follows:

$(Zn_{0.295}Fe_{0.392}Mn_{0.067})Ti_{1.094}O_3$	
$(Zn_{0.393}Fe_{0.354}Mn_{0.072})Ti_{1.077}O_3$	
$(Zn_{0.44}Fe_{0.333}Mn_{0.067})Ti_{1.067}O_3$	
$(Zn_{0.138}Fe_{0.363}Mn_{0.024})Ti_{1.22}O_3$	
$(Zn_{0.736}Fe_{0.118}Mn_{0.060})Ti_{1.029}O_3$	
$(Zn_{0.103}Fe_{0.567}Mn_{0.051})Ti_{1.13}O_3$	
$(Zn_{0.599}Fe_{0.157}Mn_{0.052})Ti_{1.082}O_3$	
$(Zn_{0.694}Fe_{0.100}Mn_{0.053})Ti_{0.996}O_3$	
$(Zn_{0.056}Fe_{0.397}Mn_{0.016})Ti_{1.022}O_3$	
$(Zn_{0.071}Fe_{0.512}Mn_{0.019})Ti_{1.172}O_3$	
$(Zn_{0.485}Fe_{0.329}Mn_{0.070})Ti_{1.034}O_3$	
$(Zn_{0.585}Fe_{0.247}Mn_{0.053})Ti_{1.042}O_3$	
$(Zn_{0.589}Fe_{0.187}Mn_{0.067})Ti_{1.067}O_3$	
	Figure 5. Classification of Ecandrewsite and Zinc bearing Ilmenite in triangular diagram with three end members ZnTiO3-FeTiO3-MnTiO3 (Mitchell & Liferovich, 2004).

The dispersion diagram shows lack of correlation between Zn and Mn contents (Fig: 7), whereas the correlation between Fe and Zn is significant and both are very well correlated (Fig.6).

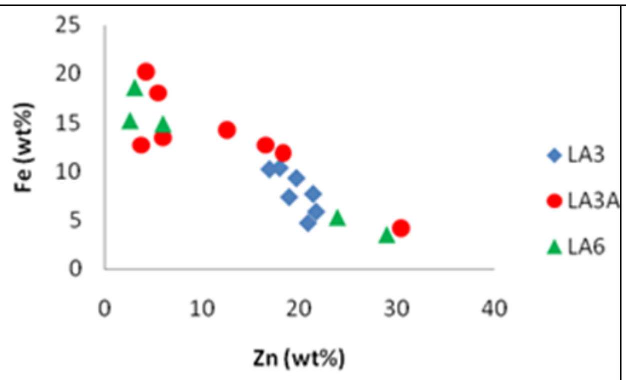
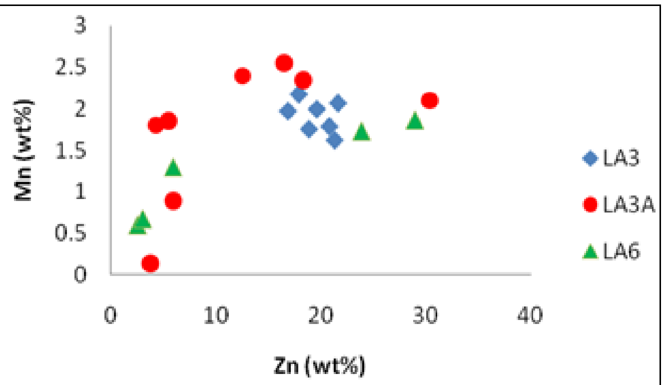
	

Fig: 6 Dispersion diagram showing correlation between for Fe & Zn	Fig: 7 Dispersion diagram showing correlation between for Mn & Zn

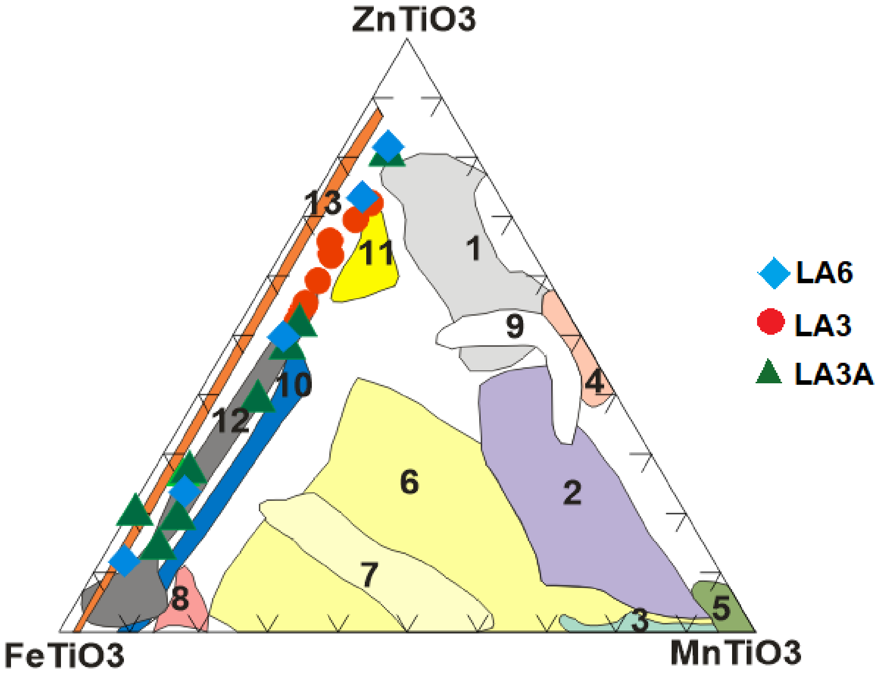


Fig: 8 Composition of minerals from ilmenite group in coordinates ZnTiO3- FeTiO3- MnTiO3, mol%. Numerals in figure: (1-3) sequence of ilmenite generation in lujavrite (from early to late), Pilansber Complex, South Africa (Mitchell and Liferovich, 2004); (4,5) Pocos de Caldas lujavrite, Brazil (Mitchell and Liferovich, 2004); (6) Dmitrovka alkaline metasomatic rocks, Azov region, Ukraine (Sharygin and Krivdik, 2011); (7) miaroles in Kuiqi Futian alkali granite, China (Suwa et al., 1987); (8) syenite and miaroles in alkali rhyolite at Cape Ashizuri, Japan (Nakashima and Imaoka, 1998); (9,10) alkali granite pegmatites in Belye (white). Tundras massif (Lyalina et al., 2006), (11) Cherty metasedimentary rocks from Melbourne Rockwell and Little Broken Hill Mines in Australia and San Valentin Mine in Spain(Birch et al., 1988); (12) metamorphosed massive sulfide ores and wall-rock metasomatic rocks in the Rocky Mountains, Colorado, United States (Heimann et al., 2005); Central Jebel, Morocco (Essaifi et al., 2001); sulfide deposits from Betul Belt, Central India (Ghosh and Praveen, 2007, 2008); (13) kyanite schist in Dead valley, California (Whitney et al., 1993).

Sample no.	**LA3A**	**LA3A**	**LA3A**	**LA3A**	**LA3A**	**LA3A**	**LA3A**	**LA3A**	**LA6**	**LA6**
Rocktype	**Quartz-mica-schist**									
TiO2	56.78	65.20	57.72	55.37	54.35	64.51	51.97	57.73	52.68	50.74
FeO	18.30	16.33	23.21	16.37	15.26	17.28	5.34	26.07	6.87	4.57
MnO	3.09	0.17	2.39	3.30	3.03	1.15	2.71	2.33	2.23	2.41
ZnO	15.61	4.65	6.80	20.57	22.83	7.42	37.89	5.34	29.70	36.03
TOTAL	95.16	90.20	90.74	96.50	96.35	91.23	98.93	91.98	92.42	97.27
Cations calculated on the basis of 3 oxygen atoms										
Ti	1.09	1.20	1.14	1.08	1.07	1.22	1.03	1.13	1.08	1.00
Fe	0.39	0.33	0.51	0.35	0.33	0.36	0.12	0.57	0.16	0.10
Mn	0.07	0.00	0.05	0.07	0.07	0.02	0.06	0.05	0.05	0.05

Zn	0.30	0.08	0.13	0.39	0.44	0.14	0.74	0.10	0.60	0.69

Sample no.	**LA6**	**LA6**	**LA6**	**LA3**	**LA3**	**LA3**	**LA3**	**LA3**	**LA3**	**LA3**
Rocktype	**Quartz-mica-schist**									
TiO2	56.27	58.59	61.08	45.35	46.72	45.98	46.50	48.68	48.00	48.77
FeO	19.65	19.21	24.00	13.20	13.37	12.01	9.92	9.50	7.56	6.07
MnO	0.77	1.67	0.87	2.54	2.80	2.57	2.09	2.26	2.66	2.30
ZnO	3.16	7.38	3.77	21.00	22.29	24.44	26.59	23.51	26.98	25.94
TOTAL	90.85	87.60	91.05	84.20	86.51	85.89	86.05	84.88	86.02	84.04
Cations calculated on the basis of 3 oxygen atoms										
Ti	1.02	1.18	1.17	1.02	1.03	1.03	1.04	1.08	1.07	1.09
Fe	0.40	0.43	0.51	0.33	0.33	0.30	0.25	0.24	0.19	0.15
Mn	0.02	0.04	0.02	0.06	0.07	0.07	0.05	0.06	0.07	0.06
Zn	0.06	0.15	0.07	0.46	0.48	0.54	0.59	0.51	0.59	0.57

DISCUSSION AND CONCLUSION

The NSMB holds all the critical fundamental controls on regional scale which are very important for the formation of gold deposits. According to Arogyaswamy and Dutta (1948), the auriferous ore shoots occurring as en-echelon pattern are present within the metasedimentary rock units in the area. The auriferous quartz veins are milky white-grey in colour. The surface indications of mineralization are present as malachite and azurite stains along with euhedral pyrite within the country rock. Petrographic study of the samples suggests the sulphide association as chalcopyrite, pyrite, pyrrohotite, covellite, sphalerite and cinnabar. There exists a distinctive generation of sulphide and associated oxides in association with gold mineralization. The presence of oxides such as ecandrewsite and gahnite in the mineralized assemblage has bearing on the oxidation conditions present at the time of ore formation and precipitation.

This is the first report of the presence of ecandrewsite in auriferous quartz veins of NSMB. Earlier, ecandrewsite occurrences have been documented across the globe in diverse geological settings, including quartz-rich metasediments, quartz-gahnite exhalites, kyanitic schists, nepheline syenites, metamorphosed volcanic-hosted massive sulfide (VHMS) mineralizations, and albitites (María José Espeche & Raúl Lira, 2022).

Ecandrewsite, a zinc-bearing variety of ilmenite, is assessed through four major components: geikielite ($MgTiO_3$), pryophanite($Mn\ TiO_3$), Ecandrewsite itself ($ZnTiO_3$) and ilmenite ($FeTiO_3$). The samples examined from the Lawa mines reveal the presence of two disctinct compositional groups (Zn-poor and Zn-rich) within the ilmenite-ecandrewsite solid solutions (Fig 4d). Although definitive evidence is lacking at this stage, the formation of Zn-rich ilmenite and ecandrewsite may potentially result from the desulfidation of sphalerite, as suggested by Whitney et.al.

Ecandrewsite, a zinc-bearing variety of ilmenite, is assessed through four major components: geilielite ($MgTiO_3$), pyrophanite ($MnTiO_3$),ecandrewsite ($ZnTiO_3$) and ilmenite ($FeTiO_3$). The samples examined from the lawa mines reveal the presence of two distinct compositional groups (Zn-poor and Zn-rich) within the ilmenite-ecandrewsite solid solution (Fig 4d).Although definitive evidence islacking at this stage, the formation of Zn-rich ilmenite and ecandrewsite may potentially result from the desulfidation of sphalerite, as suggested by Whitney at.al. (1993). On the other hand, the Zn-poor ilmenite could likely form from the metamorphic recrystalization, which might have diluted the zinc content within the sphalerite.

Whitney et al. (1993), from his experimental data, considering the system to be ideal, suggested that the mixing in ilmenite-ecandrewsite and the Zn-Fe exchange equilibrium among these minerals, can be elucidated by the following reaction:

$ZnTiO_3 + FeAl_2O_4 = FeTiO_3 + ZnAl_2O_4$

Zincian ilmenite containing more than a few mol% of the ZnTiO3 component will only be found alongside aluminate spinel under specific conditions. These conditions include instances where the spinel is almost entirely composed of ZnAl2O4, or when temperatures significantly exceed the levels typically reached during regional metamorphism (above 800 °C). According to experimental research and thermodynamic considerations, the formation of zincian ilmenite and Ecandrewsite has been observed and is associated with several geological processes. These processes include:

1. The alteration of sphalerite in sedimentary rocks through desulfidation.
2. The subsolidus transformation of early magmatic zinc-bearing zirconosilicates and titanosilicates, specifically within alkaline igneous complexes such as Sakoma and Martin (2002), Mitchell and Liferovich (2004), Lyalina et al. (2006), and Sharygin and Krivdik (2011).
3. The metamorphism of massive sulphide ores at amphibolite and granulite metamorphic grades. This has been documented by Whitney et al. (1993), Birch et al.(1998),Essaifi et al.(2001), Heimann and Spry (2005), Ghosh and Praveen (2007,2008).
4. The occurrence within hydrothermal fluids, formed as a result of the subsolidus replacement of annite with muscovite. This process takes place within cavities of hydrothermally altered wall rocks in sulfide-hosted deposits, as noted by Prochazka et al.(2010), Suwa et al.(1987) and Nakashima and Imaoka(1998).

The composition of zincian ilmenite and Ecandrewsite have allowed for their categorization and genetic association with various geological environments, as illustrated in the ternary diagram ZnTiO3-FeTiO3-MnTiO3 (Fig.8).

Mineral chemical analysis reveals that the compositions of ilmenite species within the examined samples from the study area, exibit a continuous variation along a solid-solution tranjectory. This trend spans from ferron ecandrewsite to ilmenite with intermediate stages including ferroan ecandrewsite, zincian ilmenite and pure ilmenite. The fluctuations in zinc content are governed by the replacement of zinc with iron, a relationship supported by the observed negative correlation between iron and zinc, as depicted in Figure 6. This correlation underscores the impact of hydrous oxidized melt on sulfide-rich crustal rocks, potentially leading to the decomposition of sphalerite, particularly during the prograde metamorphic process. Additionally, the presence of a negative correlation between zinc and manganese in most crystals contributes to the sporadic appearance of these crystals, as evident in the back scattered Electron (BSE) image shown in Figure 4d. These observations along with previous findings (Essaifi et al.,2001; Ghosh and Praveen, 2007).

This study marks the initial documentation of Ecandrewsite (ZnTiO3), a zinc-bearing variant within the ilmenite series, within auriferous quartz veins found in the metasediments of the NSMB's Lawa mines. The coexistence of zincian ilmenite, ecandrewsite, and the iron-end member ilmenite confirms a genetic connection between the region and its associated gold mineralization, rooted in metamorphosed sulfide deposits. The presence of these minerals, indicative of heightened oxidation conditions and elevated oxygen fugacity, suggests that both the ore and the surrounding country rock underwent at least upper amphibolite-grade metamorphism. This metamorphism produced a significantly oxidized melt that interacted with sulfide-bearing crustal rocks. This interaction transpired during retrograde metamorphism along the crustal-scale shear zones present in the area. This interplay fostered conditions favorable for the deposition of zincian ilmenite and ecandrewsite. The emergence of these minerals played a pivotal role in the formation and precipitation of gold within the auriferous quartz veins of the area. Although gold likely originated from magma containing sulfide-bearing components under reducing conditions, the intricate interplay between oxygen fugacity (fO2) and sulfur fugacity (fS2) created a dynamic oxidative environment, which led to the precipitation of gold within the auriferous quartz veins restricted within the shear zones in the NSMB.

ACKNOWLEDGEMENT
The authors are grateful to Dr. L.P.Singh, former DDG, NCEGR, GSI, Faridabad for extending necessary support, guidance and his valuable comments on the manuscript that allowed us to make improvements to the paper. The authors are indebted to Dr. Dipayan Guha, Dy. Director General, Geological Survey of India, State Unite: Jharkhand for fruitful discussion and guidance during the course of work. The authors express their sincere thanks to Dr. Pankaj Kumar, Director, Geological Survey of India, State Unit: Jharkhand for his guidance, support and the facilities provided during field visits. The authors are also thankful to all the officers and staff of NCEGR, Geological Survey of India, Faridabad for their active co-operation and help to execute the research work.

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