# CHAPTER 4

## MATERIALS AND METHODS

Detailed fieldwork has been carried out from the central part Visakhapatnam domain up to the northern part near the Phulbani domain of the EGP. As the present study is aimed to understand the geological evolution of the orthogneissic rocks, the focus was laid on the granite, charnockite, syenite and mafic granulite, examining their field relationship, occurrences and associations. Small-scale mapping was done to delineate field relations and are shown respective map (Fig. 4.1 a, b, c, d). Samples from the rocks under investigation presented in Table 5.1 and 6.1, were collected for petrographic, geochemical and geochronological analyses. Thin sections were examined using a polarizing microscope (Nikon) to understand textural characters of the rocks in details. Thin sections were studied both under transmitted polarized light and reflected light (for opaque phases). Images of thin sections were taken using a digital camera attached to the microscope.

### Scanning Electron Microscopy (SEM)

In order to study charnockite and granite samples a scanning electron microscope (SEM) model JEOL JSM IT500 is used at Presidency University. Additionally, high-resolution backscatter electron (BSE) images are produced at 50-60 na probe current with a working distance of < 10 mm operated at 20 kV acceleration voltage. These images are utilized to identify specific regions for chemical analysis performed by an electron microprobe.

For the characterization of sulphide minerals in mafic granulite, a Vega-Tescan scanning electron microscope at Presidency University was employed, and EDS data were obtained from spots to identify the elements present within pyrite and pyrrhotite grains across various samples. In order to understand intricate textural relation between oxide-sulphide-silicate, backscatter electron (BSE) image has been taken at 15kV acceleration voltage with a working distance (WD) of <25mm.

### Electron Probe Micro Analysis (EPMA)

Mineral chemical analyses for charnockite samples were done with a Cameca SX Five Tactics Electron Microprobe Analyzer (EPMA) at the National Centre for Earth Science Studies (NCESS), Thiruvananthapuram, Kerala, India. The instrument was operated with 15 kV accelerating voltage,

20 nA beam current, and 1 μm beam diameter. Respective background intensities were measured on both sides of the peak for half the peak times. Data reduction has been carried out using X-Phi method.

The analyses of mafic granulite samples were conducted at the Indian Institute of Technology, Kharagpur, India, using a CAMECA SX100 electron microprobe. The instrument operated at an acceleration voltage of 15 kV with a current of 12 nA. Point analyses were performed using a probe diameter of 1 μm. Calibration was carried out using natural silicate and oxide standards, except for Ti and Mn, which utilized synthetic standard materials. Raw data were corrected using the ZAF matrix correction routine. Chemical mapping was also done in feldspar grains to understand the chemical variation.

## Xray Fluorescence (XRF) spectrometry

For whole rock chemistry, representative samples were crushed using a jaw crusher followed by a pulverizer (Fritsch) at the Presidency University. Strict precautions were taken to prevent any potential cross-contamination. The analysis of major and trace elements in 12 representative samples was conducted at NCESS, Thiruvananthapuram. Major elements were examined using WD-XRF (Bruker S8 Tiger sequential WD X-ray spectrometer) with pressed pellets. The standards utilized for this analysis were BHV01, G2, GSN, and W2a. Detailed information on the analytical procedures and accuracy can be found in Dev et al. (2021) and Dasgupta et al. (2022).

## Inductively Coupled Plasma Mass Spectrometry (ICPMS)

The analysis of rare earth elements (REE) was conducted at M/s Acme Laboratory in Vancouver, Canada, specifically at Bureau Veritas Commodities Canada Ltd. Specific trace and REE concentrations in 10 representative samples using the litho-geochemistry program LF100 were chosen. The studies were carried out by the Acme Laboratory using the ICP-MS technique and the STD-SO-19 reference material. The details of the analytical protocol and detection limits for elements are provided in the laboratory's webpage at (https://www.bvna.com/sites/g/files/zypfnx386/files/media/document/Bureau-Veritas-USD-Fee-Schedule-2022.pdf). The GCDKit program was used to calculate the CIPW norm and producing geochemical plots (Janouek et al., 2006).

## Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The major, trace, and rare earth element compositions of the selected samples of granites were examined at the Australian Laboratory Services Pty. Ltd. (ALS) in Brisbane, Australia. The analysis was done using whole rock package (ME-ICP06) and Lithium Borate Fusion ICP-MS (ME-MS81). The $H_2O$/LOI content was determined by subjecting the samples to heat in a Thermo Gravimetric Analysis (TGA) furnace (ME-GRA05). The following standards were used for major, trace and REE analyses: CGL208, OREAS120, OREAS460, OREAS-100a and SY-4. The minimum detectable concentrations for the major element oxides were 0.01%, with the exception of $Cr_2O_3$, which had a minimum detectable concentration of 0.002%. As for the trace and rare earth elements, their respective detection limits were as follows: Ba, Sn, and W at 0.5 ppm; Ce, Ga, La, Nd, Sr, Ta, and Y at 0.1 ppm; Cr and V at 5 ppm; Cs, Ho, Lu, Tb, Tm at 0.01 ppm; Dy, Gd, Hf, Nb, Th, U at 0.05 ppm; Er, Sm, Yb at 0.03 ppm; Eu and Pr at 0.02 ppm; Rb at 0.2 ppm; and Zr at 1 ppm.

## Laser Ablated Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS)

To conduct zircon U-Pb analyses, approximately 2 kg of each sample underwent manual crushing, followed by refining the grain size to approximately 300 μm diameter using an agate ball mill (Fritsch Pulverisette 0). With the help of a disposable sieve cloth, the powdered samples were collected in water, and heavy minerals were manually separated with the utmost care to avoid any potential cross-contamination. Zircon grains were meticulously selected by hand from each heavy mineral fraction and put on a typical epoxy disc with a diameter of 25 mm. The mounts were then polished to expose the maximum amount of the zircon grains' surface area. On the CAMECA SXFiveTactics electron probe, microanalyzer at NCESS, the interior structures of these grains were analyzed using cathodoluminescence (CL) and backscattered electron (BSE) imaging.

For single spot U-Pb isotope and trace element analyses of the zircons, the samples were analyzed at the Isotope Geochemistry Facility, NCESS, utilizing a Teledyne CETAC Nd: YAG (213 nm) solid-state laser coupled with an Agilent 7800 quadrupole ICP-MS. The analytical protocol followed the same procedures as described in Dev et al. (2022). Data reduction, as well as the calculation of isotopic ratios and ages, were performed offline using Iolite 4.4 software (Paton et al., 2011). The isotopic ratios and elemental concentrations were processed using Isoplot 4.1 (Ludwig, 2008). For U-Pb analysis, 91500 zircons (LA-ICPMS $^{206}Pb/^{238}U$ age ca. 1062 Ma;

Weidenbeck et al., 1995) was used as the primary standard whereas BB11 (LA-ICPMS $^{206}Pb/^{238}U$ age 562±9 Ma, Santos et al., 2017) and Plesôvice ($^{206}Pb/^{238}U$ ID-TIMS age 337±0.37 Ma; Sláma et al., 2008) zircons were analyzed for quality monitoring. During the analytical session, BB11 and Plesôvice yielded weighted mean $^{206}Pb/^{238}U$ ages of 557±3 Ma (n=30, MSWD = 1.2) and 337.9±2.2 Ma (n= 29; MSWD = 0.043) respectively. We have calculated group ages based on the $^{206}Pb/^{238}U$ data following the logic of Spencer et al. (2016). For in situ trace element measurement, NIST 610 (Pearce et al., 1997) was used as the primary reference material with $^{29}Si$ (IS value=14.98%) as the internal standard. All errors are reported in 2σ confidence.

The sample of monzosyenite was examined utilizing BSE and CL techniques with a JEOL JSM-7500F scanning electron microscope at the Department of Earth and Planetary Systems Science, Hiroshima University. This examination aimed to comprehend the internal morphology and identify specific positions within the grains. The sample was further analyzed for U-Pb isotopes using a 213 nm Nd-YAG Laser (New Wave Research UP-213) in conjunction with the Thermo Fisher X-series-II ICP-MS at the Department of Earth and Planetary Systems Science, Hiroshima University. This process employed a mixed He-$N_2$-Ar carrier gas system, featuring a small volume ablation cell, sample aerosol stabilizer (buffering chamber), and charcoal filter attachment. For the analysis, a laser spot diameter of 25 μm and a repetition rate of 4 Hz were selected. Details are further discussed in Das et al. (2017) and Saha et al. (2016b). For correction of U-Pb ratio and Th/U ratio standard of FC1 and glass standard NIST SRM 610 was used respectively. The initial data underwent processing through PepiAge (Dunkl et al., 2008). A correction for common Pb was applied by considering the measured $^{204}Pb$ and utilizing the common Pb composition model suggested by Stacey and Kramers (1975). Graphical representations of the data were generated using Isoplot software (version 3.75, Ludwig, 2012). For all plots and group-age calculations, errors are presented as 2σ values. To calculate group ages, the $^{206}Pb/^{238}U$ age (near-concordant) was employed for samples with dates less than 1.0 Ga (Gehrels et al., 2008).

## Phase equilibria modeling using Perple_x

Phase equilibria modeling was carried out on samples of coarse-grained charnockite. The pre-metamorphic evolution of coarse-grained charnockite was modelled using the software Perple_X 6.9.0 (Connolly, 2005, 2009). Phase equilibrium analyses were carried out in the pressure-

temperature (P-T) range of 6-11 kbar and 600-1200 °C. To take into account the evolution of mineral assemblages, phase diagram calculations were done using the $Na_2O$-CaO-$K_2O$-FeO-MgO-$Al_2O_3$-$SiO_2$-$H_2O$-$TiO_2$ (NCKFMASHT) system. The computations were performed using a total of nine bulk compositions. Since hydrated basalt can partially melt under the influence of a $CO_2$-rich fluid to form charnockite magma, the hypothetical compositions of the fluid were considered as 0.7 wt.% $H_2O$ and 0.3 wt.% $CO_2$. Gt (HP), Augite(G), O(HP), Augite(G), Pheng (HP), Bio (TCC), Pl(h), San, Ilm (WPH), cAmph(G), and melt(G) were among the solution models and hp633.ver data file is used in the calculations. The melt compositions were further calculated and compared using a TAS diagram in GCDKit program.

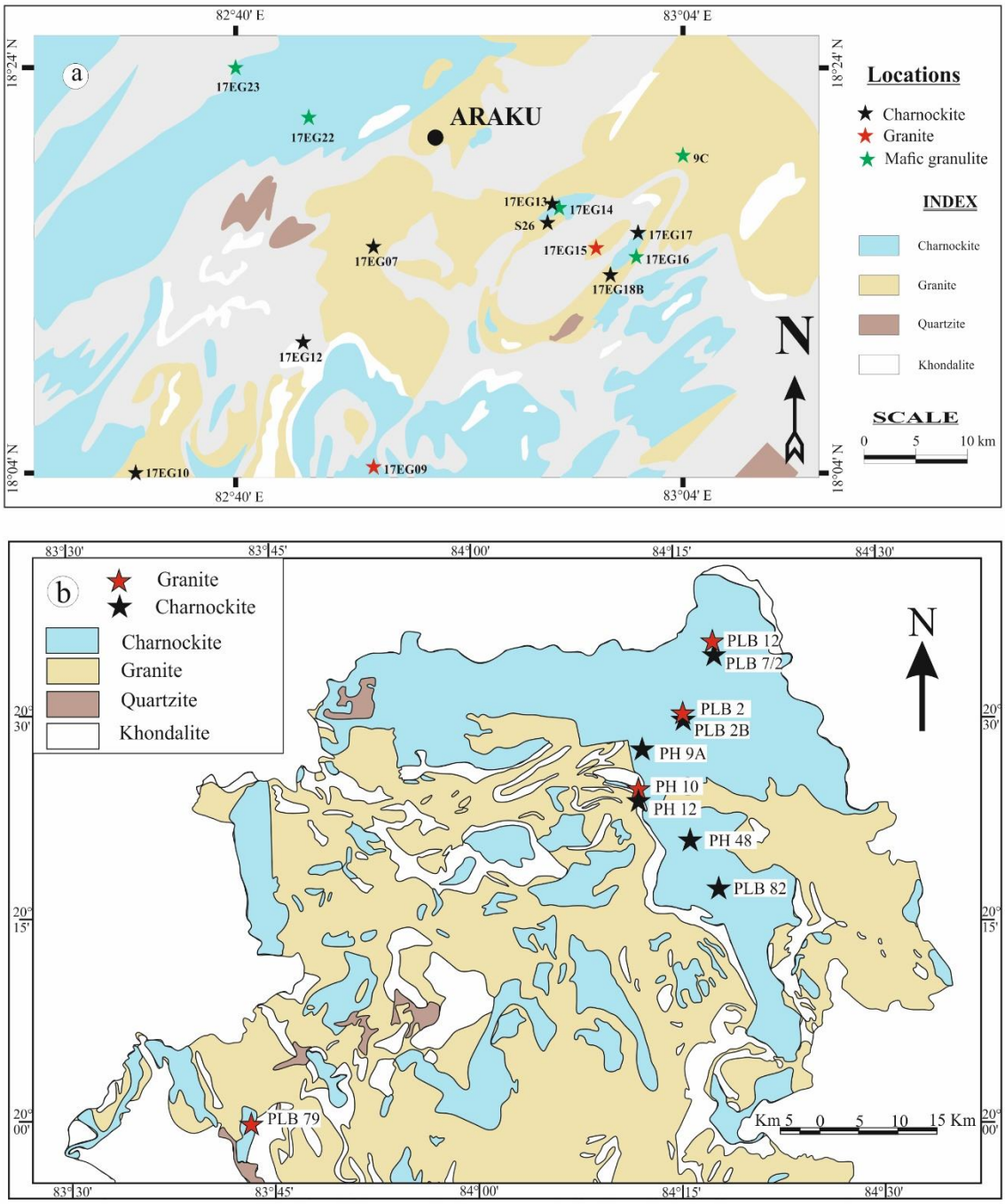


Fig 4.1 (a) Broad geological map of part of the central Eastern Ghats Province showing major lithological units and sample locations (modified after Ramakrishnan et al. 1998). (b) Geological map of Phulbani area modified after resource maps of Khandamal district by Geological Survey of India (2002).

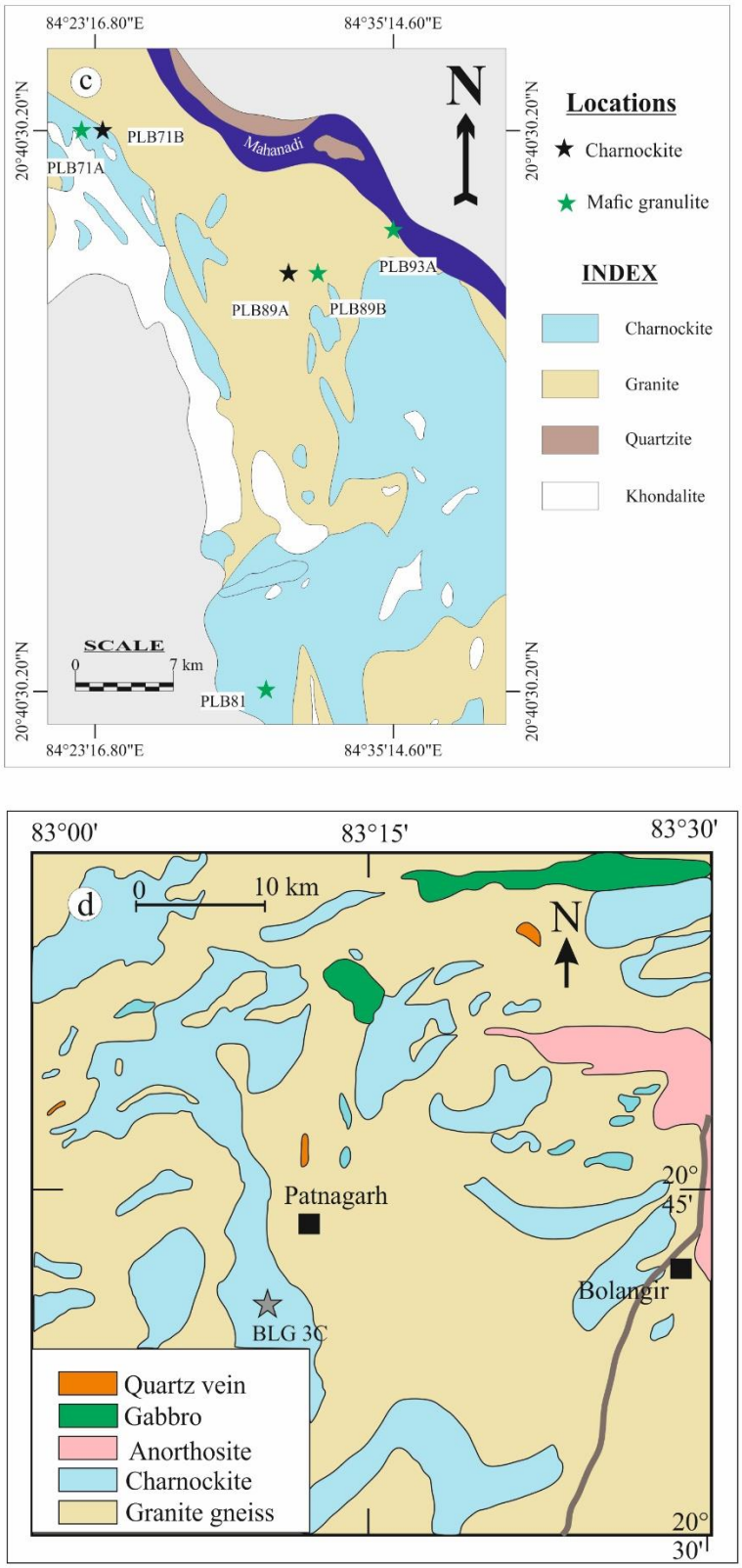


Fig. 4.1 (c) Broad geological map of Boudh area northern part of Eastern Ghats Province. (d) Geological map of Bolangir area north-western part of Eastern Ghats Province modified after district resource map by Geological Survey of India (2002).