Chapter 2

METHODOLOGY AND INSTRUMENTAL TECHNIQUES

2.1 Introduction

The petrogenesis of any lithounit is based upon the basic hypotheses primarily framed during the field observation and subsequently collection of representative rock samples, laboratory treatments of the samples and testing the hypothesis one by another based on the result to arriving on viable genetic model. The chapter provides detailed methodology of field and analytical techniques used in the present investigation.

2.2 Field Techniques

The geological field work has been carried out in the western part of Arunachal Himalaya mostly along the West Kameng corridor keeping in view of two major objectives; first to map the felsic bodies establishing their relationships with the other metasedimentaries present in the area, and second is to collect adequate number of representative samples along with field data of granitoids and associated lithounits of the area. The base map used to achieve the above mentioned objectives is the degree sheet of Northeastern region of India published by Survey of India, Google images of the various traverses of Kameng valley and earlier published geological maps (e.g. Dikshitulu et al., 1995; Srinivasan, 2001). As the area is rugged and unapproachable, close traverse mapping has been carried out to cover the area. Traverses have been planned mostly along road cuts, river sections and foot tracks, where fresh outcrops are present. Light to heavy-duty hammers, chisels, brunton compass, hand lens, measuring tape, handheld Kappameter (Magnetic Susceptibility Meter), GPS (Global Positioning System: Garmin GPS12), and digital camera are some of the essential field equipments used while conducting the geological and MS-mapping.

Field investigations in the study area were performed carefully to understand the geology of the area, nature and type of the various felsic plutonic bodies and
associated lithounits, and their mutual field relations. During intensive field surveys, field data such as GPS locations (latitude, longitude and elevation above mean sea level) of the studied outcrops, mineralogical and textural variations of granitoid bodies, field relation between granitoids and associated lithounits, magnetic susceptibility (MS) measurements and collection of fresh rock samples have been carried out. However, there are some limitations while using GPS for exact locations as it needs line-of-sight to satellites. It does not work in forests or steep valleys and therefore there is need to rely only on the conventional methods locating the positions with the help of toposheet and bearings from compasses from the known locations.

The magnetic susceptibility (MS) of granitoids was measured on smooth surface in the field using hand-held SM-20 MS meter (version-2) which operated at of 10 KHz frequency with a sensitivity of $1 \times 10^{-6}$ SI unit. The instrument can operate within a temperature range of 10 - 60º C. Measuring time of each reading is < 3 seconds per sample in two steps. The MS meter is placed preferably on fresh and smooth rock surface larger than 60 × 60 mm area and measure button is pressed shortly. MS is then taken away (at least 30 cm) from the rock surface in the air again measured button is pressed shortly. Then the actual MS value ($\times 10^{-3}$ SI unit) is displayed on the LCD screen. The MS values can be further corrected using factors for degree of surface unevenness; 1 mm = 1.07, 2 mm = 1.15, 3 mm = 1.23, 4 mm = 1.32, 5 mm = 1.41, 6 mm = 1.51, 7 mm = 1.61, 8 mm = 1.72, 9 mm = 1.84, 10 mm = 1.96. However, surface unevenness was not observed more than 5mm.

### 2.3 Method of Sample Preparation

#### 2.3.1 Thin section preparation

After collection of representative rock samples, the next step is to select proper rock sample for further analytical work to generate the petrographical, petrological and geochemical (mineralogy and whole-rock geochemistry) database. Rock thin sections were prepared to document important textural features of petrogenetic significance and for volume % estimate of constituent minerals. The rock-chips for thin section preparation have been cut in three directions and in view of major structures, if any. Rock-chips were grinded and polished to a recommended thickness using different grades (sizes) of corundum powders. The polished section is then mounted on 1:3
inches glass slides and then again grinded and polished on glass plates using silicon carbide powder till the desired thickness of 0.03 mm is achieved. The glass slides were washed and dried, and then polished on emery and cloth polishing sheets. The rock thin section for petrographic studies under microscope is covered with a glass cover slip, and the slide for microprobe analysis was carbon coated.

2.3.2 Fine powdering

The representative granitoid samples were further selected for major and trace including rare earth elements determinations using XRF and ICP-MS techniques. Weight of each rock sample is about 2 kg, which is chopped, crushed and grinded to a fine powdered sample. The chopped pieces of rock samples were crushed (Jaw Crusher) making fragmentary pieces (coarse powder) of several millimeters size. The coarse powder was homogenized, and about 200 gm of sub-sample was separated by coning and quartering method, into several steps. The coarse powder then powdered again in cleaned agate Teema mill for 5-7 minutes (about 5 minutes for felsic rocks and 10 minutes for mafic samples) to obtain fine powder of -200 mesh grade. The working platform, Jaw Crusher as well as Teema mill were cleaned after processing each sample by air blower, water and acetone to minimize contamination. The -200 mesh fine powdered sample was then homogenized, coned and quartered for getting about 1 gm of the fine powder of sample, which was used for chemical analysis.

2.3.3 Loss on ignition (LOI) determination

Loss on ignition (LOI) is a measure of the freshness of any rock sample and the presence of the volatiles (along with moisture) in it. The basic principle behind the LOI determination is that the weight loss of a powdered rock sample due to moderate to high heating (700 - 900° C) is proportional to the volatile content of the hard rock.

One g of the fine powder of a rock sample is kept on labeled butter paper with the help of electronic balance and cleaned spatula at room temperature. It is better to weigh the sample for LOI determination just after the fine powdering of the rock sample to avoid absorption of excess moisture available in the atmosphere to the rock
powder. The pre-ignition weighing measurement should be noted properly in LOI log book. The weighed rock-powder sample is kept into cleaned and desired crucible.

The ignition of weighed samples used to carry out in a muffle furnace where the weighed powdered sample is kept in teflon crucible. The temperature of furnace is raised up to 900º C gradually with in time duration of 45 minutes. The gradual heating of sample in crucible evaporates almost all the volatile material or compounds from the powdered rock sample. The crucibles have to remove from the furnace when they are cool enough, ideally between about 50º C to 200º C with the help of proper handles. Samples with crucibles then stored in the desiccators to cool at room temperature until the post-ignition weighing.

The samples kept in desiccators after drying are weighed again practically as soon as possible to avoid the re-hydration of the samples. Pour out the dried sample on butter paper and weigh. The difference between the weight of the powdered rock sample before and after the heating is observed which in turn called as Loss on Ignition (LOI) of sample. The formula used to calculate the LOI is:

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\text{%LOI} = 100 \times \frac{(\text{weight change during ignition})}{(\text{fresh sample weight})}
\]

It is necessary to keep all samples at temperature nearly 60º C during the loss on ignition procedure as the powdered rock samples as well as the sample containers (crucibles etc.) may absorb moisture from the laboratory air which may lead to error within calculations.

2.4 Analytical methods

2.4.1 Microscopic methods and modal mineral analysis

The identification of rock forming phases and their mutual relationship require rock thin sections study, which has been carried out in the present research work with the help of Polarising microscope of Nikon400 make for petrographic studies. The microscope is fitted with a camera attached with vario tube and unioocular phototube. Mineral assemblages and various optical properties such as colour, habit, texture, mineral relationship etc. of rock thin sections were studied under plane
polarized light and cross nicols under differential magnifications 10X, 40X, 50X, 100X, 200X and 500X, and the textural features of petrogenesis were documented.

Modal mineral analysis (volume %) is a quantitative expression of constituting mineral contents commonly used for classification of the plutonic igneous rocks. The modal mineral analysis was carried out on rock thin sections using James Swift electronic point counter (Modal F415C) attached with the petrographic microscope. Rock forming and accessory minerals observed in rock thin sections were counted with an average of ca 2000 counts per section. The estimation of modal volume percentage was also rechecked by conducting the modal analysis on two-three rock thin sections of rock samples so that the modal results can be reproduced within the range of ± 15 % particularly for the major constituting minerals.

2.4.2 Electron Probe Micro analysis (EPMA)

Major element concentrations of the mineral phases were obtained by wave length dispersive microprobe technique on optically studied and carbon coated polished thin sections (48×30×2 mm size of glass slide) of rock samples from each felsic unit. The carbon coating of polished rock thin sections provides better conductivity, where coating is used to be carried out by firing pointed carbon filaments in vacuum with an electric arc in pulses. The filaments should be cleaned by outgassing. The thickness of coated carbon layer over the polished section should be uniform between 10 nm and 20 nm and the coated sample should be stored in dehumidifier cabinet or evacuated bell jar. The mineral chemical analysis has been carried out with carbon coated thin sections using CAMECA-SX-100 with (name of software) at the Electron Micro Probe Analysis Laboratory of Wadia Institute of Himalayan Geology (WIHG), Dehradun. The mineral chemical data were obtained by running the probe at 15 kv accelerating voltage, 20 nA beam current, focused beam of diameter 0.5µm, and 10 seconds as integration time for all major elements. The following natural standard minerals were used for reference: P – apatite, Ca – wollastonite, B – barite, Cr – chromite, Mn – rhodonite, Fe – almandine, Na – jadite, Mg – diopside, Al – kyanite, Si – orthoclase, K – orthoclase, Ti – TiO₂, Zr – zircon. Methods involve point and / or transect analyses across plagioclase and point analyses across biotite, muscovite, hornblende, garnet, titanite and zircon.
2.4.3 X-ray Fluorescence Spectrometry (XRF)

The X-Ray Fluorescence technique has been used in determination of major oxides (\(\text{SiO}_2\), \(\text{TiO}_2\), \(\text{Al}_2\text{O}_3\), \(\text{CaO}\), \(\text{Fe}_2\text{O}_3\), \(\text{MgO}\), \(\text{MnO}\), \(\text{Na}_2\text{O}\), \(\text{K}_2\text{O}\) and \(\text{P}_2\text{O}_5\)) and six trace elements (\(\text{Rb}\), \(\text{Ba}\), \(\text{Sr}\), \(\text{Zr}\), \(\text{Y}\), \(\text{Nb}\)) with the help of energy dispersive SIEMENS SRS 3000 sequential X-ray fluorescence Spectrometer (XRF) at Wadia Institute of Himalayan Geology, Dehradun.

2.4.3.1 Pellet preparation

The sample is used in the form of pressed pellets of fine powder. The pressed pellets were prepared by homogenizing 10 g of the powder sample in agate mortar with a medium and adhesive. The well mixed powder samples were then kept under automatic hydraulic press (40 ton) for making pressed powder pellets. The pellets were kept in tray to dry under room temperature and the proper labeling had been marked over them with permanent marker.

2.4.3.2 Instrumental and operating parameters

The SIEMENS SRS 3000 sequential wavelength dispersive X-ray fluorescence Spectrometer is fitted with Rh X-ray tube and software which is operating under computer control using the Spectra AT/3000 software for data collection. The elemental analysis was performed using pressed powder pellets following intensity based model (Lucas-Tooth and Pyne, 1964) and using international reference materials. The operating conditions for major oxide were: No filter, Vacuum path, 20/40 Kv, and for trace elements: No filter, Vacuum path, 55/60 Kv. The overall accuracy (% RSD) for major oxide is less than 5% and that of trace elements is less than 12%, the average precision being better than 1.5% in all cases. The minimum detection limit for most of the trace element is ~5 ppm.

2.4.4 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
ICP-MS technique provides the lowest possible detection limit of most of the elements of periodic table. In present study a PerkinElmer SCIEX, Model ELAN® DRCII (US make instrument) ICP-Mass spectrometer was used to determine a set of fourteen rare earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and twenty trace (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, Cs, Hf, Ta, Pb, U, Th) elements at ICP-MS Laboratory of National Geophysical Research Institute (CSIR-NGRI), Hyderabad.

2.4.4.1 Material and reagents

In ICP-MS technique the rock sample selected for analysis are in digested solution form, which essentially requires the quality reagent, ultra purified water and thoroughly cleaned crucibles and glassware. Electronic grade HF, analytical reagent (AR) grade HClO₄, distilled HNO₃ and HCl are the chemical reagents which are being used during the sample preparation. Millipore purified water (18 MΩ) was used in all investigations. PTFE Teflon beakers are used for open digestion of powdered rock samples where the teflon beakers and other glassware are cleaned with 1%HCl and Millipore purified water.

2.4.4.2 Preparation of acid digested rock solutions

The samples were prepared using open acid digestion method followed by Balaram and Rao (2003) and Roy et al (2007). The sample preparation has been done in following steps:

- Weigh 0.05 g of -200 mesh size powdered rock sample with the help of electronic balance on butter paper, where the weighing is done up to four decimal points. For making the solution, 0.05 gm of each powdered rock sample was weighed.
- Transfer the weighed sample into ultra cleaned and thoroughly dried PTFE Teflon beakers and moistened it with a few drops of ultra pure water. Label each beaker carefully.
- Add 10 ml of an acid mixture of HF, HNO₃ and HClO₄ in the ratio of 7:3:1 to each sample in Teflon beaker and swirl until sample get completely moist.
• Add 1ml of 5 µg ml⁻¹ of Rh solution to act as internal standard in the beakers, cover it with lid and keep overnight for digestion.
• Next day heat the beakers on a hot plate at 200° C after removing the lids in fume hood chamber for about 1 hours, let it evaporate until a crust or crystalline paste is obtained.
• Dissolve the crust contents of beaker with 10 ml of 1:1 HNO₃ solution and keep on the hot plate for 10 minutes with moderate heat of ~70° C. Dissolve until all suspended particles come in solution.
• Makeup solution up to 250 ml volume with purified water in a cylindrical flask.
• Keep sample in ultra cleaned polythene sample bottles for analysis with proper labeling.

2.4.4.3 Instrumental and operating parameters

Instrumental parameters

RF power – 1100 W; Argon gas flow in (i) Nebuliser – 0.86 l/min (ii) auxillary – 1.20 l/min (iii) plasma 15 l/min; Lens voltage – 5 V; sample uptake rate – 0.80 ml/min.

Acquisition parameters

Measuring mod – peak hopping; point per peak – 1; number of sweeps – 50; dwell time – 50 µs; integration time – 2500 ms; replicates – 3, internal standard – ¹⁰³Rh at an overall concentration of 20 ng/ml.

Japanese rock reference standards (JG-2, JG-1a) for granitoids were used to minimize the matrix effects. The acid digested rock solutions were used in analysis where sample introduction system in the instrument is consisted of a standard Meinhard nebulizer with a cyclonic spray chamber. All quantitative measurements were performed using instrument software.

2.4.5 Laser Ablation - Multi Collector - Induced Coupled Plasma Mass Spectrometer (LA-MC-ICPMS)

Three kilogram of rock samples, each from GGn and HBG, were crushed and sieved on a desired sized. Zircons were separated from crushed rock samples using conventional methods of magnetic separation and heavy liquid bromoform techniques
at Institute Instrumental Centre of Indian Institute of Technology (IIC-IIT), Roorkee. Zircons were manually hand-picked from the heavy and non-magnetic fractions of the samples, under the binocular microscope. Zircons were recovered in a good quantity (few hundred grains) from both the samples. Zircons in HBG are perfect euhedral and small in size, transparent and dirty in nature whereas zircons in GGn are euhedral to subhedral. The separated zircons were mounted on epoxy resin along with the standard zircons separated from GJ-1. Zircons from known and unknown samples were analysed for the simultaneous determination of U-Pb-Lu-Hf isotopes using LA-MC-ICPMS instrument at Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, P. R. China. Standard zircons were analysed after every four analysis of unknown zircons, and even standard zircons were also occasionally treated as unknown. Sixty-six spot analysis of GJ-1 zircons have yield a weighted $^{206}\text{Pb}/^{238}\text{U}$ age of 608±3.9 Ma (MSWD = 0.029; n = 66). The LA-MC-ICPMS is an assembly of Agilent 7500a quadruple (Q)-ICPMS and Neptune multi-collector (MC)-ICPMS with a 193 nm excimer ArF laser-ablation system (GeoLas Plus) appropriate for analyzing zircon U-Pb age, trace elements and Lu-Hf isotopes simultaneously. The detailed analytical methods and principles of U-Pb-Lu-Hf isotopic determinations are described by Xie et al., (2008) and Ji et al. (2009).

2.4.6 Software and rockware

Plethora’s of software are also available in geological science to keep and analyze properly the field as well as analytical database. In field of mineralogy and geochemistry various softwares are in common use to organize, calculate and plot in desired manner. In present study the field data has been further analyzed and represented with the help some GIS softwares like google earth 6.1 and global mapper12 version along with MS-Excel spreadsheet where large MS data along with the location details have been handled. Geological maps and diagrams were digitized using Surfer 9.0 version, and some figures were reframed using Corel 13 for improved presentation. For calculating and plotting the microprobe data of biotite and muscovite MS-DOS based bioterm (Yavuz and Öztas, 1997), limica (Yavuz, 2001), and mica+ 1.0 version (Yavuz, 2003) have been used where as classification of tourmaline of granitoid samples has been done by MS-DOS based programme tourmal (Yavuz, 1997). Amphibole has been studied with the help of programme amph (Yavuz, 1999)
where as feldspar composition has been calculated with *atomic formula unit programe* an excel-based spreadsheet MS-dos based *cryschem*, while several ternary plots of these minerals have been done by *statsicsta 6*. These programmes are commonly used to store data, recalculate structural formula, end-members, empirical calculations of some parameters and minerals’ variations. Intensive variables of the granitoids have also been estimated where *solvcalc 2.0* has been used for two-feldspar thermometry and menu driven *hornblende-plagioclase* barometry to estimate the pressure. Various modules of NEWPET (Daryl Clarke, 1994) and *Petrograph 2beta* (Petrelli, 2007) softwares were utilized for handling the whole-rock geochemical database, and for generating binary and ternary variation diagrams, tectonic discriminations and mesonorms and their listings, and normalized trace and REE spidergrams. The CIPW normative minerals were calculated using *sinclas* (Verma et al., 2002) programme, which calculates the standard igneous norms based on Fe₂O₃/FeO ratios as per total alkali silica (TAS) classification of igneous rocks (Middlemost, 1989). The geochemical modeling of the various felsic lithounits has been done with the help of geochemical modeling programmes such as *GPP* and *Petrograph 2beta* (Petrelli, 2007). The weighted means U-Pb ages and Concordia diagrams were constructed using *Isoplot 3.0* (Ludwing, 2003). Geochemical databases were also processed for various purposes using spreadsheet (*MS Excel, Lotus 1-2-3*). Text and tables are processed and edited on *MS Word-2007*. The standard symbols for various minerals were used according to Kretz (1983). The computer-generated figures and calculated results were always crosschecked manually following the principles and methods of programme theories.