CHAPTER 3

SAMPLING METHODS AND GEOCHEMICAL ANALYSIS

3.1 Introduction

A description of sampling procedures, analytical methods including instrumental techniques and laboratory procedures followed in the present study are presented in the present chapter.

3.2 Sampling procedures

More than 80 fresh rocks samples representative of various formations were collected from quarries, road cutting, and natural outcrops. After careful examination, 28 representative samples of quartzites (meta-arenites) and 24 samples of metapelites devoid of weathering and alteration were selected for geochemical analysis. Samples were manually chipped into 1-2 cm pieces, removing deleterious material including weathered surfaces and veins.

The chipped samples were washed repeatedly in distilled water to remove surface dust and oven- dried at $110°$ C for 24 hour prior to milling. All samples were ground to 200 mesh in agate pulverizer, maintaining the homogeneity and representativeness of the sample. Loss on ignition (LOI) values were determined by ignition in a muffle furnace at $1020°$ C. Major elements were determined by XRF (X-Ray fluorescence) techniques in the geochemical laboratory of Wadia Institute of Himalayan Geology (WIHG), Dehradun. The REE analyses were carried out at the National Geophysical Research Institute, Hyderabad by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Roy et al., 2007). International rock standards SCo-1 and GSR-4 were also analyzed and the results agree with the reported values (Govindraju 1994).

3.3 X-Ray Fluorescence Spectrometry

X-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It works on wavelength-dispersive spectroscopic principles. X-ray fluorescence analysis is a widely accepted technique for obtaining rapid chemical analyses of geologic samples with higher precision and accuracy. The pellets prepared were analyzed for major oxide concentration and trace elemental concentration with the help of energy dispersive SIEMENS SRS sequential XRF.

3.3.1 Pellets preparation

The sample is used in the form of pressed pallets of fine powder. To prepare pellets, collapsible aluminum cups were filled with a form of boric acid that acts as a binding material. Powdered sample were roasted at 1000 °C for about 14 hrs. Approximately 10 gm of 200 mesh homogenized sample of each roasted powder was sprayed upon it by uniformly covering the boric acid. Then about 15 tons of pressure was applied using press (H/100) to obtain 40 mm diameter pellets.

3.3.2 Instrumental and operating parameters

The SIEMENS SRS sequential wave length dispersive X- ray Fluorescence Spectrometer is fitted with Rh X- ray tube and software which is operative 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 oxides were no filter, Vacuum path,

20/40 KV. The overall accuracy (% RSD) for major oxides is less than 5 % and the average precision being better than 1.5 %.

3.4 ICP-MS: Inductively Coupled Plasma Spectrometry

The ICP-MS is one of the most advanced analytical techniques employed for quantitative analysis of chemical elements with atomic mass ranges 7 to 250. This encompasses Li to U in the periodic table in a variety of samples. Some masses are prohibited such as 40 due to the abundance of argon in the sample. A typical ICP-MS will be able to detect in the region of nanograms per liter to 10 or 100 milligrams per liter or around 8 orders of magnitude of concentration units. Since the last two decades it has become a powerful technique for estimation of trace, REEs, PGEs and even isotope ratios in a variety of geological materials. Unlike atomic absorption spectroscopy, which can only measure a single element at a time, ICP-MS has the capability to scan for all elements simultaneously. This allows rapid sample processing.

3.4.1 Principle of ICP-MS

The ICP-MS is the most simple and direct method of chemical analysis. The sample to be analyzed is introduced into argon based high temperature plasma by a nebulizer spray chamber system. The sample stream causes desolvation, vaporization, atomization and ionization of target elements. Ions thus generated are extracted from the plasma into a low pressure region through a sampler and skimmer cones and are allowed to pass through an electrostatic lens system, which extracts positively charged ions. These ions are separated on the basis of their mass to change ratio by quadrupole mass analyzer. A detector counts the filtered ions and a computer processes the

resulting information. ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICP-AES), including:

> Detection limits for most elements equal to or better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).

> Higher throughout than GF AAS.

> The ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source.

> Superior detection capability to ICP-AES with the same sample throughput.

> The ability to obtain isotopic information.

In the present work ICP-Mass Spectrometer, Model ELAN DRC II (Perkin-Elmer Science Instrument, US) was used. The analytical work was carried out in ICP-MS Lab, Geochemistry Division, National Geophysical Research Institute (NGRI) of Council of Scientific and Industrial Research (CSIR), Hyderabad.

3.4.2 Geological Application

The precise and accurate determinations of trace and REEs in geological samples are important to understand the evolution of the rock and to quantify the processes, which have taken place in the rock history. ICP-MS has proved to be extremely sensitive for the accurate and precise estimation of the trace elements including REE. The isotopic ratio determination in geological samples is useful to date a rock and to understand the process during evolution. Though, ICP-MS permits

accurate determination of isotope ratios, it cannot attain the precision of Thermal Ionization Mass Spectrometry (TIMS).

3.4.3 Materials and reagents

In ICP-MS techniques the rock samples selected for analysis are digested to solution form which essentially requires the quality reagents, ultra purified water and thoroughly cleaned crucibles and glassware. Electronic grade HF, analytical reagents (AR) grade $HClO_4$, distilled HNO_3 and HCl are the chemical reagents which are being used during the sample preparation. Millipore purified water (18 MΩ) was used. PTFE Teflon beakers were used for open digestion of powdered rock samples.

3.4.4 Sample Preparation of ICP-MS

For dissolving silicate rocks, acid digestion is the most widely used method in geochemical analysis using ICP techniques. In this procedure the silica vaporizes when it is attacked by acids such as Hydrofluoric acid (HF), Nitric acid (HNO_3), Perchloric acid ($HClO_4$) and Hydrochloric acid (HCl).

A test portion (0.05 g) of the sample was added to PTEE Teflon beakers. Each sample was moistened with few drops of ultrapure water. Then 10 ml of an acid mixture containing 7:3:1 HF – HNO_3 – $HClO_4$ was added to each sample. Samples were swirled until they become completely moist. The beaker were then covered with lids and kept overnight for digestion after adding 1 ml of 5 μg ml^{-1} Rhodium (Rh) solution (it act as internal standard). The following day, the beakers were heated on a hot plate at ~ 200 °C for about 1 hour. The lids were removed and the contents were evaporated to incipient dryness until a crystalline paste was obtained. The remaining residues were then dissolved using 10 ml to 1:1 HNO_3 and kept on a hot plate for 10

minutes with gentle heat (70 °C) to dissolve all suspended particles. Finally the volume was made up to 250 ml with purified water (18 MΩ) and stored in polythene bottles.

3.5 LOI (Loss on Ignition)

Loss on ignition refers to the weight loss experienced by a sample when it is placed in a furnace at a specific temperature and for a specific time period. It is used to give a general indication of the "volatile" species in the sample.

The LOI's are generally carried out at a temperature range of 850 °C – 950 °C for one hour to 90 minutes, so the weight loss reflects all of those species that are lost at this temperature and for that particular time period. It would include water (both surficial moisture as well as water of crystallization) and organic carbon species if present. In addition, carbonates decompose to oxides with the loss of carbon dioxide and sulphates decompose (but usually only partially) to oxides with .the loss of sulphur trioxide. Fluorides may also be partially lost. As a result of the complex nature of these reactions, the LOI value is best used as a general indicator of the amount of volatile species present and the post crystallization degree of alteration/hydration of the sample. It cannot be used to determine the presence of individual species. Some base metals will also be lost in this process.

3.5.1 Procedure followed for calculating the Loss on Ignition

1. Start the digital Weighing machine and let it stabilize for an hour or so, so that it equilibrates with the surrounding conditions and then set it zero.

2. Weigh the silica crucible (W_1) and note down the reading on the weighing machine.

3. Now add 2gm of the powdered rock sample very carefully into the crucible without the weighing machine after step 2 and note down the reading machine (W_2). W_2 should be approximately W1 + 2gms.

4. Repeat the same for all the samples. And store them in desiccators to avoid any moisture entering the sample.

5. Dry crucible + sample in oven (preferably 105 °C overnight).

6. Cool crucible in desiccators and reweigh (W_2).

7. Place crucible onto the furnace tray and put tray into furnace at 500 °C and leave for 4 hours.

8. Using a special tool, the crucible is then extracted from the furnace tray and then placed it over the asbestos sheet for initial cooling for 5 minutes, before placing crucibles in a desiccators to fully cool.

9. Reweigh crucible + ash (W_3).

Calculation: **Loss on Ignition (LOI) = [(W2 – W3)/ (W2-W1)] * 100**