CHAPTER VII

TECHNIQUES DEPLOYED FOR GEOCHEMICAL ANALYSIS

7.1 INTRODUCTION:

Major trace and REE of the sand size matrix of quartz pebble conglomerate, quartzite and the matrix of Kaldurga polymictic conglomerate, were determined by AAS, UV-visible spectrophotometer, XRF and ICP-MS at Geochemistry Division of National Geophysical Research Institute, Hyderabad, India. Mineral chemistry of a few feldspar minerals was also determined by EPMA at the same laboratory, whereas sulphur isotopes of pyrites separated from QPC, got analysed at Atomic Mineral Division, Atomic Energy Department, Hyderabad. The details of the analytical procedure, sampling techniques, accuracy and repeatability of the data, are discussed below.

7.2 SAMPLING:

In all 160 samples of quartz pebble conglomerate, quartzites and the matrix of the Kaldurga Conglomerate were collected from various localities. Extreme caution were taken to collect the fresh samples which have not been affected by alteration or metasomatism. A great difficulty was faced in order to collect the fresh samples from the horizon of quartz pebble conglomerate. The abundance of sulphide minerals, especially pyrite, in the matrix of quartz pebble conglomerate was the main cause for its susceptibility to chemical weathering. Hence, the subsurface fresh samples, were obtained after trenching. In the Kaldurga
Conglomerate, matrix rich samples were collected. For chemical analysis, 30 samples of quartz pebble conglomerate, 10 samples of quartzite and 49 samples of the matrix of the Kaldurga Conglomerate were selected on the basis of detailed petrographic study of thin sections. Quartzites samples were directly crushed to granules and then powdered to -200 mesh in a tungsten-carbide Herzog ring grinder. However, in case of quartz pebble conglomerate and the Kaldurga Conglomerate, fine clasts were removed by hand chipping and then the matrix was pulverized to -200 mesh in the same grinding machine. Pyrite was also separated from the matrix of quartz pebble conglomerate. For separation of pyrite the crushed matrix was sieved to -60 to -120 BSS mesh size and then washed and dried. Finally, monomineralic concentration i.e. pyrite was achieved by hand picking under a Leitz binocular microscope.

A few selected major elements of the matrix of quartz pebble conglomerate and quartzites were determined by UV-visible spectrophotometer and Atomic Absorption Spectrometer (AAS), whereas all the 10 major elements of the matrix of the Kaldurga Conglomerate were analysed by XRF. Trace and REEs including Th and U of all the samples, including pyrite samples (10) were analysed by ICP-MS. Sulphur isotopic ($\delta^{34}S$) data were generated by mass spectrometer.

7.3 SAMPLE PREPARATION FOR THE WET CHEMICAL ANALYSIS ON UVS, AAS AND ICP-MS:
7.3.1. **Solution A:**

The finely (-200) mesh powdered sample of weight 0.1 gm was fused with 15-20 pellets of sodium hydroxide in a nickel crucible. This was dissolved in 20 ml of 1:1 HCl and heated for about half an hour till a clear solution was obtained and then was made to one liter after complete cooling (Shapiro, 1975). It was used for the determination of Al$_2$O$_3$ in QPC and quartzites.

7.3.2 **Solution B:**

The 0.5 gm of the powdered sample was taken into teflon beaker of 100 ml capacity with 20-30 ml of Hydrofluoric acid (98%) and 5-6 drops of conc. H$_2$SO$_4$. The beaker was heated on steam bath till the sample was completely dried. Afterwards 10 ml of 1:1 HNO$_3$ acid was added and the contents were heated again till a clear solution was obtained. This was then made to 250 ml. This solution was used for the determination of K$_2$O, Fe$_2$O$_3$(T), MgO concentration in QPC and quartzite.

7.3.3 **Solution for ICP-MS:**

0.1 gm of sample was taken in a teflon beaker with 7 ml of HF (48%, EI grade) and 3 ml of conc. HNO$_3$. This mixture was digested by keeping the beaker over hot plate. After complete, digestion, 10 ml of HNO$_3$ of 1:1 concentration was added and further kept on hot plate till a clear solution is obtained. When solution was cooled down volume was made to 100 ml with double distilled water after adding 100 ml of 1 ppm Indium solution as an internal standard and finally stored in a 100 ml corning (Potts, 1987).
However, it was difficult to get the matrix of quartz pebble conglomerate and quartzite samples dissolved into the solution by the aforesaid method. The mere presence of rutile and zircon was making the sample resistent to go into solution completely. For such samples teflon bomb technique was used. In the method 0.1 gm of rock powder was transferred to a teflon bomb with 4 ml of HNO$_3$ (conc.), 1.0 ml of HClO$_4$ (60%) and 6 ml. of HF (48% EI grade). After sealing, the teflon bomb was kept in an oven for about 3 hours at 140°C. After the removal from oven, bomb was let to cool down at room temp. then unscrewed the bomb, and again kept on heating on hot plate at 140°C to get the complete dryness. Afterwards the same procedures were followed to make the volume as described in previous paragraph. This solution was used for all 18 trace elements (including Th and U) and REE concentration of the matrix of QPC, quartzite and the KCM.

7.4 UV-SPECTROPHOTOMETER (UVS):

A Shimadzu double beam spectrophotometer model UV-190 was used for Al$_2$O$_3$ and Fe$_2$O$_3$ (t) determinations for the matrix of quartz pebble conglomerate and quartzite samples. The instrument comprises of tungsten lamp for radiation in visible range and a deuterium lamp for ultraviolet radiations. Both the lamps cover a complete range of wavelengths suitable for elements analysed. Absorbance/concentrations of standards and samples were measured under identical conditions (Potts, 1987).

7.5 ATOMIC ABSORPTION SPECTROPHOTOMETER (AAS):

A Varian-Techtron model AA6(D) atomic absorption
spectrophotometer was used for determining other major elements. It has a modulated hollow cathode lamp for obtaining radiation of suitable frequency which is characteristic of the element to be estimated, and a burner assembly where the sample solution is aspirated through a nebuliser resulting in atomization of the sample. The emergent flame in the burner assembly enters a monochromator where the isolation of the required spectral line is achieved. A photomultiplier is used to amplify and convert the signal to a digital readout of the absorbance. Absorbance is measured in a series of natural rock and synthetic standard solutions along with the unknown samples. The concentration of various major elements, in the form of their oxides in the unknown solutions is then measured in comparison with the standards. For detail procedure please refer to Naqvi et al. (1980) and Balaram et al. (1990). The precision and accuracy of different methods is better than ±5% for most of the major elements.

7.6 **INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETER (ICP-MS):**

The concentration of 18 trace elements and all 14 rare earth elements in the matrix of QPC, quartzite, pyrite (separated from QPC) and the KCM, were determined by an inductively coupled plasma mass spectrometer (VG Plasma Quad ICP-MS). The instrument mainly comprises the following three components:

1. A standard inductively coupled plasma torch (Fassel-type)
consists of nebuliser, spray chamber, work coil and associated power supply from 2.5 KW, 271.2 MHz, RF generator which is the same as that commonly used in optical spectrometers. This torch is mounted horizontally and linked with a water cooled glass spray chamber and a Meinhard concentric nebuliser.

ii. A quadrupole mass filter and associated data collection electronics which permits rapid scanning of selected mass range between 0-300 amu.

iii. An interface unit consisting of two water cooled nickel cones each containing a small orifice at the centre, which permits sampling of the plasma gases and transfer of the ions beam into the mass spectrometer. The ion detection and data acquisition system consists of a channeltron-type electron multiplier and multichannel analyser. An IEEE 488 data base allows the transfer of data to a central control computer. An outline IBM PC/XT microcomputer facilitates data acquisition, processing and storage.

After minimising the signal on $^{115}\text{In}$ in the single ion mode, the system is operated on a mass scanning mode in the mass range m/z 45-228 covering 18 trace elements (including Th and U) and all the 14 REE as well as the internal standard (Indium). Detection limit is calculated using the count rate obtained on the 0.1% solution of the standards.

Elemental concentration for the standard reference rocks such as SY-2, BCR-1 and MRG-1 using two standard curves, are in good
agreement. Precision is better than 5% RSD (relative standard deviation) for all the elements (Balaram et al. 1990). Other details are as given in Balaram et al., (1990).

The operating parameters of the instrument are as detailed below:

1. **Plasma**:
   - Power = 1.35 KW
   - Nebulizer gas = 0.75 lit/min
   - Aux. flow rate = 0.5 lit/min
   - Coolant flow rate = 13 lit/min
   - Sample intake rate = 1 ml/min

2. **MS conditions**:
   - Vacuum stage 1 - <2.5 mbar
   - Vacuum stage 2 - <10\(^{-4}\) mbar
   - Vacuum stage 3 - <2.10\(^{-6}\) mbar

3. **Scan conditions**:
   - Mass range = 113-179 amu
   - Number of scan = 120
   - Dwell time/channel = 500 s
   - Number of channels used = 2048

7.7 **X-RAY FLUORESCENCE: SAMPLE PREPARATION**:

The ~200 mesh sample powder of the matrix of Kaldurga Conglomerate was used to prepare pellets. For determining major elements, the rock sample powder was fused at ~1200°C with lithium
tetraborate-metaborate flux with lithium carbonate added to bring
down the melting point of the flux. The sample was fused in 5%
gold-platinum crucibles using Herzog automatic fusing machine.
Sample to flux ratio was kept at 1:10 with a total weight of 10
gms having 1.0 gm of sample weight, 7.5 gm of flux and 1.5 gm
weight of Li$_2$CO$_3$. It has given pellets of 40 mm diameter.

7.7.1. X-Ray Fluorescence Spectrophotometer (XRF):

The Phillips PW-1400 microprocessor controlled, sequential
XRF with 100 KVA. X-ray generator and 72 position automatic
sample changer to load and unload, coupled to a Phillips P-851
online dedicated computer was used for calibration of regression
analysis. Japanese, Canadian and East-German standards were used
for calibration of curves. The procedure followed has an online
computer programming for dead time correction, background line
overlapping and matrix effect and gives output directly as
concentrations in percent or ppm from calibration curves. A
spinner was used to spin the sample inside the spectrometer while
measuring the counts to remove sample heterogeneity, if any. A 33
mm primary beam aperture mark was used to restrict the X-ray beam
only to the sample surface. Flow and scintillating detectors were
used for counting the X-rays, pulse height discriminator and the
fine collimator account for greater sensitivity of the data.

CT-1A, JGB-1, JB-2, BHVO-1, GSR-2, DR-N international
standards were used to calibrate the major elements data for the
matrix of the Kaldurga Conglomerate. The precision and accuracy,
reproducibility and the standard deviation from the above
mentioned is less than ±5% (Govil, 1985).

7.8 **ELECTRON PROBE MICRO ANALYSER (EPMA):**

7.8.1. **Slide Preparation:**

Doubly polished sample thin sections of 0.03 mm thickness were got prepared on 46 mm long glass slides without the coverslip. A coating of carbon of about 150Å units thickness was given by the carbon evaporation technique in a Hindivac Shadow Casting Unit at 10⁻⁶ Torr for obtaining uniform electrical conductivity.

7.8.2. **Instrumentation:**

To determine the species of plagioclase, present in the matrix of the Kaldurga Conglomerate, mineral composition was analysed by using a wavelength Dispersive Cameca make Camebax-Micro EPMA. The electronic microprobe consists of three fully focussed spectrometer (2 vertical and 1 inclined). The operating conditions were 15 KV accelerating voltage, 4.2 nA sample current, 20 seconds counting time with a beam diameter of 1-3 mm. ZAF corrections, suing the method of Bence and Albee (1968) were applied with the help of the PDP 11/03 computer. Analytical concentrations in the form of oxides wt. % were derived by applying intensity data of samples to a calibration curve established from intensity data of the standards. Precision was of the order of ±0.5-2.0% of the amount for major constituents. The following natural mineral standards were used, at wavelengths suitable for the corresponding element analysis:
<table>
<thead>
<tr>
<th>Element</th>
<th>Standards</th>
<th>Wavelength</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>Albite</td>
<td>46363</td>
<td>TAP</td>
</tr>
<tr>
<td>K₂O</td>
<td>Orthoclase</td>
<td>42765</td>
<td>PET</td>
</tr>
</tbody>
</table>