8.1 **Sampling and Sample Selection**

Sampling of BIF was mainly dependent on the availability of the open cast mines, exploration pits and fresh outcrops. Total 200 samples of BIF, basic and acid volcanics were collected from various localities for geochemical studies. Absolutely fresh BIF samples were collected from Hiremagi-Ramthal and Aihole-Sulebhavi Iron Ore Mines. Basic volcanics were collected from the hill tops near Kyadaguppi and Mulur. Acid volcanics were collected from road cuttings and nearby exposures around Kalarhatti and Mulur.

8.2 **Sample Preparation and Analytical Techniques**

Sample preparation and geochemical analysis of the samples were carried out at the Geochemical Laboratories of the National Geophysical Research Institute, Hyderabad. For chemical analysis, about 1000 gm of each rock sample was crushed into gravel-size bits using a hammer. A coarse fraction of about 250 gm was obtained by coning and quartering. These fractions were then crushed to -200 mesh size using a Herzog Swing-Grinding Mill with grinding tools made up of tungsten carbide. For BIF, stainless steel grinding tools were used. Special care was taken in cleaning the jaw crushe and the tungsten carbide/stainless steel mortar by using high purity silica sand followed by crushing a dummy sample to avoid contamination. For determination of oxygen isotopes in BIF, the iron oxide and chert band were slowly chipped.
off, and from each iron oxide and chert rich fraction, iron oxide and chert were hand picked and their degree of purity was confirmed by examining each grain under Leitz binocular microscope. Iron oxide and chert were powdered in agate mortar. Due to the fine grained nature of hematite absolutely pure chert could not be obtained. The Fe$_2$O$_3$ impurities in chert layers were also estimated by XRF.

The major and a few selected trace elements were estimated by X-ray Fluorescence Spectrometer (XRF). The trace element analysis was carried out on Atomic Absorption Spectrometer (AAS) and Inductively Coupled Plasma Mass Spectrometer (ICP-MS) while rare earth concentrations were determined by ICP-MS. Mineral compositions of coexisting phases were determined by Electron Probe Micro analyser (EPMA). Mineralogical study of SBIF was done on XRD. Oxygen isotopic study was carried out on a VG Mass Spectrometer. FeO was determined by titration method.

8.3 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)

8.3.1 Sample Preparation

0.1 gm of the sample powder was weighed accurately and placed in Teflon beakers with light lids. To each sample, 3 ml concentrated nitric acid (HNO$_3$) and 7 ml Hydrofluoric acid (HF) were added. The teflon beakers were placed in an oven for four hours at 40°C. Then the lids were removed and the beakers were placed on hot plate at a temperature of 110°C till the solution evaporated to dryness. The residue was dissolved in 10 ml of nitric acid and double distilled water (1:1). Then, 0.1% rock solutions were prepared with an overall concentration of 100 gm/ml
of indium, which serves as an internal standard. This solution was used for estimation of all 18 trace elements (including Th and U) and REE concentration.

8.3.2 Instrumentation

The instrument consists mainly of a standard inductively coupled plasma torch (Fassel-type), a quadrupole mass filter and an interface unit consisting of two water cooled nickel cones.

After minimising the signal on $^{115}$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), all the 14 REE and the internal standard (indium). Detection limit is calculated using the count rate obtained on the 0.1% solution of the standards.

Operating conditions are as follows:

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

2. **MS Conditions**:
   - Vacuum stage 1 = $<2.5$ m bar
   - Vacuum stage 2 = $<10^{-4}$ m bar
   - Vacuum stage 3 = $<2.10^{-6}$ m bar

3. **Scan Conditions**:
   - Mass range = 113-179 amu
   - Number of scans = 120
Dwell time/channel = 500 µs
Number of channels used = 2048

8.3.3 Operating Conditions

Sample solutions were introduced into the ICP with the help of a nebulizer at the rate of 1 ml/min, where the sample is heated to 8000 K and the dissolved solids are vapourised, atomised as well as ionised with a fraction of the ions getting pumped through the interface. While passing through the interface the gases expand adiabatically and are then introduced into the quadrupole mass filters, where an ion beam passes through the skimmer cones as well as a number of plates at appropriate potentials. Electrostatic fields created by these plates focus the ion beam into a form suitable for transmission through the mass filters. There is a linear relationship between the ion beam and the concentration of elements and the resultant signals are converted into concentrations by using an online IBM PC/XT microcomputer.

Elemental concentration for the standard reference rocks such as FER-1, FER-2, FER-3, FER-4, IF-G, GSR-5, SCo-1, JR-1, JR-2, JG-2, BR and JB-la are in good agreement with reported values. Precision is better than 5% RSD (Relative Standard Deviation). For detailed procedure and accuracy, see Balaram et al. (1988, 1990).

8.4 X-Ray Fluorescence

8.4.1 Sample Preparation

Two types of sample pellets in the form of (A) fused beads and (B) pressed discs were prepared. The procedure adopted are as follows:
(A) **Fused Pellet (beads)**

0.5 gm of -200 mesh sample powder was thoroughly mixed with 2.5 gm of flux (lithium tetraborate + lithium metaborate + lanthanum oxide in the ratio of 6:3:1) in a platinum gold crucible (Pt : Au :: 95:5) and heated for about 20 minutes in a Herzog automatic fusion machine (HAG 12/1500) at 1200°C. The crucible containing the sample and flux was tilted bothways with the help of a built in rocking device for 10 minutes, while heating was on, in the fusion chamber (a) to remove air bubbles and (b) also to obtain a homogenous melt. The crucible containing the melt was cooled gradually by exposing it to a flow of filtered air and vacuum suction simultaneously. The resultant pellet was of 31 mm diameter. Pellets prepared by this fusion technique were used to estimate the major elements in the samples except for Na₂O because lanthanum oxide present in the flux interferes with Na₂O. Therefore pressed pellets were used to estimate the sodium content, flux to sample ratio was changed from 1:2 in acidic samples to 1:5 in basic samples.

(B) **Pressed Pellet**

Collapsible aluminium cups were filled with 9 gm of boric acid which acts as binding material. 1 gm of -200 mesh sample powder was sprayed on it, uniformly covering the boric acid and about 15 tonnes of pressure was applied using a Herzog hydraulic press (H/100) to obtain a 40 mm diameter pellet. Such pellets were used to estimate Na₂O as well as the trace elements Zr, Y, Sr, Rb, Ba and V.
8.4.2 **Instrumentation**

Philips PW 1400 microprocessor controlled wavelength dispersive, sequential X-ray fluorescence spectrometer (Philips, Holland) with 100 KvA X-ray generator was used for analysis. It also incorporates a 72 position automatic sample changer for loading and unloading of sample pellets and has a four position internal sample turret, in which four samples can be loaded at a time. A Philips model P851 on line, dedicated computer was used to prepare calibration curves relating the concentration and intensity levels in standards as well as the unknown samples after due matrix corrections.

Software available in the computer is able to take care of dead time, background and line overlap corrections giving the output directly as concentration in oxide weight percentages or in ppm as required, after converting the counts into concentration with the help of the calibration curves. There is also a provision for calculating correction factors such as the intensity based corrections on the Lucas-Tooth-Pyne model and concentration based corrections on the DeJong and Resberry-Heinrich models. Reference iron ore standards prepared by the Geological Survey of Canada samples analysed by different methods at the Kudremukh Iron Company, Karnataka were used to prepare calibration curves for major element data of BIF. JR-1, JG-2, JG-1a, GSR-4, Cr-1a, CT-1A, JB-1a, JB-2, JA-1, JGb-1, GSR-3, GSR-5 and JB-3 standards were used to calibrate the major elements data for acid volcanics granites, basic volcanics and shales. For trace element analysis a series of synthetic standards were prepared besides using
reference standards from Canada to build the calibration curves (Govil and Gnaneshwar Rao, 1991). The major element data estimated by XRF are reproducible with a precision range of $\pm 1\%$ and for the trace elements it is $\pm 5\%$ (Govil, 1985).

8.4.3 Operating Conditions

A spinner was used to spin the samples inside the spectrometer while measuring, to obtain uniform counts. Certain elements were analysed by using a Rhodium target X-ray tube while Na, Al and Mg were estimated by a Chromium X-ray target tube since the concentration levels of these elements were very low. $P_{10} (90\% \text{Ar} + 10\% \text{CH}_4)$ gas was pumped in the flow proportional counter for ionisation and a polypropylene counter window of 1 $\mu$m was used. All the elements were estimated under vacuum media (20 pascal units).

8.5 Electron Probe Micro Analysis

8.5.1 Slide Preparation

Doubly polished sample thin sections of 0.03 mm thickness were prepared on 46 mm long glass slides without the cover slip by grinding and polishing moderately thin slabs of the rock samples using chromium and aluminium oxide powders on a glass plate as well as a metal disc covered with chamois leather. Carbon coating of 150$^\circ$A units thickness was given to the sample by the carbon evaporation technique in a Hindivac Shadow Casting Unit at $10^{-6}$ Torr vacuum for obtaining uniform electrical conductivity.
8.5.2 Instrumentation

To determine the composition of minerals and estimation of P-T-t conditions, "CAMEBAX-MICRO" (Cameca, France) electron probe was used. The electron microprobe consists of three fully focussing spectrometers (two vertical and one inclined). It has a central gun column housing the inverted 'V' shaped tungsten filament (source of the electron beam) and the Wehnelt, the anode and the electromagnetic lenses which control the size and the shape of the electron beam on its way to the sample surface. There is a co-axial binocular microscope to bring the sample into the field of view. A sample chamber with a movable stage which can take samples either as thin sections or as mounted discs is an integral part of this instrument.

8.5.3 Operating Conditions

The operating conditions were 15 KV accelerating voltage 4.2 nA sample current, 20 seconds counting time with a beam diameter of 1-3 µm. The corrections, using the method of Henoc and Maurice (1978) were applied with the help of the PDP 11/03 computer. Analytical concentrations in the form of oxide 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.

Following elemental and synthetic standards were used for corresponding elemental analysis at suitable wavelengths:

<table>
<thead>
<tr>
<th>Elements</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>
CaO       Wollastonite          38387          PET
SiO₂       Wollastonite        27737          TAP
MgO        MgO*                38499          TAP
Al₂O₃      Al₂O₃*              32463          TAP
Cr₂O₃      Cr₂O₃*              56866          LIF
MnO        MnTiO₃*             52200          LIF
TiO₂       MnTiO₃*             31416          PET
FeO(t)     Fe₂O₃               48083          LIF
BaO        Barite              31730          PET

* = Synthetic standards

8.6 X-Ray Diffraction Analysis (XRD)

XRD study of SBIF was carried out at Indian Institute of Chemical Technology, Hyderabad. Minerals were analysed on a Phillips X-ray diffractometer (PW 1730/PW-1390) with a proportional counter using Ni-filtered Cu-Kα radiation (λ = 1.5416 Å) with 40 KV and 20 mA. The chart speed was 1-2 cm/min and the goniometer speed was 1°/minute.

8.7 Stable Isotope Mass Spectrometry

The fluorinating line for extraction of oxygen from silicates and oxides is similar to that designed by Clayton and Mayeda (1963) with a minor modifications (Das Sharma et al., 1993). A typical sample run is made as follows: Previously deccicated sample is weighed (3-8 mg) and loaded quickly in the nickel reaction vessel in an atmosphere of argon. The argon present in the vessel prevents any contamination of atmospheric oxygen or moisture during sample loading. The line is evacuated slowly with rotary and diffusion pump combination. The loaded sample is
heated to about 150-200°C for two hours during pumping. This ensures expulsion of absorbed moisture by the sample and a vacuum of the order of $10^{-5}$ torr is obtained. An aliquot of twice distilled BrF$_5$ is expanded in the known volume (usually in the ratio 5:1) and is transferred to the nickel reaction vessel using liquid nitrogen. The valve of the reaction vessel is closed. The sample is then heated to about 550°C (chert) and 625°C (hematite) for 12-20 hours to liberate oxygen. The liberated oxygen is converted to CO$_2$, measured manometrically for its yield and collected in the sample collection bottle. After every 4 or 5 sample runs, usually the reaction vessel is dismantled from the line and cleaned. Two blank runs (without sample) are performed in which the first blank yield is more because of exposure of the reaction vessel to the atmosphere and the second blank is usually less than 0.5µmole. Following the second blank run, the reaction vessel is ready for next batch of sample run.

The CO$_2$ obtained is analysed by VG Mass Spectrometer having triple collector and updated to computer control using SIRA software. The sample and reference gases are alternately led into the ion source by a changeover valve. While one gas is being analysed the other gas is pumped away through the bleed pump. The gas to be analysed is ionized by bombarding with electrons emitted from a filament. The positively charged ions are then accelerated by applying an accelerating voltage of a few Kv and the beam is directed towards a magnetic field which acts in a direction perpendicular to the ion beam. Ions of different masses are separated based on the m/e ration, and collected by the Farady cup
collectors for final ration calculations by using the online computer. This is the molecular ratio of masses 44, 46 which are to be corrected to get the real isotopic ratio i.e. $^{18}O/^{16}O$. Different correction as recommended by Mook (1968) and changeover valve leakage correction as suggested by the manufacturers were applied.

The $^{\delta}^{18}O$ is reported in %, with respect to the Standard Reference Material (SMOW). The $\delta$ values are calculated on the basis of the following equation.

$$\delta^{18}O = \frac{R_{(\text{sample})} - R_{(\text{standard})}}{R_{(\text{standard})}} \times 10^3$$

where, $R_{(\text{sample})} = ^{18}O/^{16}O$ ratio in the sample

$$R_{(\text{standard})} = ^{18}O/^{16}O$$ ratio in the standard

During the course of the analysis of the present samples, two NBS 28 quartz standard gave $^{\delta}^{18}O = 9.7$ and 9.9%. as against reported value of 9.64%. relative to SMOW.