Chapter 2
MATERIALS AND METHODS

2.1 Introduction

This chapter deals with the various techniques and procedures adopted in the collection, processing and analysis of the data used for this work. The present investigation involves three parts, viz: (a) field survey and sampling, (b) laboratory investigation and (c) data processing and interpretation. Various procedures employed in the work are briefly discussed below.

2.2 Field survey and sampling

The first field survey and sampling were done in the pre-monsoon period during March to May 1996. Approximately 5-20 kg samples were collected from selected sites from upper, middle and lower reaches of Chaliyar river channel and from its major tributaries. Samples from upper and middle reaches of the channel were collected directly from exposed parts of the bed/major point bars which are exposed and stable during summer. Care was taken to avoid collecting samples that might have been contaminated by bank material. Further detailed sampling of the estuarine region and deeper part of the river course was done by undertaking a cruise in a country boat (vanchi) during April-June 1997. A stainless steel Van Veen grab was used to collect sediments from the estuary and also deeper parts of the Chaliyar river main stream. All samples were carefully transferred to neatly labeled polyethylene bags. In total 30 sites from the Chaliyar river drainage basin were selected for collection of bulk sediment samples (Fig. 2.1).

In January 1999 field visits were made to area around Nilambur for panning of sediments (using Maravi) for getting heavy mineral concentrates especially gold from different locations (including major tributaries) in order to understand the size variations, to study the surface textures and composition of gold grains and associated heavy minerals. Few gold nuggets are collected by panning the river sediments making use of the locally available wooden pans.
2.3 Laboratory investigation

2.3.1 Analytical methods

Sample preparation: Since wet chemical methods were essential and followed for the analysis, it is essential to bring the rock sample into solution. So, the samples were processed and were brought to solution by the procedures elaborated below:

Sample processing: About 20 kg of sediment sample from upper reaches and tributaries and 3-5 kg grab samples from lower reaches were dried in a hot air oven at 60°C. The samples were then homogenised, coned and quartered, and a 'quartered-fraction' was taken for finer processing and each sample crushed by hardened steel mortar. The sample powder form was thoroughly homogenised. About 15-25 g of it was ground to -300 mesh size by the help of agate mortar and pestle. Care was taken to keep the contamination at the minimum level.

Sample dissolution: Sample dissolution was done by (i) acid digestion method (major and trace elements), (ii) aqua regia digestion method (platinum group elements), and (iii) sodium hydroxide-sodium peroxide fusion method (rare earth element). Because acid digestion method uses HF and HNO₃ and does not introduce any matrix element, through flux, the 'B-solution' gives low blank value, which, in turn, increases the sensitivity of the instrument. This solution is used for the analyses of all the major and trace elements except SiO₂ which is analysed by methods described later (see section 2.3.2). Because the latter method does not allow complete dissolution of Pt group elements the sample was decomposed with 10 ml of the 1:1 mixture of HF and HNO₃ and was treated with aqua regia (2 ml HNO₃ + 4 ml HCl). This solution was used for Au determination. For the REE analysis of the samples of lower abundance, Na₂O₂-NaOH fusion method was followed. In this method, about 0.5 g of the sample was digested. The matrix of Na was scavenged by the precipitation with NH₄OH.

2.3.1.1 Preparation of 'B-solution' by acid digestion for major and trace element analysis

For the preparation of B-solution, the procedure formulated by Shapiro and Brannock (1962) modified by the geochemistry laboratory of School of Environmental Science, JNU, New Delhi was followed. 0.5 g of powdered sediment sample was digested with 10 ml conc. hydrofluoric and 5 ml conc. nitric and 1 ml...
conc. perchloric acid in a teflon crucible at a temperature range of 85°C to 90°C with lid on for 4 hours to ensure complete reaction. After 4 hours, the lid was removed and was heated till near dryness. In the second step, 5 ml conc. hydrofluoric and 10 ml conc. nitric acid were added and heated till dryness to 90°C. In the third step, only 5 ml conc HNO₃ was added and heated till dryness. In the final step 30 ml of 1N HCl was added to the dry crucible and was heated to 100°C to bring the digested sample into solution. After regular swirling, the solution was transferred to a 100 ml standard flask and was warmed in a hot plate to ensure complete dissolution of the crystalline salt. The teflon crucible was rinsed several times with 1N HCl and was allowed to cool and made up to volume with distilled water. This solution, with suitable dilution, was used for the analysis by ICP-AES and Flame Photometer. To check the reliability of the major element data duplicate analysis (XRF and ICP-AES) of few samples were also carried out (see Table 2.1).

2.3.1.2 Aqua regia digestion method

A known weight (≈ 1 g) of the well-ground sample was decomposed with 10 ml of a 1:1 mixture of hydrofluoric and nitric acids in teflon beaker. When the silica was expelled completely, the sample was treated with aqua regia (2 ml conc. HNO₃ + 4 ml conc. HCl) and evaporated to near dryness on water bath. When all the acid was expelled, 5 ml conc. HCl was added to drive off HNO₃. When dry, the residue was dissolved in 10 ml 2N HCl and made up to 25 ml. This solution was used for the Au separation.

2.3.1.3 Na₂O₂-NaOH fusion method

For REE determination, 0.5 g of powdered sample was fused with Na₂O₂ and NaOH pellets in a nickel crucible and then kept overnight in triple distilled water. The fused material was then dissolved in 6N HCl into a 500 ml beaker, and evaporated to near-dryness in a hot plate (90°C-100°C) till the silica precipitated in the form of a gel. The silica gel was filtered through whatman 42 and 41 filter papers and the residue of gelatinous silica was washed off several times with 6N HCl. The filtrate was completely dried and picked up in 30 ml of 1N HCl and transferred into a centrifuge bottle quantitatively. To this solution 10-12 drops of phenol red indicator was added. Then NH₄OH was added drop wise till the colour changes and trivalent cations precipitate. The solution was then ultra centrifuged for 10 minutes at 4000-
6000 rpm and the supernatant liquid discarded, leaving behind the precipitate in the centrifuge bottle. This precipitate contains all the REE’s and was used for the REE separation.

2.3.1.4 REE separation and pre-concentration for ICP-AES analysis

The REE separation from matrix and pre-concentration were done by cation exchange chromatography. After decanting the supernatant liquid the precipitate in the centrifuge bottle (as prepared by the above said step) was then transferred into a Teflon beaker using 6N HCl and dried (Extract-1). This Extract-1 was picked up in 30 ml of 1N HNO₃ and was loaded through a whatman 42 filter paper in 2-3 steps, into the regenerated HNO₃ quartz columns (of length 26.5 cms and an inner diameter of 1.4 cm) packed with cation-exchange resin AG 50W-X8 (100-200 mesh in Hydrogen form) up to a height of 24.5 cms. The loaded solution was then washed with 50 ml of 1.8N HNO₃ for the removal of major and trace elements and discarded. The total REE rich fraction was eluted with 180 ml of 6N HNO₃ in a Teflon beaker. The above collected solution was dried (Extract-2) in a hot plate and re-dissolved in 30 ml of 1N HCl and loaded in 2-3 steps into the regenerated HCl columns (of length 24.5 cms and an inner diameter of 1 cm) packed with the same cation exchange resin up to a height of 22.5 cms. To get rid of iron fraction collected with 240 ml of 6N HCl and dried (Extract-3) in a hot plate. This dried final cut (Extract-3) was dissolved with 4 ml of 3N HNO₃ for analysis.

2.3.1.5 Au pre-concentration for the quantitative estimation by Instrumental Neutron Activation Analysis (INAA)

Concentration of gold was determined by following the method of determination of gold in low-grade ores and concentrates by anion exchange separation followed by Neutron Activation developed by Iyer and Krishnamoorthy (1976).

Of the aqua regia digested (see section 2.3.1.2) sample solution, 10 ml was added to a thoroughly washed anion exchange resin column (2 cm long; column dimension; 6 mm internal diameter x 10 cm long; Deacidite FF anion-exchange resin; 3-5% cross linking, 200-400 mesh) and the resin was washed using 15 ml of 1N HCl. Now more than 90% of interfering elements other than platinum group
elements were eluted out from the sample. At the same time, the gold present in 1 g of the sample gets concentrated in 300 mg of resin.

The resin was then taken out of the column, dried under an infrared lamp and sealed in a polythene envelope (1.5 cm square). A standard containing ≈ 10 μg Au was prepared in a similar way.

2.3.2 Colorimetric determination of silica

Silica analysis for some of the samples were done by colorimetry using a spectrophotometer. The dissolution of the sample for this purpose was done by "A-solution" method as suggested by Shapiro and Brannock (1962).

2.3.2.1 Sample dissolution: Preparation of A-solution

A series of 75 ml nickel crucibles, cleaned with 1:1 HCl and washed with water, 10 ml portion of 15% NaOH was placed and evaporated to dryness under an infrared lamp. 0.05 g of -300 mesh samples were loaded to the crucibles and fused by Meker burner at red hot condition for 10 minutes. The crucibles were cooled and 2/3 of each was filled with H2O and kept covered overnight. The contents of the crucible with the washings were transferred to 500 ml plastic beakers containing about 300 ml H2O and 12N HCl. The contents in the beaker were quantitatively transferred to a series of 1000 ml flasks and were warmed up until the solution is clear. The volume was made up on cooling and 100 ml of each was further transferred to plastic bottles.

2.3.2.2 Determination of SiO2

Reagents used were Ammonium Molybdate solution of 7.5% and Tartaric acid solution of 8%. Ammonium Molybdate solution of 7.5% was prepared by dissolving 7.5 g of reagent grade (NH4)2Mo7O24·H2O in 75 ml of water with gentle heating and subsequent addition of 10 ml of 1:1 H2SO4 on cooling. The solution was filtered and kept in a plastic bottle.

Tartaric acid of 8% was prepared by dissolving 40 g of reagent grade tartaric acid in water and stored in a plastic bottle.

Reducing solution was prepared by dissolving 0.5 g of reagent grade anhydrous sodium sulphite in 10 ml water with subsequent addition of 0.15 g of 1-amino-2-naphthol-4-sulphonic acid and stirring till complete dissolution. Solution of 9
9 reagent grade sodium bisulphite in 90 ml water was added to the first solution and mixed thoroughly and was then stored in a plastic bottle in a dark place.

10 ml aliquot of each sample solution - A was pipetted out and transferred to a series of 100 ml volumetric flasks to which 1 ml of ammonium molybdate solution (7.5%) was added and stirred. This was allowed to stand for 10 minutes. To this solution, 5 ml of tartaric acid solution was added and thoroughly mixed. Further 1 ml of reducing solution was also added and stirred. The volume was made up to 100 ml and allowed to stand for 30 minutes.

The absorbance of each solution was measured at 650 nm with respect to "blank solution-A" used as a reference blank. This was compared with the absorbance of "solution-A" of in-house rock standards.

2.3.3 Estimation of Sodium and Potassium by flame photometer

Na and K analysis for some of the samples were done by flame photometer. The dissolution of the sample for this purpose was done by "B-solution" method (see section 2.3.1.1)

2.3.3.1 Determination of Na and K

Reagents used were NaCl (for sodium estimation) and KCl (for potassium estimation) for preparing primary stock solution. Primary stock solution of Na and K was prepared by dissolving 2.542 g of NaCl and 1.907 g of KCl respectively in distilled water and made upto 1000 ml.

Intermediate stock solution of Na and K was prepared by diluting 10 ml of the above stock solution to 100 ml with distilled water. By proper dilution of intermediate solution with distilled water different standards were prepared for Na and K.

Dilution principle:

\[
\text{(Required ppm} \times \text{amount to be made up}) / \text{Parent ppm} = \text{Vol. to be pipetted}
\]

i.e., \((10 \text{ ppm} \times 100 \text{ ml})/100 \text{ ppm} = 10 \text{ ml of intermediate solution}\)

The different standards of Na and K solution are aspirated to the flame photometer, fitted with Na and K filters respectively, under carefully controlled conditions and the photometer readings are noted down. A standard calibration curve was drawn for Na and K by plotting the concentration of the standard sodium and potassium solution respectively on the x-axes against their corresponding photometer reading on the y-axes.
5 ml of "B-solution" was diluted with distilled water and made up to 100 ml. Further, by proper dilution of the above samples they were also aspirated to the flame photometer and the corresponding photometer reading for Na and K was noted and plotted in the standard calibration curve. The concentration of Na and K was determined from the graph and computed for the whole sample. To check the accuracy of the analysis the solution of in-house rock standards was also run along with the sample solution and the analytical results are compared with the standard published values (see Table 2.2).

2.4 Analysis

2.4.1 Analysis of major, trace and REE by ICP-AES

Quantitative analysis of major and trace elements was done at SES, JNU, New Delhi and NIO, Goa by a Labtam 8440 ICP-AES and Perkin Elmer Plasma-400 ICP-AES respectively (few samples were analysed at NGRI, Hyderabad for its major elements by XRF, trace and REE's by ICP-MS). Rare earth elements were determined by a polychromator in the Labtam 8440 ICP-AES. The precision was found to be higher than \( \pm 5\% \) and \( \pm 10\% \) for major and trace elements respectively. It is found that the precision is better for samples with higher REE abundance. The accuracy of the major element analyses was better than 95%.

Standardisation for majority of the major and trace elements, (excluding REE) was based on in-house rock standards like 22-7, 22-22, VM-9 developed at JNU from the samples of the Kolar schist belt. However, due to shortage of proper rock standard and uncertainties in the internal rock standards, the accuracy for the trace elements could not be worked out.

Standardisation for REE's was done with metal standards obtained from Johnson Mathey Inc. and in-house rock standard 90-57, which was analysed several times by the isotope dilution method at SUNY, Stony Brook, USA. REE analysis by ICP-AES was done in the Geochemical laboratory under the supervision of Prof. V. Rajamani, SES, JNU, New Delhi. As a part of this the author has visited JNU from May-June 1998 and has undergone training in the analytical procedure. The data is quite consistent with the reported value (see Table 2.2). More details regarding precision and accuracy of analytical results of in-house rock standards and analytical conditions followed for ICP-AES analysis is discussed by Mohanta (1998).
Few samples were analysed for REE and trace elements using ICP-MS at the National Geophysical Research Institute (NGRI), Hyderabad, following the procedure outlined in Balaram et al. (1996).

2.4.2 Analysis of Au by Neutron Activation Analysis

The samples were analysed at BARC, Mumbai for their concentration of gold following the method of determination of gold in low-grade ores and concentrates by anion exchange separation followed by Neutron Activation developed by Iyer and Krishnamoorthy (1976). For this purpose the author has visited BARC and has undergone training in the analytical procedure during the year 1996.

The resin with pre-concentrated samples (see section 2.3.1.5) sealed in a polythene envelop and standards were irradiated for seven hours in the Apsara reactor at a neutron flux of $1 \times 10^{12}$ n/cm$^2$/sec, cooled for 5 days and then activities were measured.

The $\gamma$ activity of 412 KeV of $^{98}$Au was measured using a HPGe detector (125 cc active volume, 25% efficiency w.r.t 3" x 3" NaI(Tl) having a FWHM of 2 KeV for the 1332 KeV of $^{60}$Co) coupled to a PC based 4K multichannel analyser. The amount of Au adsorbed on the resin was thus computed, comparing the activities. From this, the concentration of Au in sample was calculated.

The sensitivity of the method depends on the weight of sample taken, length of irradiation, cooling and counting time (Iyer and Krishnamoorthy, 1976). In this work, it is found than an amount of 0.01 $\mu$g of gold in one gram of sample can easily be estimated.

2.4.3 Determination of Loss on Ignition (LOI)

Approximately 1 g of powdered sample was transferred to previously weighed silica crucible. The crucible with the sample was kept in a Muffle furnace and heated to pre set 500°C with open lids to drive off the adsorbed water. After this the silica crucible was closed with lid and heated to 1100°C to drive off the structurally held water. Then it was allowed to cool slowly. The crucible with the sample was carefully kept in a desiccator and accurately weighed. The loss of weight was computed by subtracting the weight of the heated sample from the initial weight.
2.5 Textural analysis

2.5.1 Statistical parameters

Samples (30 in numbers including major tributary samples) collected from upper (stable point bars), middle and lower reaches (grab samples) of Chaliyar mainstream were oven-dried and subjected to coning and quartering. A representative portion (100 g) was then subjected to mechanical analysis on a Ro-Tap sieve shaker using standard set of ASTM sieves at half phi (½ Ø) intervals. The fractions left over in each sieves were carefully transferred, weighed and cumulative weight percentages were calculated. Samples which contain significant amount of silt and clay fractions were subjected to combined sieving and pipette analysis as suggested by Lewis (1984).

The cumulative weight percentages of the above analyses were plotted against the respective grain sizes in phi units on a probability chart. The cumulative frequency curve is drawn and the phi values of 1, 5, 16, 25, 50, 75, 84 and 95 were recorded. The grain size parameters such as mean size, median, standard deviation, skewness and kurtosis were calculated following Folk and Ward (1957).

2.5.2 Determination of sand:silt:clay ratios

Sand, silt and clay ratios were determined using standard techniques of wet sieving and pipette analysis (Lewis, 1984). Known quantities of silt and clay rich sediments were soaked in water for dispersion. The lumps were separated and were filled with water in a 1000 ml beaker. This was kept overnight for making it free of saline content. Excess water is removed using a decanting tube and 25 ml of 10% sodium hexametaphosphate was added to the sample. The sample containing NaHPO₄ was stirred at 20 minutes intervals up to 4 hours.

The total amount of samples were transferred to a 63 μ sieve (ASTM 230 mesh) and wet sieved. The washings were continued till clear water passes through the sieve. Care was taken to limit the total amount of aliquot to less than 1000 ml. The coarse fraction obtained in the sieve was dried, weighed to know the sand fraction in the sediment samples. The volume of aliquot in the cylinder was made up to 1000 ml.
Using a stirrer the contents in the cylinder was vigorously stirred for 45 seconds. Exactly after 1 hour 40 minutes 13 seconds using a 25 ml pipette connected to a tube was lowered to 10 cm down the water level and 25 ml of aliquots containing clay were pipetted out and transferred to a previously weighed 50 ml beaker. All the aliquots were oven dried to constant weight at 60±3°C and weighed accurately after cooling at room temperature. The amount of NaHPO₄ was deducted from the weight of the sample.

Strength of NaHPO₄ = 10% (i.e., 100 g in 1000 ml)

In 25 ml amount of NaHPO₄ = 2.5 g

Amount of NaHPO₄ added to 1000 ml = 25 ml

Weight of NaHPO₄ in 25 ml of the aliquot = \((2.5/1000) \times 25 = 0.0625\) g

Weight of clay fraction in 25 ml, \(W_1 = \) Weight of sample in 25 ml – 0.0625 g

\[\therefore \text{Weight of clay fraction in 1000 ml, } W_2 = W_1 \times (1000/25) \text{ g}\]

From the known weight of sand and clay fraction the weight of silt fraction present in the samples was computed. The relative proportion of sand, silt and clay in samples was also calculated.

2.6 Mineralogical analysis

Different methods were adopted to study the mineralogical constitution of riverine sediments. Heavy mineral separation (using bromoform) were carried out in the > 63 μ fraction of Chaliyar river sediments, which is dominantly sandy.

2.6.1 Bulk mineralogy

Representative bulk samples from selected site were mounted on glass slides using canadabalsm in order to understand modal composition of sediments. Percentage distribution of minerals (assessed by point counting of grain mounts) were presented in table 4.1.

2.6.2 Mineralogy of sieved fraction

A representative portion of sand fraction was washed thoroughly, oven dried and was subjected to sieve analysis at 1/2 Ø intervals (see section 2.5). The coarse sand fraction 0.5 to 1.0 Ø (ASTM mesh size +35), which represent mean size of 33% of the samples was selected for petrologic study to facilitate comparison of data from one location to other. A total of 300 - 400 grains of the above mesh size were
mounted on a glass slide using araldiet. The sections were grinded and polished using carborandum and alumina powder respectively with a polishing machine. The individual minerals in each slide were studied under a petrological microscope and the percentage distribution of minerals (assessed by grain counting) were presented in table 4.2.

Photomicrographs of selected areas of grain mounts/polished grain mounts showing important textural and mineralogic features were taken using a Olympus polarizing microscope at the Department of Geology, University of Kerala, Kariavattom, Trivandrum.

2.6.3 Heavy media separation

In order to find out the percentage of heavy minerals in the sediments a few samples were subjected to heavy mineral separation. A representative portion of sand fraction (>63 µ in bulk sample) was washed thoroughly, oven dried and was subjected to heavy mineral separation. The bulk heavy and light minerals were separated using bromoform (CH Br₃; Sp.Gr. 2.89 g/cc) and separating funnel. The minerals thus separated were washed with acetone, dried and weighed to find out the total heavy and light minerals.

2.6.4 Mineralogy of clay fraction (<2 µ size)

Clays were separated from the bulk sediment by settling velocity employing Stoke's law. The clay mineral identification was carried out by X-ray diffraction technique.

After estimating percentage of sand, silt and clay fraction (see section 2.5.2) in the samples the contents in the cylinder was kept undisturbed. After 6 hour 41 minutes the whole aliquot upto 10 cm depth was pipetted out into a 500 ml beaker. Organic matter in the samples was removed by oxidising with 10 ml H₂O₂ and carbonate material removed with 5 ml of acetic acid. The sample was stirred well and kept overnight for settling. The top clear liquid was decanted and once again filled with distilled water and stirred well. The clay particles were allowed to settle and the water was removed. The clay-water suspensions were used to make slides of almost equal size and thickness by pipetting equal volume (~1ml) of sample and smearing on glass slides. The slides were dried at room temperature and placed in a desiccator to prevent rehydration before exposing to X-rays. These slides were
subjected to X-ray analysis at NIO, Goa using Philips PW 1840 X-ray Diffractometer with Ni filtered CuKα as the target. Clay identification were carried out by following the scheme suggested by Biscaye (1965). The untreated clay slides were scanned through 3° to 33° (2θ) with a scan speed of 0.05°/sec. The analysis was carried out at 40 kV with a current of 20 mA.

2.7 SEM analysis of quartz grains

Approximately 10 g of selected samples were washed thoroughly with distilled water. The washed samples were soaked with H2O2 to remove organic debris. The sand fraction was separated using sieves. Quartz grains between -45 and +60 ASTM size (between 250 to 355 μ) were used for present study. According to Krinsley and McCoy (1977), the quartz grains in the size range 200 to 400 μm are generally considered to record all the depositional features in any given environment. Using an optical binocular microscope, samples of quartz grains were mounted on SEM stubs using double-stick tape, sputter coated with gold for 1 minute. The gold coated quartz grains were examined with JEOL Scanning Electron Microscope, Japan at IIT, Bombay. The SEM analysis was carried out at 18 kV acceleration voltage with a probe current of 6x10^-9 AMPS. SEM photographs of few selected grains were taken to illustrate the shape and surface texture. Twenty quartz grains is thought to give a valid statistical representation of the sample and regarded as sufficient to represent the variability present in a single sample (Krinsley and Doornkamp, 1973; Baker, 1976) and accordingly twenty grains from each sample were selected for the present study.

2.8 SEM analysis of gold grains

From the panned heavy mineral concentrates gold grains were hand picked using hand lens in the field and also in the laboratory with the help of a Leica (WILD MZ5) binocular microscope, Switzerland. Gold grains from 10 different locations were studied for their size, shape etc. using a graduated eyepiece on a binocular microscope. Few gold particles from different locations were subjected to SEM and EDX analysis to understand the shape, surface texture and chemical composition. Around 50 gold particles were mounted on a stub using a double-stick tape and studied under JEOL JSM-5800LV Scanning Microscope (Japan), and few
photographs were taken at NIO, Goa. Few gold grains were also mounted on a thin film of carbon coated stub and EDX analysis was carried out at NIO, Goa. All the analysis are carried out at 20 kV and 55 \( \mu \)A. For EDX analysis of gold grains, ME-XRS multi-element X-ray reference standard was used.

2.9 EPM analysis of gold grains

Representative samples of gold grains collected from different locations were subjected to electron probe micro analysis (EPMA). The analysis were carried out on polished sections at NGRI, Hyderabad and CSIRO, Australia to understand the chemical composition, zoning etc. Few backscattered electron images were also taken at CSIRO, Australia to study the process of rim formation and differential leaching of trace elements. The EPMA conditions and standards followed for platinum group and other trace element analysis at CSIRO, Australia is given in Appendix 7.4.

2.10 Data processing and computation

Data compilation and processing were done using a personal computer. The mathematical and statistical calculations and preparations of diagrams like scatter plots were done using available software.
Fig. 2.1 Sketch Map Showing Chaliyar River And The Location Of Samples Collected
Table 2.1 Duplicate analysis of major oxides (wt. %) present in Chaliyar river sediments using XRF and ICP-AES method

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<td>0.18</td>
<td>0.17</td>
<td>0.14</td>
</tr>
<tr>
<td>LOI</td>
<td>1.66</td>
<td>1.66</td>
<td>2.04</td>
<td>2.04</td>
<td>3.49</td>
<td>3.49</td>
<td>5.56</td>
<td>5.56</td>
<td>9.34</td>
<td>9.34</td>
<td>4.92</td>
<td>4.92</td>
</tr>
<tr>
<td>Total</td>
<td>99.55</td>
<td>99.02</td>
<td>99.02</td>
<td>98.30</td>
<td>99.02</td>
<td>98.20</td>
<td>99.19</td>
<td>98.51</td>
<td>99.45</td>
<td>96.10</td>
<td>99.00</td>
<td>97.23</td>
</tr>
</tbody>
</table>
Table 2.2  Accuracy of the analyses measured by running several in-house rock standards as unknown sample. The analyte standard was not used for calibration during the analysis. All analyses are done by ICP-AES at JNU, New Delhi and NIO, Goa.

<table>
<thead>
<tr>
<th>Major elements</th>
<th>Std. 22-7</th>
<th>Std. 22-22</th>
<th>Std. VM-9</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NIO*</td>
<td>JNU1</td>
<td>JNU2</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.85</td>
<td>0.91</td>
<td>0.83</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.43</td>
<td>15.31</td>
<td>15.2</td>
</tr>
<tr>
<td>FeO (t)</td>
<td>11.31</td>
<td>11.36</td>
<td>10.87</td>
</tr>
<tr>
<td>MnO</td>
<td>0.17</td>
<td>0.17</td>
<td>0.18</td>
</tr>
<tr>
<td>MgO</td>
<td>9.42</td>
<td>10.26</td>
<td>9.87</td>
</tr>
<tr>
<td>CaO</td>
<td>11.16</td>
<td>11.34</td>
<td>11.01</td>
</tr>
</tbody>
</table>

* Present study

Analytical accuracy of SiO₂, Na₂O and K₂O of in-house rock standards. All analysis carried out at CUSAT. Si is analysed by Spectrophotometer, Na and K by Flame Photometer.

<table>
<thead>
<tr>
<th>Major elements</th>
<th>Std. 22-7</th>
<th>Std. VM-9</th>
<th>Std. 22-22</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CUSAT*</td>
<td>JNU1</td>
<td>JNU2</td>
</tr>
<tr>
<td>SiO₂</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.67</td>
<td>1.61</td>
<td>1.57</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.05</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Present study

Accuracy of REE data for in-house rock standard (90-57) analysed along with samples at JNU, New Delhi

<table>
<thead>
<tr>
<th>Element</th>
<th>Ce</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Dy</th>
<th>Er</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis</td>
<td>46.44</td>
<td>18.99</td>
<td>4.63</td>
<td>1.75</td>
<td>4.82</td>
<td>3.48</td>
<td>2.44</td>
<td>2.15</td>
</tr>
<tr>
<td>Reported</td>
<td>38.5</td>
<td>21.8</td>
<td>4.89</td>
<td>1.58</td>
<td>4.75</td>
<td>4.6</td>
<td>2.6</td>
<td>2.3</td>
</tr>
</tbody>
</table>

The data in column JNU1 and JNU2 in the above tables are as reported by Rajamani et al. (1985) and Mohanta (1998) respectively.