

CHAPTER 3

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**MATERIALS AND METHODS**

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The quality of data in geochemical studies has utmost importance. In the prevailing conditions the care has been taken to the maximum extent. The materials and machines used during data acquisition, has been chosen at par with international standards. During the analysis international geochemical standards and high class internal standards were used.

### **3.1 SAMPLE PROCESSING**

The processing is little bit different for hard rocks and soft rocks. The sediment samples of nearly one kilogram were air dried mixed and made to -60 mesh size, whereas the hard rock samples were first made to chips then nearly one kilogram of chips were crushed to -60 mesh size. Nearly 200 gms of each crushed samples (-60 mesh) were thoroughly mixed by coning and quartering and then pulverised to -200 mesh size and stored into the plastic vials for further use.

### **3.2 INSTRUMENTS AND APPARATUS**

**Weighing balance:** For weighing the samples and chemicals, an electronic balance, the METTLER 240 model with digital display and minimum capacity of  $10^{-5}$  gms, was used.

**Furnace:** The muffle furnace used for the fusion of samples was a Thermoline 10500 model, which can maintain temperature up to  $1200^{\circ}\text{C}$ , with a good thermocouple control on the attained temperature.

**Inductively coupled plasma atomic emission spectrophotometer (ICP-AES):** ICP-AES is LABTAM 8440 model, manufactured by Labtam limited, Australia, with both simultaneous and sequential detection. The instrument is equipped with a vacuum monochromator of Czerny Turner type and a vertically mounted Paschen-Runge polychromator with 10 channels for simultaneous determination of ten numbers of REE. All the elements except silica and potassium has been analysed by this instrument.

**Flame photometer:** Microprocessor based Chemito 1020 flame photo meter which has sensitivity for K is 1ppm and range of operation is 0 to 100 ppm has been used for K analysis.

**Spectrophotometer:** Spectronic 20 spectrophotometer manufactured by Bausch and Lomb was used to analyse SiO<sub>2</sub>.

**X-Ray Diffractometer:** Philips XRD (PW1140) was used to determine bulk and clay mineralogy of the samples.

**Infra red spectrometer:** Jasco FT/IR-5300 spectroscope at Chemistry department, B.H.U., Varanasi has been used to determine clay mineralogy of the samples.

**Centrifuge:** Refrigerated Hitachi himac CR 20B2 has been used in centrifuging during REE separation.

**Sieve shaker:** Sieve shaker of Fritsch anlysette and sieve of .063 mm were used in textural analysis.

**Miscellaneous:** Ultra 'F' purity graphite crucibles for the fusion of samples were procured from Ultra Carbon Corporation, Michigan, U.S.A. Quartz crucible of 50 ml size were procured from Vitresil, England. The teflon crucibles manufactured by J.N.U.- U.S.I.C. using high class teflon rods were used for the geochemical work

whereas teflon beakers were procured from Nalgene U.S.A. Local made high class Ni-crucibles were used for sample digestion. Tarson 500 ml centrifuge bottles were used to centrifuge the solution during REE separation. A grade Borosil glassware has been used in chemical work. Ashless filter papers of grade 40 and 42 were procured from Whatman International Ltd., England.

### **3.3 CHEMICAL REAGENTS USED**

**Water:** Triple distilled water was used for the preparation of standards, dilution of digested samples and ringing etc.. The last two distillations being in a pure quartz distillation plant.

**Acids:** The acids used were analytical grade HNO<sub>3</sub> (69% GR), HCl (35% GR), HF (48% GR), HClO<sub>4</sub> (70% GR), and H<sub>2</sub>SO<sub>4</sub> (95-98% GR), procured from E. Merck (India) Ltd.

**Other reagents:** Lithium metaborate (LiBO<sub>2</sub>) procured from E. Merck Darmstadt. Calgon (Ca<sub>3</sub>PO<sub>4</sub>) from S. D. Fine Chemicals, H<sub>2</sub>O<sub>2</sub> (30%) and Na<sub>2</sub>O<sub>2</sub> powder from Qualigens, NaOH pellets, Ammonia solution (25% GR), Phenol red (.02%), Tartaric acid, Sodium disulfite, Sodium sulfite, and Ammonium molybdate and Amyl alcohol from E. Merck (India) Ltd., 1-Amino-2-naphthol-4-sulphonoc acid of Sarabhai M. Chemicals were used.

### **3.4 METHODOLOGY**

#### **3.4.1 Sedimentological analysis**

The sediment samples already separated before crushing have been used for grain size analysis. The whole procedure is basically based on Ingram (1971), Galehouse (1971)

and Gale and Hoare (1991) but slight modifications have been done according to the need and lab conditions. First they were treated with H<sub>2</sub>O<sub>2</sub> and then with 1M HCl to get rid of organics and carbonates respectively (Ingram, 1971, Gale and Hoare, 1991).

The samples were again dried below 50°C in the hot air oven. The sand fraction were separated using sieve of 0.063 mm size (see Ingram, 1971). The 50 gms of each samples (less than 0.063 mm grain size) were taken into measuring cylinders of volume 1000 ml volume. Then 50 ml of 10% calgon solution were added to this and finally made to 1000 ml for the analysis. The solution were agitated at 2500 rpm for 5 minutes using mechanical analysis stirrer. The froth generated during stirring were subsided by putting few drops of Amyl alcohol. Now the cylinders were put on stable platforms. The solution in each cylinders were agitated and after 20 seconds, 20 ml of solutions were taken at the depth of 20 cm, which contained silt and clay size of sediments. Thereafter, they were again allowed to stand for 3 hours and 27 minutes to take out 20 ml of solution at the depth of 5 cm.. This contained clay fraction of the sediments. By using simple calculations sand, silt and clay percentage in the sediments were determined.

#### **3.4.2 Mineralogical analysis**

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Thin sections were made for the petrographic analysis of quartzite, whereas mineralogical analysis of the sediments, weathered quartzites and altered quartzite and pegmatite samples were done by using XRD and IR spectroscopy. For the XRD analysis following are the specifications opted for the operation during the scanning. Target: CuK $\alpha$ ; filter: Ni; range 400cps for clay fractions and 100 cps for bulk mineralogical analysis; goniometer speed: 1° of 2 $\theta$  angle per minute.; scanned angle: 2°

to 32° of 2  $\theta$  angle for clays, and 5° to 42° for bulk samples. The clay fractions have been separated by using Atterberg cylinders (Muller, 1967), and separately run on X-ray diffractometer as untreated, glycol treated (12 hours at 50°C) and heat treated (550°C for one hour) (Carrol, 1974). The minerals and their proportions were determined from the diffractograms after Griffin (1971) and Carrol (1974)

### **3.4.3 Geochemical analysis**

As we follow the wet chemical method of analysis, it is essential to bring out the samples into solution, so the samples were processed and was brought to solution by the procedures elaborated here.

#### **(1) Lithium metaborate fusion:**

In this type of method the resistant minerals like zircon, rutile, monazite are easily digested. So, this method has been used for the analysis of Zr in the sediments. In this method, sample powder is fused with LiBO<sub>2</sub> of four times the weight of the previous (in the present work 0.25 gm of -200 mesh size of sample powder was fused with 0.8 gm of LiBO<sub>2</sub>), and the molten mass is dissolved in 2N HNO<sub>3</sub> acid (Walsh, 1980). The graphite crucibles were cleaned by rubbing the inner and outer surfaces of graphite crucibles by tissue paper. They were ignited in the muffle furnace at a temperature of 800°C for 10 minutes. After cooling them they again cleaned by rubbing them by tissue paper. The 0.8 gm of LiBO<sub>2</sub> was transferred to the crucibles and at the centre 0.2 gm sample was mixed with LiBO<sub>2</sub> powder. Care was taken such that the sample should not stick to the crucible surface and kept embedded in the LiBO<sub>2</sub> flux. The crucibles with rock powder were kept in the muffle furnace in which the temperature was maintained at 700°C and gradually, the temperature was raised to

1050°C at which it was constantly maintained for 20 minutes. Then, the molten fused material were transferred into 60 ml of 2N HNO<sub>3</sub> kept in a 100 ml teflon beaker and was swirled constantly by a magnetic stirrer. When the fused material were dissolved completely without any trace of precipitation, it was transferred by repeatedly rinsing with 2N HNO<sub>3</sub> into a volumetric flask of volume 100 ml and finally the volume was made to 100 ml. Thus the 500 times diluted solution was prepared for the analysis of Zr.

**(2) Solution 'B' preparation:** For the preparation of 'B' solution the procedure suggested by Shapiro and Brannock (1962) modified by our laboratory was followed. In the open beaker acid digestion process 0.5 gm of rock sample powder (-200 mesh), 10 ml conc. HF, 5 ml conc. HNO<sub>3</sub> and 1ml conc. HClO<sub>4</sub> were added in a teflon crucible of 60 ml volume. The crucible with their lids were kept on the hot plate at a constant temperature between 85°C to 90°C for 4 hours. The lids were open and dried. In the second phase, 5 ml conc. HF, 10 ml conc. HNO<sub>3</sub> and 1 ml conc. HClO<sub>4</sub> were added and heated till dryness. In the third phase, 5 ml conc. HNO<sub>3</sub> was added and heated till dryness. For the quartzite and sands digestion 1 gm of each samples have been taken and the steps as earlier stated are repeated for the total evaporation of silica. At the last phase of digestion 20 ml of 1N HCl was added to the dry crucibles and heated to 100°C to bring the digested sample into the solution. After rinsing several times the solutions were transferred to a 100 ml volumetric flasks and the resultants of 200 times were used for trace element analysis. For the major element analysis the solutions were made to 4000 times dilution (in the case of quartz rich samples it is 100 times and 1000 times for trace and major elements analysis respectively)

**(3) Sample preparation for REE analysis:** For the REE determination samples with a flux of NaOH and Na<sub>2</sub>O<sub>2</sub> in the ratio of 1:2:2.5 were digested in the nickel crucibles at red hot condition for 15 minutes. Usually 0.5 gm samples were taken for sediments and clay rich samples, whereas 2 gm samples for the quartz rich samples were taken. On cooling the crucibles were filled with water (3/4<sup>th</sup> of the volume) and kept for overnight. The digested samples transferred to 500 ml glass beakers by scrapping and washing with 6N HCl. Then the beakers were kept on a hot plate at 80-90°C to evaporate to form the silica gel. Precipitate of silica gel were filtered and washed with 6N HCl thoroughly until the colour has disappeared. The filtrates were dried and the residue were dissolved in 30 ml 1N HCl and nearly 10 drops of phenol red solution were added in the 500 ml centrifuge bottles. By the addition of 1:1 ammonia solution to the centrifuge bottles, a change in colour from yellow to pink occur, at this stage the pH is nearly 8, and at same time the trivalent and tetravalent cations were precipitated. The bottles were centrifuged at 6000 rpm at 4°C for 30 minutes. The supernatant were discarded and precipitate were dissolved and washed with 2N HCl and dried into teflon beakers of 500 ml volume. The dried residues were dissolved in 30 ml of 1N HNO<sub>3</sub> and passed through the HNO<sub>3</sub> cation resin columns and eluets were discarded. Then the 150 ml of 3N HNO<sub>3</sub> were passed through the same columns and the eluets were discarded. Then 180 ml of 6N HNO<sub>3</sub> were passed through the columns and these eluets were collected into teflon beakers. The eluets were dried and dissolved into 30 ml 1N HCl and passed through the HCl resin columns. The eluets were discarded. 180 ml of 3N HCl were passed through the column and eluets were discarded. The 240 ml of 6N HCl were passed through the column and the eluets collected and dried into teflon beakers. Thus the samples were

processed to separate and concentrate the REE. They were analysed by the ICP in poly mode. The wavelengths characteristic for different REE for the analysis are shown in the Table 3.1.

**(4) Sample preparation for silica analysis:**

**Gravimetric method:** The silica analysis for the quartz rich samples were performed by gravimetric method. The silica gel separated during REE separation using ashless filter papers were ignited at 1000°C for 1 hour in platinum crucible. These were kept for free cooling for overnight. Next day they were weighed and silica percentage were determined. Cautions were taken during separation of silica from the solutions to avoid the loss.

**Colorimetry:** For the silica analysis of sediments method suggested by Shapiro and Brannock (1962) were performed. In this method 10 ml of 15% NaOH solution was taken into Ni crucibles and dried under infra red lamp. To this 0.05 gm of -200 mesh sample were added and the crucibles were heated over Bunsen burner at red hot condition for 10 minutes. After cooling the crucibles were filled with water (3/4<sup>th</sup> of volume) and kept for overnight. Then the content of the crucibles were transferred into 500 ml glass beakers containing 300 ml of water and 10 ml of 12N HCl. The alkaline solution was not allowed to touch the glass and was poured directly into the solution. The crucibles were rinsed thoroughly with distilled water and the cloudy solution were heated until it became clear.

The contents of the beakers were transferred to 1 litre volumetric flask and diluted to volume at room temperature. 100 ml of this was transferred into the cleaned plastic bottle and reserved for SiO<sub>2</sub> determination.

For the determination of SiO<sub>2</sub> Ammonium molybdate solution (75%) was prepared (7.5 gm of reagent grade (NH<sub>4</sub>)<sub>6</sub>MO<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O in 75 ml distilled water and 10 ml of 1:1 H<sub>2</sub>SO<sub>4</sub> was added and volume was made to 100 ml) this was stored in a plastic bottle. 8% tartaric acid was made by dissolving 40 gm reagent grade tartaric acid to the 500 ml of distilled water and stored in plastic water. To make the reducing agent 0.5 gm reagent grade anhydrous sodium sulfite was dissolved in 10 ml of H<sub>2</sub>O. To this is added 0.15 gm of 1-Amino-2-naphthol-4-sulfonic acid and stirred until dissolved. 9gm of reagent grade sodium bisulfite is dissolved in 90 ml of distilled water, and this solution was added into first solution and thoroughly mixed. The solution was stored in plastic bottle in dark place.

**Procedure:** The 10 ml of 'A' solutions of each samples and standards including blank were taken into 100 ml volumetric flask. After adding 1ml of Ammonium molybdate solution, swirled and allowed to stand for 10 minutes. Then 5ml of Tartaric acid was added to this, mixed and immediately 1 ml of reducing solution was added. After swirling the solutions to mix properly the volume was made to 100 ml distilled water and allowed to stand for 30 minutes before analysis by spectrophotometer.

**(5) Determination of Loss on ignition (LOI):** For the determination of LOI 1 gm of each samples of -200 mesh were taken into pre-weighed quartz crucibles of 50 ml volume (Maxwell, 1968). They were kept in muffle furnace without lid and temperature was raised to 500°C. Then the lids were kept on the crucibles and the temperature was increased to 1000 °C. At this final temperature they were allowed to stand for 1 hour. Then they were left for overnight for free cooling. Next day they were weighed and the

difference from untreated and heat treated sample was made to percentage, it is the loss on ignition of that sample.

### **3.5 SAMPLE ANALYSIS**

The solutions of rock samples, thus prepared were analysed in ICP-AES, AAS, flame photometer and spectrophotometer. All the elements except K (by AAS and flame photometer), and SiO<sub>2</sub> (by gravimetry and spectrophotometer) were analysed by ICP-AES. In the ICP-AES the major elements were analysed by using samples of 4000 times dilution factor (1000 times for quartz rich samples) and the trace elements with 200 times dilution factor (100 times for quartz rich samples) to ensure better data of reproducibility and precision. In the analysis of K by AAS 4000 times dilution, including 1000 ppm Cs as suppresser, of samples as well as standards and blank solutions (Sotera and Stux, 1979) have been used. For the calibration of instruments some USGS rock standards like BHVO-1, STM-1, RGM-1 and some internal standards like 21-6, 22-22, 22-7, VM9 were used. The digestion procedure used for different elements, the wavelength used for them, the percentage error between the analysis done in our lab and standard values are given in the Table-3.1. The REE analysis in our lab and by isotope dilution method using Mass spectrometer at S.U.N.Y., Stony Brook, U.S.A. is shown in Figure- 3.1.

**Table 3.1: Methods of chemical analysis**

Element	Wavelength nm	Solution	Instruments	% Error
Si			Gravimetry	1.5%
Si	650	"A"	Spectrophotometer	2.5%
Ti	336.121	"B"		1.78%
Al	396.152	"	"	0.65%
Fe	259.940	"B"	ICP	1.52%
Mn	257.610	"	"	1.78%
Mg	285.213	"	"	0.18%
Ca	317.933	"B"	"	1.10%
Na	588.995	"B"	ICP	0.56%
K	766.5	"B"	AAS	1.9%
K	766.5	"B"	Flame Photometer	1.3%
P	213.620	"	"	6.02%
Y	371.029	"B"	"	13.2%
Y	371.029	LiBO <sub>2</sub>	"	1.23%
Zr	339.198	"B"	"	10.6%
Zr	339.198	LiBO <sub>2</sub>	"	4.80%
Ni	231.604	"B"	"	6.72%
Cr	267.716	"B"	"	2.25%
Ba	455.403	"	"	1.98%
Sr	407.771	"	"	3.95%

Element	Wavelength (nm)	High Ref. STD. (ppm)
Ce	399.924	10
Nd	430.357	"
Sm	442.435	1
Eu	381.965	"
Gd	342.246	"
Dy	353.170	"
Er	326.478	"
Yb	328.937	"

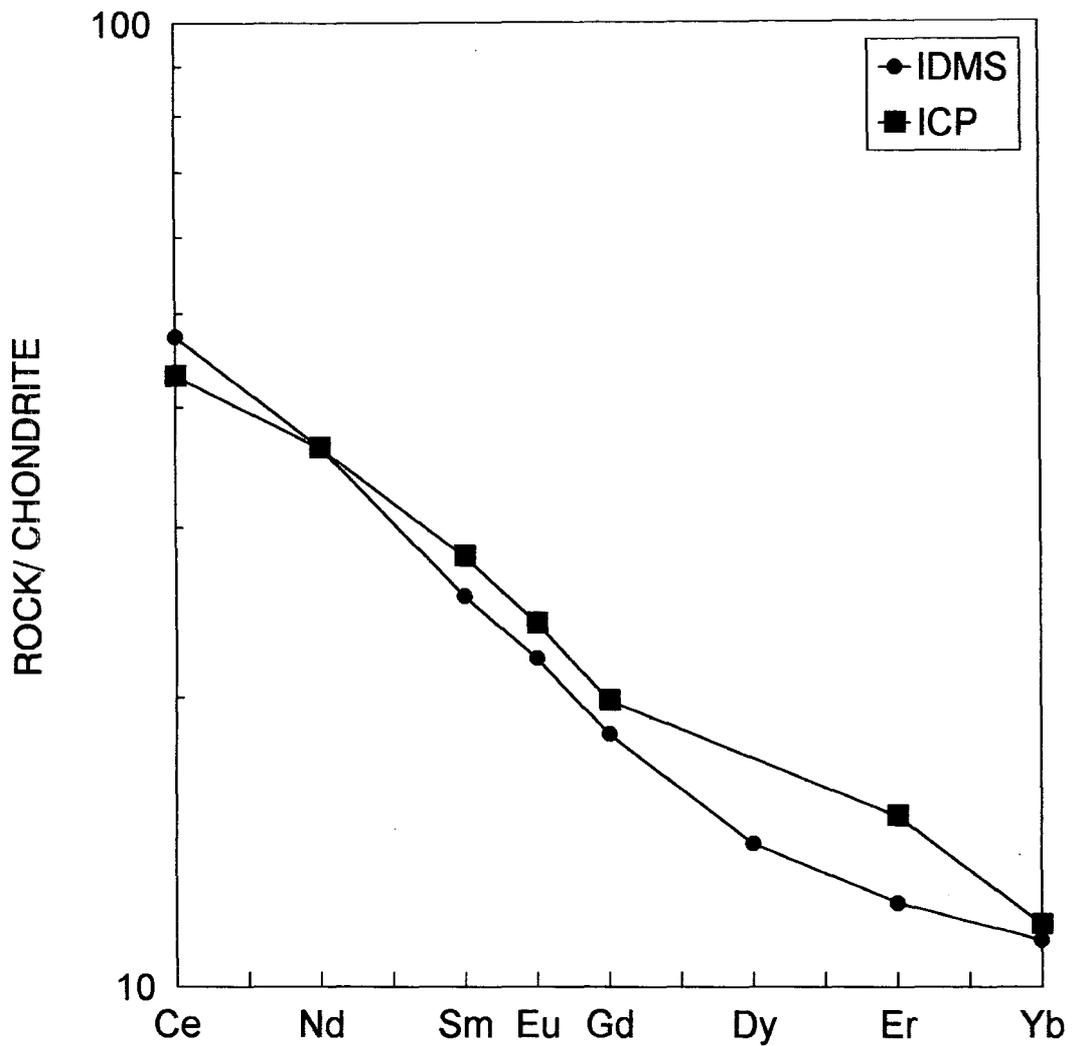


Figure 3.1: A comparison of REE analysis by ICP-AES ( J.N.U., New Delhi) and by isotope dilution method (IDMS) ( SUNY, Stony Brook, U. S. A.).

### **3.6 DETERMINATION OF CHEMICAL INDEX OF ALTERATION**

Nesbitt and Young (1984) suggested a parameter called chemical index of alteration (CIA) to be calculated from the chemical analyses of rocks and sediments. In the calculations the molar proportions of oxides of Al, Ca, Na and K are taken. This index is defined as

$$\text{CIA} = \text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \cdot 100$$

CaO\* represents the Ca in silicate fraction only. For the determination of CIA of the sediments the CaO\* has been determined by leaching the samples with cold diluted HCl (Gale and Hoare, 1991), and corrected for P<sub>2</sub>O<sub>5</sub>. The other elements were recalculated to 100% accordingly and have been used for the calculations. But for the quartzites, weathered quartzites and alteration products of quartzites and the pegmatites, the CaO\* values are taken as equal to CaO minus Ca for apatite when CaO < Na<sub>2</sub>O, otherwise the values equal to Na<sub>2</sub>O were taken for CaO\* when CaO (after P<sub>2</sub>O<sub>5</sub> correction) > Na<sub>2</sub>O (McLennan, 1993).

The molar proportions of Al<sub>2</sub>O<sub>3</sub>, CaO+Na<sub>2</sub>O and K<sub>2</sub>O; and Al<sub>2</sub>O<sub>3</sub>, CaO+Na<sub>2</sub>O+K<sub>2</sub>O, and FeO+MgO are plotted on triangular plots separately (Nesbitt and Young, 1984, 1989), which are called as A-CN-K and A-CNK-FM diagram respectively.

For the determination of palaeoweathering index of alteration, a line is projected from the K-origin in the A-CN-K plot through the sample to the weathering trend of crustal rocks (Fedo et al. 1996). The CIA value at the intersection represent palaeoweathering CIA.