Chapter: Four

Chapter 4
Materials and Methods

In this chapter, I will discuss the various samples (rocks, sediments and water) collected for this work and the experimental techniques utilized to determine their mineralogical, textural, geochemical and isotopic characteristics. The chapter is composed of two parts: the first part describes the sampling protocols followed and the second part deals with analytical techniques.

4.1 Sampling Protocol

The samples for this thesis came from the Andaman Islands including the volcanic island called the Barren Island. These were collected during three field trips to these islands during March 2007, April 2008 and March 2009. During these trips, geological mapping and volcanological studies were carried out and sampling was done. Attempts were made to identify various types of flows, sequences of events and patterns of emissions on the volcano and a stratigraphy was built, the details of which have already been presented in the previous chapter. After proper identification of different types and sequence of volcanic materials, the samples were collected; which include scoria, lava flows, minerals and loose and consolidated ash samples. The locations of the samples are presented on geological map of the volcano (Fig. 4.1) and the other details are presented in Table 4.1. Since the geochemical characteristics of the rocks are a function of degree of alteration, attempts were made to collect very fresh samples from the interior of exposed rock outcrops to avoid alteration. Representative samples from most of the formations/flows/beds were collected for this work.

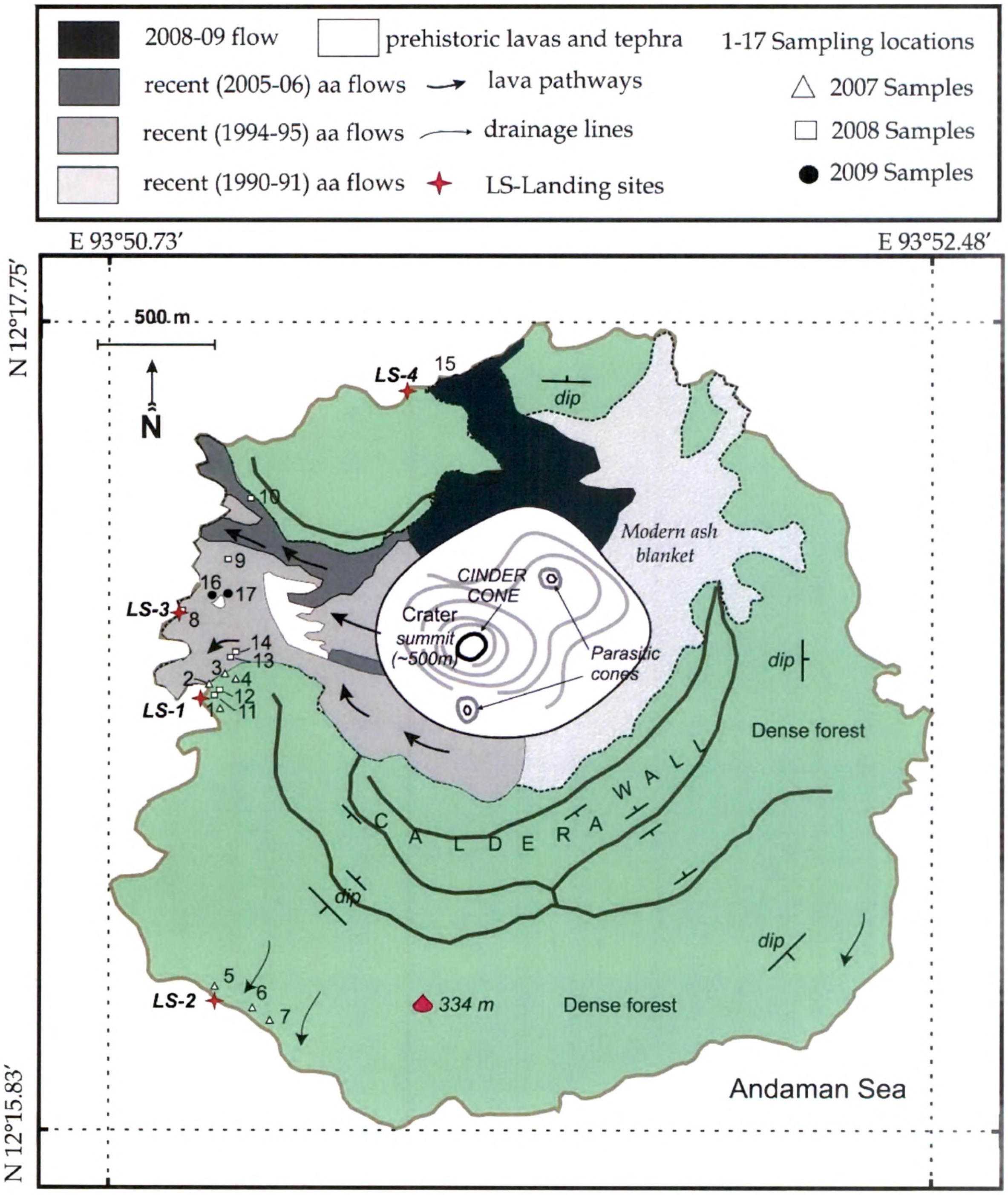

Fig. 4.1 Geological map of the Barren Island Volcano showing various lava flows and structures and sampling locations.

On the main island of the Andamans, we collected rock samples form the Ophiolite Group of rocks, particularly from those of igneous origin and samples of mud, clasts and water from the mud volcanoes. The samples from the Ophiolite Group include pillow lava, basalt, dolerite dike, gabbro, altered and fresh peridotite, andesite and plagiogranite. The sample locations are marked on Fig. 4.2 and the details of these are given in Table 4.2. Samples of mud breccia, clasts and water were collected from mud volcanoes of Baratang Island (Middle Andaman) and Hathilevel, Diglipur (North Andaman). Apart from water samples from mud volcanoes, water from springs, wells and rain were also collected. The details of these samples are given in Tables 4.3 and 4.4. All rock samples were collected in clean polythene bags, whereas water samples were collected in pre-cleaned polypropylene bottles rinsed several times with the water being sampled.

4.2 Analytical Methods

In order to achieve the scientific goals set for this thesis work, petrological, geochemical and isotopic characterization of the samples were required. Detailed and systematic approaches were adopted during this study for precise and accurate analysis of the mineralogical, major and trace elemental compositions and Sr, Nd and Pb isotopic ratios of samples. This section discusses the analytical methods utilized for the above work. Significant amount of efforts have been made during this thesis work to streamline the Sr and Nd isotope chemistry of samples in our laboratory, the details of which have been presented in next few sections.

Geochemical and isotopic characterizations of samples require well homogenization of rock and sediment samples. During this study, proper care was taken to avoid any metal contamination while powdering the

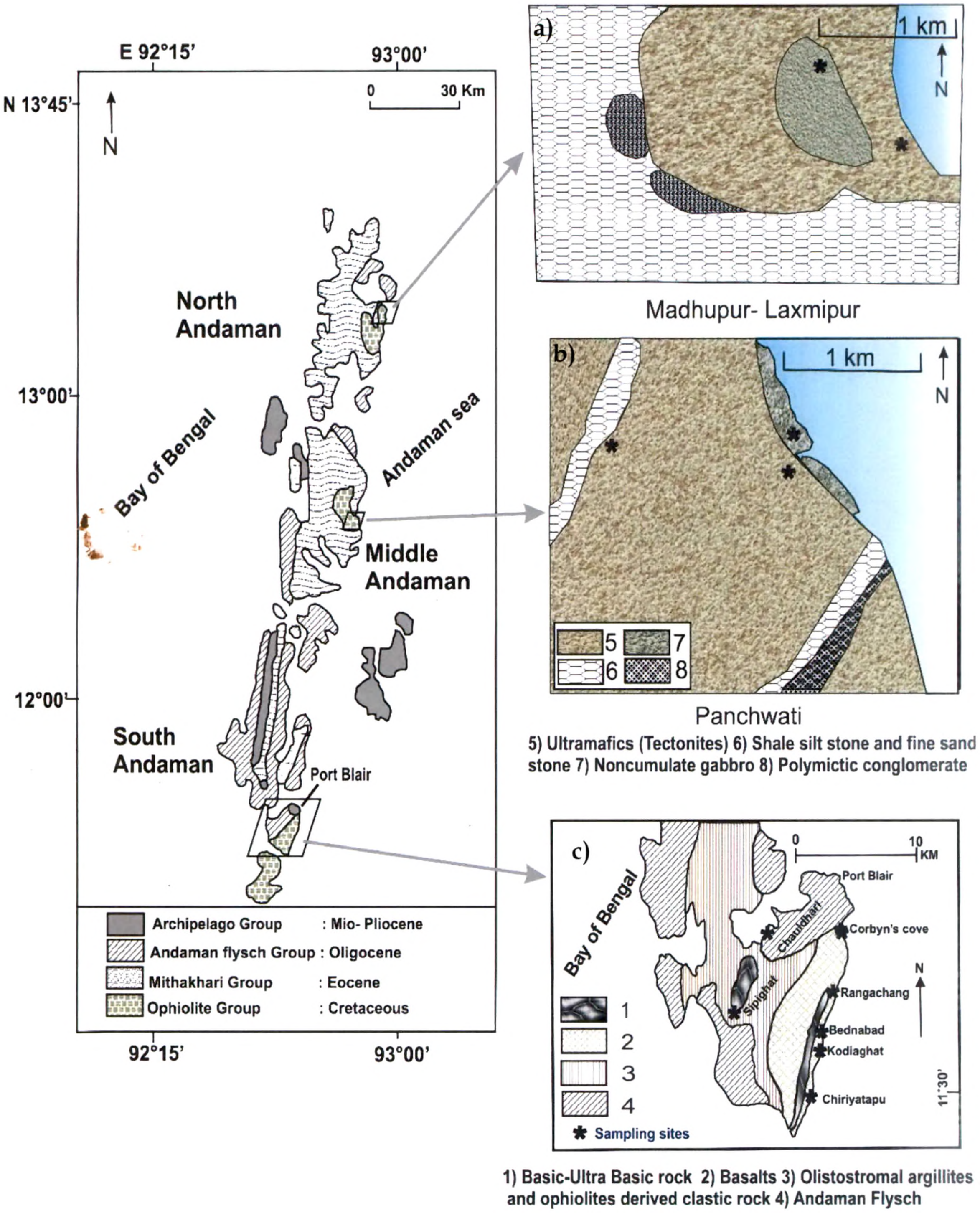

Fig. 4.2: Geological map of Andaman Islands (modified after Ray et al., 1988 and Pal and Bhattacharya 2010) with sampling locations marked on it with stars (✱); a) North Andaman b) Middle Andaman c) North Andaman

Table 4.1: Descriptions of samples form lava flows and ash beds of the Barren Island Volcano (Island Arc Group), SL: Sampling Location

Sample ID	Geographical Coordinates	Short description	Sub-group
BI-07-01	N 12° 16.797', E 93° 51.008'	Massive - jointed - old lava - caldera wall, SL-1	Precaldera
BI-07-02	N 12° 16.797', E 93° 51.008'	Red - altered - lava, below from the above sample, SL-1	Precaldera
BI-07-03	N 12° 16.874', E 93° 50.939'	Plag - cpx xenoliths bearing lava - from wall, SL-2	Precaldera
BI-07-04	N 12° 16.874', E 93° 50.939'	Scoria - flow of unknown origin (1991? Or older?), SL-2	Post caldera
BI-07-05	N 12° 16.943', E 93° 51.015'	Scoria - flow of unknown origin (1991? Or older?), SL-4	Post caldera
BI-07-06	N 12° 16.89', E 93° 51.054'	Ash - from surface blanket – mixed, SL-4	Post caldera
BI-07-07	N 12° 16.250', E 93° 50.932'	Core - lower most lava flow on caldera wall, SL-5	Precaldera
BI-07-08	N 12° 16.250', E 93° 50.932'	Red consolidated ash in between lava flows - caldera wall, SL-5	Precaldera
BI-07-09	N 12° 16.250', E 93° 50.932'	Core - middle lava flow on caldera wall, SL-5	Precaldera
BI-07-10	N 12° 16.250', E 93° 50.932'	Core - top lava flow on caldera wall, SL-5	Precaldera
BI-07-11	N 12° 16.09', E 93° 51.153'	Ash - from surface inside the forest, SL-6	Modern
BI-07-12	N 12° 16.969', E 93° 51.272'	Core - lava flow - flowed down over the caldera into sea, SL-7	Precaldera
BI-07-13	N 12° 16.969', E 93° 51.272'	Core - lava flow - flowed down over the caldera into sea, SL-7	Precaldera
BI-08-01	N 12° 17.078', E 93° 50.915'	Scoria - top of lava flow (94/95 flow?), SL-8	Post caldera
BI-08-02	N 12° 17.078', E 93° 50.915'	Toothpaste lava - surface - lava delta (94/95 flow?), SL-8	Post caldera
BI-08-03	N 12° 17.078', E 93° 50.915'	Core of an older flow - lava delta (94/95 flow?), SL-8	Post caldera
BI-08-04	N 12° 17.135', E 93° 51.010'	Scoria - older flow - lava delta (91 flow?), SL-9	Post caldera

Table 4.1 continued

Sample ID	Geographical Coordinates	Short description	Sub-group
BI-08-05	N 12° 17.310', E 93° 51.137'	Core - bottom most flow - caldera wall – north, SL-10	Precaldera
BI-08-06	N 12° 17.310', E 93° 51.137'	Core - top most flow - caldera wall – north, SL-10	Precaldera
BI-08-07	N 12° 17.310', E 93° 51.137'	Scoria - 2005 lava flow, SL-10	Modern
BI-08-08	N 12° 16.857', E 93° 50.950'	Plag - cpx xenoliths bearing lava - rolled boulders, SL-11	Precaldera
BI-08-09	N 12° 16.857', E 93° 50.950'	Ash layer - coarse - at LS2 (same as 07-TL-02), SL-12	Precaldera
BI-08-10	N 12° 16.867', E 93° 50.952'	Plag - cpx xenoliths bearing lava - from top, SL-12	Precaldera
BI-08-11	N 12° 17.083', E 93° 50.936'	Core - lava flow 20m from LS1 (94/95 flow?), SL-13	Post caldera
BI-08-12	N 12° 17.094', E 93° 50.983'	Core - lava flow - near LS1 (near toothpaste lava) 94/95?, SL-14	Post caldera
BI-08-13	N 12° 17.094', E 93° 50.983'	Top of BI-08-12 flow - 94/95?, SL-14	Post caldera
BI-08-14	N 12° 17.078', E 93° 50.915'	Core - upturned slabs - toothpaste flow, SL-8	Post caldera
BI-08-15	N 12° 17.078', E 93° 50.915'	Top - upturned slabs - toothpaste flow, SL-8	Post caldera
BI-09-01	N 12° 17.594', E 93° 50.566'	2009 lava - hot fresh lava scoria, SL-15	Modern
BI-09-02	N 12° 17.099', E 93° 50.943'	2009 ash - falling ash collected from surface, SL-16	Modern
BI-09-03	N 12° 17.099', E 93° 50.943'	Toothpaste lava - surface, SL-17	Post caldera
BI-09-04	N 12° 17.099', E 93° 50.943'	Toothpaste lava - 30 cm, SL-17	Post caldera
BI-09-05	N 12° 17.099', E 93° 50.943'	Toothpaste lava - 5m up stream, SL-16	Post caldera
Mineral-1	N 12° 16.857', E 93° 50.950'	Inclusion in ankeramite lava - plag , SL-11	Plagioclase xenolith
Mineral-2	N 12° 16.857', E 93° 50.950'	Inclusion in ankeramite lava – pyroxene, SL-11	Pyroxene xenolith

Table 4.1 continued

Sample ID	Geographical Coordinates	Short description	Sub-group
BI-07-TL-01	N 12° 16.797', E 93° 51.008'	loose ash - south of 7-1, 2007 ash?, SL-1	Modern
BI-07-TL-02	N 12° 16.852', E 93° 50.939'	coarse ash - thick layer, SL-2	Post caldera
BI-07-TL-03	N 12° 16.874', E 93° 50.939'	Old consolidated ash from a gully, SL-2	Post cladera
BI-07-TL-04	N 12° 16.243', E 93° 50.975'	Old - laminated ash - on beach section, SL-5	
BI-07-TL-05	N 12° 16.250', E 93° 50.932'	Ash bed in between lava flows, SL-5	
BI-07-TL-06	N 12° 17.094', E 93° 50.983'	Very old (bottom most) - laminated ash - on beach section, SL-14	
BI-08-TL-01	N 12° 17.310', E 93° 51.137'	Yellow ash - bottom most - on caldera wall – north, SL-10	Precaldera
BI-08-TL-02	N 12° 17.310', E 93° 51.137'	Red ash - below oldest flow on caldera wall – north, SL-10	Precaldera

Table: 4.2 Description of samples collected from the Ophiolite Group, Andaman Islands

Sample ID	Geographical coordinates	Location	Short description
PB-07-03	N 11° 30.34', E 92° 42.025'	Chiriyatapu	Buff coloured Basalt
PB-07-04A	N 11° 30.62', E 92° 42.41'	Chiriyatapu	Basalt
PB-07-05A	N 11° 31.85', E 92° 43.45'	Kodiyaghat	Plagiogranite
PB-07-05B	N 11° 31.85', E 92° 43.45'	Kodiyaghat	Basaltic flow/ Phlogopite also observed
PB-07-06	N 11° 33.96', E 92° 44.07'	Rangachang	Basalt (Coarse to medium grain)

Table 4.2 continued

Sample ID	Geographical coordinates	Location	Short description
PB-07-09	N 11° 38.38', E 92° 44.90'	Brooksabad	Pillow lava
PB-07-10	N 11° 38.28', E 92° 44.80'	Corbyn's Cove	Altered basalt (vein of Quartz / Zeolite)
PB-08-01	N 11° 31.847', E 92° 43.435'	Kodiyaghat	Plagiogranite
PB-08-02	N 11° 33.960', E 92° 42.071'	Rangachang	Trachyte vein in prismatic shaped with gabbro
PB-08-03	N 11° 33.960', E 92° 42.071'	Rangachang	Gabbro
PB-08-04	N 11° 33.960', E 92° 42.071'	Rangachang	Hydrothermal alteration product (plagio. + pyro.)
PB-08-05	N 11° 38.38', E 92° 44.90'	Brooksabad	Pillow lava
PB-08-06	N 11° 38.117', E 92° 44.814'	Quarry, Brooksabad	Low grade metamorphic basalt - green stone
PB-08-08	N 11° 39.700', E 92 °45.336'	Parade ground	Shale and sandstone
PB-08-11	N 11 °34.439', E 92 °40.055'	Nayasar	Green colour rock, chlorite rich
PB-08-12	N 11 °34.439', E 92 °40.055	Nayasar	Metamorphic Basalt, quartz vein
AND-09-17	N 12°34.146', E 92°57.901'	Panchwati	Serpentinite
AND-09-29	N 13°16.389', E 93°01.912'	Durgapur	Pillow lava
AND-09-31	N 13°16.224', E 92°57.748'	Madhupur	Altered Basalt
AND-09-32	N 13°16.224', E 92°53.435'	Madhupur	Serpentinite
AND-09-34	N 12°34.494', E 92°57.585'	Panchwati	Serpentinite
AND-09-35	N 12°34.494', E 92°57.585'	Panchwati	Limestone
AND-09-46	N 12°34.494', E 92°57.585'	Sippighat	Serpentinite

Table 4.2 continued

Sample ID	Geographical coordinates	Location	Short description
AND-09-50	N 11°36.112', E 92°40.956'	Nayasar	Serpentinite
AND-09-58	N 11°29.362', E 92°42.578'	Mundapahar	Plagiogranite
AND-09-60	N 11°31.271', E 92°43.043'	Chiriyatapu	Dolerite/ Gabbro
AND-09-62	N 11° 38.38', E 92° 44.90'	Brooksabad	Pillow lava

Table: 4.3a Description of mud breccia samples collected from Mud Volcanoes of Andaman Islands

Sample ID	Geographical coordinates	Location	Short description
Mud Breccia			
BTMV-2	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud collected from top of the cone
BTMV-3	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud relatively older
BTMV-4	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud collected from deeper part
BTMV-5	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud collected from smaller cone
BTMV-6	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud collected from another cone
BTMV-7	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud collected from smaller cone
BTMV-8	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud looking older
BTMV-9	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Green mud (serpentine)

Table 4.3a continued

Sample ID	Geographical coordinates	Location	Short description
BTMV-10	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Fine mud collected from top of the cone
BTMV-11	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Fine mud collected from another site
BTMV-12	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Green mud (serpentine)
HLMV-1	N 13°24.894', E 92°53.579'	Diglipur, North Andaman	Fine mud ,recent flow from biggest cone
HLMV-3	N 13°24.894', E 92°53.579'	Diglipur, North Andaman	Fine mud collected from 1 ft deeper level
HLMV-6	N 13°24.894', E 92°53.579'	Diglipur, North Andaman	Fine mud collected from dormant cone
HLMV-8	N 13°24.736', E 92°53.446'	Diglipur, North Andaman	Solidified mud collected from another site
HLMV-12	N 13°24.736', E 92°53.446'	Diglipur, North Andaman	Fine mud collected from cone
HLMV-15	N 13°24.660', E 92°53.442'	Diglipur, North Andaman	Fine mud collected 15 mt away from vent
HLMV-16	N 13°24.660', E 92°53.442'	Diglipur, North Andaman	Green mud (serpentine)

Table: 4.3b Description of rock clast samples collected from Mud Volcanoes of Andaman Islands

Sample ID	Geographical coordinates	Location	Short description
Rock clast			
BTMV-01-X2	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Rock clast collected from first site
BTMV-01-X5	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Rock clast collected from first site
BTMV-01-X6	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	Rock clast collected from first site

Table 4.3b continued

Sample ID	Geographical coordinates	Location	Short description
BTMV-02-X4	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Rock clast collected from second site
BTMV-03-X2	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Rock clast collected from third site
BTMV-03-X3	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Rock clast collected from third site
BTMV-03-X4	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Rock clast collected from third site
BTMV-03-X5	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	Rock clast collected from third site

Table: 4.4 Water samples from Mud Volcanoes and other water bodies, Andaman Islands

Sample ID	Geographical coordinates	Location	Date of collection	Short description
Mud Volcanoes				
BTMVW-1	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	3-Apr-09	Mud water
BTMVW-2	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	3-Apr-09	Mud water
BTMVW-3	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	3-Apr-09	Mud water
BTMVW-4	N 12°07.777', E 92°47.528'	Baratang, Middle Andaman	3-Apr-09	Mud water
BTMVW-5	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	3-Apr-09	Mud water
BTMVW-6	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	9-Dec-09	Mud water
BTMVW-7	N 12°07.926', E 92°46.834'	Baratang, Middle Andaman	12-Apr-10	Mud water

Table 4.4 continued

Sample ID	Geographical coordinates	Location	Date of collection	Short description
HLMVW-1	N 13°24.894', E 92°53.579'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-2	N 13°24.894', E 92°53.579'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-3	N 13°24.736', E 92°53.446'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-4	N 13°24.736', E 92°53.446'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-5	N 13°24.736', E 92°53.446'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-6	N 13°24.660', E 92°53.442'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-7	N 13°24.660', E 92°53.442'	Diglipur, North Andaman	5-Apr-09	Mud water
HLMVW-8	N 13°24.660', E 92°53.442'	Diglipur, North Andaman	9-Dec-09	Mud water
HLMVW-9	N 13°24.660', E 92°53.442'	Diglipur, North Andaman	9-Dec-09	Mud water
Fresh Water Sources				
NSW-1	N 13°27.185', E 94°16.527'	Narcondam Island	28-Mar-09	Narcondam Spring water
NSW-2	N 13°27.050', E 94°16.469'	Narcondam Island	28-Mar-09	Narcondam Spring water
NSW-3	N 13°27.273', E 94°16.455'	Narcondam Island	28-Mar-09	Narcondam Spring water
LBSW-1	N 13°11.625', E 93°02.181'	Diglipur, North Andaman	13-Apr-10	Lamiya bay spring water
PWSW-1	N 12°33.979', E 92°57.947'	Panchwati, Middle Andaman	14-Apr-10	Panchwati spring water
ZCWW-1	N 12°08.336', E 92°47.545'	Baratang, Middle Andaman	14-Apr-10	Well water from Baratang
PBRW	N 11°40.0', E 92°45.0'	Port Blair		Andaman rain-water, Port Blair

samples. Prior to powdering chipped sample pieces were thoroughly cleaned (repeatedly with HCl, MilliQ water and Ethyl alcohol). Powdering was done using an agate mortar and pestle. The samples were powdered to less than 75 micron size (200 mesh.), homogenized and stored in plastic bottles. These powdered samples were used for various mineralogical (powder diffraction), geochemical and isotopic studies.

4.2.1 Petrography

Petrographic studies focus on detailed descriptions of rocks in the hand specimen or under microscope or through mineralogical composition determined by techniques such as X-Ray diffractometry (XRD). As the rock is an aggregate of minerals, "petrography" deals in effect with the identification of minerals and the study of their paragenesis. For the present work, we used thin section studied for the igneous rocks and XRD studies for sediment samples from the mud volcanoes.

For our work, polished thin sections of rocks were prepared and analyses performed under petrological microscopes; Leica DM2500P microscope in IIT Bombay, Pawai and Nikon Eclipse LV100POL microscope at PRL, Ahmedabad. Based on their optical properties minerals were identified and their textural relationships determined.

XRD was done on mud breccia samples at IIT Bombay with the help of Prof. Kanchan Pande to find out different constituent minerals in mud matrix. For this purpose a Rigaku Geigarflex, X-Ray diffractometer was used. Cu - K_α (λ = 1.54056 Å) X-Ray was used as primary source. Minerals were identified from the diffractogram (Intensity vs. 2θ) using standard identification procedures (Brown and Brindley, 1980).

4.2.2 Geochemical Characterization

Major element content

The major elements are chemical elements having concentrations greater than one part per hundred (or > 1 wt %). Although concentrations of MnO, K_2O and sometimes P_2O_5 are less than 1 wt% in many basaltic rocks, they still are considered as major elements. Major elements concentrations in igneous rock help in the classification of rock types, to understand the degree of differentiation and determine trends of magma evolution. During this study, the major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5) were analyzed using X- Ray Fluorescence (XRF) spectroscopy method in an automated Phillips Axios X-Ray Spectrometer (Panalytical Limited) fitted with an Rh X-Ray tube, operated at 50kV and 55 mA, of 4kW power. The instrument is a national facility for Planetary Science and exploration Program (Planex) of Indian Space research Organization (ISRO) housed at Thaltej campus, Physical Research Laboratory, Ahmedabad. The instrument was set-up installed and calibrated for routine measurement of rock samples under this thesis work (Ray et al., 2008). The analyses for this work were done on pressed pellets method of the powdered samples.

Pressed pellets of our samples and rock standard were prepared; following the procedures given below. Four grams of samples igneous rock samples and two grams of mud samples were weighed accurately in a balance and transferred into an agate mortar. Each sample powder was mixed homogeneously with 1 g or 0.5 g of wax binder in a 4:1 ratio of sample: binder. The mixture was transferred to a 37 mm standard aluminum cup, filling up to two third of its volume. It was then placed under a compressor at a pressure of 150kN for 2 minutes. The pressure was removed slowly and pellet was recovered and labelled on the back.

Measurements were done with a wave-length dispersive X-fluorescent spectrometer which determined the intensity of X-s diffracted from sample. Concentration of a specific element was determined by comparing the X- intensity with those from several standards through a calibration procedure. For calibration, appropriate set of standards were used for a given set of samples to avoid interferences and absorptions caused by matrix. For example, igneous samples were analyzed using igneous rock standards, while sedimentary rocks were analyzed with calibration using sedimentary rock standards. Some of these standards were used as unknown for determining accuracy and reproducibility of our measurements. The precision of measurements at 2σ level, based on repeated analyses of samples/standards, for major oxides was better than 2%. The international rock standards which used for calibration of different oxides were: AGV-2, BCR-2, JA-3, JB-1a, JB-2, JB-3, JGb-1, JMS-2, MAG-1, SCO-1, SDO-1, STM-1 and W-2. Table 4.5 gives the rock type from which these standards have been prepared and their suppliers. Fig. 4.3 presents typical calibration curves, generated on the XRF using these standards, used for determination of the concentrations of various major oxides in our samples. The rock standards BHVO-2 (Basalts from Hawaiian Volcanological observatory) and BCR-2 (Basalts from Columbia River Traps) were treated as unknown to ascertain the accuracy and reproducibility of measurements. During the course of our experiment BHVO-2 (n=27) and BCR-2 (n=7) were analysed repeatedly along with the samples (Table 4.6). The measured and reported concentrations for major oxides show very good agreement within the analytical uncertainty (Fig. 4.4).

Loss on Ignition

The loss on ignition (LOI) analysis is a measure of the amount of hydrated and non-primary (i.e. not original to rock) phases. Compounds that typically contribute to the total LOI are: volatile compounds, including H_2O, CO_2, Cl, S and other added compounds, such as O_2 or CO_2 resulting from the oxidation of FeO to Fe_2O_3 and carbonate formation. The analysis is performed for several reasons: I) to obtain an estimation of the amount of alteration of a sample, II) to prepare a sample powder for major and trace elements analysis and III) to remove phases that are not original to the rock, which could influence the major/trace element composition.

Table 4.5: Rock standards used during the generation of major element data

Rock standards	Rock Types	Supplier
AGV-1	Andesite from Guano valley	USGS*
AGV-2	Andesite from Guano valley	USGS*
BCR-2	Columbia river basalt	USGS*
BHVO-2	Hawaiian Basalt	USGS*
JA-3	Japanese andesite	GJS**
JB-1a	Japanese basalt	GJS**
JB-2	Japanese basalt	GJS**
JB-3	Japanese basalt	GJS**
JGb-1	Japanese Gabbro	GJS**
JMS-2	Marine Mud	GJS**
MAG-1	Marine Sediments	USGS*
SCO-1	Cody Shale	USGS*
SDO-1	Shale	USGS*
STM-1	Napheline Syenite	USGS*
W-2	Diabase	USGS*

USGS*: United state geological survey and GJS**: Japanese geological Survey

Two grams each of moisture free sample powder (dried at 110°C) was transferred into a cleaned dry quartz crucible and accurately weighed. The quartz crucible is placed inside a muffle furnace preheated to 1050°C for igneous rocks and 1070°C for sedimentary rocks. After igniting the sample for two hours, the furnace was switched off and allowed to cool to room temperature, the sample was weighed again and the difference in measured weight is converted into LOI by the following equation:

$$LOI = \left(\frac{(W_i - W_f)}{W_i} \right) \times 100 \tag{4.1}$$

Where W_i is initial measured weight (Sample and crucible) and W_f is the measured weight after ignition (sample and crucible). LOI is expressed in %.

Table 4.6: Measured and reported major oxide concentrations in BHVO -2 and BCR-2

Major Oxide	BHVO-2 (Reported*) wt% ± 2σ	BHVO-2 (measured) mean (n=27) wt% ± 2σ	BCR-2 (Reported*) wt% ± 2σ	BCR-2 (measured) mean (n=7) wt% ± 2σ
SiO_2	49.90 ± 0.60	49.45 ± 0.33	54.10 ± 0.80	54.36 ± 0.04
TiO_2	2.73 ± 0.04	2.71 ± 0.02	2.26 ± 0.05	2.37 ± 0.02
Al_2O_3	13.50 ± 0.20	13.73 ± 0.06	13.50 ± 0.20	13.28 ± 0.01
Fe_2O_3	12.30 ± 0.20	12.50 ± 0.32	13.80 ± 0.20	13.94 ± 0.03
MnO	0.17 ± 0.01	0.16 ± 0.01	0.20 ± 0.01	0.17 ± 0.01
MgO	7.23 ± 0.12	7.34 ± 0.16	3.59 ± 0.11	3.72 ± 0.01
CaO	11.40 ± 0.20	11.52 ± 0.04	7.12 ± 0.11	7.01 ± 0.01
Na_2O	2.22 ± 0.08	2.33 ± 0.06	3.16 ± 0.11	3.26 ± 0.01
K_2O	0.52 ± 0.01	0.53 ± 0.01	1.79 ± 0.05	1.85 ± 0.01
P_2O_5	0.27 ± 0.20	0.23 ± 0.01	0.35 ± 0.02	0.38 ± 0.01
LOI	ND	-0.55	ND	ND
Total	100.24	99.94	0.20	100.34

* Values supplied by USGS and ND: Not determined

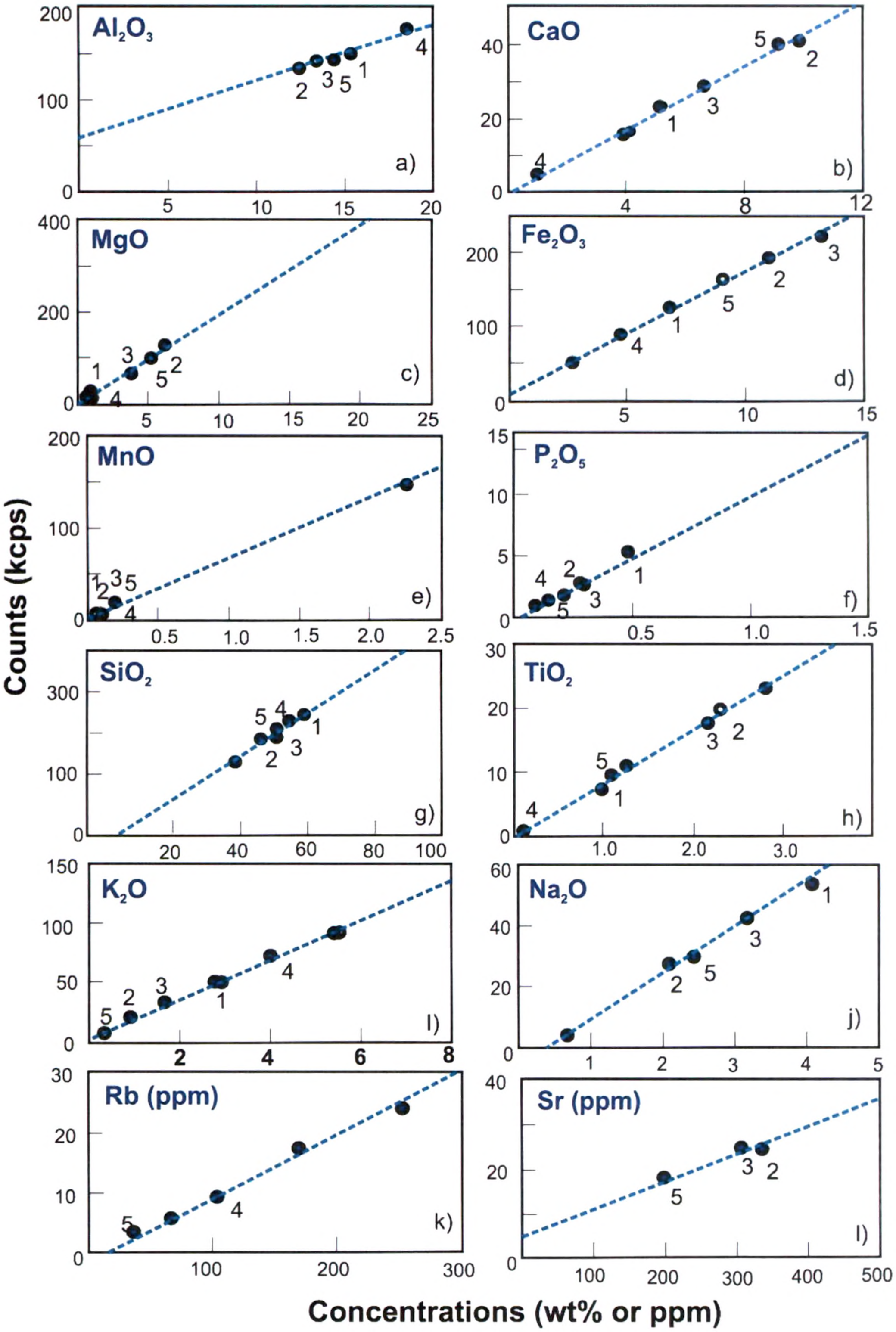

Fig. 4.3: Typical calibration curves generated using XRF for ten major element oxides (in wt %) and two trace elements (in ppm) using several international rock standards. 1) AGV-2, 2) BHVO-2, 3) BCR-2, 4) STM-1 5) W-2.

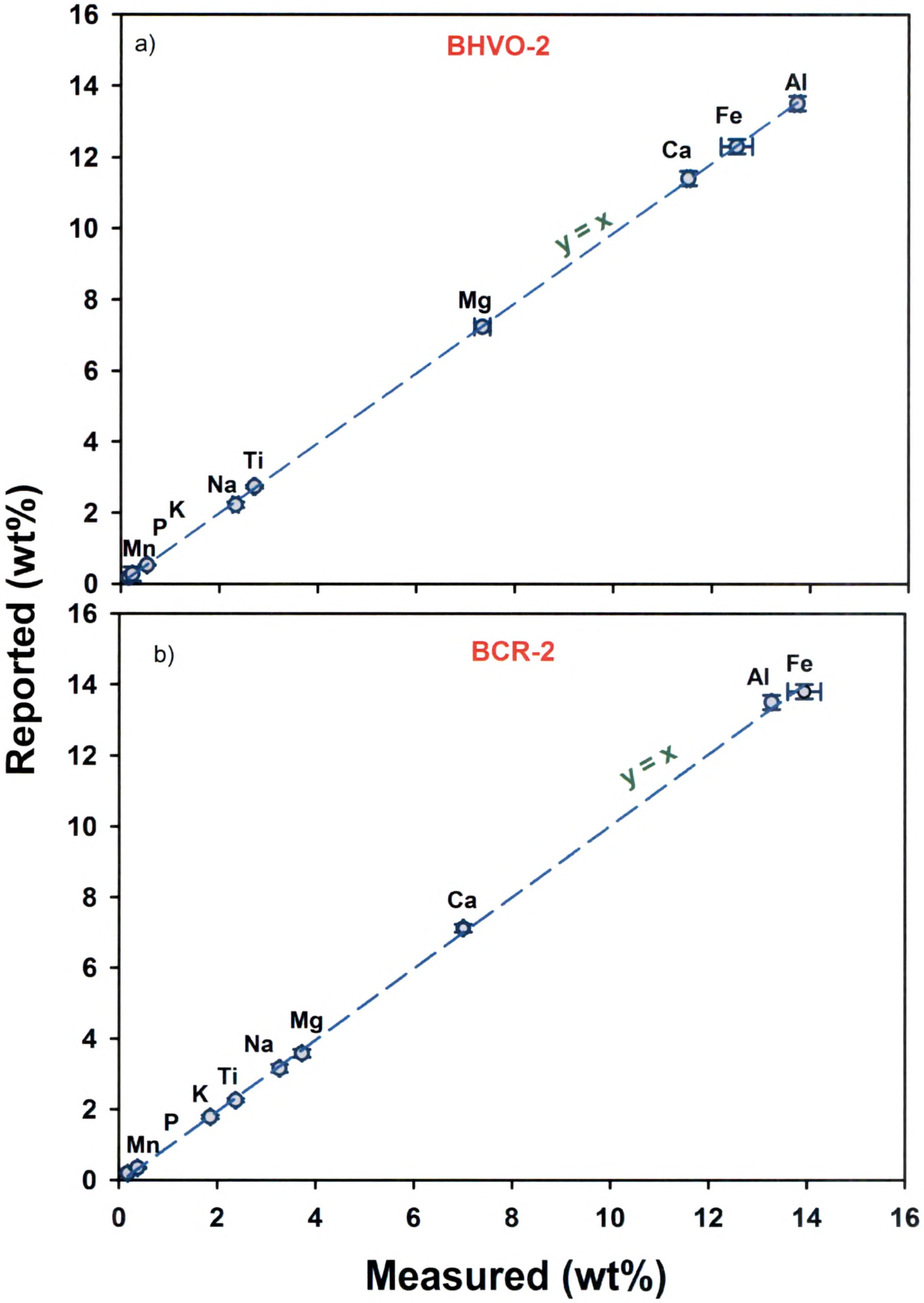

Fig.4.4: Comparison of measured and reported concentration of various major element oxides in BHVO-2 (a) and BCR-2 (b).

Trace element contents

Trace elements are chemical elements having concentrations less than 1000 ppm or 0.1 % of a rock composition. Although they do not usually form major igneous rock forming phases, but they are powerful tracers of the magmatic processes. In this work, trace element contents were measured using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Instrumental Neutron Activation Analysis (INAA) methods.

Concentrations of trace elements including 14 rare earth elements (REEs) in igneous rock samples were determined using an ICP-MS at PRL. Measurements were done on the sample solutions, in 2 % HNO_3 medium, prepared using the dissolution protocol outlined in Table 4.7

Table 4.7: Sample dissolution procedure for trace elements analysis

Step 1: ~ 50 mg of homogenized sample powder weighed into a 17ml PFA savillex teflon vial and capped with proper labelling.

Step 2: ~ 1 ml of HF + HNO_3 mixture (2:1) was added to the sample powder and thoroughly mixed.

Step 3: The vial was capped tightly and ultrasonicated for 40/60 minutes and kept overnight for complete dissolution.

Step 4: Next day, the solution vial was heated to 80°C and checked for undissolved grains. Once found completely dissolved, the solution was dried down.

Step 5: Once dried, the sample was taken back into solution using 1 ml of 8 N HNO_3.

Step 6: Making sure of complete dissolution, the solution was dried and taken back again in 8 N HNO_3.

Step 7: After the 2nd and 3rd dissolution in 8 N HNO_3, the sample was dried down and taken back into solution in 2% HNO_3.

Table 4.7 continued

Step 8: Capped sample solution vial was placed on the hotplate at 80°C for 30 minutes, to ensure that no white precipitate was left undissolved. The vial was uncapped and several drops of 2% HNO_3 were added to the cap. The dilute acid droplets were swirled around the cap so as to take back any liquid adhering to the cap.

Step 9: The sample solution was further diluted 1000 times in 2% HNO_3 and is kept in pre-cleaned 60 ml plastic bottle used as a Stock solution.

All acids used in the dissolution procedure were of ultra pure grade (from Sea-Star, Canada). For calibration purpose, an international rock standard BHVO-2 was used. Sample powder of BHVO-2, BCR-2 and AGV-2 were dissolved along with the sample with the same protocol as described in Table 4.7. Calibration curves were generated using blank and various dilutions of standard solutions. A few typical calibration curves are presented in Fig. 4.5. The isotopes ^{45}Sc, ^{51}V, ^{52}Cr, ^{59}Co, ^{60}Ni, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{93}Nb, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta and ^{232}Th, were analyzed for their respective elements. Reproducibility (external precision) of our measurements, based on the repeated analyses of sample, were better than 2% at 2σ level, for all trace elements reported here. For accuracy check, analyses of various dilutions of the international standard BHVO-2 were performed at regular intervals. It can be seen in Table 4.8, the measured and reported elemental concentrations in BHVO-2 show very good agreement within the analytical uncertainty.

Apart from analyzing them on ICP-MS some of the important trace elements in igneous rocks e.g., Ta, Rb and Th, were also analyzed using INAA for better accuracy. In addition, the samples of mud breccia that contained appreciable amounts of undissolvable organic matter were also analyzed by INAA for their trace element contents. Carefully powdered samples for INAA were dried at 110°C and packed in Al-foils and transferred to a quartz vial together with packs of BCR-1 and BHVO-2 and sealed. Blank Al foil was also packed along with the samples and standards to determine the contribution from Al foil (if any). The sealed

Table 4.8 Comparison of measured and reported concentrations for various trace elements in BHVO-2

Trace elements	Measured concentration (ppm) ± 2σ	Reported concentration* (ppm) ± 2σ
Sc	31.6 ± 3.6	31 ± 2
V	330 ± 36	329 ± 18
Cr	290 ± 31	285 ± 28
Co	48.1 ± 5.4	47 ± 4
Ni	114 ± 13.8	112 ± 18
Rb	10.5 ± 1.1	10.1 ± 1.2
Cs	0.11 ± 0.02	0.11 ±0.02
Sr	383 ±36	382 ± 20
Y	23 ± 2.4	23 ± 2
Zr	159 ± 17	160 ± 16
Nb	16.3 ± 1.9	16.4 ± 0.1
Ba	129 ± 1	128 ± 8
La	15.1 ± 1.5	15.6 ± 0.1
Ce	37.3 ± 3.6	37 ± 2
Pr	5.35 ± 0.86	5 ± 0.6
Nd	24.4 ± 3.3	24 ± 2
Sm	6.1 ± 0.76	5.8 ± 1
Eu	2.06 ± 0.23	2 ± 0.2
Gd	6.24 ± 0.78	5.9 ± 0.8
Tb	0.82 ± 0.17	0.86 ± 0.06
Dy	5.37 ± 0.58	4.9 ± 0.8
Ho	0.93 ± 0.07	0.91 ± 0.12
Er	2.59 ± 0.27	2.3 ± 0.2
Tm	0.31 ± 0.03	0.3 ± 0.1
Yb	1.95 ± 0.24	2.0 ± 0.4
Lu	0.29 ± 0.01	0.26 ± 0.08
Hf	4.13 ± 0.39	4.1 ± 0.8
Ta	0.93 ± 0.12	0.94 ± 0.14
Pb	1.61 ± 0.10	1.4 ± 0.4
Th	1.12 ± 0.19	1.18 ± 0.18
U	0.41 ± 0.07	0.44 ± 0.06

*Gao et al., (2002); kent et al., (2004); Raczek et al., (2003)

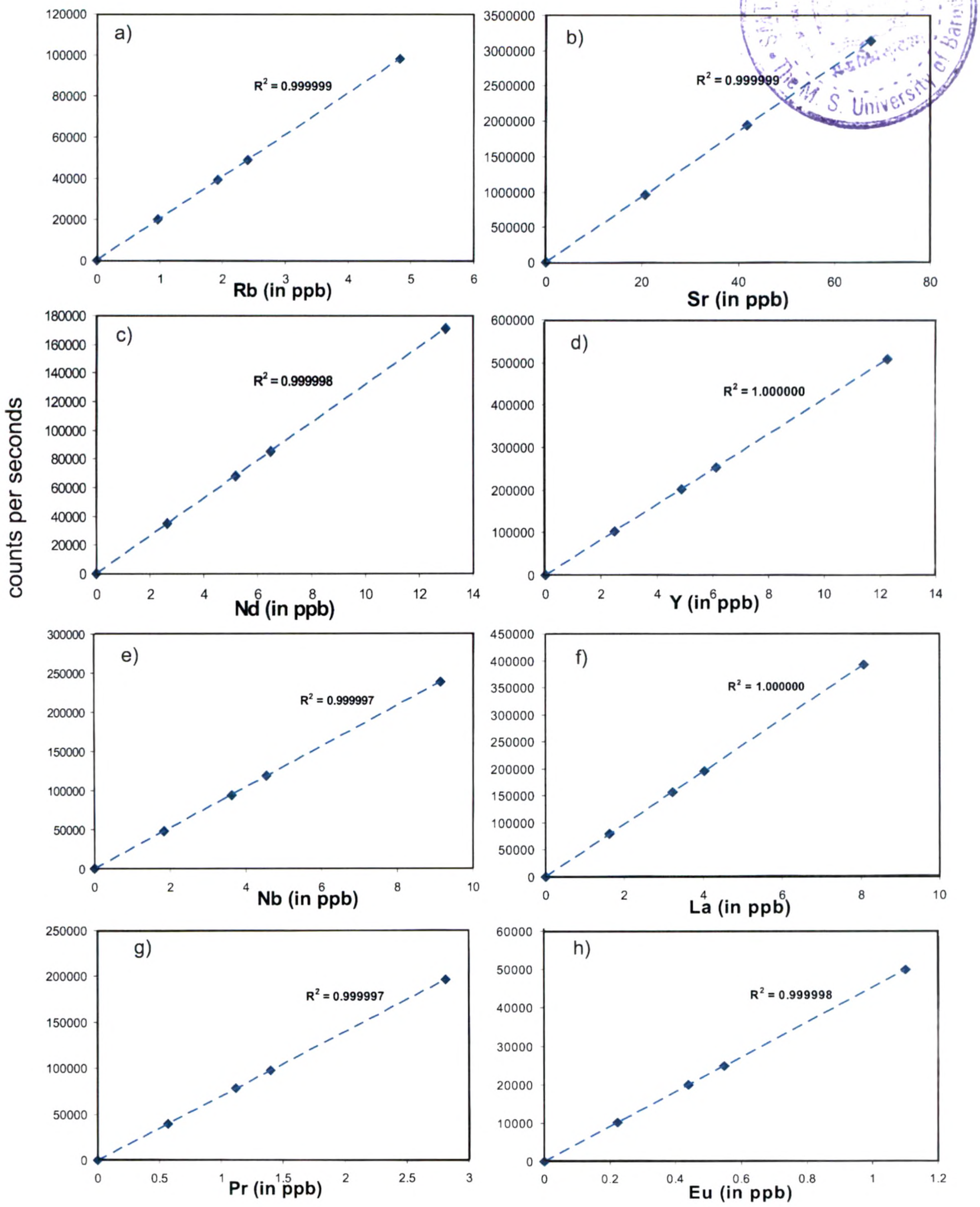

Fig. 4.5: Typical calibration curves for various trace elements generated on ICP-MS using various dilutions of a standard solution (BHVO-2).

quartz vial was subsequently transferred into a container and sent for irradiation at the CIRUS reactor of the Bhabha Atomic Research Center, mumbai, where the samples were irradiated for 15 days. The irradiated samples were counted on a Hyper Pure Germanium (HPGE) Υ- detector at PRL. The 148cc, high purity Ge-detector, has a resolution of 2.2 KeV for 1333 KeV gamma of ^{60}Co and is housed in a 10 cm thick lead shield. The counting was repeated after appropriate cooling intervals to determine both short and long lived radioisotopes. The concentration of various elements like Ta, Rb, Th, Zr, Nb and nine rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu) was measured by sample standard (BCR-1) comparative method as outlined by Flanagan (1976) and Laul (1979).

Table 4.9 Comparison of measured and reported concentrations for various trace elements in BCR-1 and BHVO-2 by INAA

Trace elements	BCR-1 Reported* wt%/ppm ± 1σ	BCR-1 Measured wt% ppm ± 1σ	BHVO-2 Reported* wt%/ppm ± 1σ	BHVO-2 Measured wt%/ppm ± 1σ
Fe	9.38 ± 0.1	9.34 ± 0.1	8.63 ± 0.1	8.51 ± 0.1
Co	38 ± 0.1	37.83 ± 0.1	45 ± 0.1	45.2 ± 0.1
Sc	32 ± 0.5	31.86 ± 0.5	32 ± 0.5	31.63 ± 0.2
Na	2.42 ± 0.1	2.42 ± 0.1	1.64 ± 0.1	1.64 ± 0.1
Ca	4.95 ± 0.5	4.73 ± 0.5	8.17 ± 0.5	8.25 ± 0.5
Rb	46 ± 1	47.15 ± 1	9.08 ± 0.5	9.9 ± 0.5
Sr	330 ± 20	367 ± 20	396 ± 10	387± 20
Ba	675 ± 1.2	676 ± 1	131 ± 5	135 ± 10
Zn	130 ± 10	123.5 ± 5	103 ± 0.5	102.4 ± 1.1
Cs	0.95 ± 0.5	ND	0.11 ± 0.05	0.13 ± 0.07
Th	6 ± 0.6	5.94 ± 0.6	1.03 ± 0.05	1.07 ± 0.04
Ta	0.79 ± 0.5	0.79 ± 0.2	1.06 ± 0.02	1.09 ± 0.01
Hf	4.9 ± 1.2	4.9 ± 0.5	4.28 ± 0.01	4.28 ± 0.04
Zr	190 ± 5	201 ± 10	172 ± 0.1	163 ±.0.16
La	25.2 ± 0.6	25.63±	15.2 ± 0.05	15.35 ± 0.07
Ce	54 ± 0.6	53.73±	37.5 ± 0.01	37.3 ± 0.02
Nd	28.7 ± 1.2	29.4±	24.5 ± 0.05	24.05 ± 0.05
Sm	6.6 ± 0.6	6.55±	6.07 ± 0.1	5.92 ± 0.03
Eu	1.94 ± 0.6	1.93±	2.07 ± 0.05	2 ± 0.02
Gd	6.67 ± 3	5.31 ± 2	6.24 ± 0.5	6.91 ± 0.06
Tb	1.07 ± 0.6	1.06 ± 0.1	0.936 ± 0.01	0.931 ± 0.04
Yb	3.36 ± 1.2	3.46±	2 ± 0.1	1.91 ± 0.02
Lu	0.50 ± 1.2	0.50±	0.27 ± 0.01	0.27 ± 0.01

* Flanagan (1976) and Laul (1979); all are in ppm expect Fe and Na in wt%

Radiogenic Isotopic ratios:

Sr and Nd isotopic ratio analyses were carried out on an Isoprobe-T Thermal Ionization Mass Spectrometer (TIMS) at the Physical Research Laboratory, Ahmedabad while the Pb isotopic ratio measurements were performed by at the Department of Earth-science, Pondicherry University, Puducherry using a Thermo-Triton TIMS. Prior to isotope ratio analyses the samples were dissolved and Sr, Nd and Pb were extracted using liquid- chromatographic techniques, the details of which are described below.

Table 4.10: Sample dissolution procedure for isotopic analyses

---

Step 1: ~ 50 mg of homogenized sample powder weighed into a 17ml PFA savillex teflon vial and capped with proper labelling.

Step 2: Add ~ 1.5 ml of HF + HNO_3 mixture (2:1) to the sample powder and mixed to ensure the acid accesses all the sample powder.

Step 3: The vial was capped tightly and ultrasonicated for 40/60 minutes and kept overnight for complete dissolution.

Step 4: Next day, the solution vial was heated to 80°C and checked for undissolved grains once found completely dissolved the solution was dried down.

Step 5: Once dried, the sample was taken back into solution using 1 ml of 8 N HNO_3 it.

Step 6: Making sure of complete dissolution of solution was dried and taken back again in 8 N HNO_3.

Step 7: After the 2nd and 3rd dissolution in 8 N HNO_3, the sample was dried down and taken back into solution in 2 ml of 6 N HCl.

Step 8: 2 ml of 6 N HCl sample was dried down to convert the elements to chloride.

Step 9: The final sample solution was prepared in 1 ml of 2 N HCl and capped for column chemistry

---

Cation-exchange chromatography was used to separate Sr and REE from other elements present in the sample. Subsequently, Nd was separated from other REE using elements specific chromatographic medium. For Sr and REE separation we used BioRad make AG 50W X 8 (200 to 400 mesh size) resin, whereas the Nd separation Ln-specific resin from Eichrom (50 to 100 µm mesh) was used. The columns used were of pure quartz and of different heights depending upon the purpose, e.g., the primary columns for Sr and REE separation were 25 cm in height and had internal diameter of 0.8 cm, where as for Nd separation smaller column (height = 15 cm, ID = 0.5 cm) were used. The elution procedures, determined through calibration, are described in Table 4.11.

Table 4.11: Protocol for Sr and REE separation from sample solution

Step 1: The Dowex 50 cation exchange resin was cleaned properly using milli-Q water to remove fine floating materials from resin.

Step 2: Cleaned quartz wool was fixed in the base of primary columns to hold the resin and maintained constant flow.

Step 3: The primary columns were filled with Dowex 50 cation exchange resin up to height of ~ 16 cm.

Step 4: Columns were cleaned with 5 ml of 6 N HCl and subsequent conditioned with 6 ml of 2 N HCl.

Step 5: 1 ml dissolved sample solution in 2 N HCl was loaded gently onto the resin bed using pipette.

Step 6: 1 ml of 2 N HCl passed to allow complete loading

Step 7: 36 ml of 2 N HCl was passed and discarded (for removal of Fe, K, Na, Rb, Ca etc.)

Step 8: Collection for Sr: 12 ml of 2 N HCl was eluted and collected for Sr.

Table 4.11 continued

Step 9: Collection for REE: 18 ml of 6 N HCl was eluted and collected for REE cut - dried down, taken in 100 µl of 0.18N HCl and capped for REE column chemistry.

Step 10: The collected Sr cut was dried down – ready for measurement on MS.

Step 11: Columns were cleaned 2 times with full volume of 6 N HCl and half full volume of milli-Q water for regeneration.

Table 4.12: Protocol for Nd separation from REE Cut

Step 1: The Ln-specific resin was cleaned properly using milli-Q water to remove fine floating materials from resin.

Step 2: Cleaned quartz wool was fixed in the base of columns to hold the resin and was maintained constant flow.

Step 3: The columns were filled with Ln-specific resin up to height of ~ 9 cm.

Step 4: Columns were cleaned with 5 ml of 2N HCl and subsequently conditioned with 2 ml of 0.18 N HCl.

Step 5: 1 ml collected and dried REE cut (100 µl of 0.18N HCl) was loaded gently onto the resin bed using pipette.

Step 6: Another 100 µl of 0.18N HCl was loaded after washing the vial for each sample

Step 7: Wash- 19 ml of 0.18 N HCl was passed and discarded (for removal of La, Ce, Pr etc.)

Step 8: Collection for Nd: 7 ml of 0.3 N HCl was eluted and collected for Nd.

Step 9: Columns were cleaned with half full volume with 6 N HCl and full volume of milli-Q water for regeneration of the resin.

Step 10: The collected Nd cut was dried down and stored for Nd-analysis.

Step 11: The columns were stored in diluted acid medium for further use.

The purified Sr from a sample was loaded with 0.1 M phosphoric acid on degassed and oxidized high purity tantalum (Ta) filament whereas for purified Nd fraction was loaded on the outer degassed Ta filament of a triple filament assembly, in which outer and inner are high purity Ta filaments, while centre contains a high purity Re filament. Sr and Nd isotopic ratio measurements were done on Isoprobe-T TIMS in static mode. The ratios were corrected for instrumental mass fractionation using exponential fractionation correction (Thrilwall 1991a) and assuming $^{86}Sr/^{88}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$. During the course of these analyses, international isotopic standard for Sr, NBS-987 and Nd isotope standard, JNdi were measured routinely. The average for $^{87}Sr/^{86}Sr$ for 131 analyses of NBS-987 was found to be 0.710227 ± 0.000028 (2σ) and for the mean $^{143}Nd/^{144}Nd$ value obtained on 53 measurements of JNdi was 0512104 ± 0.000016 (2σ), these values are well within their recommended values 0.710248 ± 0.000023 (2σ) for NBS-987 and 0512100 ± 0.000005 (2σ) for JNdi. The above value of JNdi-1 corresponds to a value of 0.511847 for the widely used La Jolla Nd standard (Tanaka et al., 2000). The variations in $^{87}Sr/^{86}Sr$ of NBS-987 and $^{143}Nd/^{144}Nd$ of JNdi-1 standards are plotted against time for the course of this study (Fig. 4.6). The consistency and absence of any systematic offset indicate that our measurements are highly precise over a long period of time. Further, USGS rock standards BHVO-2 and BCR-2 were also analyzed for their $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ to establish the accuracy of our measurements. The variations of Sr and Nd isotopic ratio of BHVO-2 (N = 14) are plotted against time during course of this study. (Fig. 4.7), and these data once again, confirm the high quality (accuracy and precision) of our measurements.

Several total procedural blanks of Sr and Nd were processed along with the samples. The procedural blanks for Sr and Nd were always below

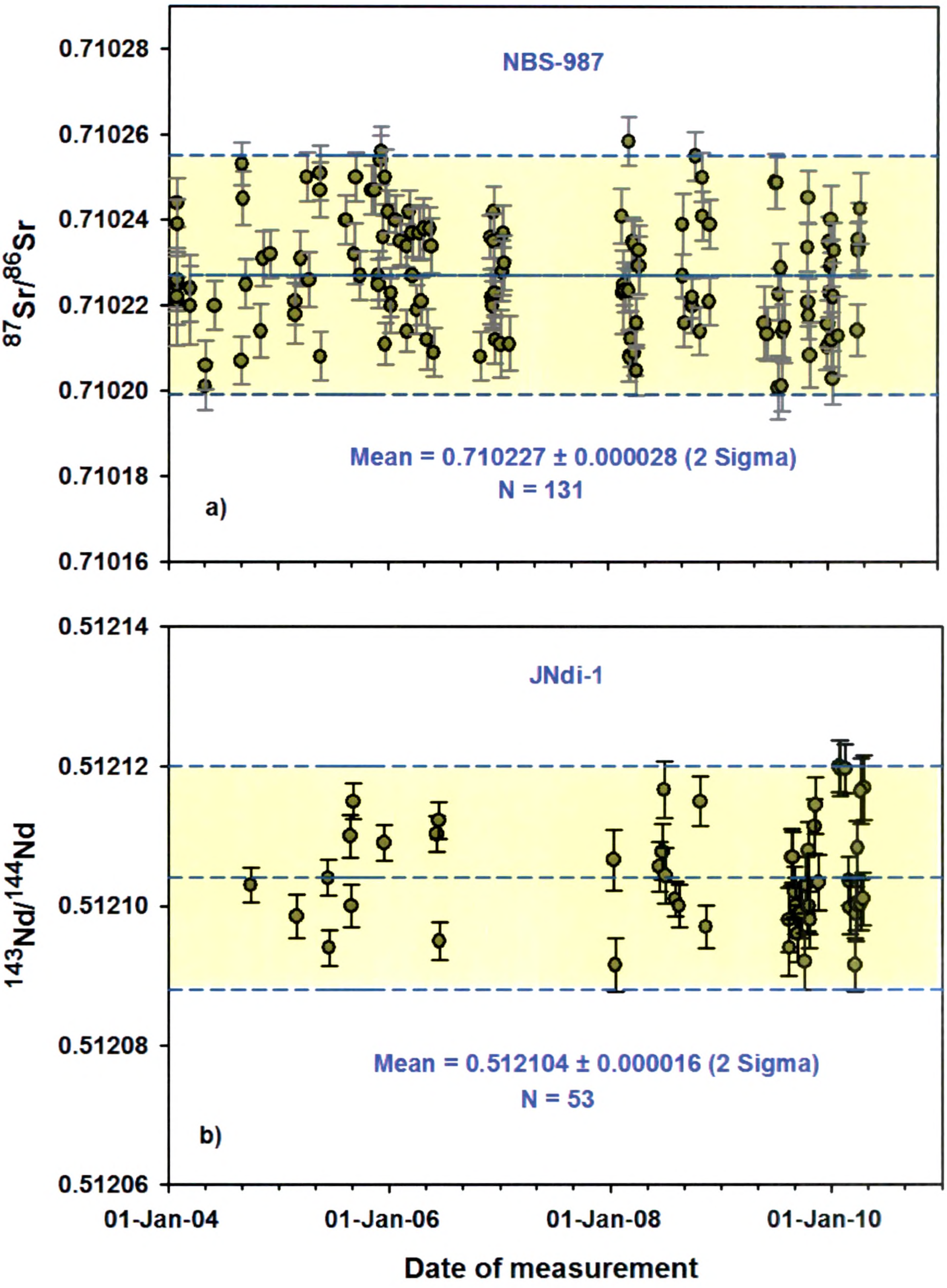

Fig. 4.6 Temporal variation of measured $^{87}Sr/^{86}Sr$ in NBS-987 (a) and $^{143}Nd/^{144}Nd$ in JNdi-1 (b). The shaded area represents mean ± SD (2 sigma) of the data points. All the data points agree well within uncertainties with the reported value.

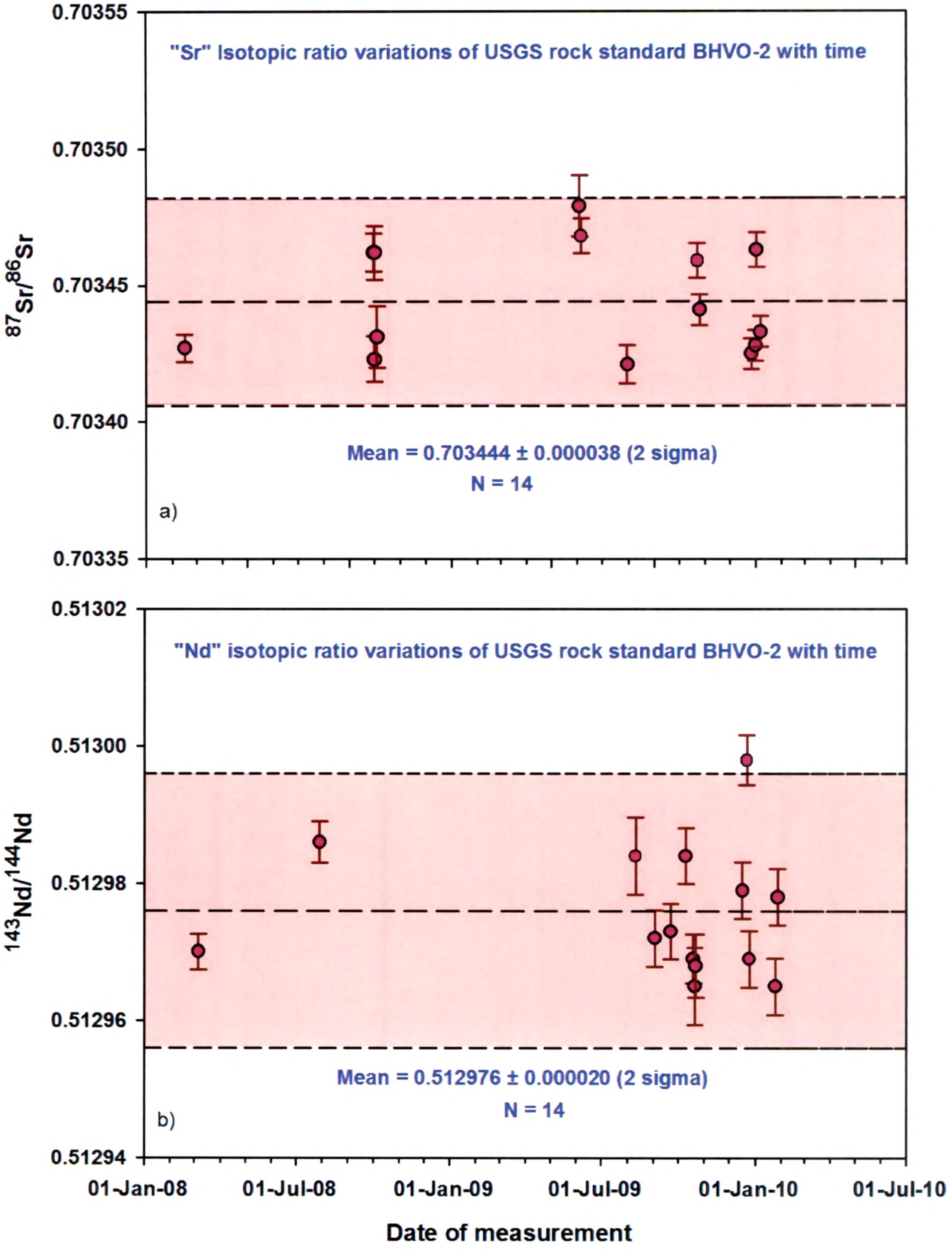

Fig. 4.7 Temporal variation of measured $^{87}Sr/^{86}Sr$ (a) and $^{143}Nd/^{144}Nd$ (b) in USGS rock standard BHVO-2. The shaded area represents mean ± SD (2 sigma) of the data points.

500pg and 400pg, respectively. These blanks are of several orders of magnitude lower than typical total Sr and Nd processed during this study and hence no corrections for blanks were made.

A few samples from Barren Island were also analyzed for their Pb isotopic ratios at Pondicherry University. About 100 mg of homogenized rock powder was digested using ultra pure HF + HCl acids on 7ml savillex vial for about one hour on hot plate at 150°C. The digested fraction was carefully decanted into another savillex vial without disturbing the undigested sample. Most of the Pb was in leachable phase because Pb prefers to go into the liquid phase (solution). Leached solution was evaporated to dryness and, a small amount of clean 1 N HBr acid was added and dried, the procedure was repeated and the final solution was prepared in 3-4 ml of 1 N HBr. Separation of Pb was then carried out using anion exchange resin following the procedure prescribed by Manhes et al. (1984). Pb was loaded on pre-cleaned high purity, degassed Re filament in chloride form with 0.1 M phosphoric acid and silica gel. Pb standard, NBS-981 was repeatedly analyzed for determining fractionation correction. The external mass fractionation correction (linear) was done taking true values from Todt et al. (1996). All reagents used were quartz distilled and total procedural blank determined was better than 200pg. During the course of these analyses, international isotopic standard for Sr, NBS-981 were measured repeatedly the average values for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ for 18 measurements of NBS-981 were found 16.9043 ± 0.0107 (1σ), 15.4462 ± 0.0138 (1σ) and 36.5595 ± 0.0447 (1σ) respectively.

Stable oxygen and hydrogen isotopic ratios

Oxygen and hydrogen isotopic ratios of water samples from the Andamans were determined at Physical Research Laboratory using a continuous flow Thermo Isotopic Ratio Mass Spectrometer (IRMS) Delta V Plus. The procedure details are given in Maurya et al. (2011).

The isotopic ratios are expressed in delta notation as follow:

$$\delta D = \left[\frac{\left(D/H \right)_{sample}}{\left(D/H \right)_{VSMOW}} - 1 \right] \times 10^3 \qquad (4.1)$$

$$\delta^{18}O = \left[\frac{\left({}^{18}O/{}^{16}O \right)_{sample}}{\left({}^{18}O/{}^{16}O \right)_{VSMOW}} - 1 \right] \times 10^3 \qquad (4.2)$$

The reproducibility of the measurement was better than 0.1‰ for $\delta^{18}O$ and 1‰ for δD based on several samples and standard measurements. The calibration experiment with international standard reference material SLAP-2 (Standard Light Antarctic Precipitation) obtained from International Atomic Energy Agency (IAEA), Vienna and Internal Laboratory standard PRL-NARM, yielded the measured values ($\delta^{18}O$ = -55.37‰ and δD = -425.1‰) for SLAP-2 and ($\delta^{18}O$ = -4.52‰ and δD = -35.78‰) with respect to V- SMOW (Vienna Standard Mean Ocean Water).

Total carbon(C) and nitrogen (N) contents in mud breccia

Prior to analysis of total C and N in mud breccia samples, the samples were treated with mild HCl to remove surficial precipitates. The cleaned samples were pulverized using mortar and pestle, and the powder was treated with 2 N HCl for 2 hours at 70°C to remove carbonates. To ensure complete removal of carbonates, the samples were again treated with 2 N HCl. The residues were cleaned several times with distilled water until a neutral pH was obtained. Finally, the residue was kept for drying in an oven at 80°C.

Total C and N were measured using a Fisons NA 1500 CN elemental analyser. About 10-20 mg of dried and powdered (In agate mortar) sediment sample was packed in an aluminum cup and was introduced through an auto sampler into the combustion chamber of the analyzer, where it was combusted completely at 1080°C in presence of high purity oxygen flow. A three-point calibration was made using international standards, low organic carbon soil standard and high organic carbon sediments standards having carbon abundance 1.65 ± 0.02% and 6.72 ± 0.17, respectively. It was cross checked by running a reference material, the Deer-river shale containing 2.53% carbon and 0.12% nitrogen. The total blank concentration, measured over a period of 200 days, was 1.31± 0.12µg C (Bhushan et al., 2001). The analytical precision for total carbon measurement is better than ±4% and for nitrogen concentration greater than 0.1% is ±8%.