Chapter 6
Discussion

In the present thesis work we have examined all the integral of the Andaman subduction zone such as obducted rocks Ophiolites Group of rocks from Andaman Islands, slab sediments (mud breccias, rock-clasts and water) which expelled from Mud volcanoes of Andaman and lava flows, ash bed samples from Barren Island volcano to understand the chemical evolution of mantle geochemistry. In present study we have used various analytical techniques (petrological, geochemical and isotopic) which have already discussed in last chapter. Apart from these techniques various models (mixing and melting) are used that is necessary to understand different processes which occur at subduction zone area. To constrain the proportion of contributions from different sources, which are affecting the pristine mantle wedge two and three components mixing models are used. Melting models are also used to ascertain degree of melting for the generation of magma beneath the arc. As we know the primary arc rock compositions control by three components; subducting slab, subducting sediments and mantle peridotite. In present study, we have considered all the above mentioned possible sources that influence the mantle geochemistry and also control the chemical composition of subduction arc lavas, these are Andaman ophiolites and serpentinite clasts as an altered oceanic crust, mud breccias as subducting sediments and I-MORB as a mantle peridotite. Water is also important constituents in subduction environment, so we have also taken a brief study of mud water that are oozing out from mud volcanoes of Andaman.

In this chapter, we have described all the models which are used in present work. The interferences of all the results that are obtained from the geochemical (major and trace elements) and isotopic studies (Sr – Nd - Pb) with various models (mixing and melting models) are described in details.

6.1 Field observations

6.1.1 Mud volcanoes of Andaman Islands

The mud volcanoes of middle and north Andaman Islands are located along faults. Gases, water and mud breccias are continuously expelled from the mud volcanoes forming large mud mounds inside dense forest. The gases appeared to be dominated by methane emissions, confirmed by their ability to catch fire. Our field observation for the first time suggests the East Margin Thrust, which is extended all over Andaman (Malik et al., 2006) along with Jarwa Thrust are the responsible for the formation of mud volcanoes of middle and north Andaman Islands.

Field observations of Barren Island volcano has already discussed in separate chapter named volcanological studies of Barren Island Volcano.

6.2 Geochemistry of mud water

Water, methane and absorbed hydrocarbon association with mud volcanoes have been attracted scientists to work at various mud volcanoes of the globe. The source and origin of the mud water is always controversial and active field of research it is because these volcanoes are considered as window to their underlying, deep fluid source and providing insight into the origin of the fluid. At depth, fluid-sediment interactions imprint the fluid chemistry and their distinct signature is brought to the surface sediments by the ascending fluid. The analysis of shallow pore fluids (tens of cms to hundreds of mts below seafloor), therefore, provides a key to constrain the reactions occurring at depth (Dahlmann and Lange, 2003). As we discussed earlier water plays an important role in subduction zone magmatism (Jarrad, 2003) and sediments which go along with lithospheric slab contain large fraction of total water volume that enter subduction zones. On a global average, the volume of pores and sediment grains each account for approximately 2.5% of the total slab volume, but approximately 40% and approximately 5%, respectively, of the mass of subducting water (Peacock 1990), therefore we took up geochemical investigations of water erupting out of Andaman's mud volcano, in addition to mud fluids some spring water and ground water were also examined, which can throw some light on the influence on overall fluid of Andaman subduction zone.

In order to study of the geochemistry of Andaman mud water considering the probable sources which can be affect the mud water chemistry are continuous input by ground water and water librated from clay mineral at shallow depth. After considering all possible sources we have utilized several models such as 'two components mixing model, Rayleigh model and water rock interaction model', all the models are described below.

6.2.1 Mixing model

Two components mixing model

Suppose we mix two components A and B which are in different proportions specified by a parameter 'f '. 'f' represent as a fractional contribution of source and is defined as

$$f = \frac{A}{A+B} \tag{6.1}$$

Where 'A' and 'B' are the weights of two components in a given mixture. The concentration of any elements 'X' in such mixture is:

$$X_M = X_A f + X_B (1-f) \quad (6.2)$$

Where X_A and X_B are the concentrations of element X in components A and B, respectively expressed in weight units and X_A and X_B are constant in any suite of samples. So X_M can be express in terms of linear equation:

$$X_M = f (X_A - X_B) + X_B \quad (6.3)$$

From equations (6.1) and (6.2), we can express two components mixing equation of isotopic ratio, such as:

$$R_M^x = \frac{R_A^x X_A f + R_A^x X_B (1-f)}{X_A f + X_B (1-f)} \quad (6.4)$$

Where R_M^x is an isotope ratio of X in a mixture of components A and B, X_A and X_B are concentrations of X in A and B.

6.2.2 Rayleigh Fractionation

Suppose there is a reservoir from which material is being removed with isotopic fractionation. Let 'N' is the total number of molecules in the system and 'R' is the ratio of the rare to abundant isotopic concentrations then the Rayleigh equation describing the evolution of isotopic composition of the reservoir is given by (Gonfiantini, 1981)

$$R = R_0 \left(\frac{N}{N_0} \right)^{\alpha - 1} \quad (6.10)$$

Where R_0 is the initial ratio, N_0 is the initial number of molecules in the system and 'α' is the fractionation factor. In terms of δ notation the equation can be written as:

$$\delta = \delta_0 \left(\frac{N}{N_0} \right)^{\alpha-1} + 10^3 \left(\frac{N}{N_0} \right)^{\alpha-1} - 10^3 \qquad (6.11)$$

Where 'δ_0'is the initial isotopic composition and $\frac{N}{N_0}$ is the fraction of initial material remaining at any time. 'δ' is defined by $\delta = \left(\frac{R_{sam}}{R_{std}} - 1 \right) \times 1000$, where R_{sam} and R_{std} are isotopic ratios in sample and standard respectively.

6.2.3 Water - rock interaction model

Suppose in the closed system condition the water–rock interaction isotopic exchange of hydrogen and oxygen can be written following two simple mass balance equations:

$$F_h \delta D^i_{fluid} + R_h \delta D^i_{rock} = F_h \delta D^f_{fluid} + R_h \delta D^f_{rock} \qquad (6.12)$$

$$F_o \delta^{18} O^i_{fluid} + R_o \delta^{18} O^i_{rock} = F_o \delta^{18} O^f_{fluid} + R_o \delta^{18} O^f_{rock} \qquad (6.13)$$

Where 'F_h' and 'F_o' are amount of hydrogen and oxygen respectively, in the water expressed in moles. 'R_h' and 'R_o' are those for the rock. Superscripts 'i' and 'f' stand for initial and final, respectively. From these two equations final rock compositions can be determined. The relations for the final rock compositions are:

$$\delta D^{f}_{rock} = \frac{\left(F_h \big/ R_h \right)\left(\delta D^{i}_{water} + \Delta^{h}_{rock-water}\right) + \delta D^{f}_{rock}}{1 + \left(F_h \big/ R_h \right)} \tag{6.14}$$

$$\delta^{18}O^{f}_{rock} = \frac{\left(F_o \big/ R_o \right)\left(\delta^{18}O^{i}_{water} + \Delta^{o}_{rock-water}\right) + \delta^{18}O^{f}_{rock}}{1 + \left(F_o \big/ R_o \right)} \tag{6.15}$$

Where $\Delta^{h}_{rock-water}$ and $\Delta^{o}_{rock-water}$ stand for the difference between final isotopic compositions of the rock and fluid (for hydrogen and oxygen, respectively). These are also respectively the carbon and oxygen isotopic fractionation factors between the rock and water, expressed in per mil (‰) units.

For the first time, in the present study we have tried to understand the chemistry of mud water from Andaman mud volcanoes through hydrogen and oxygen isotopes (Fig. 6.1). The analysis of the fluid geochemistry of Andaman mud volcanoes demonstrate that the origin of the fluid and over pressuring result from the clay mineral dehydration by the transformation of the smectite (S) to illite (I) in Andaman subduction zone. The transformation of smectite to illite (mineral dehydration) in Andaman area takes place at a greater depth of the accretionary prism is due to the sediment load and the geothermal gradient. In this process the minerals release their structural water and are transformed into secondary minerals, thereby freshening the ambient pore water. The main reactions are S - I transformation, opal dehydration, and deeper metamorphic reactions (e.g. Brown et al., 2001). The S - I transformation starts at about 60°C and is almost complete at about 160°C at depth 5 – 6 km (Kastner et al., 1991, Moore and Vrolijk, 1992). With increasing pressure and temperature the amounts of water released from the clay inter layers

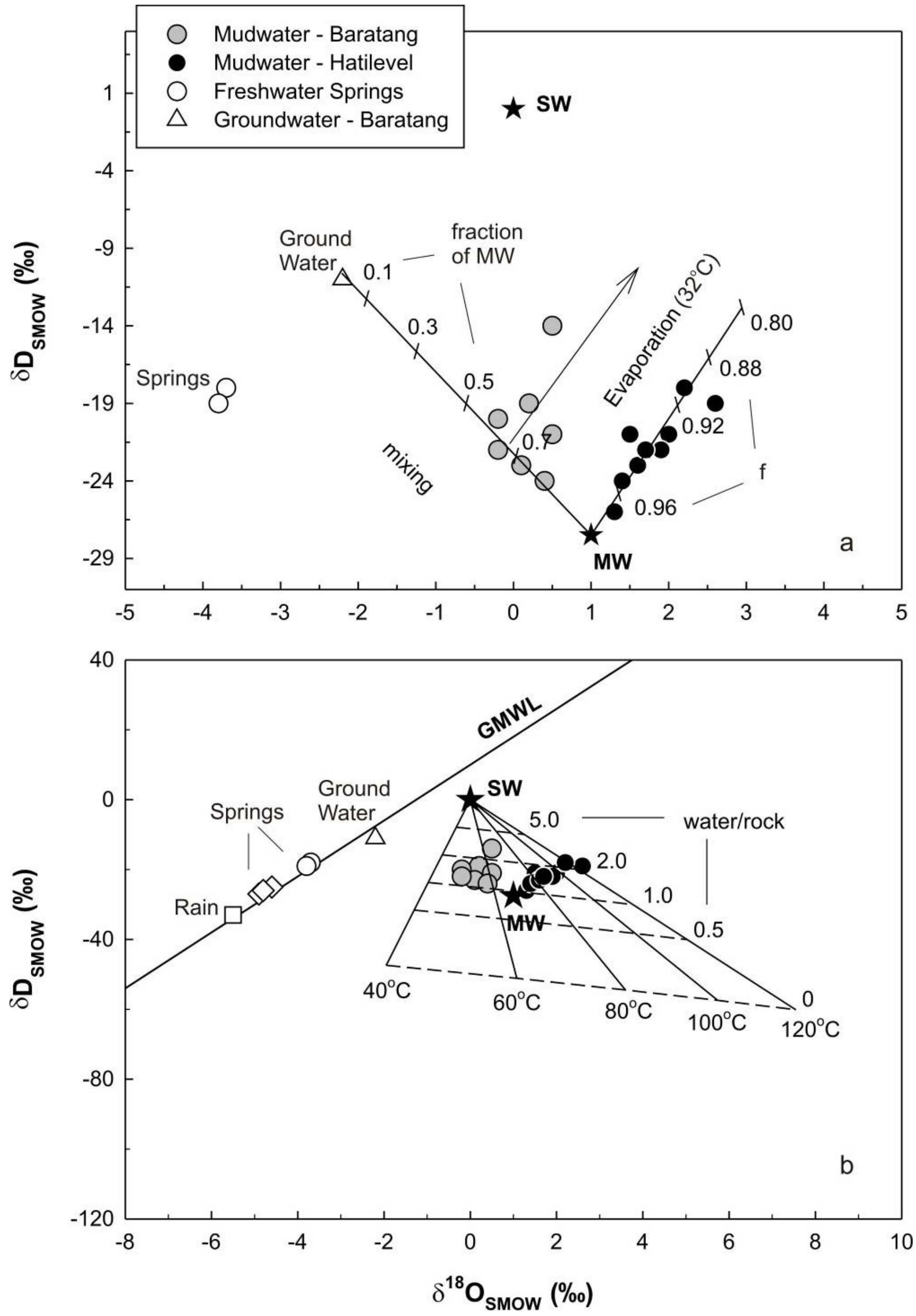


Fig.6.1 $\delta^{18}O$ and δD plots for water samples from mud volcanoes and fresh water sources of Andaman Islands (a) the data for North Andaman (Hathilevel, Diglipur) are explained by evaporation (Rayleigh fractionation) at 32°C, whereas those for middle Andaman (Baratang) are explained by binary mixing with ground water and subsequent evaporation. MW = starting compositions for mud water; f = fraction of remaining reservoir during evaporation; SW= Sea water. (b) The solid lines are evolutionary paths at different temperatures in a water-rock interaction model, where the initial water is seawater (SW) and intial rock/mineral is a smectite clay ($\delta^{18}D$ = -85 ‰; $\delta^{18}O$ = 20‰). The dashed lines join water compositions at a particular water/rock during the evolutions. GMWL = Global Mean Water Line.

increases. The interlayer water of clay minerals is generally characterized by positive $\delta^{18}O$ and negative δD values.

We have collected mud water from two different sites of Andaman Island (Middle and North). To understand the origin of Andaman mud water, we attempted a forward model and considered the initial composition of mud waters (δD = -27.5‰, $\delta^{18}O$ = 1‰) to be same for waters from mud volcanoes of Baratang and Diglipur.

The plot 6.1 shows $\delta^{18}O$ and δD isotopic compositions of mud waters and fresh waters of Andaman Islands. The analysis of mud volcano from diglipur where ground water input is absent can be best explained by evaporation of primary mud water at 32°C where as isotopic trends of most of the water from Baratang are determined to be various mixture of local ground water with the deviation of few samples from mixing line showing effects of evaporation (Fig. 6.1).

Further attempt was made to understand the isotopic components of primary mud water (δD = -27.5‰, $\delta^{18}O$ = 1‰). The composition of primary water is neither sea water nor fresh water or also not explained by mixing trends of these waters (Fig. 6.1) which are confirmed by high amount of smectite and low amount of illite at mud breccia that suggests deep smectite – illite transformation. In connection of this we have developed water rock interaction model. The results of our numerical model suggests the primary mud-water suggest that the water is derived from a mixture of seawater and water derived from dewatering of clay minerals within the forearc, at temperature ~ 70°C and depth ~ 4 km (Fig. 6.1), considering geothermal gradient of Andaman Island 15 to 20°C (Kumar et al., 2008).

6.3 Rock clasts and mud breccias from Andaman Islands

6.3.1 Petrography of rock clasts and mud breccias

A total of 25 samples of mud breccias and serpentinite clasts analyzed during this investigations. Our mineralogical data (XRD analyses) of mud breccias and clasts of mud volcanoes show Kaolinite clay mineral are dominated clay mineral with moderate amount of montmorlinite and chlorite clay minerals. Albite and small amount of muscovite are also present in these mud breccias. Calcite is also seen in XRD spectrum that is limited to Baratang mud breccias. The above mineralogical compositions suggesting mud breccias are derived from mafic rocks through alteration. The presence of calcite in mud breccias and zeolite as rock clasts from Baratang mud volcanoes suggest low grade metamorphism also play a role in this area (Orange et al., 1993).

6.3.2 Geochemistry of rock clasts and mud breccias from mud volcanoes of Andaman Islands

The geochemistry of the rock clasts and mud breccias provide important information about the sediments of subducting slab along with composition of deep seated series and can be used for revealing the evolution of the Andaman subduction zone. The geochemical analysis can also suggest the evidences of the nature of their source. In the present section, the inferences are based on major oxides and trace elements behaviours of mud volcanoes of Andaman Islands. In this study about 20 mud breccias samples and 5 serpentinite clasts (both Diglipur and Baratang areas) have been analysed.

Clues from Major oxides and trace elements

The mud breccias and serpentine clasts which are brought from mud volcanoes are plotted in the chemical classification diagram of Heron

(1988), which are extensively used for geochemical classification of mudstone and sandstone (Fig. 6.2).

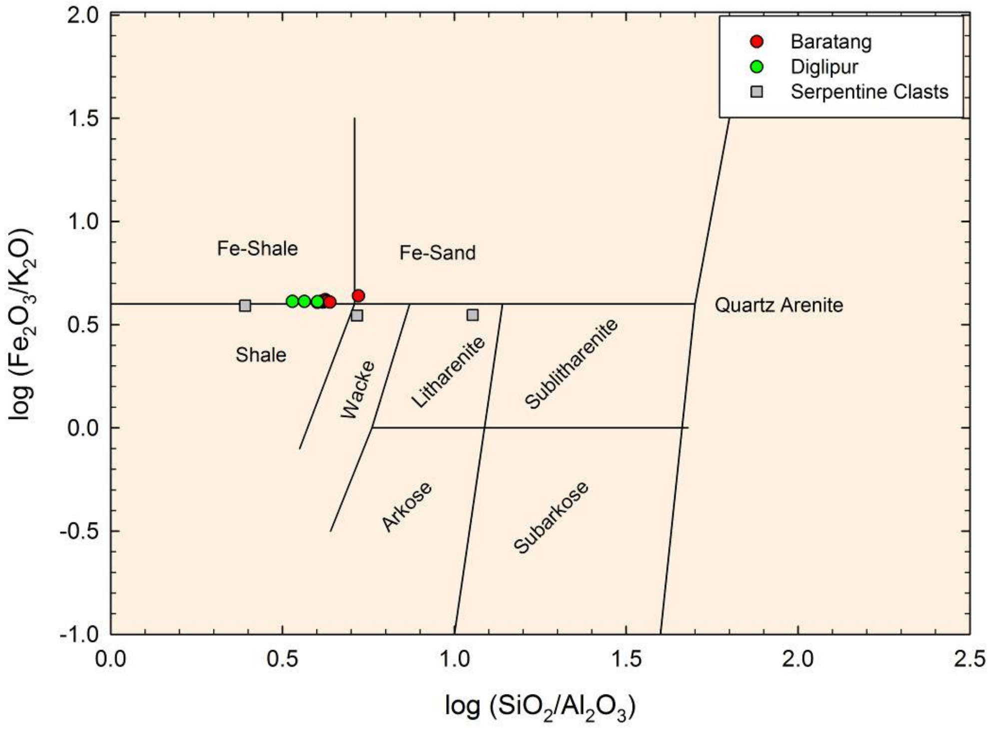


Fig. 6.2 Chemical classification of Mud breccia and serpentine clasts of mud volcanoes of Andaman using the scheme of Heron (1988)

It is observed that all the mud breccias from Baratang and Diglipur are lying on the shale and Fe shale line while serpentine clasts are scatter in the plot. The above result suggests the mud breccias are derived from deeper level in deep water regime and it has not influence by surface weathering agents.

The molecular proportions of Al_2O_3, K_2O and Fe_2O_3 of the mud breccia and clasts are plotted in the ternary diagram (Fig. 6.3). All the data are closed to Al_2O_3 suggesting clay minerals control the composition (Wronkiewicz and Condie, 1987). The serpentine clasts show the significant variation in iron content which indicate these are controlled by iron rich minerals.

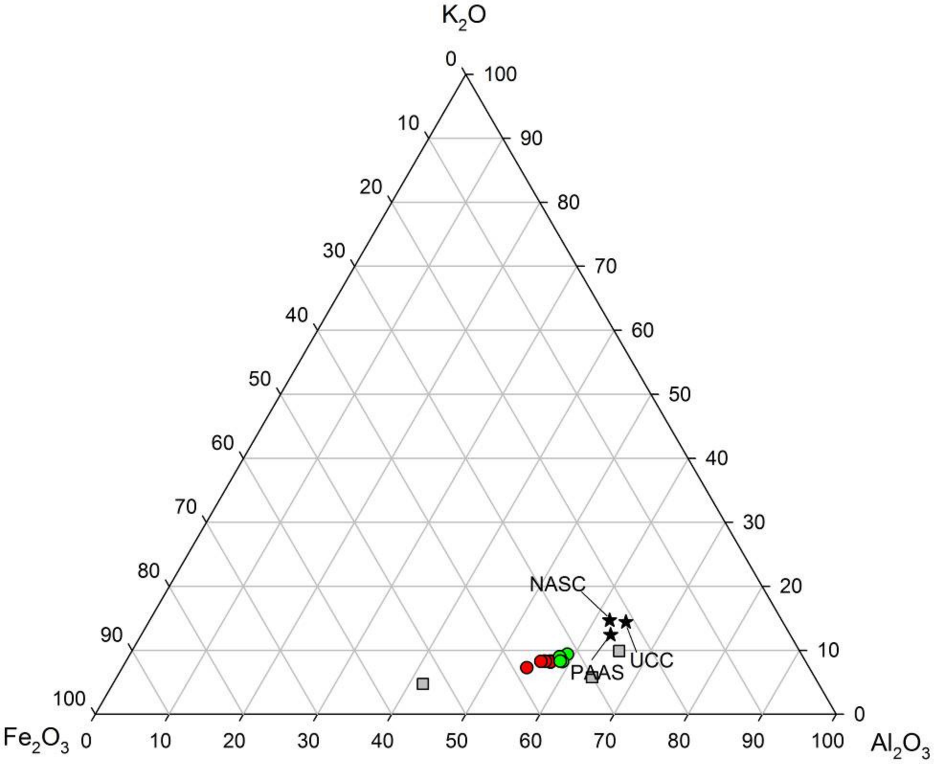


Fig. 6.3 Al_2O_3-K_2O-Fe_2O_3 *diagram for the Mud breccias and serpentine clasts of mud volcanoes of Andaman using the scheme of Wronkiewicz and Condie, 1987.*

'Al' and 'Ti' have been used to identify the source signature of Mud breccia and serpentine clasts because of their chemical resistance behaviour. We have used plotted bivariate plot between TiO_2 and Al_2O_3 the same scheme are used by McLennan et al., 1980 and Schieber, 1992, which has been in Fig. 6.4. In this plot the data of mud breccias fall closer to the mixing line of "3 granite + 1 basalt" line of Schieber (1992). While the serpentine clasts fall closer to "gabbro" field, so the source of the mud breccias and the serpentine clasts has different. The above inferences suggesting that mud breccias and clasts are derived from mafic rocks through alteration, which is also supported by their high Al_2O_3 contents.

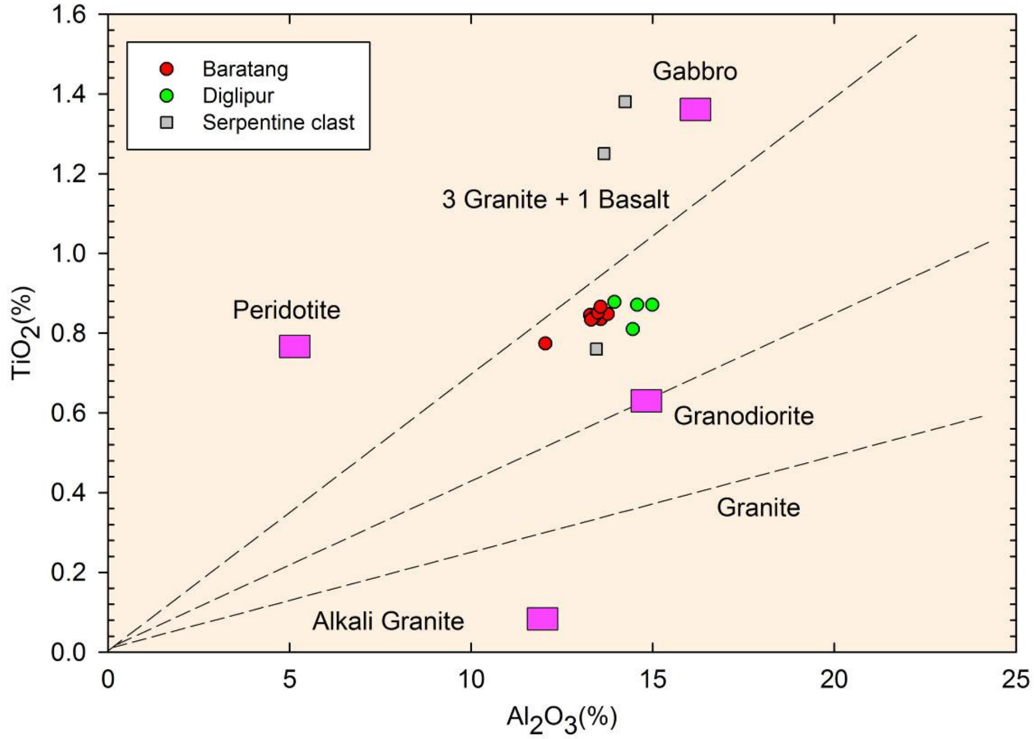


Fig. 6.4 TiO_2 vs. Al_2O_3 *plot of McLennan et al. (1980) for the Mud breccias and serpentine clasts on which data from mud volcanoes of Andaman are plotted. The 'granite' and '3 granite + 1 basalt' line are from Scheber (1992.)*

We have plotted variation diagram (Fig. 6.5) for all the major oxide with respect to 'Al'. 'Al' is an important component of particulate matter derived from continents (e.g., Taylor and McLennan, 1985) and is relatively immobile during transformation of sediments to rock (Stumm and Morgan, 1981). 'Al' is therefore frequently used to trace the abundance and accumulation of the terrestrial component (Murray et al., 1991, 1992). However, a small portion of 'Al' in the deep-sea sediments is also attributed to submarine weathering of ridge rocks and hydrothermal activity (McMurtry and Yeh, 1981).

Variation of Al_2O_3 versus other major oxides (Fig. 6.5) in mud breccias and clasts clear show that the Baratang and Diglipur mud breccias are might suggest they are derived from same source. Although clasts don't show any specific trends indicate their source has different or affected by alteration. The high concentration of Na_2O with compare to K_2O may indicate the presence of sodic feldspar in the breccia (Nohara and Kato, 1985) or preferential biological removal of Na from seawater by certain calcareous organisms (Elwakeel and Riley, 1961) which are reported by Ling et al. (1995) in mud volcano ejected breccia of Andaman Islands.

Iron contents in deep sea sediments are generally associated with lithogeneous, hydrogenous and metalliferous components (Chester and Aston 1976). In the Baratang mud volcano's breccia Fe_2O_3/ Al_2O_3 ratio is more than 0.6 which is higher then pelagic clay (0.58; Taylor and McLennan, 1985) and Diglipur mud volcano's breccias are showing pelagic clay value, indicating there is excess Fe in Baratang mud breccia. The excess Fe and constant pattern of Al and Ti in Baratang mud breccia suggest that the mud breccia is not affected by detrital clays.

Ti is known as a better tracer of terregenous fraction than Al, because of the potentially large biologically affiliated A1 flux (Murray et al., 1993), but a minor quantity is also derived from oceanic weathering of basalt (Bostrom et al., 1973). The TiO_2 content of the mud breccia (< 0.8%) is higher than pelagic sediments and nearly one and half times more concentrated than in CIB (Central Indian Basin) sediments (Pattan et al., 1995). The $A1_2O_3/TiO_2$ ratio is lower than the ratios of Post Archean Average Shale (PAAS ~ 18.9) and pelagic clay (PC ~ 20.7). This ratio is also lower in the average Pacific pelagic clay sediment (Bischoff et al., 1979), indicating an insignificant contribution of Ti from submarine weathering. Because of insignificant contribution of Ti from submarine weathering, the high Ti and Al contents of the mud breccia indicates they are derived from

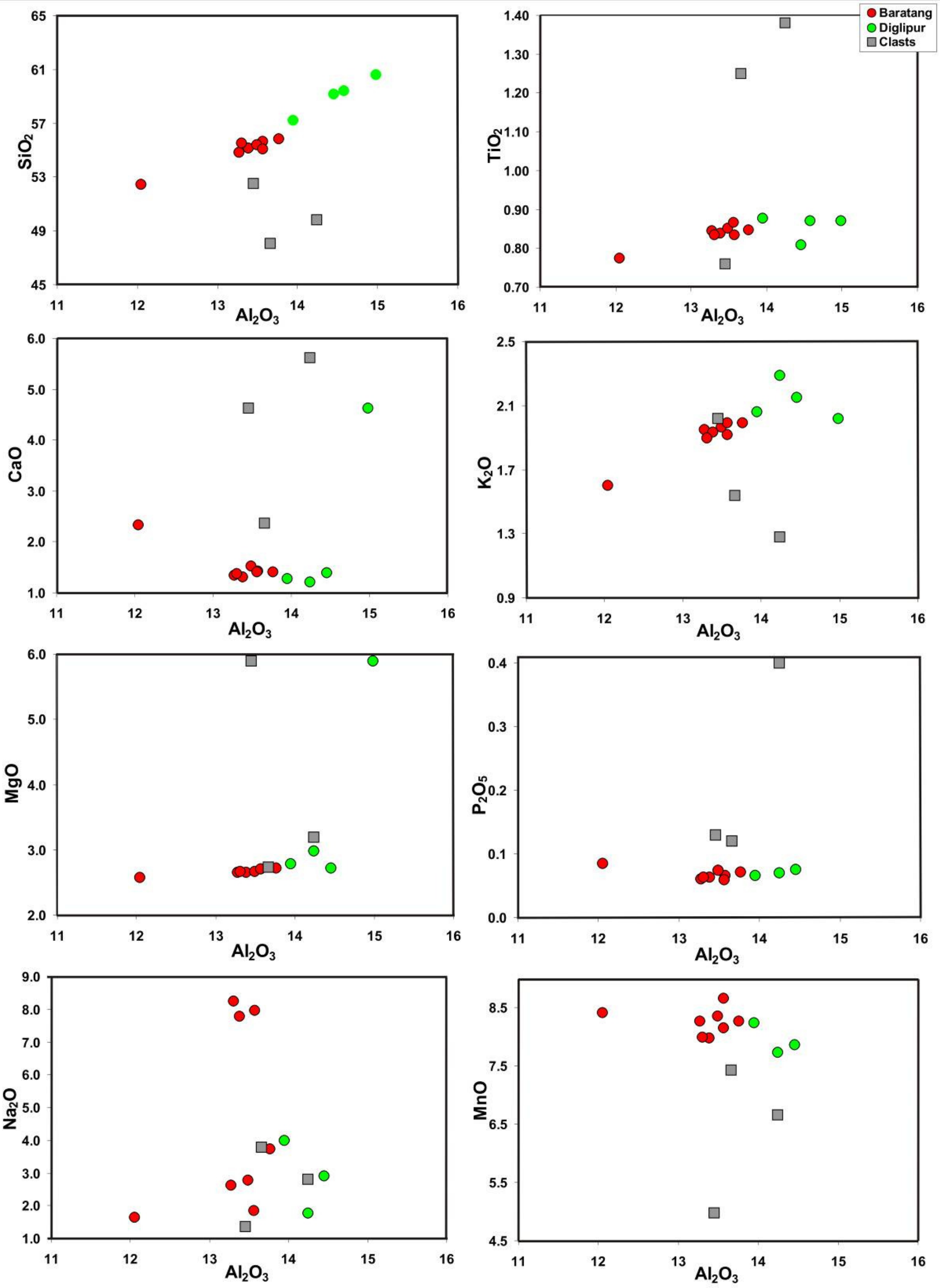


Fig. 6.5 Variation diagram of mud breccias and clasts from Mud volcanoes of Andaman Islands

'Al' rich rock or sediments. TiO_2 and $A1_2O_3$ show positive correlation (Fig 6.5) indicating their continental origin. This is supported by strong linear relation between potassium and alumina indicates lithogenous contribution.

Concentration variations in trace elements have been useful in understanding provenance, weathering and transportation. The Rare Earth Elements (REEs) patterns have been exclusively used in deciphering history of the sediments especially mud and mud stones (shale). The REEs, due to their group behaviour, immobile in water, and almost nonexistent inter element fractionation, faithfully preserved the source compositions (McLennan et al., 1989).

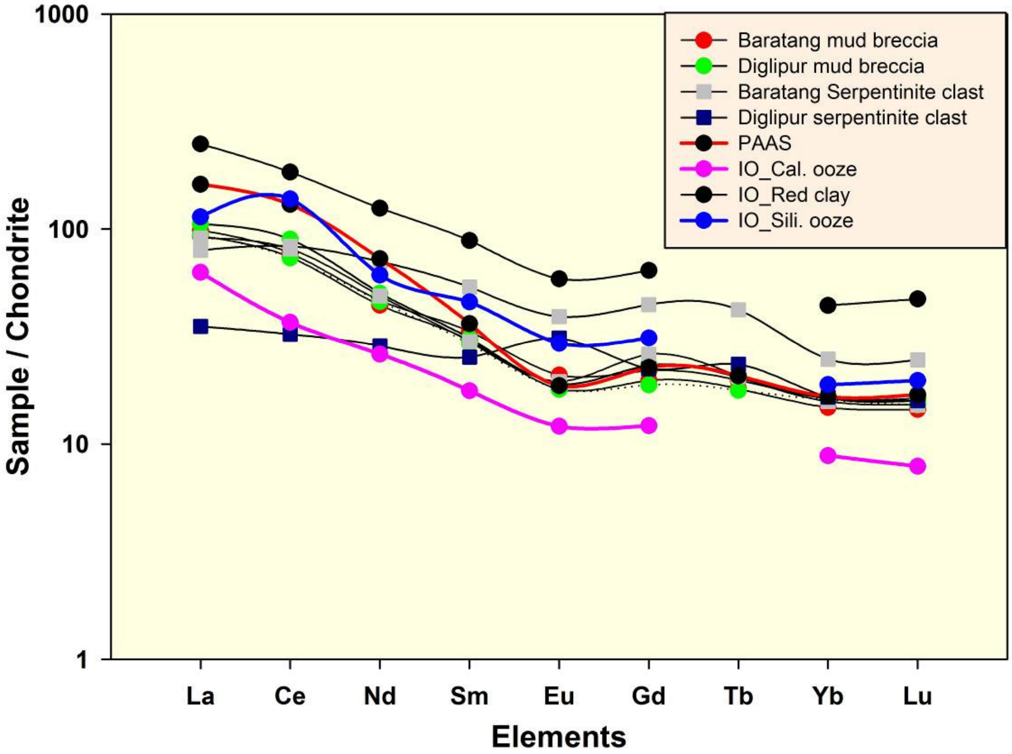


Fig.6.6 Chondrite normalized REE patterns for mud breccia, clasts compared with PAAS (McLennan et al., 1989) and Indian Ocean sediments (Pattan et al., 1995)

Chondrite normalized patterns of REE have been used for provenance studies (McLennan et al., 1989). The chondrite normalized REE patterns of mud breccia and clasts of mud volcano of Andaman along with PAAS and Indian Ocean sediments (Siliceous ooze, Calcareous ooze and red clay; Pattan et al., 1995) are plotted for comparison in Fig 6.6. The REE patterns of mud breccia are very similar to red clay of Wharton basin of Indian Ocean (Pattan et al., 1995). This suggests the source of these breccias may be red clay which is derived probably due to the supply of lateritic soil from west Australia by southeasterly winds and northeasterly aeolian transport from the adjacent Indonesian archipelago (Venkatrathnam and Biscaye, 1973), this observation are also supported by their Al_2O_3 contents.

The behaviour of serpentinite clasts of Baratang and diglipur mud volcanoes is similar except the 'Eu'. The positive 'Eu' anomaly in diglipur serpentinite clast suggests that the dominance of plagioclase in the source, as plagioclase controls the 'Eu" concentration.

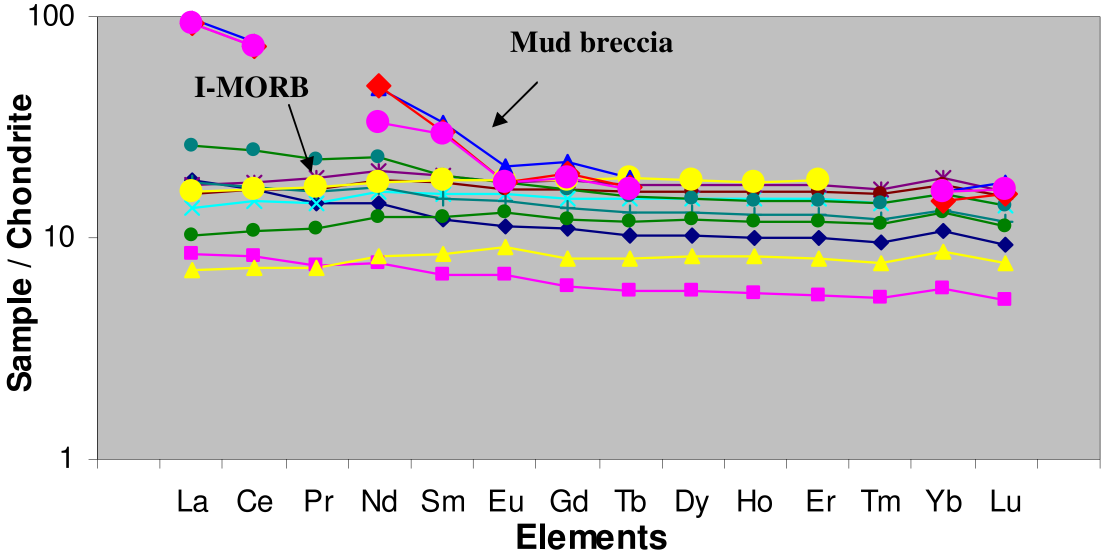


Fig.6.7 Chondrite normalized REE patterns for mud breccia, clasts compared with Indian Mid Oceanic Ridge Basalts (I-MORB) and Barren lavas

To further additional attempt was made to understand the source of mud breccias, their normalized trace elements based on a few analyses we find that the trace element patterns of mud samples are very different from average crustal materials or MORB. They are enriched in large ion lithophiles compared to MORB but depleted with respect to average crust (shale); hence the sources of mud are likely to be a mixture of both (Fig. 6.7).

6.4 Geochemistry of Andaman Ophiolite

The photomicrographs of Andaman igneous rocks are already presented in last chapter. Our petrological study on Andaman samples revel that the most of the samples are highly altered. It took place due to sea-floor weathering and the effects of serpentinization. The predominant rock type amongst the magmatic rocks in the Andaman is Basalt. In polished thin section, it is generally porphoritic and hypocrystalline and exhibits textures usually of ophitic texture and, at places, intergrannular, sub-ophitic and variolitic. Their phenocrysts are dominantly of plagioclase with a little olivine and pyroxenes and opaque minerals. Spherulite structures are also identified in a highly altered sample from the contact zone between basalt and serpentinite in the quarry, nearby to Corbyn's Cove in the island of South Andaman. This sample is a hybrid one with a relict basalt portion exhibiting typical intergranular texture, being invaded by serpentinous material, and later by a quartz vein (Fig 5.1f). The Spherulites found in Andaman Island represent eutectic intergrowth of quartz and fibrous feldspar of intrusive origin (Tyrrell p. 99) and also represent the product of alteration of glass.

Plagiogranites (Fig. 2.3a) have also collected from Andaman Islands which represent the end product of sub-alkaline tholeiitic magmatism. In Andaman, Plagiogranites are associated with cumulates, which represent its existence either by crystal-liquid fractionation process (Coleman and Peterman, 1975) or by late stage silicate liquid immiscibility process (Dixon and Rutherford, 1979). In thin section plagiogranites are medium to coarse grain, almost equigrannular and subhedral in shape recognized as hypidiomorphic granular texture (Fig 5.1a). Apart from this poikilitic and granophyric textures are also seen in which lath of plagioclase feldspars are partly enclosed by big quartz crystal and shows intergrowth of quartz and plagioclase feldspar respectively.

The Andaman ophiolites are highly serpentinized, which was confirmed by field evidence, petrography of studied basalt as well as LOI %, that varies from ~ 3 -10 %. Dick and Fisher (1984) and Niu and Hekinian (1997) reported serpentinization along with sea floor weathering significantly modify the composition of ophiolites peridotite and can show the trend of depletion of elements such as large ion lithophile with Si, Mg and Ca. Recently Niu (2004) showed that sea floor weathering is more responsible for loss of MgO with compare to serpentinization. He has also argued that Cu, Zn, Ni and Cr remain unchanged during serpentinization. In present studies we have used high field strength (HFS) elements because they are relatively immobile during low grade metamorphism, alteration and sea water weathering (Niu 2004).

Based on major oxide we have observed three compositionally different units in Andaman ophiolite group. The first group has lower silica (39 -44%), high TiO_2 (1 -1.5%) and low alumina (10-14%), the second group contains low silica (45-50%), moderate TiO_2 (0.7-1%) and high alumina (15-19%) and third group has high silica (more then 60%) low TiO_2 (0.5%), moderate alumina (10-13%) and low MgO (~2%). We have plotted MnO - TiO_2 –P_2O_5 (Fig. 6.8) discrimination diagram (Mullen, 1983) to discriminate the basaltic rocks of oceanic environment. From MnO -

TiO_2 –P_2O_5 it is evident that Andaman ophiolites compositions are MORB Island Arc and also bonitines composition.

In earlier studies was done by Shastry et al. (2001), Srivastava et al. (2004) suggested that the Andaman ophiolite suite from south Andaman is high Ti and Fe rich mafic rocks of MORB composition but our results shows it has varied from boninite to MORB composition. The origin of one group of Andaman ophiolites is boninitic parent magma as it does for many ophiolites suite (Dick and Bullan, 1984). Such type of magma has specific composition (moderate silica and high Mg). These types of magma are considered as the parental liquid for some Palaeozoic and Mesozoic ophiolites while it has been erupted throughout earth history (Orberger et al., 1995; Melcher et al., 1997). The boninitic magma is usually regarded as modern analogue of high magnesium and low Ti lavas occurring in ophiolites and common in supra subduction zone environment (Coish and Church, 1979; Cameron, 1985), and restricted to forearcs in modern tectonic environments; their presence in ancient assemblage is often taken to indicate a forcarc environment (Coish and Gardner 2004). The high Cr concentration, high Mg concentration and low Ti contents attest supra subduction zone (SSZ) setting of the Andaman ophiolites because above mentioned elements are used for the tectonic discrimination of ultramafic rocks. Pal , (2011) also suggested the Andaman ophiolite shows MORB – SSZ signature for mantle rocks on the basis of TiO_2 Vs Al_2O_3 relation of chromites. He has also proposed 10 -15 % of partial melting of mantle rock based on Cr # and TiO_2.

In the Andaman ophiolite suite we have collected dunite and hurburgite rock types, this rock types are also reported by Pal (2011). The origin of this type of rocks in subduction area, Pearce et al. (2000) documented that when the boninite melt interact with mantle harzburgite, they can produce dunite, whereas when MORB melt reacting with lherzolitic mantle can produce harzburgite. The above reported statements supported our earlier observations that are based on major oxide in which we have suggested that the formation of Andaman ophiolite is the product of are polygenetic melt (boninite and MORB melts).

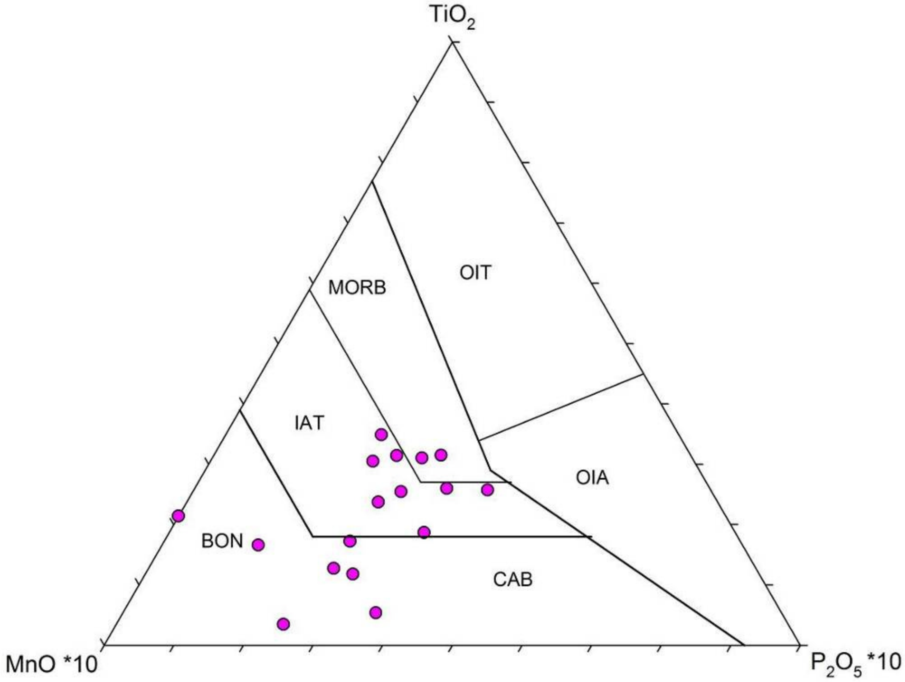


Fig 6.8 MnO-TiO_2 –P_2O_5 diagram for Ophiolite group rocks of Andaman using the scheme of Mullen, 1983. IAT: Island Arc Tholeiite, CAB: Calc-Alkaline Basalt, MORB: Mid Oceanic Ridge Basalt, OIB: Ocean Island Basalt, OIA: Ocean Island Alkaline Basalt, BON: Boninite

Pal (2011) suggests the rock types hurburgite in Andaman ophiolite is not the product of MORB melt while it is influence by subduction zone fluids which leaved a hurburgitic residue in this connection he argued that the absence of absence of any MORB extrusive rocks and presence of Island arc tholeiites (IAT) in the area, Andaman ophiolite is the product of interaction with IAT melts. Pal (2011) didn’t mention about the origination of dunite rock type which has reported by Pearce et al. (2000).

Based on comparative trace elements pattern of Andaman ophiolite and Oman ophiolite rocks, Pederson et al. (2010) differ from the conclusion of Pal (2011) and they suggested that the ophiolite rock types are the product of MORB melt. They have further added that some of the parental melts of rocks of Andaman ophiolite were contaminated by slab derived fluids and also argued that it is difficult to discriminate the formation of Andaman ophiolites whether it is formed in SSZ environment or at major spreading centre. But based on similar age of the Andaman ophiolite with Oman and Troodos ophiolites, they have suggested it may be SSZ origin.

Both Pal (2011) and Pederson (2010) argued that subduction fluids have affected the Andaman ophiolite rocks but they haven't isotopic data to prove it, in present study we did isotopic analysis. The isotopic ratios with major oxide can infer about the role of the fluids along with the source of melt composition of the Andaman ophiolite rocks. In next section we will infer the role of subducted fluids and sediments in Andaman ophiolite rocks.

6.5 Radiogenic isotopic studies of mud breccias, rock clasts of mud volcanoes and ophiolite rocks of Andaman Islands

The radiogenic isotopic studies of Sr and Nd have been used in deciphering the source composition. There are a few studies of Andaman ophiolite that are based on petrological and geochemical observation. There are also very few literature on mud volcanoes of Andaman which are mainly based on micropalentological aspects. But still there is not a single literature of these areas which deals the isotopic compositions of the Andaman ophiolite rocks and isotopic composition of mud breccia and rock clasts of mud volcanoes. So, we have undertaken isotopic studies of these rocks (Fig. 6.9 and 6.10) to ascertain its source composition.

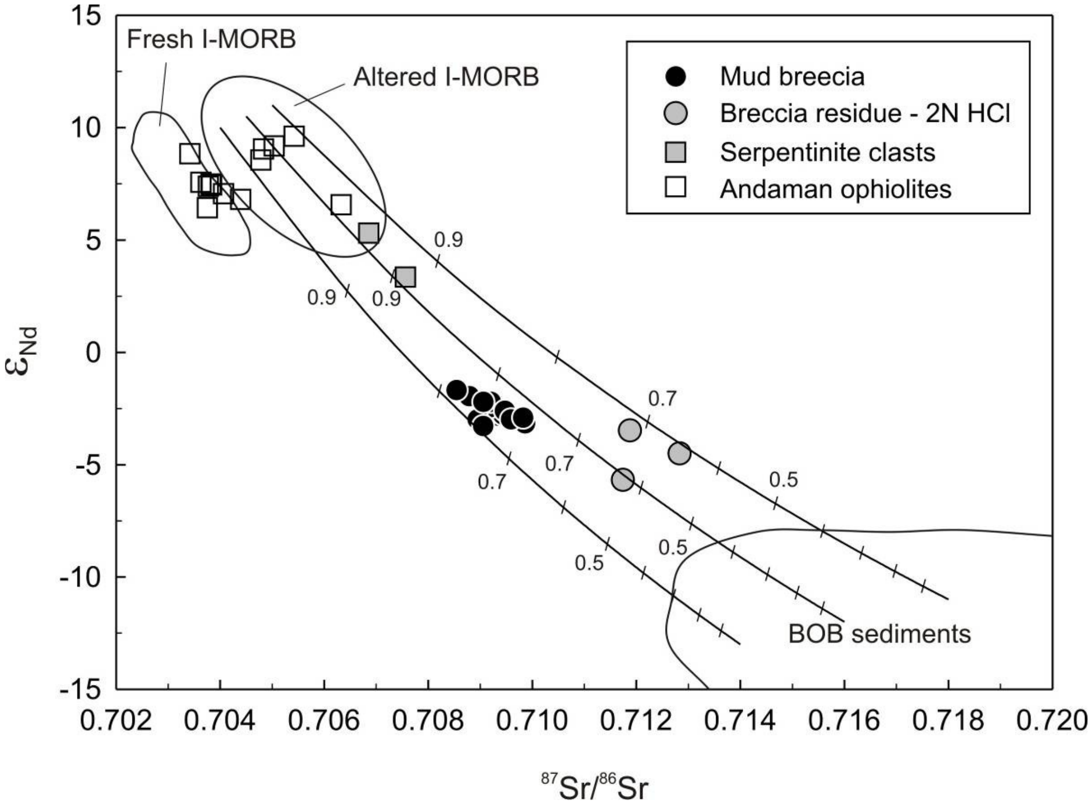


Fig.6.9: ε_{Nd} versus $^{87}Sr/^{86}Sr$ plot for mud matix, HCl- residue fraction of mud matrix and serpentinite clast samples from mud volcanoes of Andaman Islands. The plot also contains data for rocks of Andaman ophilolites. The solid lines are two-component mixing curves between altered I- MORB and BOB sediments, with the numbers on them representing amount of the former in the mixture. Data sources: fresh Indian MORB (Mohaney et al 1989; Nauret et al 2006; price et al 1986), Bay of Bengal (BOB) sediments (Derry and frence-Lanord, 1996; Plank and Langmuir, 1998).

The Fig. 6.9 is in between Sr and Nd isotopic ratios for Andaman ophiolite, Mud breccia, serpentinite clasts along with the field of BOB sediments. Here we have observed most of the ophiolites data is falling in the field of I-MORB with some exception which has high Sr value with constant Nd values indicate significantly impacted by alteration with Sea water. Further we have tried to characterize the source of mud breccias. We have developed a two component mixing curves in which two end members are altered I-MORB and BOB sediments, which are the probable source for mud breccias. Furthermore two components mixing trends show mud breccia contains ~ 70-80 % contributions from altered I-MORB and 20-30 % BOB sediments.

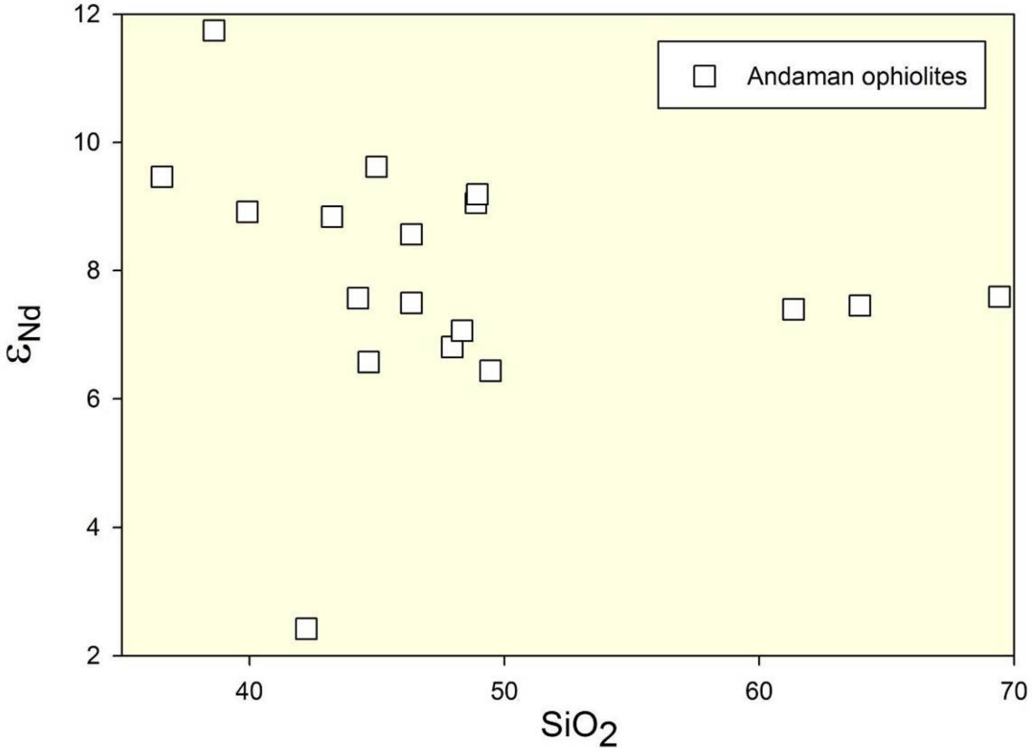


Fig. 6.10 ε_{Nd} versus SiO_2 plot for Andaman ophiolites of Andaman Islands. There is good negative correlation between Nd isotopes and SiO_2 compositions, which indicate origin of ophiolites through mixing of isotopically distinct magma sources.

As stated earlier there is not enough available data to draw conclusions of the role of subduction fluids and sediments in the melt of Andaman ophiolite rocks. However we have tried to find out the influence of fluids and sediments based on neodymium isotope and SiO_2 (Fig. 6.10). We have observed significant scatter in data, there is decrease in ε_{Nd} value with increasing SiO_2 that is consistent with isotopic variations of the ophiolite suite (Fig. 6.10) these variations in Andaman ophiolite rocks revel an important aspect of the sediment and fluid contributions. There are further observation that show appreciable change in SiO_2 and ε_{Nd}

values (high SiO_2, and high ε_{Nd} value) that suggest the parental melts of these rocks had affected by subducted fluid and subducted continental sediments source. Our inferences are well supported by Pal, (2011) that has mentioned subducted fluids and sediments infected parental melt of Andaman ophiolite. This observation also confirmed that Andaman ophiolite is related with subduction processes and its origin is supra subduction origin.

6.6 Lava flows and ash beds from Barren Island (BI) Volcano

6.6.1 Petrography of lava flows

The lavas on BI are grayish black to brownish black and highly vesiculated porphoritic basaltic rocks which show porphyritic texture with glassy ground mass and contain abundant phenocrysts of plagioclase, olivine and clinopyroxene. Many of the lava flows also contain xenocrysts of plagioclase and olivine/pyroxene that are often show resorpation boundaries. The plagioclase grains show well developed compositional zoning from core to rim, suggesting slow fractional crystallization of the lavas.

We have reported the toothpaste lava is part of the recent aa flow exposed at the landing Site 3 (N 23° 17.08′, E 93° 50.92′) on the western coast of BI (Fig. 3.9d-g), (Sheth et al., 2011). This flow issued from the cinder cone 1.5 km to the east and flowed to the coast and into the sea. Its exact eruption age is not known, since no regular monitoring of this active volcano has been in place, but Sheth et al. (2009) inferred from various evidence that it probably formed during the 1994–95 eruptions.

This flow at the coastline is notable in the entire recent aa flow field for its striking morphology. Its surface crust has been extensively broken into sheets and slabs, up to several meters across, some of which are strongly curved (Fig. 3.9e). The sheets and slabs, which we distinguish in this paper with an arbitrary boundary of 10 cm thickness, are often razor-sharp and stand on end, with meters-deep chasms in between (Fig. 3.9d). They were carried atop along a mobile aa core, well exposed at the Landing Site 3 (Fig. 3.9c). The curved sheets and slabs, including the largest ones illustrated in Figs. 3.9e, f, g are elongate in the N-S direction, i.e., perpendicular to the flow direction (due west). They are convex upstream (Sheth et al., 2011).

All the toothpaste lava samples are crystal-rich and have a few vesicles. The rocks contain up to 46.7% crystals by volume. Plagioclase is extremely abundant as a phenocryst, commonly showing zoning or twinning, sometimes both. Many plagioclase phenocrysts are very well-developed euhedral, tabular crystals and contain large numbers of glass inclusions. Olivine and clinopyroxene phenocrysts also occur, but in small amounts, the latter showing twinning as well as zoning. The zoning common in the plagioclase crystals suggests their incomplete equilibration with surrounding liquid, and Luhr and Haldar (2006) have reported that some of the plagioclase and olivine megacrysts in BI lavas are not phenocrysts but xenocrysts, representing disaggregated troctolitic cumulate from a shallow magma chamber. The viscosity of a magma or lava is strongly dependent on its temperature and composition (silica content), among other factors (e.g., Shaw, 1972). At BI, clinopyroxene crystallization is known to follow that of plagioclase, which follows that of olivine ± spinel (Luhr and Haldar, 2006). With a few available temperature estimates based on olivine melt-inclusion geothermometry (Luhr and Haldar 2006), and the extensive crystallization (including that of clinopyroxene) observed in our samples, we considered a temperature of 1100 °C suitable for input in the viscosity calculation we carried out using the major oxide data following the method of Shaw (1972). (Sheth et al., 2011).

Further, based on field observation Sheth et al. (2011) suggested that the formation of BI lava with toothpaste lava squeeze-ups was considerably cooled and crystallized, and thus highly viscous, by the time it arrived at the coast based on textural and geochemical results. They believed that the high viscosity of the BI aa flow had greatly reduced its speed of advance, and the speed might have been further retarded due to its entry into the sea, or a local shallowing of basal slope near or at the coastline.

6.6.2 Clues from Major oxides, trace elements and isotopic studies

In the absence of absolute chronology, we grouped the volcanics on BI into three categories based on their relative chronology with respect to the caldera forming event in to pre-caldera, post-caldera, modern. All our interpretations below follow the above classification

We classified the lavas for BI using the standard method using total alkalis (TA), $Na_2O + K_2O$ and silica (S) contents (Le bas et al., 1986), which is one of the most useful classification schemes available for volcanic rocks. The usefulness of the TAS diagram and reason behind choosing silica and $Na_2O + K_2O$ as a basis for classification of volcanic rocks has been discussed by Cox et al., (1979). Fig 6.11 gives the results of this classification, which reveals that BI lavas have SiO_2 in the range of 45-57 wt % and are basalts or basaltic andesite.

Interestingly lavas of precaldera eruptions have wide range of compositions varying from basalt to andesite (mainly basaltic andesite), while the post caldera and modern lavas are mainly basaltic. The MgO content ranges from 3.25 to 9.28 wt % and Mg numbers [Mg # = (Mg $^{2+}$ / Mg $^{2+}$ + Fe $^{2+}$)* 100] from 45 to 70. On the basis of Mg# BI lavas can be grouped into: evolved, moderately evolved and least evolved.

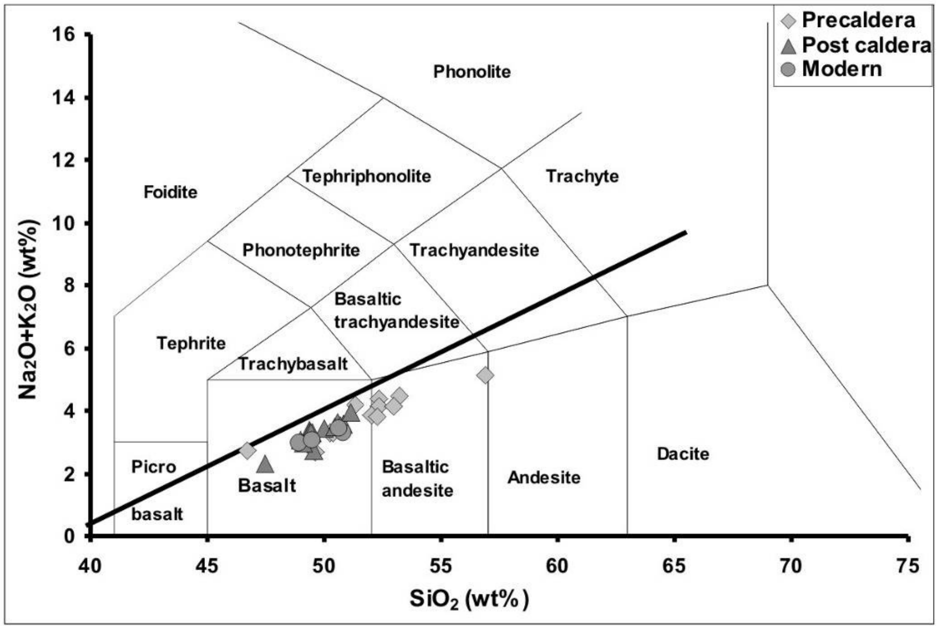


Fig. 6.11 Classification of rocks from Barren Island based on total alkali vs. Silica variation (after La Bas et al; 1986). The samples are grouped according to their chronology with respect to the caldera forming event

$MnO - TiO_2 – P_2O_5$ (Fig. 6.12) discrimination diagram (Mullen, 1983) to discriminate the basaltic rocks of oceanic environment. From $MnO - TiO_2 – P_2O_5$ ternary plot, it is evident all the BI lava flows and ash beds show Island Arc Theoliite (IAT) origin.

Variation of MgO versus other major oxides and Ni and Cr (Fig. 6.13) in BI lavas clear show that the precaldera lavas display a nice fractional crystallization trends- depicting crystallization of olivine and plagioclase for the parental magma. This might suggest that most of the

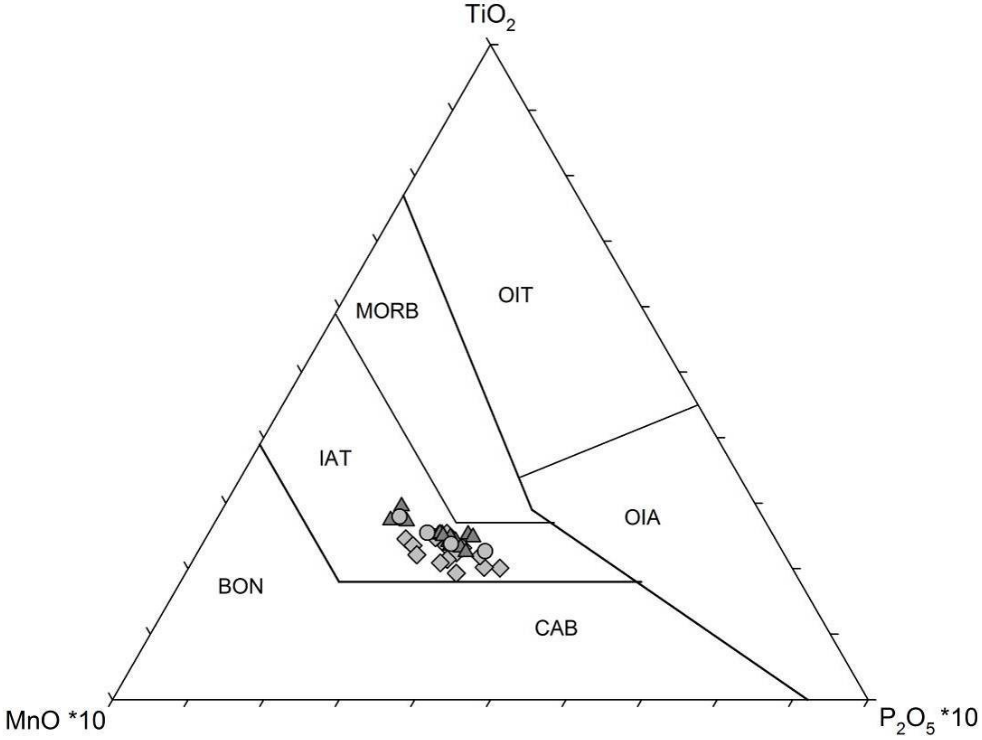


Fig 6.12 MnO-TiO₂ –P₂O₅ discrimination diagram for Barren Island lavas and ash, using the scheme of Mullen, 1983.

precaldera eruptions originated for a single magma batch. The scenario for postcaldera and modern lavas is different. Althrough they don't show any specific trends the constant CaO, Ni, Cr at varying MgO could possibly hint at magma mixing inside the magma chamber prior to their eruption.

Multiple trace-element patterns normalized to N-MORB are shown in Figure 6.14. During subduction, the oceanic slab devolatilizes and dehydrates to release fluids into the overlying mantle wedge. These fluids react with the mantle wedge and form a partial melt, which ultimately gives rise to lavas with arc signatures.

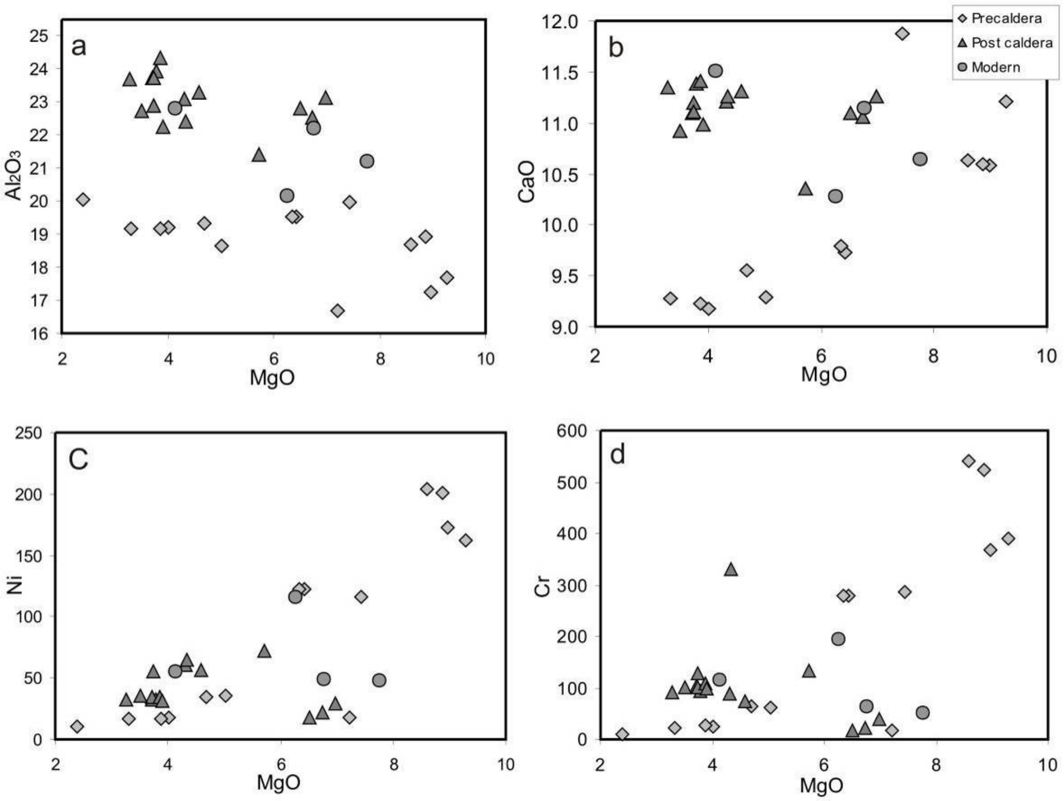


Fig. 6.13 Variation diagrams of selected major and trace elements vs. MgO in Barren Island lavas

The different fractionation stages of the samples make it difficult to directly compare with each other, but the general trend can be recognized. The modern and postcaldera lava flows and ash beds show depleted characteristics as compared to precaldera lava flows and ash beds. The N-MORB normalized trace element patterns of BI lavas show typical characteristics of arc volcanics, such as the negative Nb and Ti anomalies and positive K, Ba and Pb spikes with lesser enrichment of Sr (Fig. 6.14).

However, the magnitude of the anomalies varies between samples, and nearly all show a small depletion in Ti with respect to the REE. The relative enrichments of Ba and Rb also vary in an unsystematic way, as shown by the mafic lavas from precaldera samples. The depletion of Nb relative to large ion lithophile elements can be attributed to two processes:

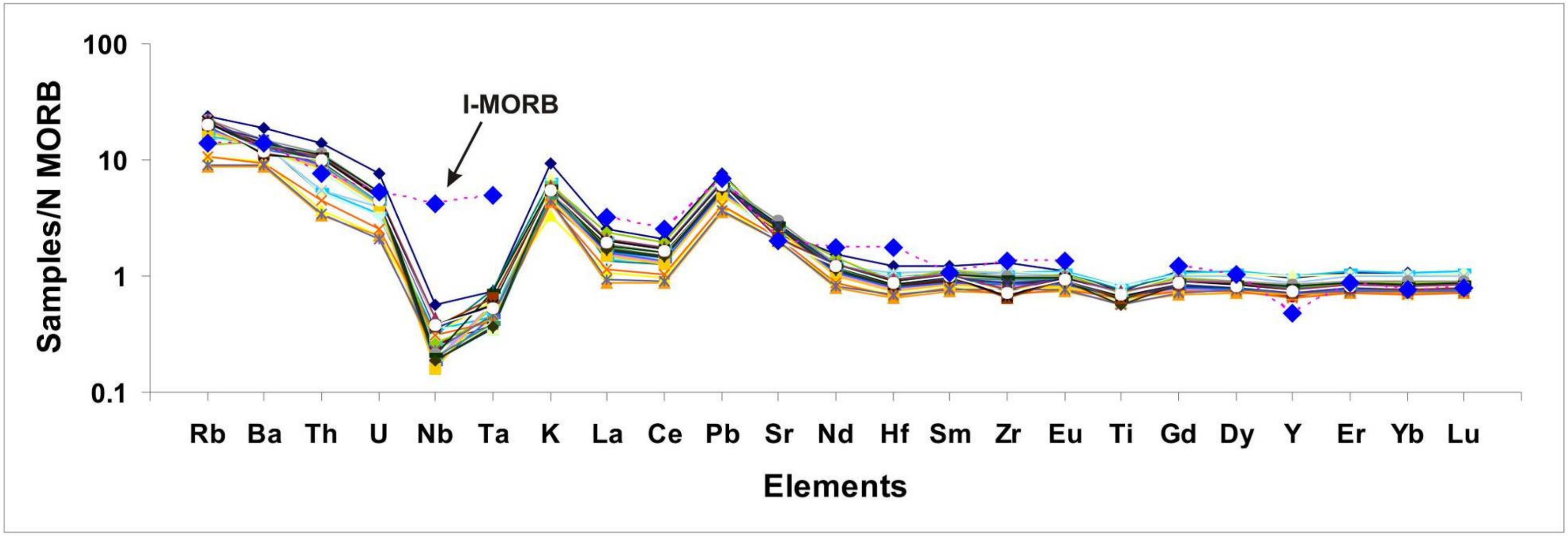


Fig. 6.15: N MORB normalized (Sun and McDonough 1989) trace element patterns for Barren Island lavas compared with the pattern of present day Indian (I) MORB

I) the addition of an LILE enrich and Nb poor fluid components to the mantle wedge or II) the preferential retention of Nb in amphibole relative to other phases in the mantle source (Howkesworth etal 1993) Similar processes can be invoked inferred for the general depletion of the high field strength elements (HFSE) Zr, Ti and Y with respect to large ion lithophile elements (LILE) in BI lavas.

The BI lava and ash samples analyzed show a variation in isotopic ratios. Although there are negative correction between Sr and Nd isotopic ratios when the full data set are considered, ^{143}Nd / ^{144}Nd ratios varies from 0.512884 to 0.512996 while ^{87}Sr / ^{86}Sr varies from 0.703760 to 0.704200.

The isotopic geochemistry coupled with trace elements of Island arc volcanic rocks gives an important clue to the understanding of subducting oceanic slab- wedge mantle interaction and recycling of crustal materials back into the mantle during subduction. So, in the next section, we have tried to understand how and at what level the different subducted components of such as fluids and sediments affected the adjacent mantle wedge.

6.6.3 Mantle source Characteristics

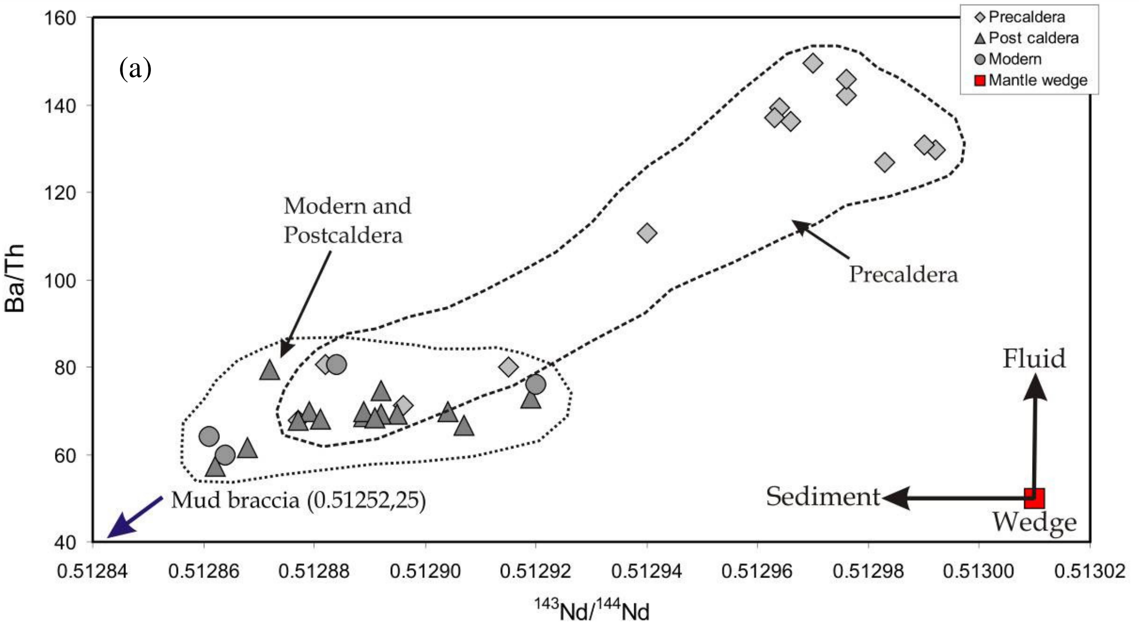
Most models of magma petrogenesis at island arcs involve three main source components: I) the mantle wedge II) the subducting slab (oceanic crust and associated sediments); III) the arc lithosphere. The majority of island arc magmas are thought to originate in the mantle wedge which has been inferred by several workers to be similar to the source of MORB (Ringwood, 1974, Ellam & Hawkesworth, 1988, Turner et al., 2003). In Andaman subduction zone, the slab is essentially the oceanic crust of Indian plate, and therefore for modelling purpose we consider

Indian-MORB (I-MORB) as the unaltered mantle wedge and sediments of Bay of Bengal (BOB) as the unaltered sediments.

In recent time the nature of the slab input to the mantle wedge is in debate because it controls the nature of the arc magma. In present studies we have tried to understand the subducted slab input for BI lavas using Nd isotopic values and some trace elements.

Experimental work (Tatsumi et al., 1986) and studies of arc lavas (McCulloch & Gamble, 1991) indicate that Nd is relatively immobile during slab dehydration, particularly with respect to the formation of aqueous fluids (Kessel et al., 2005). Ba and Ce are more mobile in fluids compared to Th, which is an indicator of sediment contribution Th is chosen over K (which gives a better discrimination between different mantle components) because it is less mobile in aqueous fluids and hence more important in the study of subducted sediments (Pearce et al., 1992). The above characteristics of trace elements were the essence of our geochemical approach and we, therefore, have used to Ba/Th, Th/Ce verse ^{143}Nd/^{144}Nd variations in BI lavas to asses the contribution of slab derived fluids and sediments to the mantle wedge (Fig. 6.15). From the variations in BI lavas it is evident that the mantle wedge initially was affected by the fluids derived from the slab, as reflected in high Ba/Th at constant ^{143}Nd/^{144}Nd in precaldera lavas. The source region was subsequently received contribution in form of particulate materials (sediments) from the slab sediments that affects both the isotopic ratios and Th content of the late precaldera, postcaldera and modern lava flows.

The high Pb/Ce and low Nb/Zr ratios in precaldera lava flows also invoked that the precaldera lavas have fluid imprints and postcaldera and modern lavas have significant sediments imprints. Comparing the ε_{Nd}



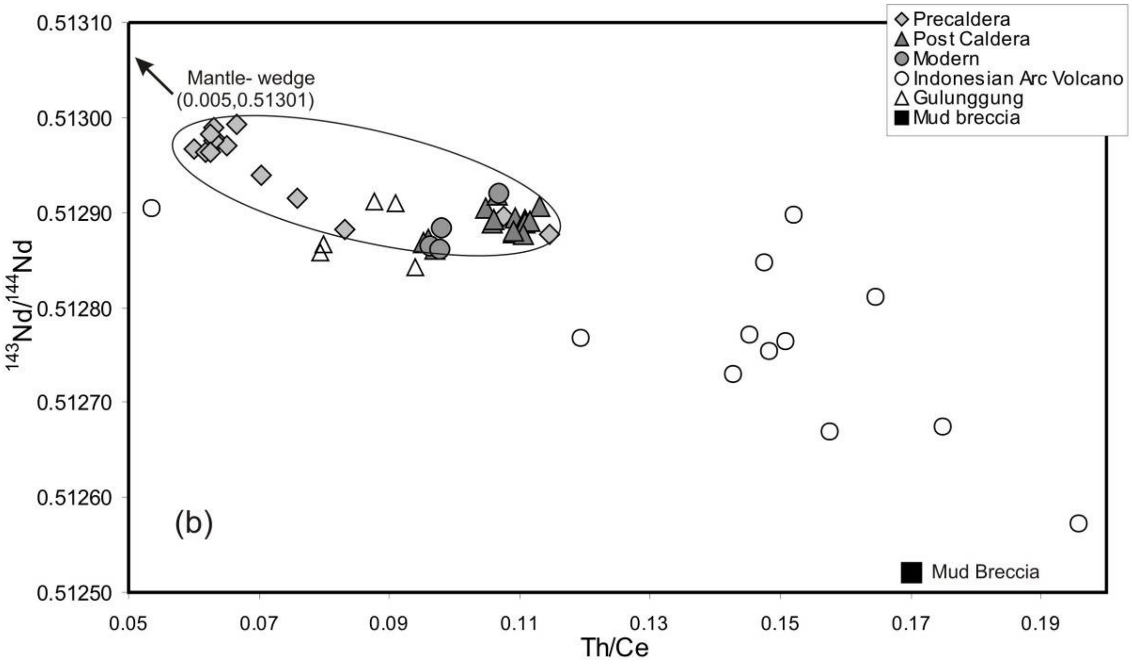


Fig. 6.15(a) ^{143}*Nd/*^{144}*Nd versus Ba/Th for Barren lavas (b) Th/Ce versus* ^{143}*Nd/*^{144}*Nd plot for Barren lavas and Indonesian arc volcano lavas (Turner and foden 2001) has been plotted for comparison*

versus of BI lavas with those of the arc lavas from Indonesia (Fig. 6.15b); we observed that the former appeared to have low contributions from slab derived materials, making them the most primitive amongst all the volcanoes in this (Fig. 6.15).

Sr and Nd isotopes are potentially more powerful indicators of the composition of the sub arc mantle and slab to mantle wedge transfer processes. Further, attempts were made to quantify the slab contributions to BI lavas using these isotopes. In this connection we developed mixing models using different end members of subduction zone components.

Fig. 6.16 shows simple binary mixing solid-solid curves between an I-MORB source and a sediment source representing Indian oceanic crust. As discussed earlier mud breccias from mud volcanoes of Andamans are deemed to represent the sediments of the subducting slab. Mixing curves are generated for different Sr/Nd ratios. Addition of 10-20 % average bulk mud sediments to I-MORB produces a curve that passes through the most isotopically primitive precaldera lavas (Fig. 6.16a). The isotopic characters of postcaldera and modern lavas, however, are inconsistent with two components mixing. Therefore we invoked a three component mixing similar to that proposed by Ellam and Hawkesworth (1988) which involved mantle wedge, subducted sediments and fluids components derived from dehydration. In stand of a fluid component we consider an altered oceanic crust (basaltic) along with I-MORB- representing the mantle wedge and mud breccia-representing slab sediments. Interaction of seawater with basalt produces significant chemical and isotopic changes (Hart et al., 1974, White & Patchett, 1984). For the altered oceanic crust end-member, we consider the serpentinite clasts found in the mud breccia since they represent material derived from the slab deep in forearc. The model curves are presented in Fig. 6.16(b) along with the data from BI

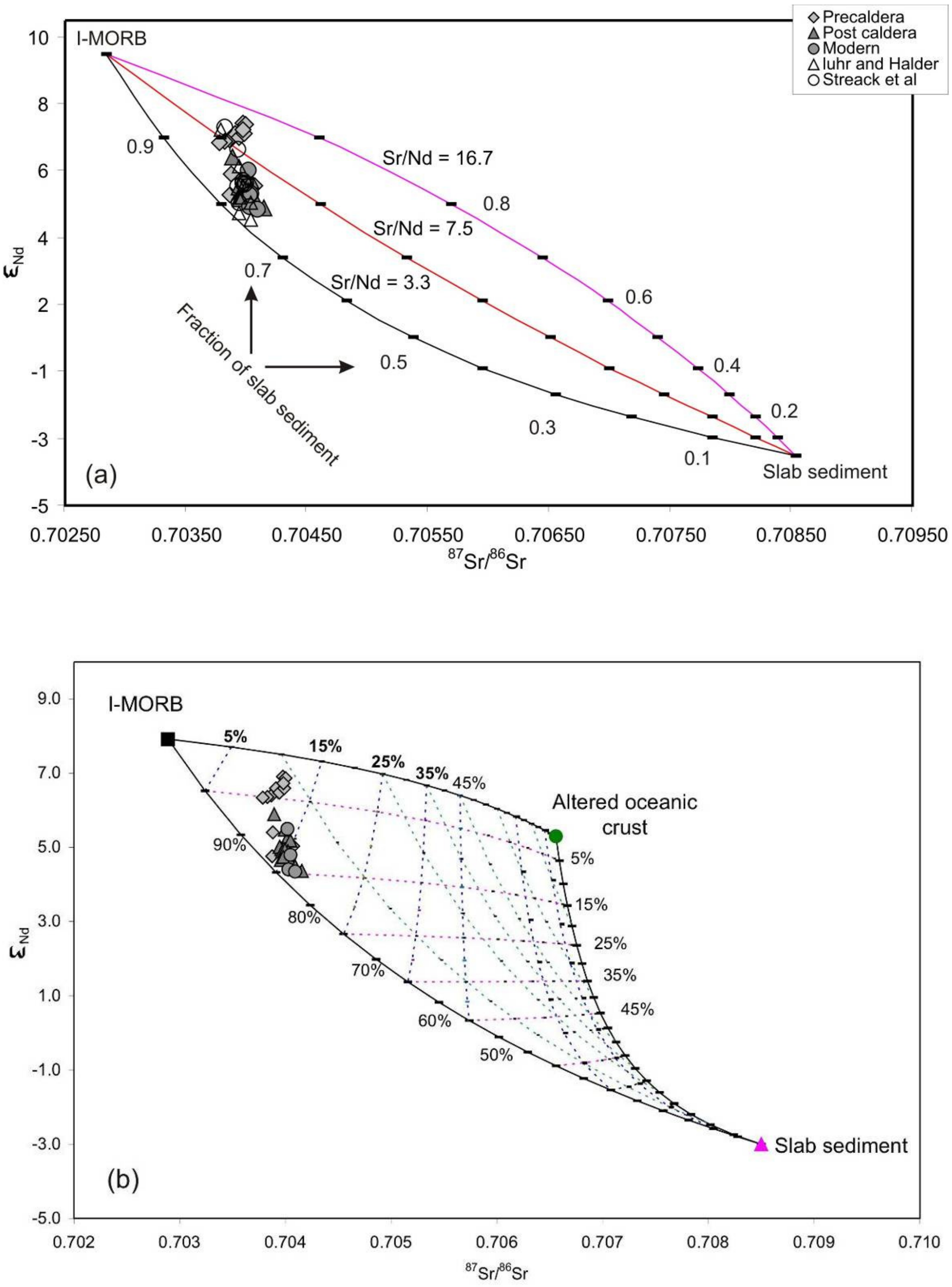


Fig.6.16 (a) $\mathcal{E}_{Nd}$ vs. $^{87}Sr/^{86}Sr$ of BI lavas compared with two components mixing curves, where I-MORB & slab components are the two end members. Mud breccia are considered to represent the slab sediments (b) The same data, as in (a) compared with three components mixing curves involving I-MORB, slab sediments and altered oceanic crust as end members

lavas. As can be seen, the precaldera lavas contain more of I-MORB compared to others indicating there primitive nature. These lavas have higher contributions from altered oceanic crust compared to sediments, whereas the postcaldera and modern lavas have higher contribution from sediments – which support our earlier inference based on trace elements geochemistry.

The Pb isotopic data can give first impression of the identify the end members involved in the magma genesis, since, unlike in Sr and Nd isotopic plots, two components mixing lines in Pb- Pb diagrams should be straight, independent of slab to mantle transfer processes.

In the Pb isotopic variation diagram, the Pb isotopic ratios in BI lavas show linear arrays and well above the Northern Hemisphere Reference Line (NHRL) suggesting pb contribution from two distinct mantle source to these lavas (Fig. 6.17 a and b). One of the sources is a non-radiogenic source, most likely the pristine Andaman mantle wedge, and the other appears to be a source affected by radiogenic Pb derived from the slab – most likely from subducted sediments from BOB. In addition of this the scatter Pb isotopes data for BI suggests variability in the subducted components to the mantle source.

To constrain degree of melting, it is important to understand the formation and compositions of the magma, which can affect the absolute concentrations of trace elements. In order to ascertain the degree of melting, we have considered the source composition (Primary basaltic melt) has 90 % mantle peridotite, 8 % of altered oceanic crust and 2 % of subducted sediments. The trace element concentrations of these sources have been taken from Kimura et al. (2010). The above % has been taken based on our previous results of three components mixing model. In the

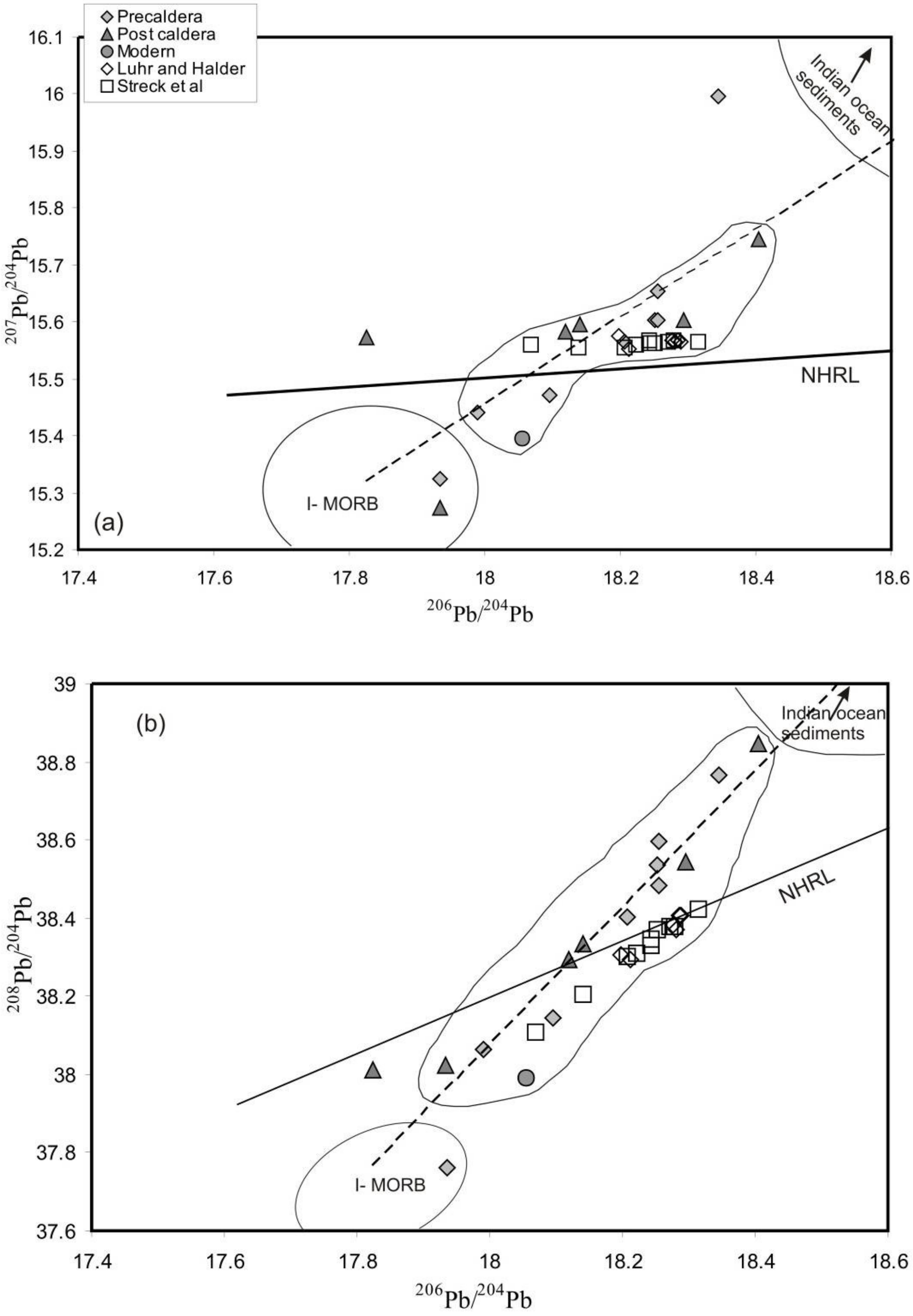
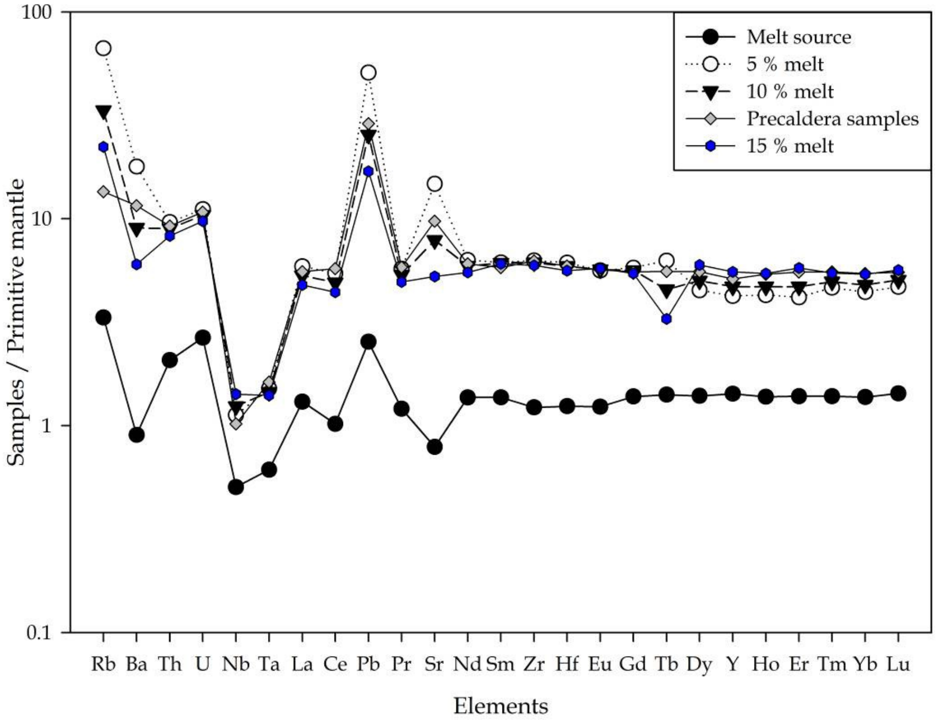


Fig. 6.17 (a) Plot of ^{208}Pb/^{204}Pb vs. ^{207}Pb/^{204}Pb (b) Plot of ^{208}Pb/^{204}Pb vs. ^{207}Pb/^{204}Pb of Barren Island lavas, NHRL (North Hemisphere Reference Line) after Hart 1984



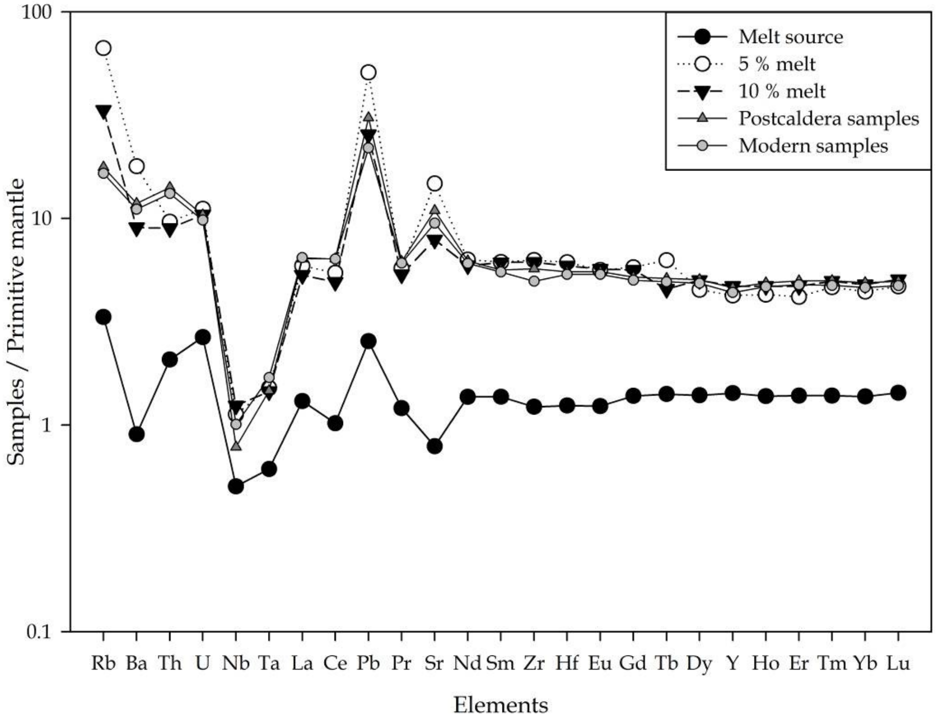


Fig. 6.18 Primitive mantle normalized trace element ratios in Barren Island lavas and its source. Based on melting model, Barren lavas show 5-15 % melting.

present melting model we have consider non batch melting in which primary melt contains 60 % olivine, 20 % orthopyroxene, 14 % clino - pyroxene, 5 % garnet and 1 % amphibole. The melt composition during melting is 10 % olivine, 10 % orthopyroxene, 33 % clinopyroxene, 39 % garnet and 8 % amphibole. The partition coefficient of all the trace elements has been taken from GERM website.

The melting model calculations for trace element abundances suggests that the precaldera lavas of Barren Island are the result of 5 -15 % of melting where as the postcaldera and modern lava produced by 5 -10 % of melting (Fig. 6.18).

Further we have tried to investigate the melting process and depth of melting through modelling of REE fractionation during partial melting. We have considered same source which we have taken for previous melting model. We have taken HREE elements (Yb, Sm, Tb) which can show both the degree/fraction of melting (F) and depth of the melt source. We estimated F using the (Yb/Sm) and (Tb/Yb) variation diagram due to its ability to resolve between F and depth of melting (Turner and Foden, 2001) because these ratios of the heavy rare earth elements (HREE) are sensitive indicator of garnet in the source and can be utilized to determine the depth of melting. Using forward modelling of mantle melting; we calculated several melting curves taking 90% mantle peridotite, 8 % Altered Oceanic Crust (AOC) and 2 % subducted sediments as a starting mantle composition (Fig. 6.19). This melting model program calculates the trace element contents of melts produced by partial melting during passive upwelling of the mantle. The path of mantle parcels through the melting zone is assumed to be governed by simple corner flow. Melting proceeds by incremental non-modal batch equilibrium melting (Shaw, 1970). The melting reaction depends on the mineral assemblage present in the parental source and also the composition in the melt.

In a plot of $(Yb/Sm)_n$ versus $(Tb/Yb)_n$ (Fig. 6.19) partial melts from mantle lherzolites occupy positions depending on the depth (and therefore, source composition – ratio of garnet to spinel in the source) and fraction of melting. The combined data from BI lavas lie close to melting path with 20-50 % of garnet in there sources. Based on garnet composition.

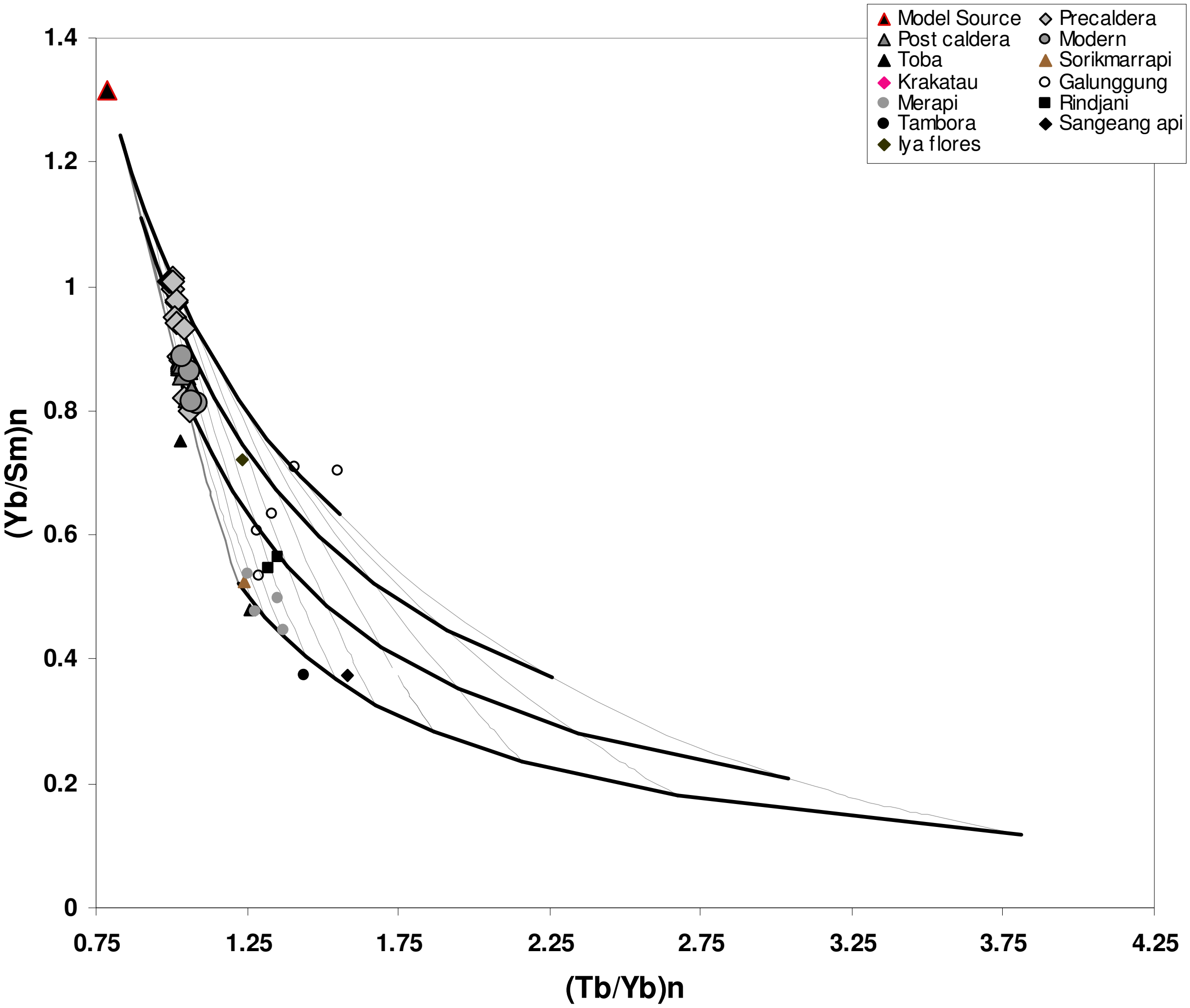


Fig 6.19 Melting model for Barren Island lavas and Indonesian arc lavas (Turner and Foden, 2001) have been plotted for comparison

in BI lavas represent 5-15 % of partial melting of a model source for precaldera lavas and 5 -10 % of postcaldera and modern lavas. These observations suggest that the BI lavas have derived from much deeper regions of the mantle wedge. Thus, a safe conclusion would be that a portion of the BI lavas may have been derived from garnet lherzolites at depths more than 100 km.