

## Sm-Nd age and mantle source characteristics of the Dhanjori volcanic rocks, Eastern India

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Trace, Rare Earth Element (REE), Rb-Sr and Sm-Nd isotope analyses have been carried out on selected basic-ultrabasic rocks of Dhanjori volcanic belt from the Eastern Indian Craton (EIC). The Sm-Nd isotopic data of these rocks yield an isochron age of  $2072 \pm 106$  Ma (MSWD = 1.56). Chondrite normalized REE plots display shallow fractionated REE pattern with LREE enrichment. In primitive mantle normalized plots also these rocks show shallow fractionated pattern with depletion of Nb and Ba and enrichment of LILE like Rb, Th and U. Depletion of Nb, Ba and Zr and enrichment of Rb, Th and U are found in N-MORB normalized plots as well. Compatible elements like Tb, Y and Yb on the other hand, show a flat pattern. Isotope, trace and REE modelling indicate that these were produced by 3–5% partial melting of a spinel lherzolite source. The Nd isotopic data suggest that an enriched ( $\epsilon_{Nd} = -2.4$ ) mantle existed below the Dhanjori basin during  $\sim 2.1$  Ga. The enrichment was possibly caused by continuous recycling of the earlier crust into the mantle whereby subducted slab derived fluid modified the surrounding mantle. The process also affected the more easily susceptible Rb-Sr systematics producing variable  $Sr_i$  (0.702–0.717). The enriched mantle material, part of a thermal plume, pierced through the deep fractures produced due to the cooling and readjustment of the Archaean continental crust and ultimately outpoured within the Dhanjori basin. The plume magmatism was manifested by the extrusion of komatiitic/basaltic flows and basic/ultrabasic intrusives. The residence time of the plume within the upper mantle was possibly very small as no depleted signature (even in Nd isotope) has been obtained. This means a deep plume was fed by a recycled oceanic crust via globally extensive subduction process, already initiated by the end-Archaean period.

### INTRODUCTION

Present day mantle is heterogeneous from mineralogical ( $\sim 1$  cm) to mantle ( $\sim 1000$  km) scale with respect to both REE, trace element composition and Rb-Sr, Sm-Nd, Pb-Pb isotopes (Dupre and Allegre, 1983; Zindler and Hart, 1986 and references therein) and to some extent Re-Os isotopic signatures as well (Lassister and Hauri, 1998; Walker *et al.*, 1999). Such heterogeneity also existed during the Precambrian time as documented by both depleted and enriched isotopic signatures

in basic and ultrabasic rocks from various parts of the world (Patchett and Tatsumoto, 1980; Dupre and Allegre, 1983; Hart *et al.*, 1986; Zindler and Hart, 1986; Hart, 1988; Smith and Ludden, 1989; Barling and Goldstein, 1990; Weaver, 1991; Cousens *et al.*, 1995; Whitehouse and Neumann, 1995; Mukasa *et al.*, 1998). A general depletion of the upper mantle with respect to Nd isotopes is observed from Precambrian to recent along with few distinct peaks during certain periods (DePaolo, 1981; McCulloch and Bennett, 1994). In addition, evidences of heterogeneity i.e., both

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enriched and depleted isotopic signatures during the same time period have also been found throughout the earth history. It is still being debated what geological process(es) causes this heterogeneity particularly enriched signatures in the mantle during the Precambrian. The problem is further compounded with the involvement of crustal contamination during the ascent of basic/ultrabasic magma and post-crystallisation alteration which can erase pristine mantle signatures. Also magmatic processes in basalts often erase mantle heterogeneity over 10 km scale length (Zindler and Hart, 1986). Therefore, to understand actual mantle processes during the Precambrian it is necessary that isotopic and geochemical studies are carried out on unaltered ultramafic/ultrabasic rocks with insignificant crustal contamination. We report here for the first time Rb-Sr, Sm-Nd systematics and complete trace, REE studies of selected and almost unaltered samples of basic volcanics and intrusives from Dhanjori volcanic belt, EIC and discuss their implications to Precambrian mantle evolution. The present investigation was undertaken with two fold purposes. Firstly to provide an absolute age for the Dhanjori volcanics and secondly to understand the nature of their mantle sources. An interesting aspect of the Dhanjori belt is the occurrence of definitive spinifex texture of komatiitic affinity, one of the few found in the EIC (Gupta *et al.*, 1985; Majumder, 1996).

### GEOLOGIC SETTING

The EIC or Singhbhum-Orissa craton comprises of Archaean nucleus of south Singhbhum and Proterozoic Dalma volcanic belt and Chotanagpur gneissic complex (CGC) in the north. This cratonic block is bounded by Copper thrust belt (CTB; also called Singhbhum Shear Zone) in the north, Sukinda thrust in the south, high grade metamorphic Satpura belt in the northwest and Eastern-Ghat granulite belt in the southeast (Naqvi and Rojers, 1987).

The oldest rocks in this craton are the amphibolite-tonalite gneiss association called the

older metamorphic group (OMG) with an age  $\sim 3.3$  Ga (Sharma *et al.*, 1994). A major part of this craton is occupied by the Singhbhum granite batholith complex covering an area of about 10,000 km<sup>2</sup>. A number of shallow basins (the supracrustals) occur within and around the periphery of this granite batholith *viz.* iron ore basins in the west containing large economic deposits of iron ores, Simlipal-Dhanjori basin comprising volcanics and volcanoclastic sediments etc.

Deposition of the Singhbhum group of metasediments and Dhanjori group of volcanoclastics followed the emplacement of Singhbhum granite. Singhbhum Group is developed along the northern flank of Singhbhum granite batholith and extends to the east and southeast and terminated with the eruption of Dalma volcanics. The Dhanjori basin, resting unconformably over the Iron Ore Group (IOG) in the NE part of the craton, consists predominantly of volcanics and volcanoclastic sediments. The vast copper deposit within its low grade metavolcanic member has been extensively mined. The Dhanjori volcanosedimentary assemblage is believed to represent a greenstone cycle (Gupta *et al.*, 1985) within south Singhbhum Proterozoics. The sequence consists a lower unit of metapelites, psammites with ultramafics and mafics (gabbro/dolerite) and an upper predominantly volcanic unit of mafic/ultramafic tuffs, intrusives, metabasalts and tuffaceous sediments. The lower ultramafics have distinct komatiitic affinity with definitive spinifex textures (Majumder, 1996). The upper Dhanjori basaltic suite comprises alkali olivine basalts grading upwards into K-poor oceanic tholeiites. An extensive granite-granophyre complex along with rhyolite, occurs along the western margin of the main Dhanjori basin.

### SAMPLING

Dhanjori basin is flanked by the CTB to its northern and eastern side, Mayurbhanj granite in the southeast, south and southwest and banded iron formation in the northwest (Fig. 1; Saha, 1994). The basic/ultrabasic rocks are well exposed in

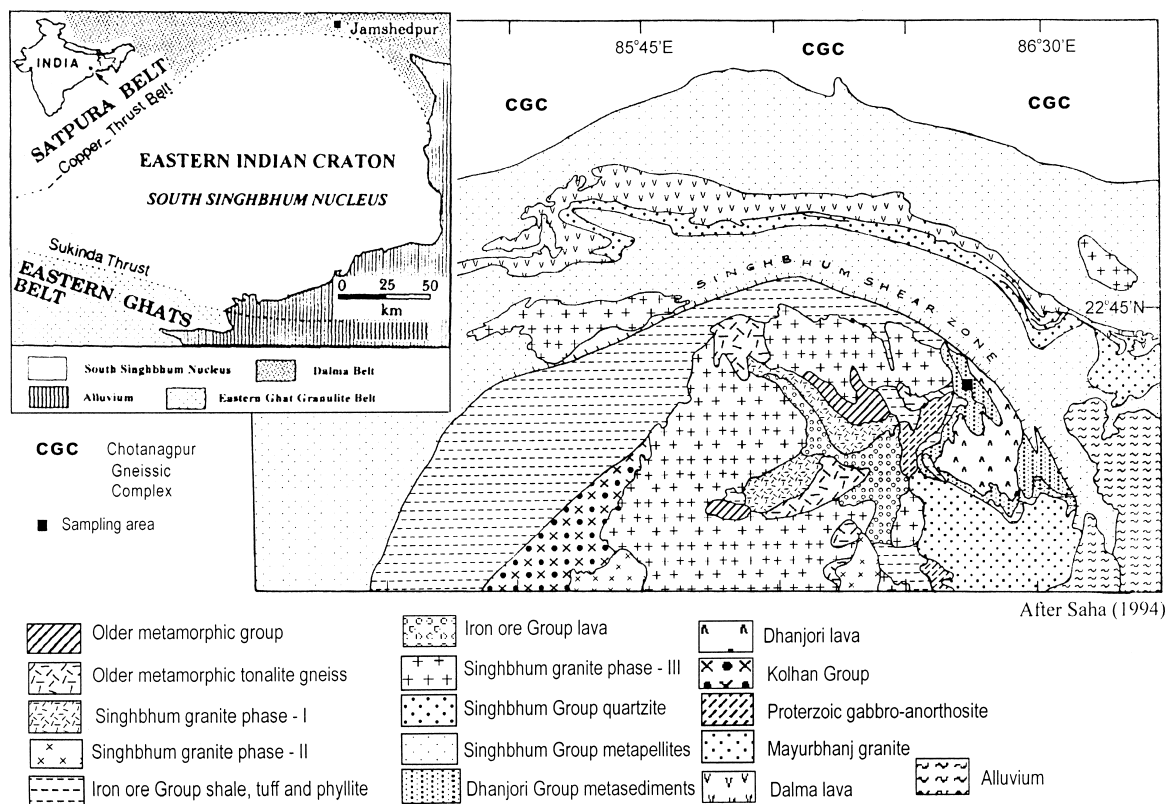


Fig. 1. Geological map of Eastern Indian Craton. Dhanjori, Kolhan, Mayurbhanj and Dalma Group of rocks are Proterozoic, rest are Archaean. The locations of Dhanjori basic and ultrabasic rocks are also shown (solid square).

various parts of this basin. Most of the coarse grained ultramafics are restricted to the lower level of the upper Dhanjori but some occurs both along the pelite-quartzite contact and also within the quartzite (Gupta *et al.*, 1985). For the present study sampling was carried out in Kulamara-Kakdha (south of Rakha mines, Fig. 1) area within a distance of ~1 km on either side of a hillock. The Dhanjori basics/ultrabasic rocks here are well exposed within the phyllite and tuffaceous country rock, part of Dhanjori. Both southern and northern margins of the basics/ultrabasic rocks from the sampling area are schistose and more or less asbestiform though coarse prismatic pyroxene grains are still preserved. The central portion was mostly massive and almost unaltered. The prismatic pyroxene phenocrysts in this part are also conspicuous and often they are so large that they

occur as xenocrysts. The metabasites are fine grained, massive and occur along both the northern and southern margins of the ultrabasic rocks. No grain size variation was found in the mafic part. The SE part of the hillock i.e., near village Kakdha the ultrabasic rocks are flanked by the gabbroic rock in which large laths of plagioclase and prismatic pyroxenes are conspicuous. In this area fine grained metabasites are also present within the ultrabasic rocks as small patches.

## PETROGRAPHY

The studied rock samples are basaltic to gabbroic in composition both containing augite and plagioclase laths. In some cases pyroxene content far exceeds that of plagioclase making them ultrabasic type rocks. Cumulates of augite

and occasional olivine are also found within the fine grained plagioclase and augite groundmass. Although occasional chloritisation of some pyroxene grains is observed, both pyroxene and plagioclase are mostly unaltered. We have used the term basic/ultrabasic to include large variety of mafic/ultramafic rocks.

#### ANALYTICAL PROCEDURE

About 5–10 kg samples for fine grained rock and 10–15 kg for coarse grained rocks were crushed into  $\sim 1 \text{ cm}^3$  size in jaw crusher. The plates of the jaw crusher were thoroughly cleaned with compressive air jet and acetone. Before crushing any sample a part of it was crushed and rejected to avoid cross contamination. After cone-quartering one quarter of the chip-samples was repeatedly washed with deionised water in ultrasonic bath and dried under the mercury lamp. The dried chips were powdered in tungsten carbide disc grinder. Care was taken to avoid cross contamination between samples by repeated washing of the grinder with de-ionized water and acetone. For isotopic analysis about 0.5 gm of powdered sample was digested in a screw-cap TEFLON<sup>®</sup> vial following the method of Todland *et al.* (1992). Typical sample digestion time was 3–4 days. Each sample solution was split into four aliquots, three of them were spiked with <sup>84</sup>Sr (80%), <sup>145</sup>Nd (80%) and <sup>154</sup>Sm (99%) for Isotope Dilution analyses (IDMS) and one aliquot for isotopic compositions of Sr and Nd. In each aliquot Sr and REE were separated using BIORAD<sup>®</sup> AG 50W- × 8, 200–400 mesh cation exchange resin column (17 cm × 0.8 cm) in 2.5N and 6N HCl media respectively (Sarkar *et al.*, 1996). Sm and Nd were subsequently separated from the bulk REE fraction using BIO-RAD 1 × 2, 200–400 mesh anion exchange resin column (4 cm × 0.4 cm) following the method of Ramakumar *et al.* (1980). REE fraction, collected from the first column, was taken into 90% CH<sub>3</sub>OH + 10% 7.5 N HNO<sub>3</sub> medium and loaded into a second column preconditioned with 90% CH<sub>3</sub>OH + 10% 7.5 N HNO<sub>3</sub>. Sm and Nd were eluted with 90% CH<sub>3</sub>OH + 10% 0.075 N HNO<sub>3</sub>

medium. The elution scheme includes rejection of first 2 column volumes followed by collection of next 7 column volume for Sm. The next 11 column volumes were discarded and final 12 column volumes were collected as Nd fraction. The entire column chemistry was carried out in the geochemistry laboratory of the Presidency College, Calcutta. Pure Sr, Sm and Nd fractions were loaded on clean rhenium filaments in nitrate medium. All isotopic analyses were carried using a double filament procedure in the Finningan MAT-261 thermal ionization mass-spectrometer at Bhabha Atomic Research Centre (BARC), Mumbai. Total procedural blanks for Sr, Sm and Nd are <1 ng, <200 pg and <300 pg respectively. Our IDMS analyses of the basaltic standard BCR-1 yielded concentrations of Sr, Sm and Nd as 332 ppm, 6.62 ppm and 28.82 ppm, respectively and in very good agreement with reported values (Wasserburg *et al.*, 1981; Kagami *et al.*, 1987; Lahay *et al.*, 1995). Overall uncertainties in Sr, Sm and Nd concentration are <0.1%. Fractionation corrections for the Sr and Nd isotopic ratios for the unspiked samples were carried out with respect to <sup>86</sup>Sr/<sup>88</sup>Sr = 0.1194 and <sup>146</sup>Nd/<sup>144</sup>Nd = 0.7219 respectively. Internal precision for <sup>87</sup>Sr/<sup>86</sup>Sr isotopic ratios was monitored by running NIST SRM 987 which gave  $0.710226 \pm 16$ . The internal precision for <sup>143</sup>Nd/<sup>144</sup>Nd ratios was checked with both La Jolla and MERCK Nd standard which gave  $0.511867 \pm 08$  and  $0.511747 \pm 06$  values respectively. Reliability of the entire analytical procedure was checked by ion-chromatographic separation of Sr and Nd from BCR-1 rock standard and their mass spectrometric measurements. This provided <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>143</sup>Nd/<sup>144</sup>Nd ratios of  $0.704971 \pm 23$  and  $0.512624 \pm 18$  and are in excellent agreement with the reported values *viz.*  $0.704998 \pm 15$  and  $0.512638 \pm 11$  respectively (Wasserburg *et al.*, 1981; Kagami *et al.*, 1987; Toyoda *et al.*, 1994). Trace element analyses were carried out by ICP-MS at National Geophysical Research Institute (NGRI), Hyderabad (Balaram *et al.*, 1996). The REE were determined both by Instrumental Neutron Activation Analysis at Tokyo Metropolitan University, Japan (for details

see Roy *et al.*, 1997) and ICP-MS in NGRI, Hyderabad mainly to check the reliability of measured elemental concentrations. Analytical errors for the ICP-MS analyses (including Rb) and INAA are <10% and <5% respectively.

## RESULTS AND DISCUSSION

As substantial amount of major element data on different basic/ultrabasic units of the Dhanjori sequence have already been reported (Gupta *et al.*, 1985; Sarkar *et al.*, 1992; Ghosh and Ray, 1994; Majumder, 1996; Deb, 1999), only few major element analysis has been carried out in the present study. On the basis of major element chemistry (SiO<sub>2</sub>: 46–50% and 49–52%, MgO: 13–25% and 3–8%, CaO: 4–10%, and 8.6%, Na<sub>2</sub>O: 0.2–1.9% and 2.5% for the peridotitic/basaltic komatiites and pillowed tholeiitic basalts respectively) these have been tentatively interpreted as bimodal suites emplaced in ocean-island (Gupta *et al.*, 1985; Sarkar *et al.*, 1992; Majumder, 1996; Deb, 1999) or transitional back-arc (Ghosh and Ray, 1994) settings. However, no isotopic data are available for any of these units; trace element/REE data are also scanty to critically evaluate the genesis of these rocks vis-a-vis tectonic setting. Apart from assessing the nature of subcrustal mantle, their tentative Proterozoic age, if true, poses interesting problems regarding the origin of such belt of komatiitic volcanism during this period.

Few major elements along with trace element and REE data for basics/ultrabasic rocks within the Dhanjori basin are given in Table 1. Chondrite normalized REE plots (Chondrite values taken from McDonough and Sun, 1995, Fig. 2(a)) display shallow fractionated REE pattern with light rare earth element (LREE) enrichment ((La/Sm)<sub>N</sub> > 2; Table 1). Deb (1999) reported REE analyses of few basaltic rocks of upper Dhanjori sequence from Mosaboni area which have been plotted along with ours in Fig. 2(b) for comparison. It can be seen from Fig. 2(b) both the data sets overlap and the REE patterns are quite similar. In primitive mantle normalized (primitive mantle data taken from McDonough and Sun,

Table 1. Major, trace and REE data for basic/ultrabasic rocks from the Dhanjori basin

Sample name	T2	T3	R5	R7
Na <sub>2</sub> O*	1.03	1.62	0.71	0.54
K <sub>2</sub> O*	0.38	0.62	0.24	0.20
CaO*	7.08	6.79	5.36	7.79
Cr <sup>I</sup>	1132	438	1934	1298
Ni <sup>I</sup>	252	332	459	308
Co <sup>I</sup>	68.80	69.60	78.70	81.40
Rb	20.18	38.73	18.23	1.50
Ba	60.03	126.20	31.12	20.04
Sr <sup>+</sup>	120.20	218.13	63.50	120.11
Nb	1.82	5.67	1.64	3.30
Hf	0.99	1.84	1.60	1.92
Zr	27.25	94.07	36.23	33.19
Y	11.93	24.85	9.53	14.08
Th	1.23	3.06	1.15	1.77
U	0.26	0.97	0.41	0.31
La <sup>I</sup>	6.39	15.39	7.17	12.20
Ce <sup>I</sup>	13.30	32.80	14.80	24.00
Pr <sup>#</sup>	1.35	3.02	1.54	2.09
Nd <sup>#</sup>	8.16	20.13	7.17	14.59
Sm <sup>I</sup>	1.72	4.49	1.50	2.89
Eu <sup>I</sup>	0.35	1.37	0.37	1.02
Gd <sup>#</sup>	2.42	3.48	1.45	2.55
Tb <sup>I</sup>	0.30	0.78	0.28	0.54
Dy <sup>#</sup>	2.25	3.31	1.09	2.61
Ho <sup>#</sup>	0.55	0.73	0.31	0.45
Er <sup>#</sup>	1.15	1.64	0.86	1.02
Tm <sup>#</sup>	0.24	0.28	0.19	0.17
Yb <sup>I</sup>	1.46	2.08	0.89	1.36
Lu <sup>I</sup>	0.20	0.25	0.16	0.18
(Ce/Yb) <sub>N</sub>	2.39	4.14	4.36	4.63
(Ba/La) <sub>N</sub>	0.92	0.80	0.43	0.16
(La/Sm) <sub>N</sub>	2.32	2.14	2.98	2.64
Th/Nb	0.68	0.54	0.70	0.54
U/Nb	1.35	2.43	1.99	22.13
Th/Yb	0.84	1.47	1.29	1.30
Ce/Yb	9.11	15.77	16.63	17.65
Ba/Rb	2.97	3.26	1.71	13.36

\*Concentration are in %; <sup>+</sup>measured by IDMS; <sup>I</sup>INAA data; <sup>#</sup>measured in ICP-MS.

All trace element concentrations are in ppm. N = chondrite normalized; T2 and T3: gabbroic with slightly higher modal clinopyroxene; R5 and R7: basaltic but R7 contains higher modal plagioclase feldspar.

1995) plots also (Fig. 3) these rocks show shallow fractionated pattern with depletion of Nb and Ba and enrichment of large ion lithophile elements (LILE) like Rb, Th and U. Depletion of Nb, Ba and Zr and enrichment of Rb, Th and U are indicated also in N-MORB normalized plots (N-MORB data from McDonough and Sun, 1995; Fig.

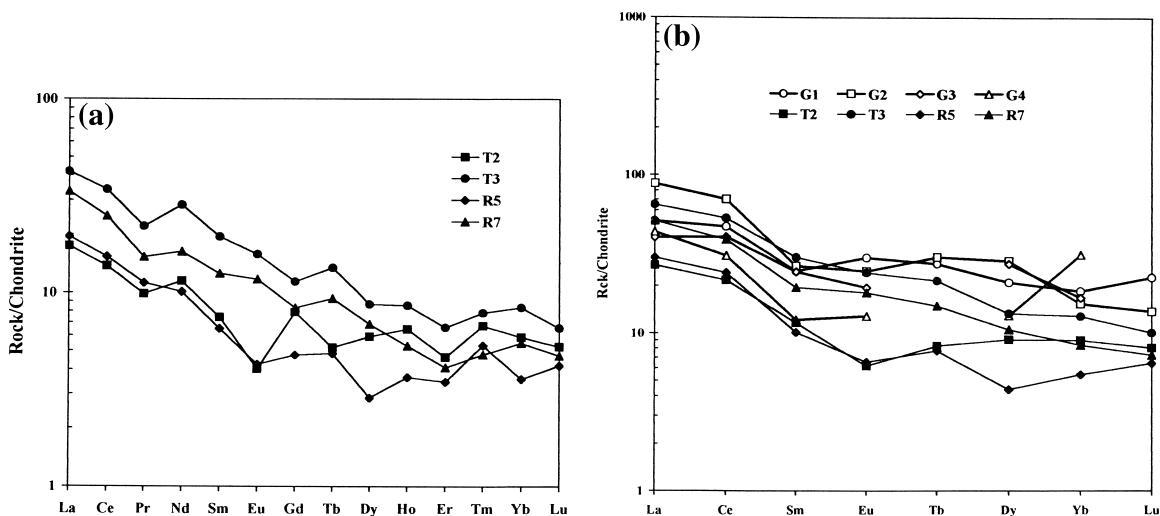


Fig. 2. (a) Chondrite normalized REE plot for Dhanjori basics and ultrabasic rocks. (b) Chondrite normalized REE plot for Dhanjori basic and ultrabasic rocks including data of Deb (1999; G-series) and present work.

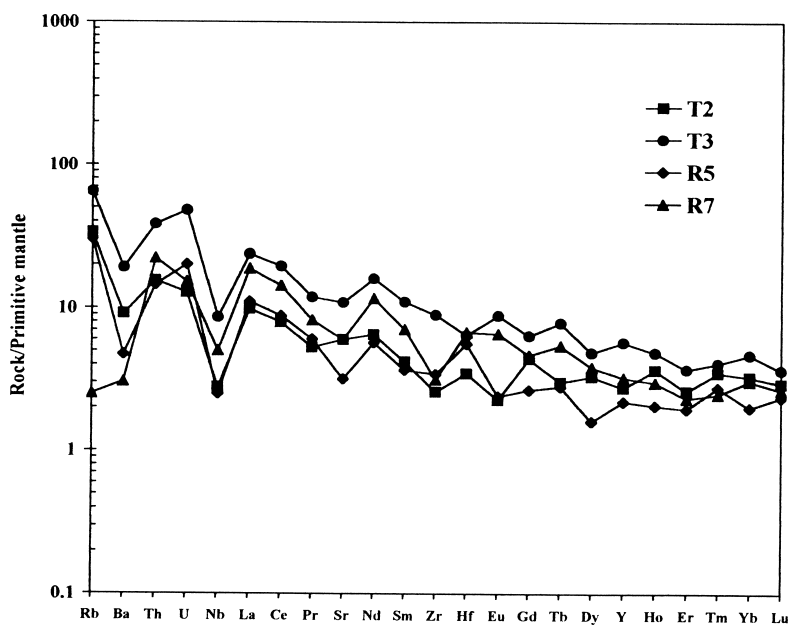


Fig. 3. Primitive mantle normalized trace element patterns for Dhanjori basics and ultrabasic rocks.

4), whereas compatible elements like Tb, Y and Yb show a flat pattern. Chondrite normalized REE pattern along with  $2 < (Ce/Yb)_N < 5$  (Table 1) of these rocks indicates that they might have formed at a relatively shallower depth close to spinel

stabilization depth (Frey, 1982). Noticeable negative anomalies of Ba, Nb and slight depletion of Zr, found in primitive mantle normalized plot are indicative of either crustal contamination during ascent of the magma or source signature. As aver-

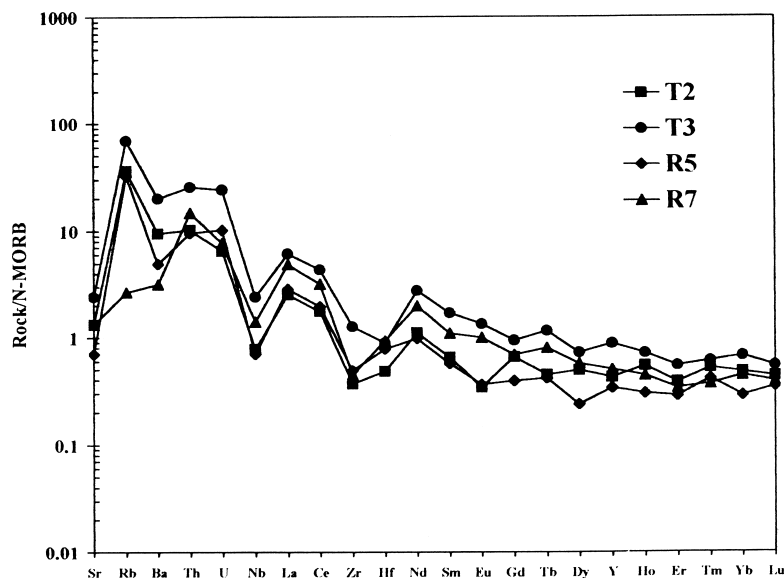


Fig. 4. N-MORB normalized trace element patterns for Dhanjori basics and ultrabasic rocks.

age continental crust contains high amount of Na and K, crustal contamination during the ascent of the basic/ultrabasic magma results relatively higher Na and K but mostly unaffacting the compatible elements like Ni, Cr and Co which occur in a very low concentration within the crust. It can also be argued that the slightly elevated LREE pattern with absence of Eu anomaly (as observed) might be due to the assimilation of the Archean TTG (Tonalite-Trondhjemite-Granodiorite; Taylor and McLennan, 1985). However, Low Na and K, high Ca, Cr and Ni content (Table 1) along with fractionated REE pattern with no Eu anomaly and  $(Ba/La)_N < 1$  of these basic/ultrabasic rocks, indicate least chance of crustal contamination (Polat *et al.*, 1997). Hence depletion of Ba, Nb and to some extent Zr in these rocks are not due to the crustal contamination rather they represent the source signature. N-MORB normalized trace element plots (Fig. 4) also display general enrichment of the incompatible elements, slight depletion of compatible elements and Ba but a strong depletion of Nb in addition to Zr.

Isotopic data for these rocks are given in Table 2. The  $^{87}Rb/^{86}Sr$  and  $^{87}Sr/^{86}Sr$  ratios of these rocks vary between 0.036 and 0.833 and 0.71770

and 0.73400 respectively.  $^{147}Sm/^{144}Nd$  and  $^{143}Nd/^{144}Nd$  ratios vary between 0.0607 and 0.1502 and 0.510652 and 0.511859 respectively. While Rb-Sr data show large scatter, Sm-Nd data show a reasonably good linear correlation (Fig. 5). Interpreted as an isochron this line corresponds to an age of  $2072 \pm 106$  Ma (MSWD = 1.56) and an initial ratio ( $I_{Nd}$ ) of  $0.509829 \pm 0.000082$  ( $\epsilon_{Nd} = -2.4$ ). The large error in age calculation is possibly due to the limited spread in Sm/Nd ratio of the samples. The low Sm/Nd ratios (e.g., 0.0607 etc.) in some samples are due to relatively higher modal plagioclase feldspar. At present, establishing a link between the genesis of these rocks and specific tectonic settings, based on trace element and isotopic compositions, seems to be difficult task. More than one single mechanism can produce the observed patterns and concentrations which are discussed below.

The negative Ba and Nb anomalies with high Th/Nb (Table 1) can be explained by metasomatism of overlying mantle wedge at source induced by the fluid coming out from some subducted crust. It is possible that due to the subduction of the earlier oceanic (mafic) crust, fluid ( $\pm$ silicate melt) was squeezed out from the slab

Table 2. Rb-Sr and Sm-Nd isotopic data for basic/ultrabasic rocks from the Dhanjori Basin

Sample No.	T2	T3	R5	R7	R8	R9
Sm (ppm)	2.00	5.34	1.74	3.20	3.95	3.43
Nd (ppm)	8.07	23.07	9.02	18.05	23.79	34.18
$^{147}\text{Sm}/^{144}\text{Nd}$	0.1502	0.1400	0.1165	0.1072	0.1003	0.0607
$f_{\text{SmNd}}$	-0.24	-0.29	-0.41	-0.46	-0.49	-0.69
$^{143}\text{Nd}/^{144}\text{Nd}$	$0.511859 \pm 10$	$0.511741 \pm 07$	$0.511448 \pm 11$	$0.511317 \pm 08$	$0.511163 \pm 08$	$0.510652 \pm 08$
$\epsilon_{\text{Nd}} (2.072)$	-2.91	-2.51	-2.02	-2.11	-3.29	-2.80
$T_{\text{DM}} (\text{Ma})$	2832	2696	2494	2462	2520	2372
Rb (ppm)	20.18	38.73	18.23	1.50	nd	nd
Sr (ppm)	120.20	218.13	63.50	120.12	nd	nd
$^{87}\text{Rb}/^{86}\text{Sr}$	0.486	0.514	0.833	0.036	nd	nd
$^{87}\text{Sr}/^{86}\text{Sr}$	$0.71923 \pm 19$	$0.717701 \pm 18$	$0.734002 \pm 16$	$0.718660 \pm 18$	nd	nd
$\text{Sr}_i$	0.70457	0.70220	0.70890	0.71757	nd	nd

nd = not determined.

$$f_{\text{SmNd}} = [(^{147}\text{Sm}/^{144}\text{Nd})_{\text{sample}} / (^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}}] - 1.$$

CHUR (chondrite uniform reservoir):  $^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ ,  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ .

$$\epsilon_{\text{Nd}} (T) = \epsilon_{\text{Nd}} (0) - 25.09 \cdot T \cdot f_{\text{SmNd}}$$

Used in model age calculation, DM (depleted mantle):  $^{147}\text{Sm}/^{144}\text{Nd} = 0.2137$ ,  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51315$ .

$\lambda$  = decay constant of  $^{147}\text{Sm} = 6.54 \times 10^{-12}$ .

All errors quoted are  $2\sigma$  error.

R8 and R9: basaltic.

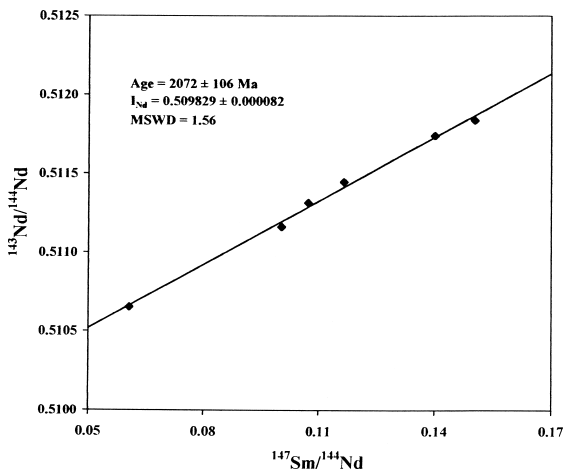


Fig. 5.  $^{147}\text{Sm}/^{144}\text{Nd}$ - $^{143}\text{Nd}/^{144}\text{Nd}$  whole rock isochron diagram of the Dhanjori intrusives. The isochron age is calculated using ISOPLOT program (model 1 solution; Ludwig, 1988).

and incorporated into the overlying mantle wedge. As this fluid generally contains  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and chloride ions, it will be enriched in less acidic elements like Th and U (particularly in slightly oxidised condition) and depleted in very strong acidic element like Nb (Meen *et al.*, 1989; Keppler, 1996)

which can result in the high Th/Nb and U/Nb ratios (Keppler, 1996; Kelemen *et al.*, 1993; Davies *et al.*, 1989; Karsten *et al.*, 1996; Tatsumi and Kogiso, 1997; Kogiso *et al.*, 1997). It also enriches moderately strong acidic elements like Rb, Ba and Sr. Among Rb, Ba and Sr, Rb is of least acidic character. Furthermore, solubility and mobility of Rb in chloride medium is higher compared to Ba and Sr (op.cit.). This could explain the relative depletion of Ba and Sr compared to Rb. However, Ba depletion has also been reported to be due to the presence of Ba-depleted sediment subduction-component at source (Smith *et al.*, 1986). The high Ce/Yb and Th/Yb ratios (Table 1) relative to the primitive mantle of these rock suites also indicate selective enrichment of Th and Ce due to the invasion of fluid coming out from subducted slab (Hawkesworth *et al.*, 1984; Peltonen, 1995). Depletion of Zr in N-MORB normalized plot (Fig. 4) can be explained by the fractionation of accessory minerals like zircon and rutile in the source (Green, 1994). Furthermore, negative  $\epsilon_{\text{Nd}}$  value (-2.4) indicates the presence of an enriched source. The  $T_{\text{DM}}$ - $^{147}\text{Sm}/^{144}\text{Nd}$  plot (Fig. 6) of these rock suites which shows a crude hyperbolic mix-



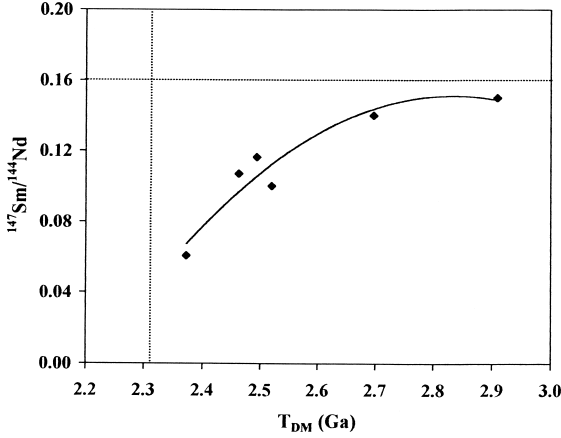


Fig. 6.  $T_{DM}$ - $^{147}\text{Sm}/^{144}\text{Nd}$  plot of basic and ultrabasic rocks from Dhanjori basin. Note a hyperbolic mixing relation at the source.

ing relation, attests a short term enrichment in the source. The two asymptotes of this hyperbolic mixing line indicate that an enriched component was mixed up with a relatively depleted component ( $\sim^{147}\text{Sm}/^{144}\text{Nd} = 0.15$ ) during  $\sim 2.3$  Ga i.e., just before the emplacement of these rock suites at around 2.1 Ga. It is also to be noted that  $\text{Sr}_i$  values (calculated back to 2.1 Ga) of these rocks considerably vary from 0.702 to 0.717 where as  $\epsilon_{\text{Nd}}$  values do not. This indicates two possibilities. Either the Sr isotopic signature has been disturbed by low-grade metamorphism and/or post crystallisation alteration (albeit insignificant) without affecting Nd-isotope systematics or the source itself was heterogeneous (mixing of different source components) at least in terms of Rb-Sr systematics. It should be mentioned in this context that for the present work Rb was measured by the ICP-MS method. The analytical error (monitored by the analyses of rock standard JB-2) for this is  $\sim < 5\%$ . Even considering the inter-aliquot heterogeneity and analytical error together ( $\sim 15\%$ ), no correlation has been observed between  $^{87}\text{Sr}/^{86}\text{Sr}$  and Rb/Sr ratios and hence the scatter indeed is real. The variation in  $\text{Sr}_i$  (calculated back to 2.1 Ga) is, therefore, also real. The Nd isotopic data, however, indicate a near-uniform but slightly enriched source.

### Nd isotope and REE modeling

The  $\epsilon_{\text{Nd}}$  values can be used to estimate the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio of the mantle source of these rocks during 2.072 Ga by using the following relationship (DePaolo, 1988):

$$f_{\text{Sm/Nd}}^{\text{source}} = \frac{\epsilon_{\text{Nd}}}{Q(T_S - T_X)}$$

where,  $T_S$  = model age of the magma source and  $T_X$  = crystallisation age of the rocks. Considering  $T_S = 4.55$  Ga where from accretion of the earth started,  $T_X = 2.1$  Ga,  $\epsilon_{\text{Nd}} = -2.4$  (taken from Isochron) and  $Q = 25.09 \text{ Ga}^{-1}$  (calculated using present day values of  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}} = 0.1967$  and  $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$ ; Jacobsen and Wasserburg, 1984), the  $f_{\text{Sm/Nd}}^{\text{source}}$  value has been calculated to be  $\sim -0.04$ . Again,

$$f_{\text{Sm/Nd}} = \frac{(^{147}\text{Sm}/^{144}\text{Nd})_{\text{source}} - (^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}}}{(^{147}\text{Sm}/^{144}\text{Nd})_{\text{CHUR}}}$$

Using  $f_{\text{Sm/Nd}}^{\text{source}} = -0.04$  in the above equation,  $(^{147}\text{Sm}/^{144}\text{Nd})_{\text{source}} = 0.189$  has been obtained which is about  $\sim 4\%$  lower than the average chondrite.

Taking  $f_{\text{Sm/Nd}}^{\text{source}} = -0.04$  and  $f_{\text{Sm/Nd}}^{\text{rock}} = -0.43$  (average of the six samples, Table 2) values, fractionation factor ( $\alpha$ ) has been calculated using the following relationship of DePaolo (1988):

$$\alpha_{\text{Sm/Nd}} = \frac{1 + f_{\text{Sm/Nd}}^{\text{rock}}}{1 + f_{\text{Sm/Nd}}^{\text{source}}}$$

which gives the value of  $\alpha_{\text{Sm/Nd}} = 0.594$ , i.e.,  $\sim 41\%$  depletion in the Sm/Nd ratio of the precursor of these rocks at source. This requires very low degree of partial melting (DePaolo, 1988) of the spinel lherzolite source which was already enriched at a scale of 4% with respect to Sm-Nd isotope.

As a first approximation shallow fractionated pattern in chondrite normalized REE plot indicates its derivation from partial melting of a less fractionated REE source. In the trace element modelling, it is difficult to get a unique solution. This is mainly due to the improper estimation of the initial source composition. Using the measured REE concentrations, Nd isotope signatures and partial melting model of Allegre and Minster (1978), the probable source composition of these basic/ultrabasic rocks and the extent of melting have been assessed. Partition coefficient (D) values, used in this model, are taken from Shaw (1970) and McKenzie (1995). The modelling shows that ~3–5% partial melting of a slightly enriched source with REE concentration of ( $\sim 2.5 \times$  chondrite LREE values and  $2 \times$  chondrite HREE values) and spinel lherzolite composition (Ol:Opx:Cpx = 60:25:15) can give rise to Dhanjori basaltic or gabbroic end products. Weight fraction of liquid contributed by each phase during melting is Ol:Opx:Cpx = 10:35:55. Since modal percentage of pyroxenes is higher and  $(Ce/Yb)_N > 1$ , initial rock composition and melting mode have been considered as discussed above (for details see Roy *et al.*, 1997). This estimation is consistent with the Nd isotope modelling of these rocks.

#### Source enrichment

The foregoing discussion indicates that at 2.1 Ga i.e., early Proterozoic, the mantle below the Dhanjori basin was enriched which had a relatively short residence time whereas it was heterogeneous in terms of Rb-Sr isotopic character. Trace element signatures also indicate that the mantle enrichment could be the result of invasion of fluids originated from subducted slab. This resulted in low Nb, Ba with enriched LREE pattern in chondrite normalized REE plot, high Th/Nb ratio and enriched Nd isotopic signature.

However, apart from the fluid-invasion (subducted slab of altered oceanic crust? Smith *et al.*, 1986), the lower Nb i.e., high Th/Nb ratio and higher Rb of these basics and ultrabasic rocks can as well be explained by the contribution of delaminated continental crust at the source itself

(Rudnick and Fountain, 1995). In the first case, fluid coming out from the subducting oceanic crust (hydrated), enriched in LILE like Rb, Th and U and LREE and depleted in HFSE like Nb, Ta and Zr and occasionally Ba (if Ba depleted sediment is subducted; Ben Othman *et al.*, 1989; Smith *et al.*, 1986; Jahn *et al.*, 1999), is mixed up with upper mantle wedge resulting Nb and Ba depleted but LREE and LILE enriched upper mantle (Schiano *et al.*, 1995). The second case i.e., delamination of continental crust occurs when the continental crust is thicker and differentiated (Rudnick and Fountain, 1995). With progressive crust building activities the metamorphosed lower part of thicker continental crust becomes denser. If the density of lower crust exceeds that of the immediate neighbouring upper mantle, density inversion i.e., sinking of a part of the lower crust within the upper mantle occurs. The upper mantle material instead occupies the volume left behind by the detached lower crust. After a considerable time, mixing of the delaminated lower crust with the mantle results a hybridised upper mantle with enriched Nd isotopic and variable Sr isotopic signatures (McKenzie and O'Nions, 1983) along with LILE enrichment and Nb depletion.

Though it is difficult to choose either of these two processes, higher Th/Nb, Th/Yb, Ce/Yb, low but variable Ba/Rb ratios and variable  $Sr_i$  of these rocks favour more a source affected by subduction induced fluid rather than delamination of continental crust. If slightly higher amount of low Ba bearing sediments, which are generally characteristic of hemipelagic sequence, are subducted, the fluid coming out from these sediments will also be slightly enriched in U and Th but depleted in Ba, Nb and Zr, resulting in Ba, Nb and Zr depleted upper mantle (Smith *et al.*, 1986; Ben Othman, 1989). This of course does not suggest any tectonic setting (subduction or otherwise) for basic/ultrabasic rocks of Dhanjori but merely suggests a process of modification of the source. It is not possible to comment about the exact time of source enrichment, however, Nd isotope data indicate it to be prior to ~2.3 Ga i.e., lower Proterozoic time. The modified mantle material might come up

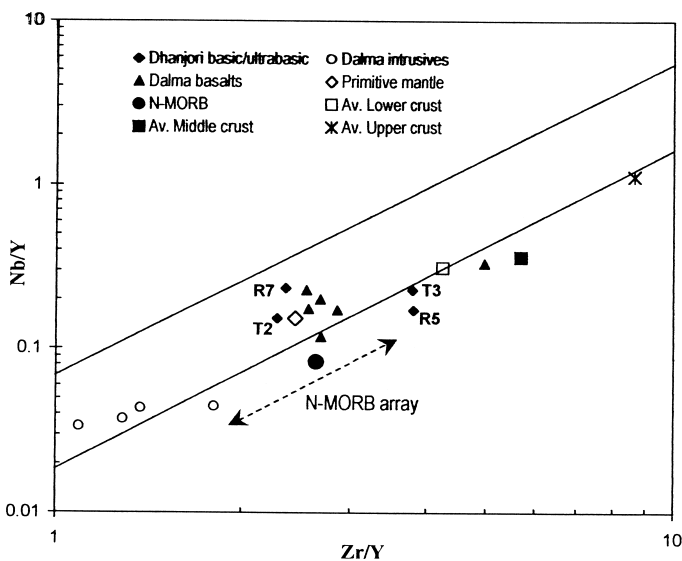


Fig. 7. Nb/Y-Zr/Y discriminant plot for the Dhanjori basics/ultrabasic rocks (present work) Dalma intrusives and tholeiites (data taken from Bose *et al.*, 1989; Saha, 1994; Roy, 1998); Primitive mantle and average N-MORB data from McDonough and Sun (1995); Average lower, middle and upper crust data from Rudnick and Fountain (1995); note that both the Dhanjori and Dalma basic/ultrabasic data fall within the plume array (for details see text).

through a number of tectonic settings including plumes which, according to many, was responsible for generating all the komatiitic (or high MgO basaltic) melts like those of Dhanjoris (McKenzie and Bickle, 1988; Campbell and Griffith, 1992; Arndt *et al.*, 1997). In this regard,  $\Delta Nb$ , a parameter which is insensitive to the effects of variable degrees of mantle melting, source depletion through melt extraction, crustal contamination of the magmas and post crystallisation alterations (Fitton *et al.*, 1997) can be used for source characterisation. Since both continental crust and N-MORB are depleted in Nb, the low abundance of Nb in the upper mantle cannot be explained by simple mass balance calculation involving extraction of continental crust at the expense of upper mantle. The lost Nb, possibly stored in the subducted oceanic crust, is recycled back through mantle plumes (Saunders *et al.*, 1988). This produces relatively higher Nb concentration in plume magma compared to that of N-MORB. On a Nb/Y-Zr/Y plot the present day plume basalts from Iceland have been shown to fall on an array which runs exactly parallel to the N-MORB array but

with significantly higher Nb/Y ratios (Fitton *et al.*, 1997). Crustal contamination, in this plot, is easily discernible from low Nb/Y-high Zr/Y array deviating from either plume or N-MORB array.  $\Delta Nb$  ( $= 1.74 + \log(Nb/Y) - 1.92 \log(Zr/Y)$ ) with positive and negative values indicate plume and MORB sources respectively (op.cit.). Owing to the non-availability of precise trace element data for majority of Dhanjori komatiitic lavas it has not been possible to use Nb/Y-Zr/Y discriminant diagram (a potential diagram to identify plume related volcanism) and compare (and compile) the Nb/Y-Zr/Y ratios between komatiites and basic/ultrabasic rocks under investigation. However, when plotted on this discriminant diagram two samples of Dhanjori basic/ultrabasic rocks (T2 and R7) have been found to lie exactly within the plume array close to primitive mantle but away from crustal contamination whereas other two samples (T3 and R5) are slightly deviating (Fig. 7). While the sample T3 falls very close to the lower boundary of the plume array ( $\Delta Nb \sim 0$ ),  $\Delta Nb$  for R5 is  $\sim -0.14$  occurring quite close to the N-MORB along the N-MORB-Crust array. The nega-

tive  $\Delta\text{Nb}$  of R5 might be due to the mixing between the N-MORB and crust as both have negative  $\Delta\text{Nb}$  values. Based on few major and compatible element concentrations we earlier indicated minimum chance of crustal contamination. Additionally, depletion of Ba compared to the other incompatible element like Rb along with high Th/Yb and Ce/Yb in Dhanjori basics/ultrabasic rocks also negates crustal contamination during emplacement. The geochemistry of these rocks rather indicates other geological process(es) operative at source. We have also plotted in Fig. 7 Nb/Y-Zr/Y ratios of mid-Proterozoic (~1.6 Ga; Roy *et al.*, 1999, 2002a) Dalma basalts, komatiites and ultrabasic intrusives all of which have been found to be depleted mantle products (in terms of both REE and  $\epsilon_{\text{Nd}}$ , data taken from Bose *et al.*, 1989; Saha, 1994; Roy, 1998, Roy *et al.*, 2002a). Interestingly, all these units of Dalma belt also fall within the plume array and together they indicate that the plume magmatism was quite active during the Proterozoic of the EIC. The fundamental difference between Dhanjori and Dalma plumes are that the former possibly represents tapping of an enriched part of a plume while the later represents a depleted part. This is consistent with the prevalent idea of large compositional spectrum encompassed by different kinds of plume (MacDougall, 1988). It is, therefore, concluded that the Dhanjori basic/ultrabasic rocks are genetically connected to a plume which was fed by fluid derived from an ancient subducted altered oceanic crust and not related to crustal delamination process. Since the Dhanjori basic/ultrabasic rocks are uniformly enriched (both geochemically and isotopically), it is tempting to speculate that possibly the plume originated at deep crust-mantle boundary and rapidly pierced through the crust without any contamination (and stalling or residence) with shallow depleted upper mantle (Fitton *et al.*, 1997). A deep seated plume with enriched signature can show depleted components only if it travels slowly or stalls within the depleted upper mantle for a long time by acquiring an envelope of depleted component (Kerr *et al.*, 1995).

## IMPLICATIONS

It has been well documented that by early Proterozoic the crust in the south Singhbhum nucleus was considerably thick due to the emplacement of vast Singhbhum granite (Saha, 1994). Hence, the Dhanjori basalts including komatiites (and gabbros), if related to plume magmatism, must have had access to some weak zones through which they were extruded/emplaced. It is envisaged that number of small isolated basins like Dhanjori, Simlipal etc. were formed within the Singhbhum nucleus towards the early Proterozoic time possibly due to the readjustment in proto-crustal stability and resetting of tectonomagmatically active margins (Gupta *et al.*, 1985). During the end-Archaean period cooling down of the vast intrusion of granite batholith (Singhbhum Granite) took place which possibly induced an isostatic readjustment. Local tensional regimes and deep seated fractures, thus produced, might have culminated in the formation of small isolated basins. Subsequent upwelling of an enriched plume from the deeper mantle through these weak zones accentuated the basin evolution resulting in outpouring of basaltic/komatiitic magma with basic and ultrabasic intrusives.

It is also noticeable that an enriched mantle (in terms of trace elements, REE and Nd isotopes) existed below the Dhanjori basin during ~2.1 Ga or early Proterozoic period. The enrichment was possibly caused by the continuous recycling of the earlier crust into the mantle whereby subducted slab derived fluid modified the surrounding mantle, a process which started much earlier below the EIC as evident from the  $\epsilon_{\text{Nd}}$  values of 2.6 Ga old ultramafic rocks associated with Newer Dolerite dykes (NDD; Roy, 1998; Roy *et al.*, 2002b). The Nd isotopic data of these Archaean dyke (the data are being published separately) bodies indicate that the mantle below the EIC was heterogeneous displaying both early depleted and later enriched components (op.cit.). The 2.6 Ga time is a period of major global crust building activities and initiation of recycling of enriched

component(s) to the mantle via subduction (McCulloch and Bennett, 1994). As the crustal recycling continued, the underlying mantle became more and more enriched and homogeneous by 2.1 Ga as manifested by uniformly enriched  $\epsilon_{Nd}$  values of Dhanjori basic/ultrabasic rocks. The process also affected the more easily susceptible Rb-Sr systematics producing variable  $Sr_i$  of the basic/ultrabasic rocks from Dhanjori basin. The enriched mantle material, part of a thermal plume, not only produced the basic/ultrabasic rocks of the Dhanjori group but also aided extrusion of high temperature komatiitic flows. That the komatiites are possibly product of plume magmatism has been convincingly demonstrated (Kerr *et al.*, 1995; Arndt *et al.*, 1997). The residence time of the Dhanjori plume within the upper mantle was possibly very small as no depleted signature (even in Nd isotope) has been obtained. This means a deep plume was fed by recycled crust via globally extensive subduction process already initiated during the end-Archaeon period (op.cit.).

### CONCLUSIONS

(1) The Sm-Nd isotopic analyses of basic-ultrabasic rocks of Dhanjori basin from the EIC yield an isochron age of  $2072 \pm 106$  Ma (MSWD = 1.56) indicating their age as early Proterozoic.

(2) Chondrite normalized REE plots display shallow fractionated REE pattern with LREE enrichment. Also in primitive mantle normalized plots these rocks show shallow fractionated pattern with depletion of Nb and Ba and enrichment of LILE like Rb, Th and U. Depletion of Nb, Ba and Zr with enrichment of Rb, Th and U are found in N-MORB normalized plots as well. Compatible elements, like Tb, Y and Yb, on the other hand, show a flat pattern.

(3) Isotope, trace and REE modeling indicate that these are produced by 3–5% partial melting of spinel lherzolite source. The data suggest that an enriched ( $\epsilon_{Nd} = -2.4$ ) mantle existed below the Dhanjori basin during ~2.1 Ga which had a relatively short residence time in the mantle. The en-

richment was possibly caused by the continuous recycling of the earlier crust into the mantle whereby subducted slab derived fluid modified the surrounding mantle. The process also affected the more easily susceptible Rb-Sr systematics producing variable  $Sr_i$  (0.702–0.717).

(4) The enriched mantle material, part of a thermal plume, pierced through the deep fractures produced due to the cooling and readjustment of the Archaean continental crust and ultimately outpoured within the Dhanjori basin. The plume magmatism was manifested by the extrusion of komatiitic/basaltic flows and basic/ultrabasic intrusives. The residence time of the plume within the upper mantle was possibly very small as no depleted signature (even in Nd isotope) has been obtained. This means a deep plume was fed by a recycled oceanic crust via globally extensive subduction process already initiated by the end-Archaeon period.

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