

Crustal growth processes as illustrated by the Neoarchaeon intraoceanic magmatism from Gadwal greenstone belt, Eastern Dharwar Craton, India

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Abstract

Geochemical studies on metavolcanic rocks of the Gadwal greenstone belt (GGB), eastern Dharwar craton, have documented several rock types that are indicative of subduction zone tectonics reflecting on the crustal growth processes in the Dharwar craton. The dominance of komatiites in the western Dharwar craton (WDC) and the arc volcanics in the eastern Dharwar craton (EDC) is an indication for the predominance of plume magmatism in the WDC and the intraoceanic subduction zone processes in EDC which together played a significant role in the growth and evolution of continental crust in the Dharwar craton. Boninites of GGB are high calcic type with high MgO (13–24 wt.%) and a characteristic MREE depleted U-shaped REE patterns whereas the basalts have flat REE patterns with no Eu anomalies. Nb-enriched basalts exhibit slightly fractionated REE patterns with high Nb (8–26 ppm) content compared to arc basalts. Adakites of GGB are Sr depleted with highly fractionated REE patterns and no Eu anomaly compared to rhyolites. The occurrence of boninites along with arc basalts, Nb-enriched basalts–basalt–andesite–dacite–rhyolites and adakites association in Gadwal greenstone belt indicate the intraoceanic subduction zone processes with a clear cut evidence of partial melting of metasomatized mantle wedge (boninites), melting of subducting slab (adakites) and residue of adakite–wedge hybridization (Nb-enriched basalts) which have played a significant role in the growth of continental crust in the Dharwar craton during the Neoarchaeon.

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1. Introduction

Magmatism along destructive plate margins is the widely preferred hypothesis for generation of new continental crust. Most estimates suggest that the average crust is andesitic in composition and andesite is thought to be the most abundant rock type erupted along the continental margin arcs (Taylor and McLennan, 1985). Although most arcs are basaltic (Ellam and Hawkesworth, 1988), intracrustal melting is also required to generate an andesitic crust (Rudnick and Goa, 2004). Many recent models for Archaean continental evolution indicate a peak of crustal growth during the Neoarchaeon, and parts of Archaean crust is considered to evolve through terrane accretion including amalgamation of oceanic plateaus and island arcs at convergent margins (Polat et al., 1998; Kerrich and Polat, 2006).

All the products of these magmatic and tectonic processes are apparently well preserved in the Neoarchaeon greenstone belts of Superior Province, Canada [Schreiber–Hemlo, White River–Dayohessarah (Polat et al., 1998), Wawa (Polat and Kerrich, 2001), Birch–Uchi (Hollings and Kerrich, 2000), Abitibi greenstone belt (Kerrich et al., 1998)] which are characterized by two types of volcanic associations. Tholeiite–komatiite suites are interpreted to erupt from mantle plumes and tholeiitic to calc–alkaline suites erupted in island arc setting (Polat et al., 1998, 1999; Wyman et al., 1999; Kerrich et al., 2000; Wyman et al., 2002; Manikyamba et al., 2004; 2005a; Kerrich and Polat, 2006). Late Archaean greenstone belts contain a great compositional diversity of subduction related volcanic rocks such as basalt–andesite–dacite–rhyolite (BADR), adakites, low and high TiO₂ basalts (Polat and Kerrich, 2002; Wang et al., 2004; Samsonov et al., 2005; Niu et al., in press). In addition to bimodal tholeiite–calc–alkaline suites of basalts to rhyolites; there are adakites, Mg-andesites, Nb-enriched basalts and boninites, which have been reported from few Archaean greenstone

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belts of Superior Province, Canada, Greenland, Quebec, Baltic Shield and Western Australia (Kerrick et al., 1998; Hollings and Kerrich, 2000; Polat and Kerrich, 2001; Boily and Dion, 2002; Kerrich and Polat, 2006). Individual suites of boninites and adakites were identified from other greenstone belts of the world (Smithies, 2002; Polat et al., 2002; Polat and Munker, 2004; Smithies et al., 2005; Samsonov et al., 2005; Niu et al., in press). Kerrich and Polat (2006) have compiled the Archaean hot subduction volcanic rocks and their Phanerozoic analogs reported from different cratons of the world; they discuss their geodynamic processes, demonstrated the operation of plate tectonics with a thin oceanic crust and shallow angle subduction during Archaean.

Boninites are a large variety of primary to near-primary magmas with a wide variation in $\text{CaO}/\text{Al}_2\text{O}_3$ (<0.55 to >0.75), U-shaped REE patterns with <52 wt.% SiO_2 and $\text{Mg\#} > 60$ ($\text{Mg\#} = \text{Mg}/(\text{Mg} + \text{Fe}^{\text{total}})$; Crawford et al., 1989). Adakites are Al- and Na-rich, intermediate to felsic calc-alkaline volcanic rocks having low Y and Yb contents and high $(\text{La}/\text{Yb})_n$ values (Drummond et al., 1996; Martin, 1999; Polat and Munker, 2004). Mg-andesites are primitive, intermediate calc-alkaline volcanic rocks having high Mg#, Cr and Ni contents (Sajona et al., 1996; Rapp et al., 1999; Polat and Munker, 2004). Nb-enriched basalts are mafic volcanic rocks possessing high Nb (>7 ppm) and high $(\text{Nb}/\text{Th})_{\text{pm}}$ and $(\text{Nb}/\text{La})_{\text{pm}}$ than normal arc basalts where Nb <2 ppm (Defant et al., 1992; Kepezhinskias et al., 1996; Polat and Munker, 2004). The geochemical characteristics of these volcanic rocks are consistent with diverse petrological processes operative in Archaean subduction zones including slab melting, slab dehydration, mantle wedge metasomatism and crustal recycling that played a significant role in the growth and evolution of continental crust in the Dharwar craton.

Volcanic rocks from Indian greenstone belts have not been understood properly due to few studies with high precision REE, HFSE and isotopic data (Zachariah et al., 1996; Naqvi et al., 2002; Manikyamba et al., 2004, 2005a). Due to this gap, whenever the crustal growth and crust–mantle geodynamic models are discussed, Indian greenstone belts are not generally considered, although these greenstone belts have varied lithologies reflecting on diverse tectonic settings and provide significant constraints either on collision or accretion processes. Although terrane accretion has been established from different greenstone belts such as Holenarsipur, Chitradurga, Sandur, Ramagiri, Penakacherla, Kushtagi; (Kunugiza et al., 1996; Zachariah et al., 1996; Manikyamba and Naqvi, 1997, 2002; Naqvi et al., 2002), boninites–adakites formed during subduction–accretion processes and responsible for the crustal growth during Archaean, have been recognized only from few greenstone belts of the Dharwar craton (Manikyamba et al., 2005a, Manikyamba and Khanna, 2005; Naqvi et al., 2006). Previous workers have inferred the gravity driven deformation in Holenarsipur and Chitradurga (Bouhallier et al., 1993), and incipient sagduction of greenstone within the basement due to gravity process (Chardon et al., 1996; Choukroune et al., 1997). However, the work carried out by Kunugiza et al. (1996) suggest that the Holenarsipur belt was formed by ocean floor spreading and the terrane accretion model has been clearly demonstrated at Sandur Superterrane

(SST; Manikyamba and Naqvi, 2002; Manikyamba and Kerrich, in press). However, this model also needs the rigorous radiometric and reflection seismological data.

Irrespective of their age, and mode of formation, there are at least two types of greenstone belts found in the Dharwar craton: 1) dominated by siliciclastic turbidites with moderate abundance of volcanic rocks (present in western Dharwar Craton (WDC); 2) greenstone belts predominantly made up of a variety of volcanic rocks and subordinate sediments (found in the eastern Dharwar Craton (EDC); Table 1). The latter (EDC type) appears to have formed by intraoceanic processes together with the impingement of mantle plumes at various accretionary stages (Zachariah et al., 1996; Naqvi et al., 2002; Manikyamba et al., 2004, 2005a,b; Naqvi et al., 2006). For example, the late Archaean Ramagiri greenstone belt in the eastern Dharwar craton is made up of three genetically different mafic metavolcanic dominated blocks separated by granitic rocks. The metavolcanic rocks are serpentinites, mafic and felsic in composition associated with minor bands of banded ferrugeneous quartzite, argillite and volcanoclastic rocks which have different chemical composition and diverse origin. According to Zachariah et al. (1996), serpentinites represent the subducted oceanic lithosphere; and the mafic to felsic volcanic rocks were derived from a tectonic setting similar to present-day island arc volcanic suites. The collage of lithologies is found juxtaposed within a matrix of granitic rocks and the age of accretion was constrained at 2450 Ma (Zachariah et al., 1996). The northern part of Ramagiri belt, extending up to Hungund in the EDC, has a series of volcanic-dominated greenstone belts which accreted at various stages (Manikyamba et al., 2004).

Table 1

Lithotectonic differences between the western and eastern sectors of Dharwar cratons

Western Dharwar craton (WDC)	Eastern Dharwar craton (EDC)
1. Large widespread greenstone belts covering ~75% surface area. Greenstone belts are surrounded by gneisses and granitoids.	Small and linear greenstone belts (15–20%) surrounded by vast outcrops of gneisses and granitoids.
2. Predominance of sedimentary rocks over volcanic rocks.	Volcanic rocks are predominant and sedimentary rocks are sparse.
3. Sedimentary sequence starts with QPC, followed by volcanics, banded iron and banded manganese formations, greywackes, shales. Carbonaceous shales are predominantly developed.	Small-scale development of banded iron formation. Manganese formation and carbonaceous shales are not present.
4. Stromatolites are well developed.	Stromatolites are absent.
5. Komatiites are predominant.	Komatiites are rare whereas island arc basalts and other volcanic rocks are predominant.
6. Kimberlites are absent.	Kimberlites are predominant.
7. Volcanic rocks in these greenstone belts are of 3.4–2.7 Ga.	Volcanic rocks in these greenstone belts are of ~2.7–2.8 Ga.
8. Lower greenschist to upper amphibolite grade metamorphism.	Lower amphibolite to upper amphibolite grade metamorphism.
9. Intracontinental to intraoceanic to shelf facies deposition of volcano-sedimentary sequences.	Mostly intraoceanic island arc type tectonic setting.
10. Average crustal thickness is 39 km.	Average crustal thickness is 37 km.

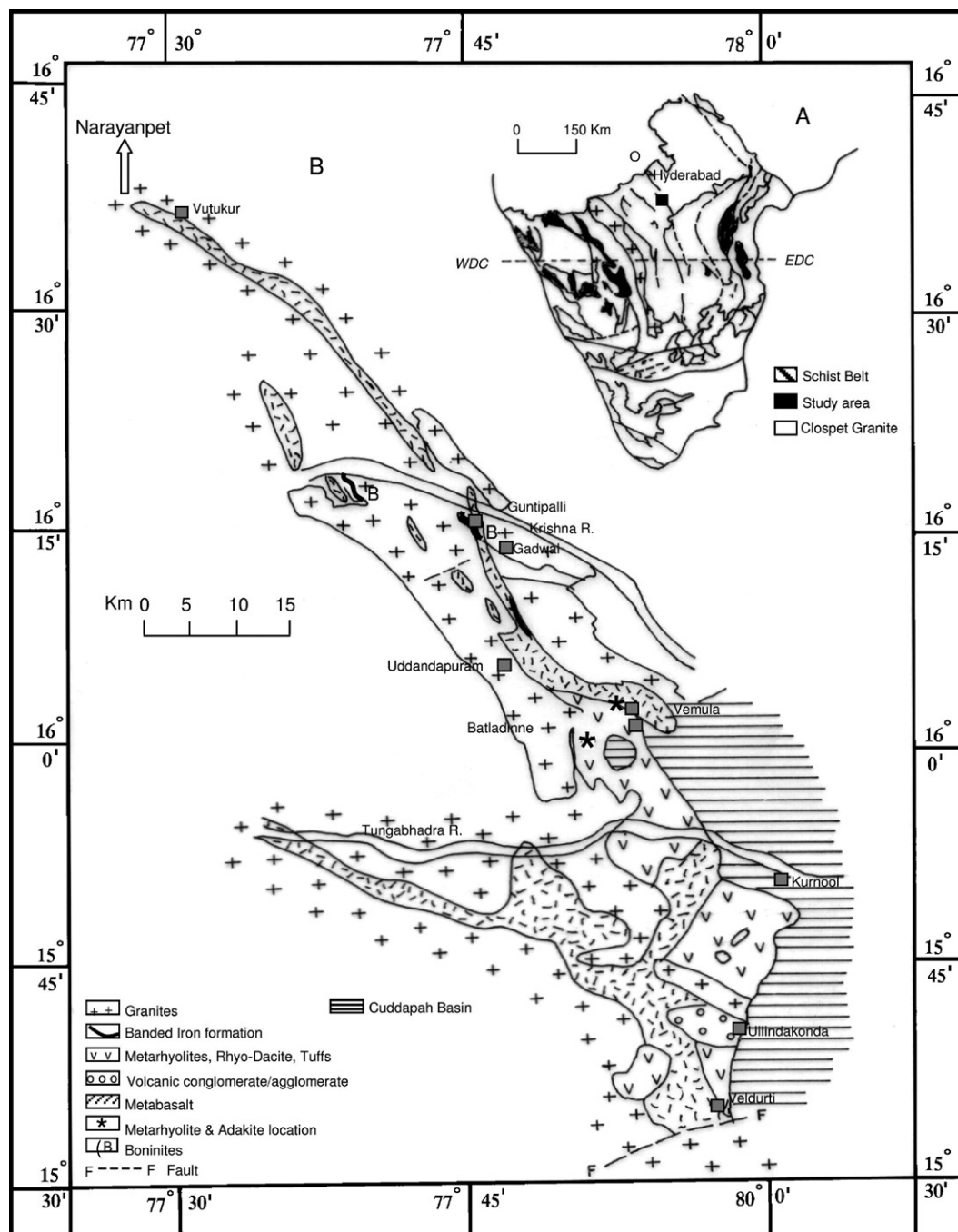


Fig. 1. (A) Simplified geological map of southern Peninsular India showing the location of the area along with other greenstone belts of the Dharwar craton. (B) Generalized geological map of Gadwal greenstone belt (after Srinivasan, 1990).

Similarly in the Sandur Superterrane (SST), eight blocks of volcanic-dominated terranes which have different lithologies, structure, stratigraphic succession and metamorphism are juxtaposed along with three accretionary planes (Manikymba and Naqvi, 1997, 2002; Naqvi et al., 2002; Manikymba and Kerrich, in press). Therefore, in these greenstone belts, komatiites, tholeiites, transitional and alkali basalts (OIB type), boninites, Nb-enriched basalts–adakites, calc–alkaline basalts, andesites, dacites and rhyolites are found at various places (Hanuma Prasad et al., 1997; Manikymba and Naqvi, 1997; Manikymba et al., 2005a,b; Manikymba and Khanna, 2005;

Naqvi et al., 2006). Some of these rock types have recently been identified from the Gadwal greenstone belt and are indicative of intraoceanic arc environment. The results of these studies on Gadwal greenstone belt are discussed here in connection with their role in the growth and evolution of continental crust during late Archaean period in the Dharwar craton.

2. Geological setting of Gadwal greenstone belt (GGB)

Gadwal greenstone belt of eastern Dharwar craton is a linear belt running discontinuously from Narayanpet in the north to

Veldurti in the south. It disappears below the Cuddapah basin and reappears at the south of Cuddapah basin near Veldurti. The belt is 85 km long and ~1–15 km wide (Fig. 1A). Apart from different events of volcanic activity within the greenstone belt, the emplacement of kimberlites has been dated at 1094 ± 8 Ma from the Siddampalli area of Gadwal belt (Manikyamba et al., 2005b), which appears to be coeval with the emplacement of other kimberlite pipes in the EDC. EDC has got certain unique characteristics that are not found in WDC (Table 1). The seismic tomographic data has shown comparatively thinner nature of the crust in EDC (35 km) than in WDC (55 km; Gupta et al., 2003; Rai et al., 2003) which is different from the estimate by gravity and magnetic study of Ramdass et al. (2006) (average crustal thickness of WDC=39 km; EDC=37 km). The geological setting and lithologies of the greenstone belts of both the sectors of Dharwar craton along with their comparative crustal thickness appears to reflect the different geodynamic setting of these two parts of Dharwar craton (Krogstad et al., 1989; Newton, 1990; Peucat et al., 1993a,b; Krogstad et al., 1995; Jayananda et al., 1995, 2000; Chadwick et al., 2000; Moyen et al., 2001, 2003).

Gadwal belt is made up of metabasalts along with felsic and intermediate volcanic rocks, thin band of pyroxenites and minor banded iron formations (Fig. 1B). This belt has been intruded by granitoids of different phases which have not been studied and dated as yet, although Moyen et al. (2003) have identified four types of granitoids like 1) TTG, 2) Sanukitoid, 3) biotite granite and 4) Closepet granite (high-Mg, high-HFSE type) in the eastern Dharwar Craton. The rocks of this belt have been subjected to three phases of deformation and metamorphosed to amphibolite facies (Matin, 2001). The Rb–Sr whole rock isotopic age on adakites of Gadwal belt is 2825 ± 45 Ma, which has been interpreted as the emplacement age of these rocks in this belt (unpublished data of Manikyamba).

3. Sampling and analytical methods

For geochemical studies, least weathered samples have been collected and screened for alteration through petrographic studies. Data for representative samples are summarized in Table 3. However detailed analytical data with precision and accuracy are available from the authors upon request. The samples have been powdered to –240 mesh using an agate mortar and major elements were analysed by XRF (Philips MAGIX PRO Model 2440) under pressed pellets; relative standard deviation (RSD) are within 5% and totals were all $100 \pm 1\%$. HFSE and other trace elements were analysed by ICP-MS (Perkin Elmer SCIEX ELAN DRC II) at National Geophysical Research Institute (Balaran and Rao, 2003). The samples have been dissolved in HF–HNO₃ acid mixture in Savillex vessels, following the procedure of ICP-MS laboratory of University of Saskatchewan, Canada, using the protocol of Jenner et al. (1990) with standard addition, pure elemental standard for external calibration and BHVO-1, JB-2 and JR-1 as reference materials for monitoring the accuracy of the data. Wet chemistry operations were conducted under clean laboratory conditions. Distilled acids, distilled deionized water and procedural blank yielded levels of <1 ppb for REEs, Th, Nb, Zr and Hf. The average of five values along

with the reported values of Govindaraju (1994) and relative standard deviation are reproduced in an Appendix A. RSD for REE and trace elements is between 2% and 6%. Boninites and basalts have been analysed by using the international reference material BHVO-1 and JB-2 whereas JR-1 was used for rhyolites and adakites. The values of Sun and McDonough (1989) were used for chondrite and primitive mantle normalizations.

4. Salient features of the metavolcanics of GGB

The petrological and geochemical data obtained on the amphibolites conclusively showed that these amphibolites are neither mineralogically nor compositionally homogenous. To address the primary compositional characteristics, the elements that are relatively least mobile (HFSE and REE) are mostly considered suitable for interpreting the tectonic setting. Based on their chemical composition, the metavolcanic rocks of Gadwal belt have been differentiated into 1) boninites, 2) basalt–andesite–dacite–rhyolite (BADR), 3) Nb-enriched basalts and 4) adakites.

4.1. Boninites

Boninites are high-Mg basaltic to andesitic rocks with low Ti, high LILE, high Al₂O₃/TiO₂, and low (Gd/Yb)_n compared to primitive mantle. Modern boninites are exclusively found in convergent margins and record important thermo-tectonic implications indicative of subduction of young and hot oceanic lithosphere. The mineralogy of Gadwal boninites is summarized in Table 2 (Fig. 2A). These boninites are both olivine normative

Table 2

Mineralogy and textures of different volcanic rocks present in Gadwal greenstone belt

	Primary mineralogy	Texture	Accessory mineralogy
Boninite	Olivine (relict), pyroxene, tremolite–actinolite	Inequigranular porphyritic with crystalline matrix	Serpentine, chromite, magnetite, titanite.
NEB	Amphibole, plagioclase (phenocrysts + groundmass)	Inequigranular, phaneritic texture	Magnetite, illmenite.
Basalt	Pyroxene (relict), hornblende, plagioclase	Inequigranular, aphanitic texture	Magnetite, illmenite, titanite, titanomagnetite
Andesite	Plagioclase, quartz, hornblende	Equigranular aphanitic texture	Biotite, chlorite, apatite, zircon, titanite.
Dacite	Plagioclase, quartz, K-feldspar, hornblende	Equigranular aphanitic texture	Biotite, apatite, zircon, titanite
Rhyolite	Quartz, K-feldspar, plagioclase	Inequigranular porphyritic texture	Biotite, sericite, apatite, zircon, titanite, fluorite
Adakite	Plagioclase (phenocrysts + groundmass), Amphibole	Inequigranular porphyritic texture	Quartz, biotite, apatite, zircon, titanite, titanomagnetite

Meta is implicit to all the rock types and most of the textures have been metamorphosed.

and quartz normative consisting of diopside, hypersthene, olivine, ilmenite, haematite, chromite and titanite. Keeping in view of the mobility of CaO, K₂O, Na₂O and SiO₂ during hydrothermal alteration and metamorphism, previous workers have used the term “boninitic series” for older metamorphosed lavas which share low TiO₂, Zr, Nb contents and high Al₂O₃/TiO₂ ratios, U-shaped REE patterns (Stern et al., 1995; Kerrich et al., 1998; Bédard, 1999). Polat et al. (2002) have used the term “boninitic” for the boninites of Isua greenstone belt which are low Ca-type with positive Zr anomalies. Gadwal boninites are characterized by a narrow range of SiO₂ (45–52 wt.%), high MgO (13–24 wt.%), Mg# (0.71–0.82), Ni (423–1184 ppm), Cr (943–2763 ppm), low TiO₂ (0.22–0.36 wt.%) and high Al₂O₃/TiO₂ (29–50; Manikyamba et al., 2005a). These rocks have

lower Ti/Zr, higher Zr/Y, Hf/Ta and Hf/Th ratios than the associated tholeiitic basalts (Manikyamba et al., 2005a).

4.2. Basalts–andesite–dacite–rhyolites (BADR)

The mineralogical characteristics of these rocks are summarized in Table 2 (Fig. 2B and C). Tholeiitic basalts are characterized by SiO₂=51–55 wt.%, MgO=6.1–9.6 wt.%, TiO₂=0.52–1.91 wt.%, Fe₂O₃=8.7–14.7 wt.%, Mg#=0.55–0.69, Zr/Y=0.6–2.6. The chemical composition of the Gadwal metabasalts resembles with Phanerozoic intraoceanic arc basalts (Hawkesworth et al., 1993) and intraoceanic arc basalts of the Archaean Ramagiri–Hungund belt (Manikyamba et al., 2004). Based on major, trace including REE abundances and

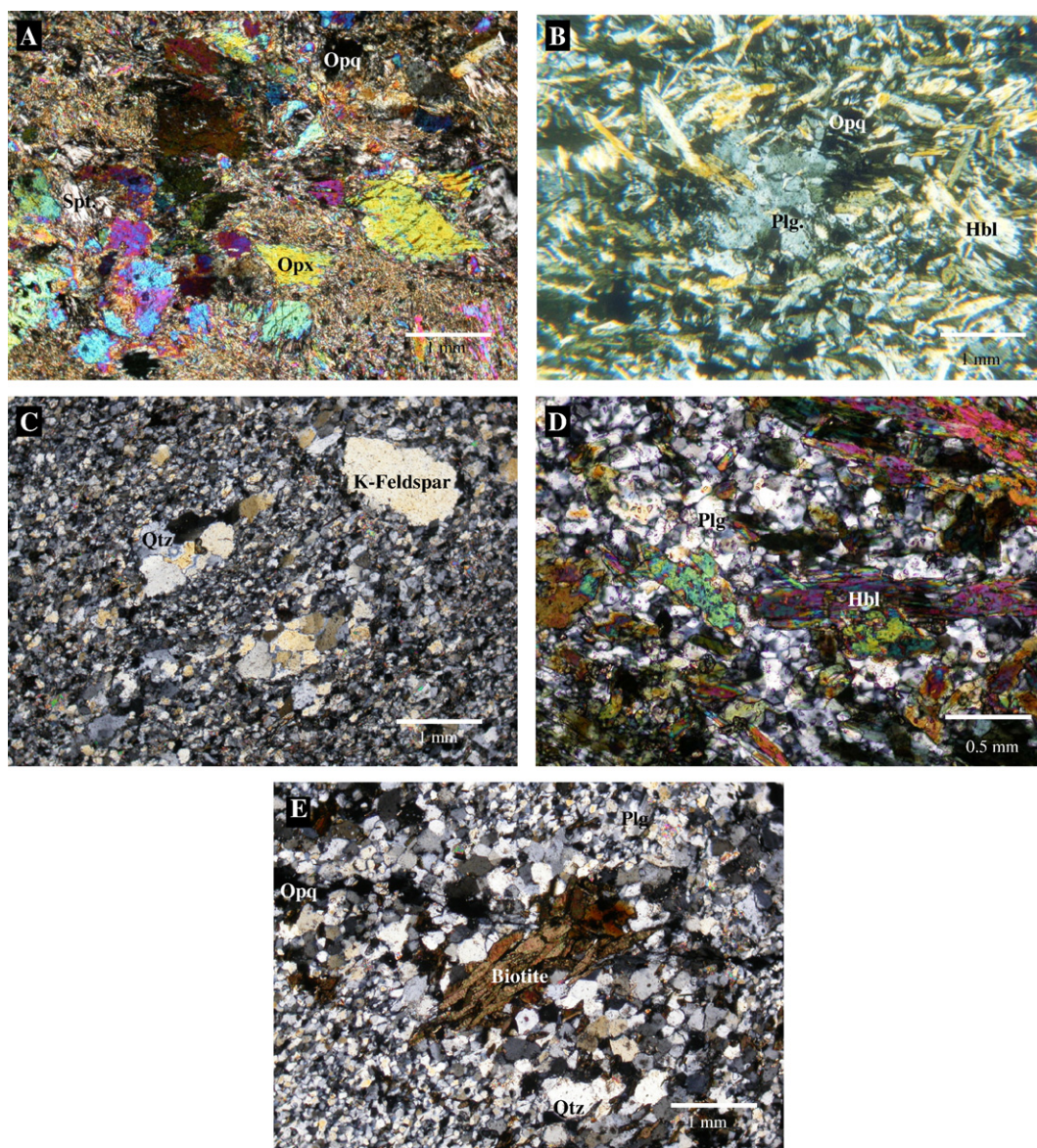


Fig. 2. (A) Photomicrograph of boninites showing the predominance of pyroxenes, serpentinized olivine, tremolite–actinolite along with other opaques. (B) Photomicrograph of basalt indicating the radiating amphiboles along with plagioclase, and opaques. (C) Photomicrograph of rhyolite showing the presence of quartz, feldspars, and plagioclase. (D) Photomicrograph of Nb-enriched basalt with amphiboles (hornblende), plagioclase and opaque. (E) Photomicrograph of adakite indicating the presence of biotite, quartz and plagioclase.

interelemental behaviour and ratios, the felsic metavolcanic rocks of Gadwal belt have been divided into rhyolites and adakites. Although there is an overlap in the SiO₂ content of both these rock types, K₂O, Na₂O, Sr, Y and Yb distinguishes them as separate groups. Rhyolites have high SiO₂ (74–75 wt.%) with comparatively lower Al₂O₃ (13.5–14 wt.%) and Na₂O/K₂O less than 1. Their MgO is between 0.13 and 1.6 wt.%, Sr=64–68 ppm with a comparative enrichment in Rb content (Table 3). Rhyolites have higher concentration of Zr, Hf, Th, U, Y and Yb along with Cu, Zn, Tl and Sb than adakites.

4.3. Nb-enriched basalts (NEB) and high Nb-basalts (HNB)

These rocks mineralogically resemble with metamorphosed tholeiitic basalts (Table 2; Fig. 2D). NEB are mafic volcanic rocks containing more than 7 ppm Nb with high (Nb/Th)_{pm}, (Nb/La)_{pm} exhibiting positive or smaller magnitude of negative Nb anomalies (than intra oceanic arc basalts; Sajona et al., 1996). In GGB, these rocks have a narrow range of SiO₂ (50–52 wt.%), MgO (7.7–9 wt.%), TiO₂ (0.64–0.94 wt.%) with almost similar contents of LILE and HFSE with associated tholeiitic basalts except in Nb content (8–26 ppm). According

Table 3

Range of chemical composition for boninites, NEB and basalt along with rhyolites and adakites of Gadwal greenstone belt

	Boninite ^a (n=22)	Nb-enriched basalt (n=4)	Basalt (n=19)	Rhyolites		Adakites	
SiO ₂	45.2–52.3	50.75–51.93	51.05–55.42	75.00	74.11	65.03	64.83
TiO ₂	0.22–0.36	0.64–0.94	0.52–1.91	0.20	0.19	0.70	0.64
Al ₂ O ₃	8.78–12.76	11.89–14.29	10.64–15.23	13.53	14.06	12.96	16.47
Fe ₂ O ₃	9.96–12.37	11.33–12.22	8.75–14.73	1.30	0.92	7.07	5.38
MnO	0.13–0.18	0.14–0.17	0.10–0.25	0.05	0.04	0.07	0.06
MgO	12.9–24.1	7.72–9.02	6.15–9.62	0.16	0.13	3.22	2.30
CaO	7.73–12.02	10.55–13.06	8.7–12.85	0.52	0.25	5.59	4.07
K ₂ O	0.10–0.61	0.14–0.6	0.04–0.64	5.69	7.60	1.35	1.47
Na ₂ O	0.23–1.32	2.14–2.52	1.10–3.39	3.52	2.68	3.78	4.55
P ₂ O ₅	0.01–0.04	0.08–0.1	0.07–0.30	0.02	0.02	0.23	0.22
Mg#	0.71–0.82	0.59–0.63	0.55–0.69	0.20	0.22	0.47	0.46
Cr	943–2763	195–592	11–583	1.37	1.52	27.54	14.50
Co	61–86	49–51	33–489	0.44	0.88	19.75	13.61
Ni	423–1184	135–189	62–489	0.78	0.96	6.80	5.96
Rb	2.1–308	12–34	1.95–58	182	217	50	90
Sr	9–142	137–189	76–272	64	68	420	402
Cs	1.3–29.7	1.66–4.22	0.12–21.4	2.35	2.88	4.12	38.37
Ba	9–97	60–131	33–215	180	198	475	426
Sc	14–59	18–25	17–38	3.23	3.24	12.08	9.65
V	57–141	95–220	64–232	5.02	6.35	191	154
Ta	0.02–0.13	2.21–3.28	0.16–0.39	1.38	1.47	0.58	0.79
Nb	0.31–6.26	8.40–26.45	1.86–5.48	16	17	7.33	10.07
Zr	12–23	17–61	11–83	254	250	150	185
Hf	0.32–0.72	0.75–2.65	0.53–2.42	6.55	6.67	3.19	3.94
Th	0.15–0.73	0.65–1.61	0.34–2.10	27	27	8.13	10.56
U	0.09–0.25	0.20–0.22	0.14–0.63	5.86	6.34	1.54	2.38
Y	10–19	17–24	18–45	28	27	18	18
La	1.41–3.76	4.70–6.37	3.34–10.25	51.14	49.79	30.18	34.54
Ce	2.61–7.71	11.84–15.18	8.46–23.48	98.02	96.54	55.62	63.60
Pr	0.33–0.98	1.79–2.04	1.29–3.66	10.24	10.03	5.90	6.73
Nd	1.80–4.01	8.30–8.83	5.87–17.2	37.32	35.92	23.25	26.96
Sm	0.48–1.14	2.31–2.70	1.79–5.47	6.78	6.79	4.60	5.15
Eu	0.20–0.45	0.86–1	0.67–2.13	0.66	0.63	1.38	1.48
Gd	0.84–1.70	2.66–3.36	2.29–6.67	5.34	5.28	3.68	4.00
Tb	0.19–0.32	0.46–0.6	0.44–1.24	0.82	0.78	0.56	0.58
Dy	1.43–2.78	2.90–3.96	2.9–7.93	3.94	3.85	2.64	2.65
Ho	0.38–0.68	0.39–0.87	0.66–1.71	0.69	0.67	0.45	0.45
Er	1.12–1.99	1.64–2.38	1.84–4.51	2.29	2.16	1.43	1.37
Tm	0.18–3.10	0.27–0.39	0.26–0.70	0.37	0.35	0.21	0.21
Yb	1.10–1.84	1.72–2.60	1.84–4.53	2.38	2.32	1.34	1.24
Lu	0.18–0.33	0.26–0.39	0.28–0.62	0.38	0.37	0.21	0.20
Cu	10–216	14–182	8–193	1.02	1.29	8.05	13.51
Zn	40–700	49–69	36–83	35	29	79	61
Tl	0.03–0.85	0.07–0.17	0.05–0.25	0.77	1.03	0.17	0.42
Pb	2.7–15.6	2.69–2.99	2.61–3.54	24.83	25.09	25.08	25.54
Sb	0.16–0.59	0.16–0.44	0.15–0.75	0.88	0.82	1.15	1.87

All the values are recalculated to 100% volatile-free.

^a Samples are from Manikyamba et al. (2005a).

to Sajona et al. (1996), more than 20 ppm Nb are considered as high Nb basalts (G 35; Table 3). The associated tholeiitic basalts have Nb content from 1.8 to 5.5 ppm.

4.4. Adakites

The mineralogy of metamorphosed adakites is summarized in Table 2 and the thin section photo is given in Fig. 2E. Adakites of GGB are characterized by a moderate content of SiO_2 (65 wt.%), higher Al_2O_3 (12.9–16.5 wt.%), Fe_2O_3 (5.4–7.0 wt.%), MgO (2.3–3.2 wt.%), Y (18 ppm), Sr (402–420 ppm), Yb (1.2–1.3 ppm), Mg# (0.46–0.47), Ni (5.9–6.9 ppm), and Cr (14.5–27.5 ppm) than associated metarhyolites.

4.5. Major, trace and REE behavior in the metavolcanic rocks of GGB

When we observe the MgO and SiO_2 behaviour of Gadwal metavolcanics, rhyolites and boninites define two end members due to the enrichment of MgO in boninites and its depletion in rhyolites. Due to its basaltic nature, NEBs form a cluster with basalts. Adakites are comparatively enriched in MgO with a relative depletion in SiO_2 than rhyolites occupying a separate position. The spectrum of different types of volcanic rocks from

GGB is distinct from each other in their SiO_2 vs. MgO behavior (Fig. 3A). The enrichment of Nb in NEB and HNB compared to other tholeiitic basalts is clearly visible on the Nb vs. Zr plot where basalts are depleted in Nb. Among the felsic volcanic rocks, rhyolites are enriched in Zr and Nb when compared to adakites (Fig. 3B). Similar distinctions can be made in their TiO_2 and Zr behavior. Ti/Zr ratio of boninites from different areas is between 22 and 113 comparable with GGB boninites (70; Manikyamba et al., 2005a; Table 3). The TiO_2 –Zr relationship of Gadwal boninites shows similarities with Phanerozoic boninites (Fig. 3C; Manikyamba et al., 2005a). Distinction between these rock types can be clearly seen on the Zr vs. Zr/Nb plot (Fig. 3D) in which NEB have low Zr content at a very low Zr/Nb ratio.

Boninites exhibit unique concave upward REE patterns with MREE depletion and slight enrichment in LREE ($(\text{La/Yb})_n = 0.73$ –1.29; $(\text{Gd/Yb})_n = 0.56$ –0.66) and absence of Eu anomalies ($\text{Eu/Eu}^* \sim 1$). Chondrite-normalized trace element variation diagram show a pronounced trough at Nb, Ta, V and Sr with positive U and low order negative Zr, Hf and Ti anomalies (Fig. 4A, A'; Manikyamba et al., 2005a). However, boninites of Isua greenstone belt have positive Zr anomalies resembling with some of the Tertiary boninites such as Bonin Islands and Mariana Trench (Cameron et al., 1983; Stern et al., 1991; Pearce

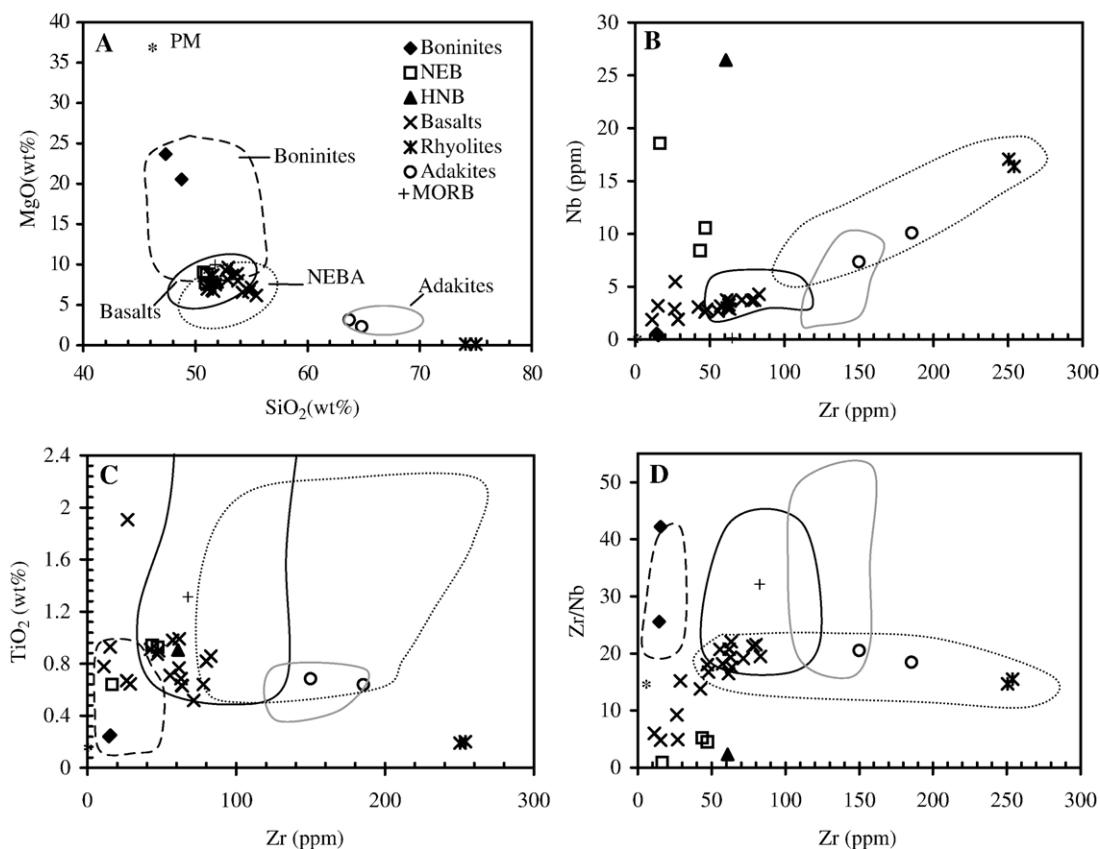


Fig. 3. (A) SiO_2 vs. MgO distinguishing different types of volcanic rocks from Gadwal belt. NEB – Nb-enriched basalts; HNB – high Nb-basalts; PM – primitive mantle, MORB – mid oceanic ridge basalt. Same symbols are followed for other panels. (B) Nb vs. Zr plot exhibiting the enrichment of niobium in Nb-enriched basalts and high-Nb basalts and enrichment of Zr and Nb in rhyolites compared to adakites. (C and D) TiO_2 vs. Zr and Zr/Nb vs. Zr plots distinguishing different types of volcanic rocks from Gadwal greenstone belt. Fields of Canadian boninites from Kerrich et al. (1998), Arc basalts, Nb-enriched basalts and adakite are from Polat and Kerrich (2001).

et al., 1992; Taylor et al., 1994; Polat et al., 2002). Basalts have flat REE patterns with $(La/Yb)_n = 1.0–1.5$ (Fig. 4B). Few transitional type of basalts are also found associated with these basalts which have slightly fractionated REE patterns ($G = 52$; $(La/Yb)_n = 3.6$). Multielement variation diagrams are characterized by pronounced negative Nb, Ti, V anomalies; slight negative Zr and Hf anomalies and negative to positive Sr anomalies (Fig. 4B'). Nb/Ta, Zr/Hf, Zr/Sm are less than the primitive mantle values of 51, 36 and 25. Nb-enriched basalts of GGB exhibit slightly fractionated chondrite normalized REE patterns $((La/Yb)_n = 1.3–2.6$; Fig. 4C) with $Zr/Y = 2.5$ slightly more than Primitive mantle value of 2.4 and displaying very strong positive Nb anomaly ($Nb/Nb^* = 1.7–5.2$) along with weak negative Ti, V, Zr, Hf and V anomalies (Fig. 4C'). Nb/Ta, Zr/Hf and Zr/Sm are less than the primitive mantle and the associated tholeiites. Among the felsic volcanic rocks of Gadwal belt, rhyolites are comparatively enriched in their total REE (163–262 ppm) than adakites (89–155 ppm) in which rhyolites exhibit fractionated REE patterns $((La/Yb)_n = 15)$ with pronounced negative Eu anomaly $((Gd/Yb)_n = 1.8$; $Eu/Eu^* = 0.32$) whereas adakites lack in Eu anomaly ($Eu/Eu^* \sim 1$) displaying fractionated REE $((La/Yb)_n = 16–20)$. Multielement variation figures display enrichment in Th and U with negative anomalies of Nb, Ta, Sr and Ti (Fig. 4D, D', E, E').

4.6. Interelement relationship – implications on source/tectonic setting

Al_2O_3/TiO_2 is one of the most important ratios in discriminating komatiites from boninites. The former are generated by anhydrous melting of the mantle plumes and the latter form by the hydrous melting of the refractory mantle wedge in subduction zone complex, both being high Mg-magmas (Hickey and Frey, 1982; Arndt, 2003; Kerrich and Polat, 2006). Al_2O_3/TiO_2 ratio is higher in GGB boninites (Fig. 5A; Manikyamba et al., 2005a) than associated tholeiitic basalts (6–26; Table 3), and resembles Cenozoic boninites (30–60; Pearce et al., 1992; Manikyamba et al., 2005a). $(Gd/Yb)_n$ ratio also exhibits variation in boninites–arc basalts–rhyolites and adakites. On Al_2O_3/TiO_2 vs. $(Gd/Yb)_n$ diagram, NEB and HNB plot along with other tholeiitic basalts. Rhyolites have higher Al_2O_3/TiO_2 ratio and low order fractionation of HREE than adakites $((Gd/Yb)_n = 1.8$; Fig. 5A). Negative Nb anomaly which is a characteristic feature of subduction zone magmatic rocks (Polat and Kerrich, 2001) is clearly displayed by Gadwal metavolcanic rocks through $(Nb/La)_{pm}$ vs. $(Th/Nb)_{pm}$ plot where boninites, tholeiitic basalts, adakites and rhyolites occupy their place below one (of $(Nb/La)_{pm}$), whereas NEB and HNB have more than one due to Nb-enrichment and subsequent positive Nb anomalies (Fig. 5B).

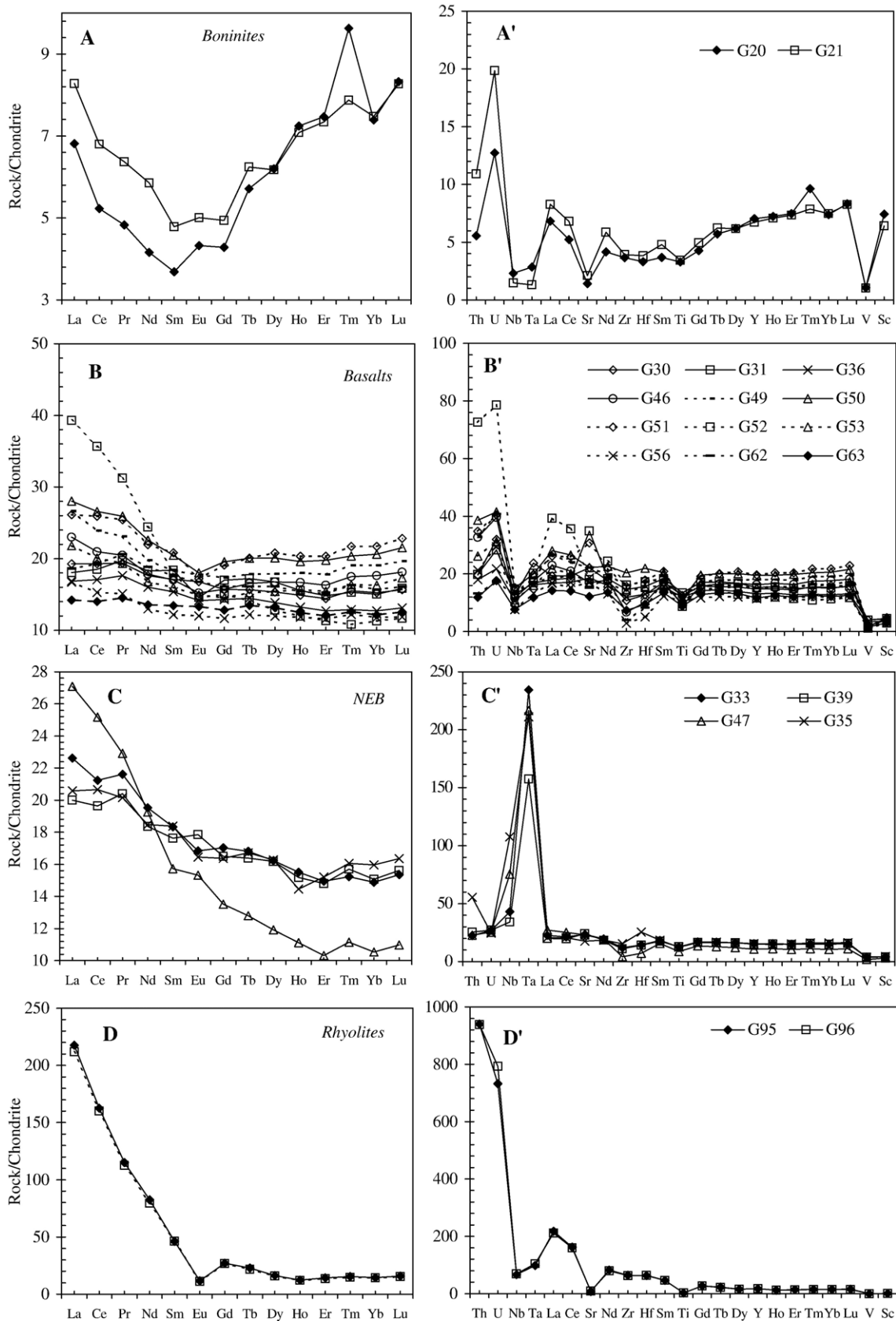
5. Discussion and conclusions

Boninites are reported from Archaean greenstone belts of Superior Province, Isua greenstone belt of Greenland, Frotet–Evans greenstone belt of Opatika Subprovince, Quebec, Karelian greenstone belt of Baltic shield, Whundo greenstone belt of

western Australia and in a few Proterozoic sequences (Kerrich et al., 1998; Polat et al., 2002; Boily and Dion, 2002; Shchipansky et al., 2004; Smithies et al., 2005); they have not been reported in the greenstone belts of Dharwar craton except the recent reports from Gadwal and Kushtagi belts (Manikyamba et al., 2005a; Naqvi et al., 2006). Boninites–Nb-enriched basalt–adakite association has not been found in other Archaean greenstone belts in general (except Abitibi and Baltic shield) nor in India in particular. A few rocks having boninitic affinities have been documented from 3.865 Ga Isua greenstone belt of Southern Greenland (Polat et al., 2002), 3.5 Ga Barberton greenstone belt of South Africa (Parman et al., 2001), 2.95 Ga Mallina Basin from the Central Pilbara Craton (Smithies, 2002), 2.7 Ga greenstone belts of Abitibi, Superior Province (Kerrich et al., 1998; Wyman, 1999) and Bastar Craton of Central India (Srivastava et al., 2004). Nb-enriched basalts have been reported from few greenstone belts of Abitibi and Karelian greenstone belt of Baltic shield (Hollings and Kerrich, 2000; Wyman et al., 2000; Polat and Kerrich, 2001; Hollings, 2002; Shchipansky et al., 2004). Although TTG are extremely widespread in Archaean, adakites have also been reported from many Archaean greenstone belts of different places (Tomlinson et al., 1999; Puchtel et al., 1999; Hollings and Kerrich, 2000; Wyman et al., 2002; Cousens et al., 2002; Boily and Dion, 2002; Percival et al., 2003; Wang et al., 2004; Svetov et al., 2004; Samsonov et al., 2005; Manikyamba and Khanna, 2005; Naqvi et al., 2006). Generally, active adakitic magmatism is found along Circum-Pacific margins and all are related to subduction (Martin, 1999). Defant and Drummond (1990) compiled the geochemical data on subduction-related magmas and showed that adakitic magmas are produced when the subducting slab is younger than 30 Ma and BADR magmas are generated when the subducting slab is older than 30 Ma. Drummond et al. (1996) described two types of tonalite–trondhjemite–dacite (TTD) suites in which one type is Cenozoic adakites and the other type Archaean high Al–TTG that are considered to represent slab melting with garnet–hornblende–clinopyroxene residue (adakites) and garnet–amphibole–eclogite residue (TTG). However, Rapp et al. (1999) have shown that Archaean TTG could be produced by melting of hydrous metamorphosed basalt with an eclogitic residue but also by a garnet–amphibolitic residue. Wherever Nb-enriched basalts (or high Nb-basalts) are found they are closely associated with adakites whereas adakites can occur alone (Sajona et al., 1996; Zhang et al., 2005). According to Defant et al. (1992), the NEB generation is closely related to that of adakites. According to Sajona et al. (1996), NEB–adakites association results from the formation of adakitic liquids by the shallow subduction of young and hot oceanic lithosphere. Many modern examples of flat subduction (along Andean and Central American margins) show strong association of adakites and NEB (Defant and Drummond, 1993; Drummond et al., 1996; Gutscher et al., 2000; Smithies et al., 2003). Zhang et al. (2005) evaluated different models for the generation of NEB which includes 1) the crustal contamination via sediment incorporation, 2) partial melting of subducted oceanic crust and 3) partial melting of enriched mantle and proposed the melting of hybridized mantle wedge for the generation of Nb-enriched basalts from north west China. It is

commonly believed that boninites originate from sub-arc mantle wedge during the subduction of young and hot oceanic lithosphere which provides favourable conditions for the melting of

subducting slab. The fluids metasomatize the mantle wedge, which on partial melting generates boninites (Kerrick et al., 1998; Polat and Munker, 2004). The geochemical similarities of



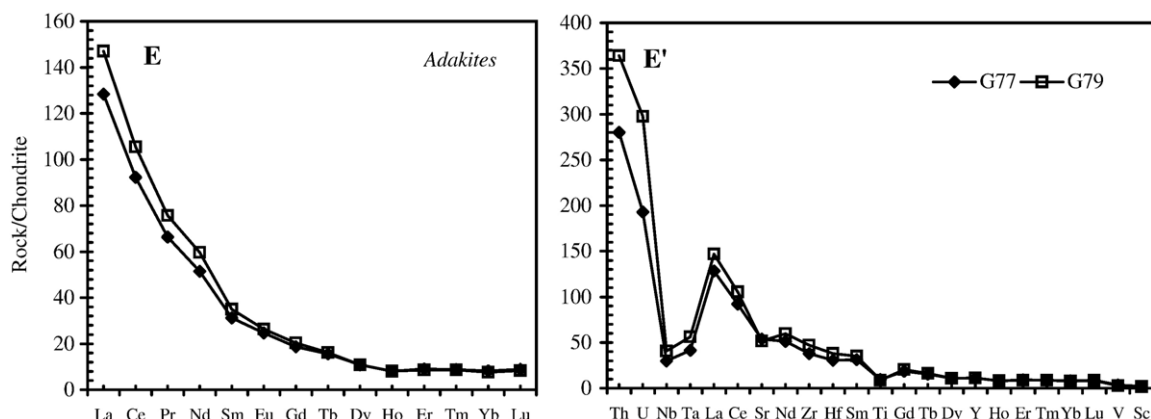


Fig. 4 (continued).

GGB boninites with Cenozoic boninites indicate similar type of intraoceanic tectonic setting for their genesis. Recent finding of adakites from the continental setting of Himalayan orogen (Chung et al., 2003; Hou et al., 2004) suggests that adakites could occur in accretion and collision settings as well.

5.1. Sr depletion in Dharwar adakites

Defant and Drummond (1990) reported high Sr content (400–2000 ppm) as a typical feature of adakitic magmas. However, there are exceptions like Austral Volcanic Zone (AVZ) in southern Andes (545 ppm) and Taitao Peninsula (280 ppm) where low concentration of Sr has been observed (Arth and Hanson, 1975; Stern and Kilian, 1996). In general, Sr anomalies are attributed to the minor amount of plagioclase formation during the fractional crystallization in a magma chamber (Martin, 1999). Martin et al. (2005) reported two different kinds of adakites. High silica adakites (HSA) with Sr average about 500 ppm which is very similar to Archaean TTG and low silica adakites (LSA) with average Sr of 2000 ppm. HSA are considered as slab melts whereas the LSA are supposed to be metasomatized mantle derived. According to them high Sr contents and positive Sr anomalies are not characteristics of all adakites. GGB adakites are displaying small-scale negative Sr anomalies and Sr depletion in adakites appear to be the characteristic feature of Dharwar craton as adakites analysed so far from Kushtagi and Sandur Superterrane are characterized by 178–300 and 180–237 ppm, respectively (Manikyamba and Khanna, 2005; Naqvi et al., 2006) which may reflect on mobility of Sr in Archaean volcanics. However, Sr depletion in Gadwal adakites (101–420 ppm) along with the adakites from the other greenstone belts of Dharwar craton resembles with some of the volcanic adakites assemblage from the late Archaean Karelian greenstone belt of Baltic shield (Samsonov et al., 2005). The

association of adakites with tholeiitic basalts indicates intraoceanic setting. Rhyolites are also depleted in Sr (64–269 ppm), which is a characteristic feature of calc–alkaline volcanic rocks in general reflecting on their genesis through partial melting and fractional crystallization of the basaltic material from the mantle wedge.

5.2. Intraoceanic setting for the metabasalts of GGB

Ti, Sc, V and Zr discrimination diagrams have been used by previous workers (Gamble et al., 1994; Polat et al., 1999) to discriminate between arc, back arc and MOR basalts. The metabasalts of GGB indicate their intraoceanic nature by occupying the field of arc and back arc basalts on Ti/Zr, Ti/Sc and Ti/V vs. Zr plots (Fig. 6A, B and C). At 11–83 ppm of Zr concentration, Ti/Zr varying between 44 and 152 (with three outliers) resembling with island arc basalts of Penakacherla belt (shaded region drawn from Manikyamba et al., 2004; Fig. 6A). Though Ti/Sc and Ti/V exhibit a scatter, most of the GGB metabasalts are within/nearby the fields of arc and back arc reflecting an intraoceanic setting for the generation of these rock types.

5.3. Melting of low Mg-amphibolite – generation of Gadwal adakites

The low abundance of HFSE compared to LILE with a characteristic depletion of Nb and Ta provides important constraints on the genesis of island arc volcanic rocks. Nb/Ta is believed to be important incompatible element ratio, which distinguishes adakites from TTG (Condie, 2005). TTG have low Nb/Ta and high Zr/Sm than Primitive mantle (16.7 and 25.2; Sun and McDonough, 1989) compared to adakites, which display near primitive mantle values of Nb/Ta ratio reflecting on melting of rutile-bearing eclogite. Nb/Ta ratio of continental crust is 10–

Fig. 4. (A and A') Typical MREE depleted U-shaped chondrite normalized REE patterns and trace element variation figure for the boninites of Gadwal belt. Data is taken from Manikyamba et al. (2005a). Chondrite values are from Sun and McDonough (1989). (B and B') Chondrite normalized flat REE patterns and trace element variation figure of metabasalts of GGB exhibiting negative Nb, Ti, V, Zr and Hf anomalies. (C and C') Slightly fractionated chondrite normalized REE patterns of Nb-enriched basalts (NEB) with trace element variation figure, which is characterized by a pronounced positive Nb anomaly. (D and D') Strongly fractionated chondrite normalized REE patterns of rhyolites exhibiting negative Eu anomalies along with multielement variation figure characterized by enrichment in U and Th, a trough at Nb and Ta with negative Sr, and Ti anomalies. (E and E') Strongly fractionated Chondrite normalized REE patterns of adakites with no Eu anomaly and the trace element variation figure characterized by a pronounced trough at Nb, Ta with small negative Sr and Ti anomalies.

14 (Rudnick and Fountain, 1995; Plank and Langmuir, 1998), which is lower than the Primitive mantle value. The Nb/Ta and Zr/Sm ratios of Gadwal adakites range between 9 and 13 and between 33 and 58, respectively, indicating melting of low Mg-amphibolite with garnet being the residual phase. Experimental studies have shown that low Mg-amphiboles are able to cause greatest fractionation between Nb/Ta and Zr/Sm (Foley et al., 2002). Therefore, melting of low-Mg amphibolite causes depletion in Nb/Ta ratio.

Rapp et al. (1999) conducted experimental studies on natural hydrous basalts at 1–4 GPa and compared the experimental slab melts with adakites from Philippines, southern Andes, central America and northern Japan. They have explained that low-Mg# adakites are consistent with slab melting source whereas high-Mg# adakites are derived from a hybrid and/or mantle source and established a clear-cut relationship between the slab melt and hybrid melt on the basis of their SiO₂ and Mg# relationship. Gadwal adakites are low Mg# type and occupy the field of slab melts at 1–4 GPa of Rapp et al. (1999). Boninites of this region (Manikyamba et al., 2005a) are occupying a distinct place with high Mg# and exhibiting its hybrid nature (i.e. melting of metasomatized mantle wedge; Fig. 7). Earlier, Moyen et al.

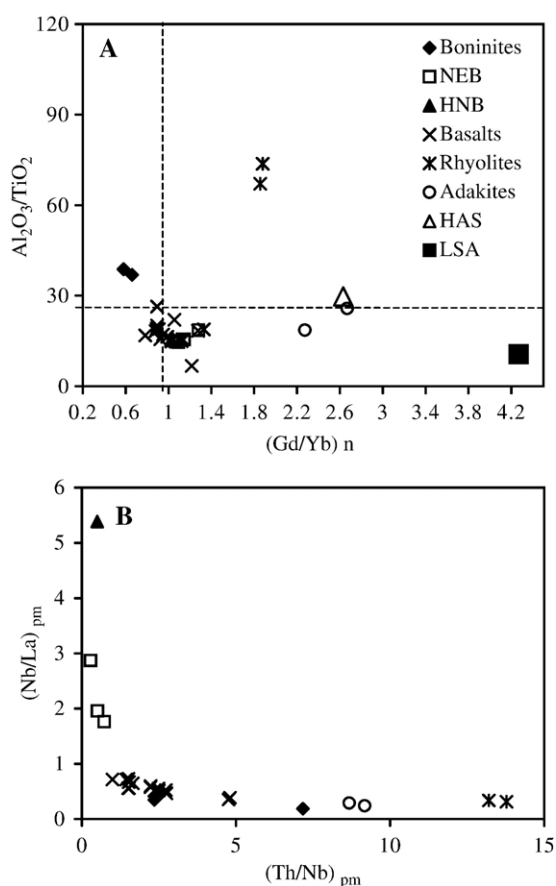


Fig. 5. (A) Al₂O₃/TiO₂ vs. (Gd/Yb)_n plot to discriminate between boninites with other metavolcanic rocks of Gadwal belt. The dotted lines represent the chondritic ratios. (B) (Nb/La)_{pm} vs. (Th/Nb)_{pm} binary plot documenting the negative Nb anomalies in the Gadwal metavolcanics, which is the characteristic feature of island arc volcanic rocks. Nb-enriched basalts and high-Nb basalts display enrichment in Nb. LSA and HAS data are from Martin et al. (2005).

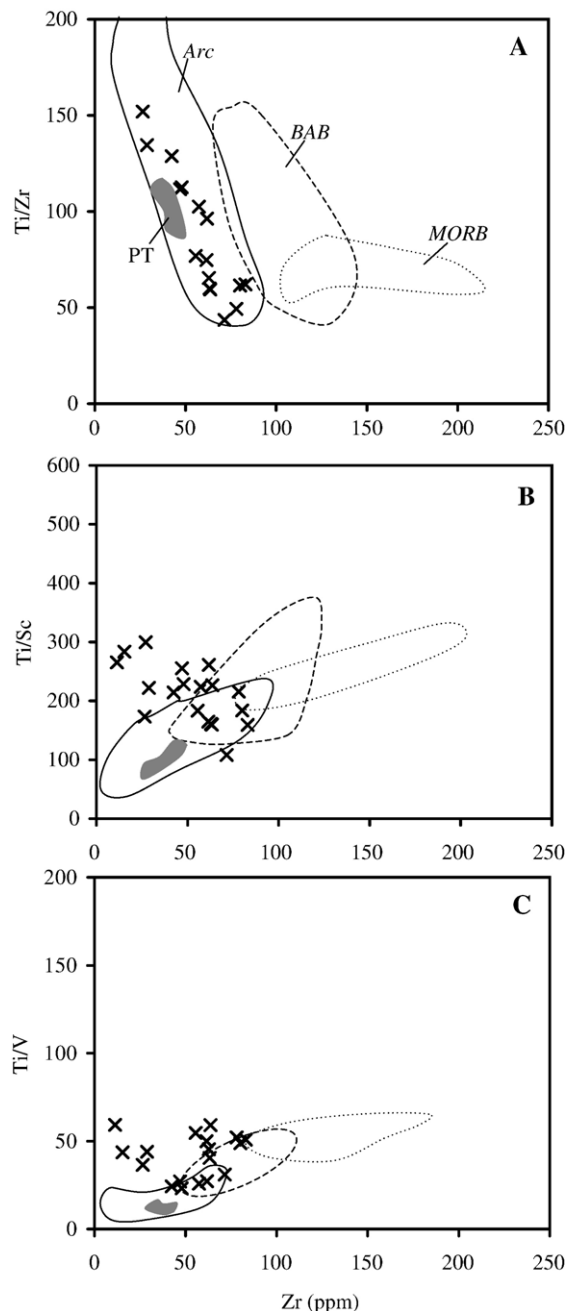


Fig. 6. Plots of Zr vs. (A) Ti/Zr, (B) Ti/Sc and (C) Ti/V (after Gamble et al., 1994) for the metabasalts of Gadwal greenstone belt. Shaded area represents the arc basalts of Penakacherla belt drawn from Manikyamba et al. (2004).

(2001) have suggested the evidence of interaction between adakitic magma and mantle peridotite to explain the formation of Closepet Granite that has been generated by melting of mantle wedge metasomatized by assimilation of adakitic (TTG) magmas.

The occurrence of boninites–arc basalts–Nb-enriched basalts–adakites and BADR association from GGB indicates subduction of young and hot oceanic lithosphere similar to certain Cenozoic subduction zones took place even in Archaean. The presence of transitional basalts along with adakites–BADR indicates melting of slab and mantle wedge under the influence of raising slab fluids along with some component of hotspot

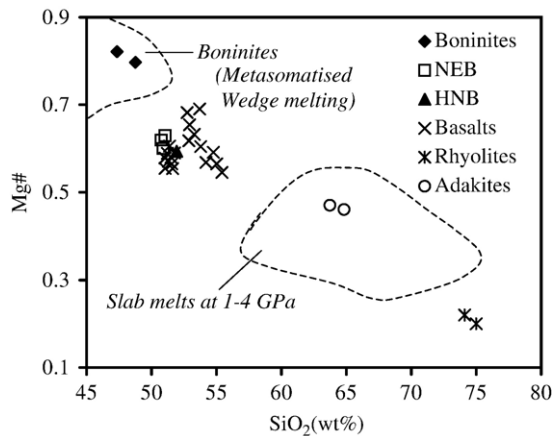


Fig. 7. SiO_2 vs. Mg# indicating the genesis of adakites through slab melting and boninites through the melting of metasomatized mantle wedge.

(Wyman, 2003). Since the age of Archaean lithosphere is estimated to be around 20 Ma (Hargraves, 1986; Martin, 1999) and the Cenozoic NEB–adakites are also the product of subduction of 20–30 Ma old oceanic lithosphere; it is proposed that rapid production and consumption of oceanic lithosphere during the Archaean resulted in the faster crustal growth due to different accretionary events (Kerrick and Polat, 2006). One of the main conclusions drawn from these studies is that irrespective of time and space, whenever and wherever hot and young lithosphere is subducted (even in Archaean), the assemblage of boninites–NEB–adakites is present. If a hotspot has been able to reach in this setting, its signatures as transitional basalts are also expected in this environment.

5.4. Model

The petrographic and geochemical data obtained from different volcanic rocks of the Gadwal greenstone belt indicate a heterogeneous source, namely the mantle wedge and subducting slab in a subduction zone environment. The boninite and arc basalts possibly derived from the partial melting of mantle wedge whereas the adakites have been generated from the melting of the subducting slab. The proposed model is explained through a cartoon expression (Fig. 8) where a hot and young lithosphere is obliquely subducted which gets melted during the initial stage of subduction and provides LILE

enriched fluids to the mantle wedge. Fractional crystallization of the basaltic magma generated the basalt–andesite–dacite–rhyolite (BADR) suite. Melting of the residual slab gave rise to adakites. Boninites form in two stages of melting process. High degree partial melting of mantle peridotite during the first stage, leaves a residue depleted in Ti, LREE–MREE. In the second stage, hydrous fluxing of the residue adds LREE, generates melts with a characteristic MREE-depleted concave patterns. NEB are interpreted to represent the residue of hybridized mantle wedge that melted at greater depth from induced convection in the wedge (Defant et al., 1992; Yogodzinski et al., 1995; Keleman, 1995; Kepezhinskis et al., 1996; Benoit et al., 2002; Kelemen et al., 2004; Smithies et al., 2005; Kerrich and Polat, 2006).

According to Von Huene And Scholl (1991), continental crust is recycled into the mantle at a rate of $1.6 \text{ km}^3/\text{year}$ which is being added as juvenile crust. However, it is generally considered that the subduction of young crust cannot be associated to significant sediment subduction and the thickness of the sediment on the oceanic crust is proportional to its age. Defant et al. (2002) proposed the term ‘adakite metasomatic volcanic series’ for the genetically related volcanic rocks that incorporate adakite during their genesis, because of the involvement of the young crust subduction associated with hydrous slab fluids for the formation of boninites, NEB–adakite suite.

Martin (1999) suggested that geothermal gradient plays an important role in the degree of interaction between the slab melt and mantle peridotite. The higher geothermal gradient during Archaean caused the melting of subducted slab at shallow plagioclase stability field. According to Zhang et al. (2005), higher geothermal gradient ($25\text{--}30^\circ\text{C}/\text{km}$) and low pressure (8–18 kbar) along the Benioff zone in the Archaean has resulted to relative enrichment of HREE in both adakites and NEB compared to their Cenozoic counterparts due to lesser incorporation of garnet in the residue. The absence of positive Sr anomaly in these rocks has been accounted for calcic plagioclase being in the residual phase. Martin (1999) attributed the relatively lower concentration of transition elements (Cr and Ni) and MgO to the less efficient mantle melt interactions due to shallow angle subduction and thin mantle wedge and the shallow depth of slab melting.

The entire process appears to have taken place within a short duration by the subduction of hot and young oceanic

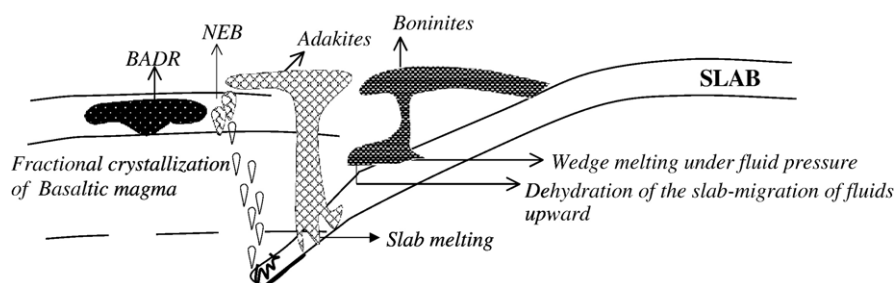


Fig. 8. Cartoonic expression to show the generation of different rock types of the convergent margin tectonic setting of Gadwal greenstone belt indicating melting of mantle wedge and subducting slab. BADR – basalt–andesite–dacite–rhyolite suite; NEB – Nb-enriched basalts.

lithosphere. The Archaean geothermal gradient, size and dynamics of plates and shallow angle subduction collectively played a significant role for the generation of these rock types. The studies carried out by different workers on Archaean greenstone belts have shown that at Neoarchaean convergent margins, bimodal arc magmatism involved slab dehydration, wedge melting to generate arc basaltic liquids as in Phanerozoic (Pearce and Peate, 1995; Wyman, 2003; Kerrich et al., 2005). The secular trend in Mg, Cr and Ni from 3 to 2.7 Ga TTG has been explained by Martin and Moyen (2002) and Martin et al. (2005) with a flat to shallow angle subduction in which at 3 Ga, TTG traverse with no or little mantle wedge due to flat subduction (low-Mg, Cr and Ni contents) whereas the shallow angle subduction during Neoarchaean (2.7 Ga) allowed the TTG to interact more with the mantle wedge (high Mg, Cr and Ni contents). The dissipation of higher thermal energy of the Earth could have been possible at that time by longer ridge system with frequent ridge subduction and numerous short-lived mantle plumes. The frequency of these processes has to be much higher than what we see today or in Cenozoic. Instead of 150 Ma average age of oceanic lithosphere, 20–30 Ma of age and its faster return to the surface with a short incubation can explain the geochemical, structural and isotopic data which is found in the greenstone belts of Dharwar craton.

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Appendix A

Major, Trace concentrations and RSD of BHVO-1, JB-2, JR-1 obtained from XRF and ICP-MS

(Wt %)	BHVO-1			JB-2			JR-1		
	A	RSD %	B	A	RSD %	B	A	RSD %	B
SiO ₂	48.97	1.80	49.94	53.15	3.51	53.20	73.52	2.24	75.41
TiO ₂	2.43	3.26	2.71	1.14	3.59	1.19	0.12	4.72	0.10
Al ₂ O ₃	14.04	1.97	13.8	14.87	1.86	14.67	12.56	4.24	12.89
Fe ₂ O ₃ (T)	12.41	2.91	12.23	13.71	2.42	14.34	0.92	2.81	0.96
CaO	11.55	3.02	11.4	10.17	2.36	9.89	0.69	3.02	0.63
MgO	6.53	1.49	7.23	4.52	2.02	4.66	0.11	4.14	0.09
Na ₂ O	2.30	2.90	2.26	2.10	1.85	2.03	3.89	2.94	4.10
K ₂ O	0.50	3.67	0.52	0.43	3.47	0.42	4.87	3.55	4.41
MnO	0.13	3.97	0.17	0.18	3.11	0.20	0.16	3.51	0.10
P ₂ O ₅	0.16	3.09	0.23	0.10	4.38	0.10	0.03	13.98	0.02

Appendix A (continued)

(Wt %)	BHVO-1			JB-2			JR-1		
	A	RSD %	B	A	RSD %	B	A	RSD %	B
(ppm)									
Sc	32	6.48	31.8	59	5.55	54	5.91	3.59	5.16
V	308	8.91	317	565	3.32	578	9.77	2.38	
Cr	282	4.33	289	27	5.07	27	2.91	3.06	2.30
Co	46	4.42	45	41	3.37	40	0.77	4.89	0.65
Ni	125	6.05	121	15	2.72	14	0.63	3.27	0.66
Cu	141	7.05	136	226	3.29	227	1.59	4.82	1.40
Zn	104	3.91	105	109	4.88	110	30.35	4.94	30.00
Ga	24	7.10	21	15	3.27	17	19.91	3.27	17.60
Rb	11.13	5.61	11	6.51	2.92	6.20	258	1.85	257
Sr	413	1.86	403	176	1.77	178	31.33	2.48	30.00
Y	27.44	3.95	27.60	24.71	2.39	24.90	48.04	2.37	45.40
Zr	181	2.99	179	49.33	3.30	51.40	105	2.58	101
Nb	19.14	2.40	19.00	0.82	3.60	0.80	17.21	3.96	15.50
Cs	0.16	6.25	0.13	0.83	1.90	0.90	20.38	2.76	20.20
Ba	142	4.73	139	211	2.50	208	42	2.87	40
Hf	4.33	3.41	4.38	1.45	3.14	1.42	4.97	4.34	4.67
Ta	1.26	3.67	1.23	0.18	4.60	0.20	2.03	3.10	1.90
Th	1.08	3.68	1.08	0.23	3.82	0.23	27.25	3.32	26.50
U	0.41	7.63	0.42	0.21	3.37	0.16	9.91	3.44	9.00
La	16.20	1.99	15.8	2.51	2.96	2.37	20.06	1.30	19.70
Ce	40.66	2.30	39	6.25	2.43	6.77	49.54	3.15	47.10
Pr	5.86	2.58	5.7	1.20	3.53	0.96	6.01	3.62	5.62
Nd	25.50	2.35	25.2	6.55	2.34	6.70	22.33	2.99	23.50
Sm	6.50	5.68	6.2	2.27	2.70	2.25	6.14	2.09	6.07
Eu	2.15	3.33	2.06	0.76	1.71	0.86	0.25	3.64	0.30
Gd	6.41	5.87	6.4	2.89	3.65	3.28	5.23	2.96	5.24
Tb	0.98	8.87	0.96	0.65	5.66	0.62	1.07	5.16	1.02
Dy	5.53	6.63	5.2	3.40	3.14	3.66	5.80	2.00	5.78
Ho	1.07	6.16	0.99	0.86	4.96	0.87	1.20	2.59	1.10
Er	2.54	6.58	2.4	2.52	2.21	2.63	3.93	1.75	3.78
Tm	0.33	4.65	0.33	0.45	5.51	0.45	0.76	4.46	0.67
Yb	2.16	5.23	2.02	2.47	2.49	2.51	4.57	2.85	4.49
Lu	0.30	5.65	0.29	0.43	3.05	0.39	0.63	2.67	0.71

Note: A, Present study average of five values; B, Reported values from Govindaraju (1994); RSD, Relative Standard Deviation, calculated with respect to the values given in Column "A".

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