



## Platinum Group Elements (PGE) geochemistry of komatiites and boninites from Dharwar Craton, India: Implications for mantle melting processes



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### ABSTRACT

High MgO volcanic rocks having elevated concentrations of Ni and Cr are potential hosts for platinum group elements (PGE) owing to their primitive mantle origin and eruption at high temperatures. Though their higher PGE abundance is economically significant in mineral exploration studies, their lower concentrations are also valuable geochemical tools to evaluate petrogenetic processes. In this paper an attempt has been made to evaluate the PGE geochemistry of high MgO volcanic rocks from two greenstone belts of western and eastern Dharwar Craton and to discuss different mantle processes operative at diverse geodynamic settings during the Neoproterozoic time. The Bababudan greenstone belt of western and Gadwal greenstone belt of eastern Dharwar Cratons are dominantly composed of high MgO volcanic rocks which, based on distinct geochemical characteristics, have been identified as komatiites and boninites respectively. The Bababudan komatiites are essentially composed of olivine and clinopyroxene with rare plagioclase tending towards komatiitic basalts. The Gadwal boninites contain clinopyroxene, recrystallized hornblende with minor orthopyroxene, plagioclase and sulphide minerals. The Bababudan komatiites are Al-undepleted type ( $Al_2O_3/TiO_2 = 23-59$ ) with distinctly high MgO (27.4–35.8 wt.%), Ni (509–1066 ppm) and Cr (136–3036 ppm) contents. These rocks have low  $\Sigma$ PGE (9–42 ppb) contents with 0.2–2.4 ppb Iridium (Ir), 0.2–1.4 ppb Osmium (Os) and 0.4–4.4 ppb Ruthenium (Ru) among Iridium group PGE (IPGE); and 1.4–16.2 ppb Platinum (Pt), 2.8–19 ppb Palladium (Pd) and 0.2–9.8 ppb Rhodium (Rh) among Platinum group PGE (PPGE). The Gadwal boninites are high-Ca boninites with  $CaO/Al_2O_3$  ratios varying between 0.8 and 1.0, with 12–24 wt.% MgO, 821–1168 ppm Ni and 2307–2765 ppm Cr. They show higher concentration of total PGE (82–207 ppb) with Pt concentration ranging from 13 to 19 ppb, Pd between 65 and 180 ppb and Rh in the range of 1.4–3 ppb compared to the Bababudan komatiites. Ir, Os and Ru concentrations range from 0.6 to 2.2 ppb, 0.2 to 0.6 ppb and 1.4 to 2.6 ppb respectively in IPGE. The PGE abundances in Bababudan komatiites were controlled by olivine fractionation whereas that in Gadwal boninites were influenced by fractionation of chromite and sulphides. The Al-undepleted Bababudan komatiites are characterized by low  $CaO/Al_2O_3$ ,  $(Gd/Yb)_N$ ,  $(La/Yb)_N$ , with positive Zr, Hf, Ti anomalies and high Cu/Pd, Pd/Ir ratios at low Pd concentrations suggesting the derivation of parent magma by high degrees (>30%) partial melting of mantle under anhydrous conditions at shallow depth with garnet as a residual phase in the mantle restite. The komatiites are geochemically analogous to Al-undepleted Munro type komatiites and their PGE compositions are consistent with Alexo and Gorgona komatiites. The S-undersaturated character of Bababudan komatiites is attributed to decompression and assimilation of lower crustal materials during magma ascent and emplacement. In contrast, the higher  $Al_2O_3/TiO_2$ , lower  $(Gd/Yb)_N$ , for Gadwal boninites in combination with negative Nb, Zr, Hf, Ti anomalies and lower Cu/Pd at relatively higher Pd/Ir and Pd concentrations reflect high degree melting of refractory mantle wedge under hydrous conditions in an intraoceanic subduction zone setting. Higher Pd/Ir ratios and S-undersaturation of these boninites conform to influx of fluids derived by dehydration of subducted slab resulting into high fluid pressure and metasomatism of mantle wedge.

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## 1. Introduction

Mantle derived magmas in different tectonic settings provide important clues to understand the chemical evolution of mantle through time and its role in crust generation processes (Rollinson, 2007; Condie and Kröner, 2013). Mantle melting at higher degrees and greater depth, under high pressures and anhydrous conditions in a hot mantle plume generate ultramafic magmas of komatiitic affinity, whereas low pressure hydrous melting of refractory mantle peridotite metasomatized by fluids above a subduction zone produces boninitic magmas (Arndt, 2003). Thus, the formation of high MgO magmas is attributed to a mantle source which has been either unusually hot or rich in volatiles with variations in degrees and depths of melting (Arndt and Nisbet, 1982; Arndt, 2003). The contrasting origin of high MgO magmas in different tectonic settings provide valuable constraints on the chemical composition of the mantle, particularly the platinum group element (PGE) content of the mantle (Keays, 1995; Bockrath et al., 2004). The Archean greenstone belts preserved in the ancient cratonic nuclei of the continents are potential candidates to evaluate mantle evolution and metallogenic processes that operated during the early evolution of the Earth. The volcanic associations of Archean greenstone belts are dominated by komatiite–tholeiite rocks and tholeiitic to calc-alkaline basalt–andesite–dacite–rhyolite (BADR) with boninites, arc-picrites, adakites, high-Mg andesites and Nb-enriched basalts which preserve the geochemical signatures of plume magmatism and subduction–accretion processes in convergent plate margins (Dostal and Mueller, 2013). These diverse magmatic suites are juxtaposed in most of the greenstone terranes through subduction–accretion processes and offer important insights into mantle processes during Precambrian. The association of plume magmatism with calc-alkaline intermediate to felsic volcanic rocks has been ascribed to plume–arc interaction in convergent margin settings (Hegner et al., 2007; Smithies et al., 2009; Barnes and Van Kranendonk, 2014; Manikyamba et al., 2004a,b, 2009, 2012; Manikyamba and Kerrich, 2012). The high MgO rocks occurring in the volcano–sedimentary sequences of Archean greenstone belts are important source for orthomagmatic ores like chromite (Cr), magnetite (Fe, Ti and V), gold, Ni–Cu sulphides and platinum group elements (PGE; Keays, 1995; Mondal, 2011).

Komatiites are ultramafic (MgO > 18 wt.%) volcanic rocks that predominantly occur in Archean greenstone belts (Arndt and Nisbet, 1982; Arndt, 2003; Furnes et al., 2013). Archean komatiites are considered to have been derived by high degrees (>30–50%) of partial melting at great depths under 3–10 GPa melting pressures within hot and dry mantle plumes (Herzberg, 1992; Ohtani et al., 1989; Campbell and Griffiths, 1990; Herzberg and O'Hara, 1998; Sproule et al., 2002; Stiegler et al., 2012). These are considered as low-viscous, rapid eruptions of high temperature mantle melts that primarily flowed over long distances and covered large areas. However, they also occur as submerged oceanic plateaus (Leshner et al., 1984; Huppert and Sparks, 1985; Barnes et al., 1988; Hill et al., 1995; Williams et al., 1998; Polat and Kerrich, 2000; Sproule et al., 2002). Komatiites have been classified as Al-depleted, Al-undepleted, Ti-enriched and Ti-depleted types based on TiO<sub>2</sub> content, CaO/Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and (Gd/Yb)<sub>N</sub> ratios (Jahn et al., 1982; Hanski et al., 2001; Sproule et al., 2002; Gangopadhyay et al., 2006; Jayananda et al., 2008; Manikyamba et al., 2008, 2013; Tushipokla and Jayananda, 2013; Manikyamba and Saha, 2014). These compositional variations of komatiites reflect variable source compositions and mantle melting conditions, which provide important constraints on thermo-chemical structure and metallogenic characteristics of Archean mantle.

Subduction of oceanic crust and the formation of volcanic arcs above the subduction zone are important components in Earth's

geological and geochemical cycles (Straub and Zellmer, 2012). Subduction consumes and recycles material from the oceanic plates, releasing fluids and gases that enhance magmatic activity, feed hydrothermal systems, and generate ore deposits. Boninites are erupted during the early stages of subduction and carry distinct signatures of interaction between mantle wedge and subducting slab (Kusky et al., 2014; Zhou et al., 2014). Chemically boninites have high SiO<sub>2</sub> (52–58 wt.%) coupled with high MgO (9 wt.% or more), as well as several hundred parts per million (ppm) of Cr and Ni but low TiO<sub>2</sub> (0.2–0.5 wt.%), Zr (20–40 ppm) and (~5 wt.%) dissolved water (Le Bas, 2000; König et al., 2010). Boninites are significant in terms of their unique petrogenesis and their exclusive occurrence in intraoceanic environment. Their chemical compositions represent primary magmas derived from the partial melting of a strongly depleted mantle source in high geothermal gradient at shallow levels. Some of the important requirements for boninite eruption are (1) addition of hydrous fluids to the refractory mantle peridotite which lowers the solidus temperature and generate partial melting, and (2) high temperature (1150–1350 °C) at shallow depth (<50 km) in a subduction zone environment (Smithies, 2002; Crawford et al., 1989; Polat et al., 2002). The geochemical characteristics of boninites suggest that they are formed in an intraoceanic subduction zone at fore arc region through two stage melting process and metasomatism of the mantle wedge. Variable enrichment or depletion of incompatible elements suggests that boninites are derived from refractory peridotite which has been metasomatically enriched in LREE, Sr, Ba and alkalis (Resing et al., 2011).

Platinum group elements [PGE: Pt, Pd, Rh, Ir, Os, Ru] show strong chalcophile and siderophile affinity and are therefore considered as sensitive indicators of processes involving segregation and accumulation of sulphide melts from silicate magmas, core-mantle differentiation, mantle evolution and magma genesis (Zhang et al., 2005; Mondal, 2011; Zhou et al., 2014). PGE compositions of mantle-derived ultramafic–mafic magmas are significant tools to understand their petrogenetic evolution and sulphide saturation history as PGE behaviour and their abundance is controlled by several factors like mantle heterogeneity, enrichment–depletion processes of the mantle, partial mantle melting, melt percolation, sulphide segregation, crystal fractionation, etc. (Zhang et al., 2005; Naldrett, 2010; Mondal, 2008, 2011). PGE abundances in mantle derived rocks have been documented by various workers (Pattou et al., 1996; Röhkamper and Hofmann, 1997; Snow and Schmidt, 1998; Handler and Bennett, 1999; Lorand et al., 1999, 2000, 2004; Bennett et al., 2000; Lorand and Alard, 2001; Lee, 2002; Luguët et al., 2003; Irvine et al., 2003; Pearson et al., 2004; Dale et al., 2008; Said et al., 2011 and references therein). Using low degree partial melts like basalts, understanding of PGE compositions of mantle is difficult as these are saturated with sulphides which retain PGE in the source and fractionates them during magma ascent and eruption. However, the conditions for generation of komatiites, including high degrees of partial melting of hot and dry peridotite, sulphur undersaturation, rapid ascent, minimum differentiation and contamination prior to eruption, facilitate extraction of large proportions of compatible elements from mantle (Arndt, 2003; Keays, 1995; Barnes et al., 1985; Herzberg and Zhang, 1996; Puchtel and Humayun, 2001; Puchtel et al., 2004; Fiorentini et al., 2011). Thus, komatiites being high magnesian lavas, trap the siderophile element content of the mantle and provide information on PGE abundances of mantle (Puchtel and Humayun, 2001; Puchtel et al., 2004). In a supra-subduction zone setting, a spectrum of magmas from high-Si, high Mg boninitic compositions to low-Si, high Mg picritic or olivine tholeiitic end members are generated under hydrous conditions, ~1300 °C temperature and within 20–100 km depth. Two of the world's largest platinum-group element deposits (the Bushveld and Stillwater

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