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Satyanarayanan Manavalan*, Surya Prakash Singh, Vysetti Balaram, and Mohanty Niranjana Geochemistry of the Madawara Igneous Complex, Bundelkhand Craton, Central India: Implications for PGE Metallogeny

DOI 10.1515/geo-2015-0016

Received March 25, 2014; accepted September 10, 2014

Abstract: The southern part of the Bundelkhand craton contains a series of a E-W trending mafic and ultramafic rocks, about 40 km in length and 2–4 km wide, that occur as intrusions within the Bundelkhand Gneissic Complex (BnGC). They are confined between the Madawara-Karitoran and Sonrai-Girar shear zones. Dunite, harzburgite, lherzolite and websterite are the commonly occurring ultramafic rocks that have high MgO, Ni, Cr, PGE and low Al_2O_3 , CaO, K_2O , TiO_2 and V contents, and shows peridotitic affinity. A distinct trend of crystallization from peridotite to komatiitic basalt has been inferred from geochemical plots, which also indicates the occurrence of at least two varieties among the ultramafic suite of the Madawara ultramafic complex, namely, Group I comprising dunite, spinel peridotite, harzburgite and lherzolite, and Group II consisting of pyroxenite, websterite and olivine websterite. In several places, the rocks of Group II have an intrusive relationship with Group I, and are relatively enriched in total platinum group elements (PGE ~ 300 ppb). The discrimination diagrams suggest that the PGE are enriched in low sulphur-fugacity source magma at moderate to deeper depths by high degree of partial melting of the mantle.

Keywords: PGE mineralization; Madawara; Bundelkhand Craton; Central India

1 Introduction

Mafic/ultramafic intrusions related to intracratonic magmatism occur in several shield areas [1]. Mineral systems associated with these events include Ni-Cu-PGE miner-

alization in mafic-ultramafic rocks and base metals in metavolcanic rocks (VHMS type) in the Kaapvaal craton, Barberton greenschist belt and Superior Province [2]. Hence these lithologies have attracted attention in recent years for their potential to host viable metallic mineral deposits. The genesis of these metal associations within the host lithologies have now been established, apart from understanding the mantle evolution and its contribution to crustal growth [1–3]. The Bundelkhand craton preserves the different phases of Archean magmatism, metamorphism and deformation events [4] which were followed by emplacement of Bundelkhand granitoids (BG), quartz reef [5] and mafic dykes during the Paleoproterozoic [6–8]. The Meso to Neoproterozoic Bundelkhand gneissic complex (BnGC) comprises high grade rocks reaching up to granulite facies followed by low grade metamorphic rocks of greenschist facies of Bundelkhand Metasediments and Metavolcanics (BnMM) rocks [9, 10] and the mafic-ultramafic intrusions occurring along the E-W trending Mauranipur-Mohar-Babina shear zone in the central part [11] and Madawara-Karitoran shear in southern parts of the craton [12]. The Madawara Igneous Complex (Figure 1) occurs as giant lensoidal intrusion into the BnGC and is nearly undeformed and unmetamorphosed [12–14]. The occurrences of PGE within the Madawara Igneous Complex (MIC) of the Bundelkhand craton were first reported by Farooqui and Singh (2006) [15]. The identification of sperrylite and other important PGMs in these rocks based on the SEM-EDX data [16–20] suggest that MIC could be a new potential prospect for PGE deposits in the Indian shield. Hence the detailed geochemical study of ultramafic and associated rocks are presented here.

2 Geological framework

The Bundelkhand craton is considered as one of the oldest nuclei in the northern part of the Indian shield. It is delineated by the E-W trending Son-Narmada lineament/faults from the Mahakoshal group of rocks in the south, the WNW-ESE trending Yamuna fault in the north from the foreland basin of Himalaya and the NE-SW trending Great Boundary Fault (GBF) from the Aravalli belt [4].

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Figure 1: Geological map of Madawara Igneous Complex (inset showing study area in Bundelkhand craton) (After Singh *et al.* [16]).

A detailed stratigraphy of the area modified after Singh *et al.* (2010) [16] is given in Table 1. Geological studies around the southern part of the craton revealed occurrences of E-W trending, high grade metamorphosed rocks of BnGC (gneisses, migmatites, granite-gneisses, amphibolites, hornblende-biotite gneisses) around Rajola and north of Madawara, followed by less deformed and low grade metamorphosed rocks of Bundelkhand metasedimentary rocks and metavolcanic rocks (banded magnetite-quartzite, quartzite, mica schist) [7] that are exposed at Girar and Baraitha. The ultramafic rocks of Madawara trending E-W and ENE-WSW and associated with peridotite, pyroxenite and diorite/gabbro occur as scattered lensoidal bodies in the area covering more than 400 km² and have been reported from the southern part of the Bundelkhand craton (Figure 1) [5, 12, 14, 21, 22]. These ultramafic bodies are subparallel and are confined between the Madawara – Karitoran shear zone in the north and Sonrai – Girar shear zone in the south. The sheared relationship between ultramafic rocks of the MIC and BnGC has been recorded at several places, where the ultramafic rocks are mylonitised and recrystallised, and in places altered to serpentine-talc-chlorite schists [7]. The presence of pegmatites and thick zones of mylonites and phyllonites indicate hydrothermal activity in the area that may be responsible for alteration of ultramafic rocks at several places.

Madawara Ultramafites: The ultramafic rocks at Madawara town represent the largest exposure. It is about 3 km wide and 4-5 km long, comprising dunite, peridotite,

spinel-bearing peridotite, pyroxenite and websterite followed by gabbro and diorite in subsequent stages. The rocks are relatively hard and compact, dark bluish gray and are medium to coarse grained. Chromespinel occurs as disseminated crystals while granular crystals of olivine, magnetite and pyroxenes are common. Porphyritic texture is rare. Sulphides are visible at many places. Globular aggregates of altered olivine in pyroxenites (2-10 cm in diameter) are common in the southern part of the Madawara ultramafic rocks. The gabbro/diorites intrude into these ultramafic rocks in the southern part of Madawara.

Pindar Ultramafites: These ultramafic rocks are medium to coarse grained and consist of peridotite, Cr-spinel bearing peridotite, harzburgite, lherzolite, dunite and pyroxenite. However, the area is dominated by peridotite and dunite. The olivine websterite is very dark bluish gray coloured, hard and compact, characterized by coarse grained cumulates of olivine (Figure 2a). They occur as small to large size lenses (up to 8-10 metres in length and 4-5 metres in width) and close to peridotite and websterite in composition. The contact of these lenses with BnGC is normally crushed, altered and at some places, they are sheared and mylonitised. Talc-chlorite schist occurs along the sheared contact, while websterites are scattered bodies within the ultramafic rocks and their orientation is also parallel to the main ultramafic complex.

Ikauna Ultramafites: The PGE bearing Ikauna ultramafic body is 3500 m long and 90-180 m wide [15]. It strikes E-W and dips 50° to 70° to the north. The high grade meta-

Table 1: Stratigraphy of Bundelkhand Craton (After Singh *et al.* [15]).

Vindhyan Supergroup (1400-700 Ma)	Lower Vindhyan limestone and dolomite, quartzite, Kaimure sandstone, Rewa sandstone and shale, Bhandar carbonate
Bijawar/Gwalior Group (1800-1600Ma)	Sandstone, quartzite, mica quartzite, meta-basalts, fer-ruginous shale and sandstone, limestone and dolomite
Mafic emplacement (2000-1800Ma)	Dolerite, gabbro, lamproites, quartz veins and reefs, granites
Late phase granitic emplacement (2300-2000Ma)	Quartz reef, Granitoids, Pegmatites, diaspore and pyro-phyllites
Bundelkhand Granitoids (BG) (2600-2500 Ma)	Leucogranite, biotite granite, hornblende granite, hornblende-biotite granite
Madawara Ultramafic Complex	Peridotite, dunite, harzburgite, spinel bearing peri-dotite, pyroxenite, gabbro, diorite, granite, talc chlorite schist
Bundelkhand meta sedimentaries and metavolcanics (BMM) (3300-2600 Ma)	BMQ, rhyolite, andesite, rhyodacite, quartzite, mica-ceous quartzite, chlorite schist, talc schist, pyroxenite, gabbro, peridotite and calc-schist
Bundelkhand Gneissic Complex (>3300 Ma)	Granite-gneisses, calc silicate gneisses, quartzites, gar-netiferous gneiss, sillimanite-cordierite gneiss, amphi-bolite, TTG

Figure 2: (A) Peridotite showing serpentine veins, (B) Outcrop of ultramafic rock in Ikauna, (C) Photomicrograph under crossed nicols of olivine (Ol) cumulates, (D) Chromite (Cr) within altered olivine.

morphic rock, which hosts these ultramafic rocks, contain several E-W trending subvertical shear zones, dipping to the north. The ultramafic body of Ikauna is almost flat with small hillocks of nodular lenses of pyroxenite. These lensoidal dark coloured pyroxenites are strongly crushed at their margin, in places crenulated and are few metres (10-50 m) wide and 15-100 m length. The contact is altered, in places shows rotation signatures, and is partially enveloped by chlorite + talc-actinolite schists. The chrome-spinel -bearing ultramafic rock has also been traced for more than 1 km along the strike length. The contact of the intrusive body with gneisses or diorites is marked by mylonite. The Ikauna ultramafic body is also cut by NW- SE trending faults in several places. Most of the ultramafic rocks are commonly altered to serpentine, talc and chlorite schists along the shear zone (Figure 2b).

3 Petrography

The ultramafic rocks of the Madawara Igneous Complex (MIC) are medium to coarse grained, more or less uniform in texture and ranges from peridotite to pyroxenite. Detailed petrographic and geochemical analyzes indicate that the peridotites are represented by lherzolite and harzburgite, while the pyroxenites are mostly olivine-rich orthopyroxenites (websterite). The lherzolite and harzburgite consist of olivine cumulates where interstices are filled with chromite, magnetite and sulfides. Olivine grains are cumulus and are medium to coarse grained (Figure 2c). The interstitial space is either occupied by orthopyroxene or clinopyroxene with fine grained chromite and magnetite (Figure 2d). SEM-EDS (Hitachi®, Japan) studies have indicated presence of sulfide phases, for example, pentlandite, pyrrhotite, chalcopyrite, with inclusions of chromite and platinum group minerals (PGM) like sperrylite, wolframite and an Ir-tungstate alloy occur as disseminated grains in the inter-spaces of olivine or along the cleavage in pyroxenes (Figure 3a-b) [16, 17]. The fine- to medium- grained chromites, magnetite, titanomagnetite and granular aggregates of pentlandite occur in olivine-rich orthopyroxenites, where these minerals are also present along the cleavages of pyroxene and intra-granular spaces of olivine. The alteration of olivine, pseudomorphic texture, and appearance of talc, chlorite and serpentine as secondary minerals were also recorded in few thin sections, indicating very low-grade metamorphism at the marginal area of deformed zones.

3.1 Methodology

Major oxides, minor and trace elements (including REE and PGE) were determined in fifteen representative samples representing rocks from Madawara, Pindar and Ikauna. Major elements were analyzed at the National Geophysical Research Institute (NGRI), India by XRF (Phillips® 234 MAGIX PRO Model 2440), with a relative standard deviation of < 3% [23]. For trace elements, the sample powders were dissolved in reagent grade HF:HNO₃ mixture in Savillex screw top vessels and heated at 140°-146°C. Solutions were analyzed by ICP-MS (Perkin Elmer SCIEX ELAN DRC II) at NGRI. ¹⁰³Rh was used as an internal standard [24]. External drift was corrected by repeated analyzes of a 1: 5000 solution of UB-N (certified reference material obtained from ANRT, France), which was also used as a calibration standard. Instrument response was corroborated relative to two independent digestions of the JP-1 (certified reference material obtained from GSI, Japan). Precision and accuracy are better than 5% (1σ) for the majority of trace elements, but varied up to 10% (1σ) in the case of HREE. Mg# is calculated as $Mg/(Mg+Fe_{total})$. Chondrite and primitive mantle normalisation values are taken from Sun and McDonough [25]. Analysis of PGE and Au was carried out by following the NiS-fire assay method with Te co-precipitation and ICP-MS described in Balaram *et al.* [26]. The certified reference material WPR-1 was used as calibration standard and WMG-1 was analyzed as an unknown to check accuracy. The overall precision of PGE analysis was better than 10% (1σ) at ppb levels. Most abundant and recommended isotopes relatively free from isobaric interferences were used for all elements and were selected based on their abundance levels and the lack of interferences from other elements normally present in rock samples.

4 Results

The whole rock analyzes of representative ultramafic rock samples from the MIP are presented in Table 2 and are characterized by high MgO, Ni, Cr, and PGE, and extremely low Al₂O₃, CaO, K₂O, TiO₂ and V contents. The geochemical characteristics of the ultramafic rocks exposed around Madawara shows variation from high MgO (~47 wt %; picritic) to moderate MgO (~32 wt %; gabbroic). A Jenson cation plot (Figure 4) shows that these rocks were derived from melt which is peridotitic in nature. The norm mineral classification and petrographic study reveal that these ultramafites are lherzolite, olivine websterite, orthopyroxen-

Figure 3: SEM-EDS image showing (A) Sperrylite [sr] associated with the chalcopyrite [cy] in the matrix of pyroxene [cy], (B) Dumble shaped Iridium-Tungsten alloy.

ite, harzburgite in composition. The relatively clear to partial linear regression relationship between MgO and SiO₂, TiO₂, CaO, Cr, Ni and total PGE (Figure 5a-f) indicate crystallization trend from peridotite composition of primitive magma to Mg-olivine fractionation followed by differentiated Fe-rich olivine, spinel/magnetite and sulfide crystallization. There is a broad range of Ni and Cr concentration in the ultramafic rocks and their associated rocks from Madawara. Maximum concentration of Ni (up to 2655 ppb) and Cr (up to 5538 ppb) are recorded in dunite while the lowest value of Ni and Cr is in diorite. A decrease in the Mg# in these ultramafites leads to their corresponding gradual decrease in Ni and Cr concentrations. A strong linear correlation of SiO₂ vs. Zr, Al₂O₃ vs. Y, TiO₂ vs. Zr and Y vs. Zr (Figure 6a-d) shows that these rocks have undergone high degree of partial melting at shallow to moderate depths.

The REE plots and spider diagram show at least two types of trend (Figure 7a-b) for ultramafites and associated rocks from Madawara, Ikauna and Pindar. The REE patterns of dunite, spinel peridotite, harzburgite and lherzolite show essentially a strong Eu negative anomaly (termed here as Group I) (Figure 7a). These rocks display a relatively uniform and unfractionated REE trend, and are characterized by low MgO, high CaO, SiO₂, Ni, Cu and relatively high PGE. The flat LREE pattern, with mild positive Eu anomaly pattern (Figure 7b) is recorded in differentiated variety of ultramafic rocks representing pyroxenite and peridotites II (termed here as Group II) and are inevitably associated with Group I type of MIP representing the last intrusive phase. Besides REE patterns, the spider diagrams of these two categories (Figure 8a-b), show distinct trend for each group, although they both display slight LILE enrichment, especially for pyroxenites, with values ranging in between those of N-MORB and E-MORB.

The mantle normalized spider diagram of Group I and Group II shows negative and positive anomalies for Ti respectively. A strong Nb negative anomaly is also present in Group I when compared to Group II suggesting partial melting of primary melt component associated with crustal inputs. This is also supported by the overall high positive anomalies of Rb, K, La, Sr and Sm values and strong depletion in U, Nb, Hf.

4.1 PGE geochemistry

The PGE and Au values of ultramafic rocks from Madawara listed in Table 1 indicate a narrow range of Ir and Ru contents varying from 7.2 to 17.6 ppb and 41.8 to 100.2 ppb respectively. Rhodium contents are fairly constant with a range from 1.4 to 11.2 ppb, whereas Pt contents vary from 6.8 to 131.6 ppb and Pd from 6.8 to 77.2 ppb. Gold also displays a wide variation, ranging from 21.8 to 1426.8 ppb. Both Group I and II of ultramafic rocks have a similar primitive mantle normalized siderophile element pattern (Figure 9a-b) and are enriched in PPGE (Rh, Pt, Pd) and Cu relative to IPGE (Ir and Ru) and Ni. MgO displays a relatively good correlation with PGE. Thus it is inferred that the fractionation of olivine, pyroxene and spinel has significantly influenced the PGE distributions in these rocks. The geochemical studies indicate that olivine, chrome-spinel and/or sulfides are the most compatible mineral phases for PGE-enrichment [3, 27, 28]. The Pd/Ir and Pd/Rh ranges from 0.6 to 5.0 (average 1.7) and 1.3 to 20.3 (average 5.6) respectively. The strong positive Au and Pt anomalies, corroborated with REE and multi-element diagram, indicate the presence of chloride and carbonate enriched fluid components in the system during magmatism [29].

Table 2: Geochemical data representing ultramafic rocks from Madawara (MD), Pindar (P) and Ikauna (I) localities in Madawara Igneous Complex ("Data from Balaram *et al.*, 2013 [18]). H-Harzburgerite, L-Lherzolite, W-Wehrilite, O-Orthopyroxene.

Analyte	MD24	MD25	MD29	MD-8	MD19	P-64*	P-65*	P-66*	P-67*	P-68*	I-37	I-38	I-39	I-40	I-41
Rock type	H	H	O	O	O	W	W	W	W	W	L	L	L	L	H
Group	II	I	I	II	I	II	II	II	I	I	II	I	I	I	I
Major oxides (in wt %)															
SiO ₂	43.7	43.1	50.9	44.5	44.7	41.7	41	40.1	41.8	42.8	42	41.4	41.7	40.1	40.2
Al ₂ O ₃	0.87	0.87	0.88	0.73	0.85	2.06	2.69	2.35	2.67	2.02	2.57	2.72	3.88	5.16	1.86
FeO	8.8	8.8	10.3	10.7	10.4	4.6	4.8	4.9	4.5	4.7	5.4	4.7	4.9	8.7	4.9
Fe ₂ O ₃ T	11.5	11.6	13.4	14.1	13.5	6	6.2	6.4	5.8	6.2	7.1	6.1	6.5	11.4	6.4
MnO	0.14	0.14	0.13	0.1	0.14	0.12	0.14	0.12	0.11	0.11	0.15	0.12	0.15	0.2	0.06
MgO	35.4	35.6	29.5	34.5	34.2	46	45.3	45.2	45.1	45.8	41.3	42.2	41.1	31.6	47.3
CaO	2.31	1.72	1.61	0.08	0.07	0.66	1.41	1.63	1.34	0.44	3.53	3.67	2.55	2.18	0.64
Na ₂ O	0.02	0.01	0.01	0.02	0.02	0.06	0.11	0.04	0.06	0.03	0.05	0.06	0.04	0.02	0.04
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.03	0.03	0.03	0.04	0.02	0.03	0.03	0.04	0.03	0.03
TiO ₂	0.53	0.46	0.27	0.1	0.45	0.17	0.21	0.18	0.19	0.16	0.18	0.17	0.24	1.71	0.16
P ₂ O ₅	0.03	0.03	0.02	0.01	0.01	0.02	0.02	0.02	0.2	0.02	0.07	0.02	0.02	0.08	0.02
LOI	5.6	7.23	2.2	6.87	6.55	4.06	3.65	4.68	3.22	2.95	3.47	4.08	4.24	8.27	3.76
Sum	100.1	100.7	99	100.9	100.5	100.9	100.8	100.7	100.5	100.5	100.3	100.6	100.4	100.8	100.5

Table 2: Cont.

Analyte	MD24	MD25	MD29	MD-8	MD19	P-64*	P-65*	P-66*	P-67*	P-68*	I-37	I-38	I-39	I-40	I-41
Rock type	H	H	O	O	O	W	W	W	W	W	L	L	L	L	H
Group	II	I	I	II	I	II	II	II	I	I	II	I	I	I	I
Trace elements (ppm)															
Sc	13.8	12.5	7.2	7.1	11.4	10	12.3	10.7	11.7	10.9	14.3	12.5	13.4	44.3	9.4
V	88.6	83	33.2	27.8	81.4	47.4	62.4	52.3	57.1	50.1	63.8	55.5	63.5	363.5	44.1
Cr	4810	5538	955	2540	5280	2703	3150	2297	2890	2721	2547	3021	3248	1922	3840
Co	116	116	61.5	168	90.9	137	133	131	127	119	132	124	133	149	121
Ni	1728	1740	1483	2064	1738	2655	2616	2434	2581	2466	2260	2259	2278	915	2606
Cu	23.7	20.2	18	62.7	18.1	11.2	16	24.9	11.4	63	44.5	28.2	15.3	18.8	16.7
Zn	37.1	40.5	39.3	52.4	52.8	111.4	476.7	253.5	84.1	611.8	540.5	153.8	73.8	331.5	142.8
Ga	4.5	4.3	6.7	1.3	4.1	3.9	5.2	4.4	4.8	4.7	5.2	6.2	6.7	25.4	5.6
Rb	0.88	0.64	0.44	0.7	0.6	0.81	1.11	1.15	1.65	2.12	1.03	0.97	1.93	0.72	0.69
Sr	21.3	9.5	6.3	8.5	4.6	4.8	18.5	5.1	5.2	9.4	13.6	11.8	6	2.7	3.7
Y	3.5	3.1	3.7	1	2.7	2.8	4.2	3.6	3.8	4.3	4.2	3.8	3.8	3.7	2.9
Zr	9	8	18	1.5	8.1	4.7	11.2	4	5	6.1	6.9	5.7	5.6	64.9	5.3
Nb	0.28	0.22	0.37	0.12	0.28	0.08	0.09	0.04	0.1	0.08	0.09	0.09	0.13	1.28	0.07
Cs	0.13	0.07	0.05	0.06	0.09	0.37	0.41	0.52	0.44	0.45	0.23	0.35	0.57	0.06	0.15
Ba	11.2	16.5	12.3	17.1	13.1	1.7	3.2	2.7	4.6	7.8	6.2	2	5.1	2.5	1.4
La	0.94	0.77	0.73	0.5	0.55	1.59	2.29	2.12	2.01	3.87	2.28	2.27	2.65	8.8	1.24
Ce	2.8	2.3	2.3	1.4	1.9	3.3	4.4	3.9	4	8.2	4.7	4.4	5.8	18.1	2.6
Pr	0.36	0.31	0.33	0.18	0.28	0.27	0.37	0.32	0.32	0.58	0.37	0.35	0.44	1.43	0.22
Nd	1.6	1.4	1.6	0.8	1.2	1.3	1.9	1.5	1.7	2.8	1.9	1.8	2.1	7.1	1.1
Sm	0.44	0.38	0.49	0.17	0.35	0.34	0.48	0.4	0.43	0.64	0.5	0.44	0.53	1.62	0.32
Eu	0.14	0.12	0.09	0.08	0.08	0.11	0.15	0.12	0.11	0.13	0.14	0.12	0.13	0.18	0.09
Gd	0.58	0.5	0.57	0.22	0.42	0.42	0.6	0.48	0.53	0.75	0.59	0.55	0.59	1.58	0.38
Tb	0.1	0.08	0.1	0.03	0.07	0.08	0.12	0.1	0.1	0.13	0.11	0.11	0.12	0.23	0.08
Dy	0.59	0.53	0.61	0.16	0.43	0.47	0.69	0.58	0.61	0.75	0.7	0.64	0.67	0.94	0.49
Ho	0.14	0.12	0.13	0.03	0.1	0.1	0.15	0.13	0.14	0.16	0.15	0.14	0.15	0.16	0.11
Er	0.41	0.35	0.41	0.09	0.31	0.32	0.45	0.4	0.42	0.47	0.47	0.41	0.45	0.47	0.32
Tm	0.07	0.06	0.07	0.02	0.05	0.06	0.07	0.07	0.07	0.07	0.08	0.07	0.07	0.07	0.05
Yb	0.38	0.37	0.4	0.09	0.31	0.31	0.41	0.37	0.38	0.43	0.42	0.39	0.43	0.45	0.3
Lu	0.07	0.06	0.07	0.01	0.05	0.05	0.06	0.05	0.06	0.07	0.06	0.06	0.07	0.09	0.05
Hf	0.19	0.16	0.36	0.04	0.17	0.1	0.29	0.1	0.12	0.13	0.15	0.14	0.14	1.29	0.13
Ta	0.03	0.02	0.04	0.03	0.02	0.02	0.02	0	0.05	0.03	0.07	0.04	0.03	0.27	0.03
Pb	10.4	9.5	12.3	10.6	14.2	12.3	12.4	11.2	8.2	23	13.2	11.4	9.7	12.6	11.7
Th	0.17	0.14	0.31	0.06	0.16	0.07	0.1	0.09	0.09	0.18	0.13	0.13	0.13	0.27	0.07
U	0.09	0.1	0.19	0.18	0.11	0.06	0.1	0.21	0.09	0.22	0.11	0.14	0.08	0.16	0.06

Table 2: Cont.

Analyte	MD24	MD25	MD29	MD-8	MD19	P-64*	P-65*	P-66*	P-67*	P-68*	I-37	I-38	I-39	I-40	I-41
Rock type	H	H	O	O	O	W	W	W	W	W	L	L	L	L	H
Group	II	I	I	II	I	II	II	II	I	I	II	I	I	I	I
Precious elements (ppb)															
Ru	81.4	83.4	72.6	100.2	74.6	41.8	48.6	59.4	66.8	52.4	65.6	54.2	53.6	44.4	59.6
Rh	11.2	3.8	1.4	2.4	5.4	2.8	3.4	3	4.2	8.2	5.4	4.6	5.6	2.4	3.8
Pd	48.8	77.2	13.4	17	26.8	13.6	10.8	9.8	15.2	14.4	66	10.8	12.4	8.2	12.2
Ag	784.6	57	58.6	79.4	226.6	26.6	62	41.4	56.6	69.6	165.4	84.2	148.4	130.4	129.6
Re	355.8	44.8	77.4	210.2	290.2	10.4	11.6	12	14	9.4	36.4	164.2	93	172.2	233.8
Os	6.6	4	2.2	7.6	6	65.2	24.2	54.8	28	63.8	46.4	22	38.6	9	59.8
Ir	17.6	15.4	7.2	9.4	13.8	10	11.8	12.6	14.6	12.6	17.2	13.6	15.2	4.4	16.8
Pt	49.6	86.4	6.8	131.6	35	24.6	29	27	28.6	30.4	47	33.8	23.4	31.8	29.4
Au	59.4	56.6	52.8	42.2	1426.8	29.8	29.6	21.8	38.6	35.6	49.2	28.6	39.8	26.2	27.8

Figure 4: Jensen cation plot from the ultramafic rock of MIC. (Modified after Jensen (1976) [52]).

5 Discussion

The geochemical data from the ultramafic rocks presented here reflect their mineralogy and allows them to be distinguished into two main groups of ultramafic rocks: (1) harzburgites, spinel peridotites and dunites and (2) pyroxenites and peridotites II. There are linear correlation between certain elements (like Cr, Co, Ni) in the ultramafic rocks which suggest that they basically represent a melt that was extracted from the peridotite and subsequently contaminated by crustal components and fractionated at several stages as shown in Figure 5d-e. The pyroxenite has high PGE, LREE and LILE, and hence differs from the other ultramafic rocks and associated diorites. The presence of high Ir-low Pd (Figure 10a), high MgO and HREE suggests partial melting for these ultramafites at relatively high temperature. The partial melting of the primitive mantle may lead to the formation of either S-saturated or S-undersaturated melts [3, 30]. It is advocated that where S-undersaturated magma is formed by high degrees of partial melting, the PGE remain in the primary melt, leading to enrichment of PGE, especially PPGE [28]. The Pd/Rh vs. Ni/Cu and Pd/Ir vs. Ni/Cu variation diagrams (Figure 10b-c), proposed by Barnes [31], display that most of the ultramafic rocks show peridotitic affinity. The negative correlation between Pd/Ir and Ni/Cu ($r^2 = -0.4$) (Figure 10c) suggests that Pd may have behaved like Cu and was removed, whereas Ir associated with Ni and was retained

during melt-rock interaction. The range of Ni/Cu and Pd/Ir (0.83 to 31.9) ratios for the ultramafic rocks from Madawara suggests sulfide under saturated conditions.

REE contents normalized to chondrite values show variable enrichments in LREE [(La/Sm)_N between 1.45 and 2.0] with mild positive Eu anomalies (Eu/Eu* from 1.08 to 2.26) and nearly flat HREE patterns [(Gd/La)_N 0.94–1.49] for the pyroxenites. The (Gd/La)_N is similar to those of pyroxenites analyzed from elsewhere [32–34, 34]. The pyroxenites in ultramafic massifs are normally considered as depleted in LREE and highly enriched in HREE contents [32]. In contrast to this, LREE enrichment and higher contents of Zr, Nb and U and very low HREE have been reported from a few locations, for example, Hungary and the French Massif Central [32, 33], Herbeira massif [34] and harzburgite of Herbeira [35]. Hence, the trace element concentrations including PGE appear unique and differ from those of other pyroxenites in ultramafic massifs reported elsewhere, for example, Ronda, Ortegal, Horoman, Cabo-Ortegal, Alpine, Ronda massifs, Beni Boussera, the Alps, massive pyroxenites from Herbeira.

The mafic rocks and pyroxenites from orogenic peridotites show a characteristic depletion in incompatible elements [36, 37]. The absence of such depletion from the Group II rocks suggests that the source area of pyroxenite parental melts should originally be either enriched in incompatible elements or had received LILE enrichment by reaction with carbonic fluids or by metasomatism of carbonatite related fluids. The last hypothesis is preferred

Figure 5: Variation diagrams showing plots between MgO and (a) SiO_2 , (b) TiO_2 , (c) CaO, (d) Cr, (e) Ni and (f) Total PGE. (MD-Madawara; P-Pindar; IK-Ikauna).

Figure 6: Bivariate plots showing strong linear correlation between (a) SiO_2 vs. Zr, (b) Al_2O_3 vs. Y, (c) TiO_2 vs. Zr and (d) Y vs. Zr.

Figure 7: Chondrite-normalized REE patterns of ultramafic rocks representing (a) Group I and (b) Group II. Normalization values are from Sun and McDonough [25].

Figure 8: Primitive-mantle normalized spidergram representing (a) Group I and (b) Group II. Normalization values are from Sun and McDonough [25].

Figure 9: Primitive-mantle normalized siderophile element patterns of ultramafics indicating (a) Group I and (b) Group II. Normalization values are from Sun and McDonough [25].

(a)

(b)

(c)

Figure 10: PGE variation diagrams showing (a) Ir vs. Pd (Chondrite ratio from Sun and McDonough [25]), (b) (Ni/Cu) vs. (Pd/Rh), and (c) Ni/Cu vs. Pd/Ir. (Fields for 10 b-c are from modified after Barnes and Maier [2]).

here, as it would also account for the depletion of LILE in peridotites. The melt percolation into interstitial space of harzburgite due to partial melting of asthenosphere proposed by Zhou *et al.* [38] and Chen *et al.* [39] may also be considered for the genesis of pyroxenite. The enrichment in LILE associated with a generalised, although variable LREE enrichment from peridotites and pyroxenites have been reported from other places, and hence the enrichment of LREE is considered as possibly due to metasomatism of carbonatite related fluid or crustal contamination [34, 35]. Therefore, such variation in LREE enrichment of rocks from Madawara is noteworthy. LREE-enriched rocks with flat patterns have also been described from the Horman, Cabo Ortegal, Alpine and Ronda massifs [36, 37, 40]. The presence of such occurrences are limited and their origin is not well constrained. The origin of pyroxenites enriched with crustal elements, has also been caused by thinning and upwelling of asthenosphere and late melt percolation into the harzburgite. Recently, Gruau *et al.* [41] have proposed various mechanisms for selective LREE enrichment in peridotites. In the present case, and by comparison with the models proposed by Gruau *et al.* [41], the REE trend points to high-temperature contamination of the ultramafic rocks through interaction with LREE-rich melts.

5.1 Magma evolution

The physical and chemical changes recorded across the harzburgite–dunite–pyroxenite suite in the Madawara complex could have been theoretically generated by increasing degrees of partial melting [42–44]. Different types of REE pattern have been described for the evolution of ultrabasic magma. The U-shaped REE patterns of peridotites reported from Oman ophiolite has been explained as the product of interaction of peridotites with LREE-enriched melts [45, 46]. The processes that include a mantle origin involving disequilibrium mechanisms [47], the effect of melt transportation [48] and the entrapment of small melt fractions [49] are important points during the course of crystallisation of ultrabasic magma. The variation in REE patterns of peridotites has been interpreted in terms of the contamination by assimilated continental crustal material [41]. The positive correlations between Zr vs. SiO₂, Y vs. Al₂O₃, TiO₂ vs Zr and Zr vs Y (Figure 6a–d), in Madawara ultramafic rocks are similar to those recorded globally in anhydrous peridotites [50] and indicate a similar source for evolution of the magma. The decrease in Pd/Ir ratios close to chondrite (Figure 10a) suggests that early/initial phase of magma was perhaps developed from fertile mantle under sulphur under-saturated conditions, whereas the py-

roxenites and Group II type magma, which are presumably enriched in sulphides, are developed in the subsequent stages. The range of Pd/Ir (0.7 to 5.0) and Pt/Au (0.03 to 3.1) ratios indicate that sulphur and chloride rich fluid activity causes the mobilisation of the Pt and Au from the magma. The LREE depleted pattern is characteristic of late Archean ultramafites and is generally believed to indicate that these magma originated by a high degree of partial melting of the mantle. The strong negative Eu anomaly reflects plagioclase fractionation in the melt. The Pd/Rh vs. Ni/Cu and Pd/Ir vs. Ni/Cu variation diagrams (Figure 10c–d) proposed by Barnes *et al.* [51] and HREE fractionation trend support the view that Group I ultramafic rocks of Madawara are close to mantle composition and are less fractionated, whereas Group II type of rocks are more evolved and are enriched with dissolved sulphur

6 Concluding remarks

The ultramafic rocks of the Madawara Igneous Complex are enriched in Ir, Pt, Au, Ni, Cr and depleted in Cu, Al, Ca and V. The field relationship and geochemical study suggest two distinct categories. The geochemical and petrological data show that they are derived from variable degrees of partial melting of a primitive mantle composition. Based on major and trace-element systematics, and published experimental melting studies, it is inferred that these ultramafites represent high degree of partial melt equivalent to those that represent a batch melt extracted from a primitive fertile mantle composition at pressures between 1 and 3 GPa [1]. Different suites of magma were developed due to the variations in the degree of partial melting that are not easily related to a simple lithospheric column generated during a single upwelling event. The relatively high Ir and low Pd/Ir ratio are usually considered as signatures for high degree of partial melting of fertile mantle at moderate to greater depth. The high degree of partial melt would promote HREE enrichment in the melt, leaving a strongly LREE-depleted source. The high values of IPGE in a few samples and flat to slightly enriched LREE may be considered as having formed due to the dissolved sulphur and chloride fluid phases and carbonatite metasomatism.

Acknowledgement: The authors (MS and VB) are grateful to the Director, CSIR-National Geophysical Research Institute (NGRI), Hyderabad, for his support and permission to publish this paper. Profs. L.G. Gwalani and D.I. Groves are profusely thanked for critical evaluation

and providing useful suggestion for improving the final manuscript. This work forms part of the Ministry of Earth Sciences, Government of India funded project vide letter no. MoES/PO(Geosci)/4/2013.

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