Geochemistry of PGE in mafic rocks of east Khasi Hills, Shillong Plateau, NE India

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The mafic rocks of east Khasi Hills of the Meghalaya Plateau, northeastern India, occur as an intrusive body which cut across the weakly metamorphosed Shillong Group of rocks. Other than Shillong Group of rocks, high grade Archaean gneissic rocks and younger porphyritic granites are also observed in the study area. The studied mafic rocks of east Khasi Hills cover an area of about 4 km² and represent structurally controlled intrusion and varying grades of deformation. Structurally, these mafic rocks can be divided into massive type of mafic rocks, which are more or less deformation free and foliated type of mafic rocks that experienced deformation. Petrographically, this massive type can be classified as leuco-hornblende-gabbro whereas foliated type can be designated as amphibolite. On the basis of major oxide geochemistry, the investigated mafic rocks can be discriminated into high titanium (HT) (TiO₂ > 2 wt%) and low titanium (LT) types (TiO₂ < 2 wt%). Use of several geochemical variation diagrams, consideration of chondrite-normalized and mantle-normalized REE and PGE plots suggest role of magmatic differentiation (with almost no role of plagioclase fractionation) in a subduction controlled tectonic environment. The PGE trends of the studied rocks suggest relative enrichment of palladium group of PGE (PPGE) compared to iridium group PGE (IPGE). Critical consideration of Sm *vs.* La, Cu *vs.* La, Pd *vs.* La and Cu/Pd *vs.* La/Sm plots strongly favours generation of the parent magma at a columnar melting regime with batch melting of cylindrical column of the parent mantle to the tune of ~25%. The characteristic PGE behaviours of the presently investigated mafic rocks of east Khasi Hills can be typically corroborated as 'orogenic' (discordant) type. These rocks have an enriched mantle affinity with a co-magmatic lineage and they have been generated by slab-dehydration, wedge-melting and assimilation fractional crystallization process at a continental margin arc setting.

1. Introduction

Platinum group of elements (namely Pd, Pt, Rh, Ru, Ir and Os) are associated with mafic or ultra-mafic intrusions, which are products of crystallization of a parental magma containing several ppb levels of Pd or Pt (Momme *et al.* 2006). The platinum group of elements (PGE) are commonly subdivided into the Pt group (*viz.*, Pd, Pt, Rh) and Ir

group (*viz.*, Ru, Ir, Os). Ir group of PGE are normally compatible during moderate to high degree of batch melting of cylindrical column or during fractional crystallization. On the other hand, Au, Pd, Pt and Rh are normally incompatible and they would tend to be concentrated into the melt phase. However, Au, Pt group PGE, and Ir group PGE all have a tendency to be incorporated into the sulphide minerals (Vaillancourt *et al.* 2003). In other

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words, the extremely high distribution coefficient (K_D) for PGE between sulphide and magma suggest that PGE rich magmas can only form, if all the sulphides are melted out of the mantle (Momme et al. 2006). It is generally considered that the average degree of mantle melting should exceed 20%, assuming standard peridotite mantle contains 250 ± 50 ppm sulphur (McDonough and Sun 1995). The importance of PGE had been widely appreciated and those PGE were extensively studied to identify basic geochemical control for their formation and characterization in the earth's crust, which is in turn related to primary mantle derived magmatic process (Brüggmann et al. 1993; Rekhamper et al. 1999; Momme et al. 2002, 2003; Crocket and Paul 2004; Balaram 2008; Qi and Zhou 2008; Song et al. 2009; Keays and Lightfoot 2010; Mondal 2011). Geochemistry of PGE has also been used for elucidation of PGE deposits in different geological and tectonic settings (Li et al. 2009; Naldrett 2010). During magmatic crystallization, the chalcophile elements can be broadly divided into compatible group (Ni, Co, Os, Ir, Ru) and incompatible group (Cu, Ag, Au and Pd). During magmatic crystallization, the PG elements are partitioned more favourably to the sulphides rather than to Ni and Cu. Therefore, the magmas which have suffered removal of sulphides will be depleted in PGE (Barnes and Maier 1999). In general, the ultramafic igneous bodies (which have good prospect of PGE studies) could be broadly divided into two categories (Balaram et al. 2013) on the basis of their occurrence which are as follows:

- PGE as by-product in massive Ni–Cu deposits (Hudson et al. 1978; Lesher and Barnes 2009) and
- dominant PGE deposits with Ni–Cu as by-product (Maier et al. 1996; Maier 2005; Naldrett et al. 2009).

In contrast to the global scenario, attempts for PGE investigations in Indian context are still very limited (Srivastava et al. 2010; Balaram et al. 2013). However, PGE have been reported from several plutonic to hypabyssal Indian magmatic intrusions of Archean–Paleoproterozoic age (Balaram 2008; Mukherjee 2010). Some of the path-breaking studies in Indian scenario include Sukinda and Baula-Nausahi of Orissa in Singhbhum craton (Auge et al. 2002; Mondal et al. 2007), Sittampundi complex of Tamil Nadu, Southern Granulite Belt (Satyanarayanan et al. 2008, 2010b) and Hanumalapura of Karnataka in Dharwar Craton (Devaraju et al. 2005; Alapieti et al. 2008) and in Ikauna–Madawara areas on Bundelkhand Craton, central India (Farooqui and Singh 2006; Singh et al. 2010a, b; Satyanarayanan et al. 2010a, 2011;

Balaram et al. 2013). Beside these above studies, PGE investigations have also been carried out (in small areas though) in other parts of India (Mukherjee 2010; Nathan 2010; Dora et al. 2011). PGE studies have immense importance in unravelling petrogenetic aspects and tectonic implications of the source rock. Hence, in this paper, an attempt has been made to highlight the significance of newly generated PGE data on mafic rocks of east Khasi Hills. A fresh batch of 11 samples of mafic rocks of east Khasi Hills have been analyzed for major, minor, trace (including REE) and PGE contents and the output data have been presented in this paper. Such PGE studies on investigated mafic rocks of east Khasi Hills of northeastern India have been taken up for the first time and they play important role in constraining petrogenetic aspects considered in conjunction with REE and other data. The major, minor, trace, and PGE contents have been presented in tables 1–3.

2. Geological setting

The different rock units exposed in Meghalaya plateau are: Archean gneissic complex, Shillong Group of rocks (previously known as Shillong series), mafic rocks of east Khasi Hills (known as ‘Khasi greenstone’ in previous literature), porphyritic granite, Sylhet traps, and younger sediments. Geological succession of the Meghalaya plateau was presented by Mazumder (1986) based on the original work of West (1949). From the geological succession it is apparent that the mafic rocks of east Khasi Hills occur as intrusives into the Shillong group of rocks and might be invaded by the younger porphyritic granite. The generalized succession (after Mazumder 1986) is given below:

Table 1. Major oxide data (wt%) of Khasi mafic rocks.

Sp. no.	SH-11B	SH-29	SH-113	SH-119	SH-120	SH-13B	SH-26	SH-59	SH-116	SH-118	SH-108C
SiO ₂	49.55	49.15	49.57	50.67	49.28	52.03	48.19	56.34	49.23	48.27	49.02
TiO ₂	4.30	2.35	2.13	3.83	2.55	1.81	1.41	1.37	1.53	1.69	1.54
Al ₂ O ₃	10.79	12.38	11.55	11.14	12.57	11.55	13.13	12.58	12.82	13.05	15.10
*Fe ₂ O ₃	3.56	3.11	2.79	3.37	3.48	4.12	3.21	3.37	2.65	3.07	2.81
*FeO	9.98	8.70	7.80	9.43	9.75	11.53	8.99	9.43	7.42	8.59	7.88
MnO	0.34	0.22	0.21	0.29	0.22	0.28	0.22	0.19	0.18	0.19	0.20
MgO	6.35	8.28	10.12	6.28	6.58	3.32	9.61	2.02	10.60	10.60	9.05
CaO	8.22	8.72	8.67	8.51	8.22	6.59	9.04	4.51	9.79	9.02	9.01
Na ₂ O	3.52	2.81	3.09	2.24	2.76	4.01	2.14	4.35	2.06	2.12	2.09
K ₂ O	1.20	1.59	1.01	1.55	1.23	2.01	1.32	2.96	0.88	0.75	1.14
P ₂ O ₅	0.65	0.35	0.28	0.48	0.45	0.50	0.19	0.22	0.18	0.25	0.20
LOI	0.52	0.98	1.60	1.22	1.50	0.70	1.20	1.33	1.34	1.09	0.75
Total	98.98	98.64	98.81	99.00	98.60	98.45	98.65	98.66	98.69	98.69	98.79
Na ₂ O + K ₂ O	4.72	4.40	4.10	3.79	3.99	6.02	3.46	7.31	2.94	2.87	3.23
**Mg#	39	49	56	40	40	22	52	18	59	55	53
CIPW norm											
Quartz	0.89	—	—	6.52	1.48	1.10	—	5.12	—	—	—
Orthoclase	7.09	9.40	5.97	9.16	7.27	11.88	7.80	17.49	5.20	4.43	6.74
Albite	29.79	23.78	26.15	18.95	23.35	33.93	18.11	36.81	17.43	17.94	17.68
Anorthite	10.10	16.47	14.66	15.76	18.28	7.58	22.32	6.06	23.13	23.88	28.45
Diopside	21.48	19.82	21.28	18.94	15.99	18.45	17.23	12.69	19.46	15.49	12.06
Hypersthene	14.29	11.72	11.55	15.18	19.80	14.24	15.52	11.18	21.46	22.13	22.92
Olivine	—	6.70	8.88	—	—	—	8.70	—	3.49	5.49	2.73
Magnetite	5.16	4.51	4.05	4.89	5.05	5.97	4.65	4.89	3.84	4.45	4.07
Ilmenite	8.17	4.46	4.05	7.27	4.84	3.44	2.68	2.60	2.91	3.21	2.92
Apatite	1.51	0.81	0.65	1.11	1.04	1.16	0.44	0.51	0.42	0.58	0.46
D.I.	37.77	33.18	32.12	34.63	32.10	46.91	25.91	59.42	22.63	22.37	24.42

* FeO and Fe₂O₃ proportions discriminated using stipulated FeO/Fe₂O₃ ratios (Cox *et al.* 1979).

**Mg# = [MgO/(MgO+FeO)] × 100.

3. Petrographic notes

3.1 Massive type

It comprises coarse grained, inequigranular rocks, essentially composed of plagioclase, actinolite, relict pyroxene, biotite and opaque minerals (either magnetite or ilmenite, see Hazra *et al.* 2008). Carbonate minerals are seldom present. Plagioclase crystals are medium grained, lath shaped and highly saussuritized. Actinolite grains occur mostly as secondary after pyroxene (Ray *et al.* 2013). Some of the actinolite grains contain inclusions of lath shaped plagioclase and opaque minerals mostly magnetite. Sometimes quartz grains occur in association with recrystallised plagioclase as small, equidimensional irregular grains and also as inclusions within amphibole.

3.2 Foliated type

It includes medium grained variety consisting of plagioclase, actinolite with biotite, epidote, sphene, magnetite, ilmenite and apatite as accessory

minerals. In this type, plagioclase occurs as medium to fine grained lath shaped subidioblastic grains. Some of the grains are coarse in nature occurring as large porphyroblast. Most of the plagioclase grains are saussuritized and show cloudy appearance due to the presence of secondary minerals like muscovite, sericite and epidote. Actinolite is secondary in nature and formed from primary pyroxene. Sphene occurs as tiny idioblastic rhombic crystals whereas apatite occurs as elliptical grains. Well developed opaque grains are formed at the expense of relict pyroxene and actinolite. Texturally, these rocks show an overall nematoblastic texture defined by the prismatic amphibole grains. These mafic intrusives have undergone low grade metamorphic reconstitution (Ray *et al.* 2013).

It is important to note that both the massive type and foliated type have broadly identical mineral assemblages. But from field and petrographic studies it appears that (i) the massive type retains igneous textures and (ii) the foliated type is reconstituted due to later deformation. In view of retention of igneous signature, it would therefore be worthwhile to classify the massive

Table 2. Trace element data ($\mu\text{g/g}$)[§] of Khasi mafic rocks.

Sp. no.	SH-11B	SH-29	SH-113	SH-119	SH-120	SH-13B	SH-26	SH-59	SH-116	SH-118	SH-108C
Cr	0.73	4.07	4.10	1.21	2.06	0.73	2.98	0.60	3.15	3.25	3.11
Co	35.97	74.81	78.99	57.82	37.15	39.44	62.23	33.11	55.41	53.04	57.12
Ni	0.45	3.69	5.34	0.74	1.65	0.35	18.37	0.36	13.77	11.76	13.26
Rb	14.37	28.13	17.16	24.05	20.14	32.50	32.72	30.23	13.02	11.08	10.21
Sr	136.50	180.61	141.21	113.20	169.10	120.71	163.34	73.01	148.86	162.58	150.23
Cs	9.28	42.80	10.66	57.66	16.48	26.09	85.30	11.68	18.17	34.56	18.34
Ba	343.20	698.75	219.18	731.33	509.92	1170.11	290.40	890.04	307.70	186.10	306.70
Sc	68.16	59.24	58.65	70.72	54.53	41.85	42.03	25.76	43.77	51.05	42.77
V	346.49	630.40	544.45	680.43	505.09	13.35	347.22	4.76	382.76	445.35	381.76
Ta	0.17	0.08	0.07	0.12	0.10	0.19	0.04	0.59	0.04	0.05	1.04
Nb	0.60	0.26	0.21	0.41	0.35	0.66	0.13	2.30	0.14	0.16	0.24
Zr	57.33	15.34	23.71	41.31	27.93	93.42	5.95	192.75	6.72	10.06	7.72
Hf	1.72	0.54	0.73	1.26	0.87	2.80	0.22	5.57	0.24	0.33	0.28
Th	1.42	0.57	0.46	1.02	0.92	2.39	0.23	4.50	0.23	0.26	0.24
U	0.43	0.17	0.16	0.33	0.31	0.71	0.07	1.05	0.08	0.09	0.08
Y	58.30	34.13	28.98	48.22	43.63	78.24	16.65	110.22	17.18	20.39	18.17
Cu	34.09	205.09	234.84	482.31	226.20	24.10	21.06	98.35	107.78	163.99	108.78
Zn	87.55	70.30	89.38	99.83	68.93	97.27	76.87	76.52	54.22	59.38	52.22
Pb	20.24	13.91	14.93	16.72	24.01	18.01	22.27	30.06	13.60	20.05	14.60
Ni/Co	0.01	0.05	0.07	0.01	0.04	0.01	0.30	0.01	0.25	0.22	0.23
Ni/Cu	0.01	0.02	0.02	0.00	0.01	0.01	0.87	0.00	0.13	0.07	0.12
Th/Ta	8.63	6.88	6.72	8.68	9.34	12.49	5.79	7.67	6.03	5.38	0.23
Rare earth element data ($\mu\text{g/g}$) [§]											
La	4.71	2.10	1.75	3.00	3.07	5.43	1.01	12.80	1.05	1.23	1.10
Ce	11.96	5.70	4.79	8.06	8.13	14.98	2.80	31.88	2.84	3.33	2.93
Pr	1.68	0.80	0.67	1.13	1.13	1.98	0.39	4.13	0.39	0.47	0.34
Nd	11.35	5.41	4.59	7.64	7.49	12.76	2.70	25.77	2.71	3.31	2.80
Sm	3.87	1.91	1.62	2.71	2.57	4.34	0.96	8.16	0.97	1.18	0.97
Eu	1.19	0.79	0.64	0.98	0.95	1.43	0.39	2.54	0.42	0.52	0.43
Gd	5.82	3.05	2.50	4.21	4.00	6.59	1.50	11.90	1.55	1.84	1.54
Tb	1.21	0.65	0.53	0.92	0.85	1.46	0.32	2.41	0.33	0.40	0.34
Dy	7.60	4.30	3.59	5.88	5.52	9.78	2.07	15.08	2.16	2.59	2.16
Ho	1.82	1.07	0.91	1.51	1.41	2.50	0.54	3.61	0.55	0.67	0.53
Er	6.31	3.79	3.21	5.39	4.89	9.09	1.90	12.22	1.88	2.28	1.89
Tm	1.20	0.70	0.61	1.03	0.92	1.76	0.35	2.21	0.37	0.42	0.38
Yb	7.09	4.20	3.64	6.15	5.43	10.97	2.10	12.69	2.14	2.51	2.15
Lu	1.17	0.66	0.60	1.01	0.86	1.78	0.35	1.96	0.34	0.41	0.36
ΣREE	66.97	35.12	29.63	49.61	47.21	84.83	17.37	147.35	17.68	21.15	17.91
(La/Yb)	0.66	0.50	0.48	0.49	0.57	0.49	0.48	1.01	0.49	0.49	0.51
(La/Sm) _N	0.79	0.71	0.70	0.71	0.77	0.81	0.68	1.01	0.70	0.67	0.73
(La/Sm)	1.22	1.10	1.08	1.11	1.19	1.25	1.05	1.57	1.08	1.04	1.14

[§]($\mu\text{g/g}$)=ppm.

type of mafic rocks on the basis of IUGS recommended plagioclase–pyroxene–hornblende (actinolite) triangular diagram (Streckeisen 1976). The foliated type (as this is reconstituted), on the other hand, would be better classified in terms of triangular diagram (amphibole–plagioclase–quartz + biotite) recommended for basic metamorphic rocks (Suk 1983).

For massive type, the plots fall mainly within hornblende–gabbro field with a rare spill to pyroxene–hornblende–gabbro/norite field (Streckeisen 1976).

The modal data of the foliated type are clustered in the field of amphibolites (Suk 1983).

4. Analytical method and sample location/characterization

Major and minor oxides (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O and P_2O_5) were determined in all the samples by XRF (Phillips MagiXPRO-PW2440) at the CSIR–National

Table 3. Platinum group of elements data (ng/g)[§] of Khasi mafic rocks.

	SH-11B	SH-29	SH-113	SH-119	SH-120	SH-13B	SH-26	SH-59	SH-116	SH-118	SH-108C	Primitive mantle*	Chondrite value*
Ru	7.47	4.50	5.90	4.35	5.45	8.99	4.85	4.80	3.94	7.63	6.11	5	710
Rh	2.04	1.52	2.11	3.74	4.21	3.18	4.62	3.00	2.12	2.59	1.78	0.9	130
Pd	34.88	17.55	10.00	1.76	23.40	37.30	17.65	15.60	8.80	15.30	14.70	3.9	550
Ag	4586.50	1665.60	9679.00	677.20	11496.00	686.00	1938.62	501.80	3452.80	1333.40	1168.10	8	200
Re	4.66	23.31	79.20	435.00	90.40	49.42	23.55	212.00	21.44	21.50	94.10	0.28	40
Ir	0.97	0.66	0.41	0.28	0.51	0.54	0.48	0.59	0.49	25.00	0.48	3.2	455
Os	0.53	0.53	0.32	0.33	0.36	0.57	0.38	1.45	0.51	0.46	0.29	3.4	490
Pt	16.38	7.56	5.80	4.39	6.40	8.90	5.29	5.86	5.16	7.27	4.45	7.1	1010
Au	164.80	166.00	116.30	170.00	207.80	394.80	131.30	178.80	105.80	210.80	265.00	1	140
ΣPGE	4818.23	1887.23	9899.04	1297.05	11834.53	1189.70	2126.74	923.90	3601.06	1623.95	1555.01	32.78	3725
Pd/Ir	35.96	26.59	24.39	6.28	45.88	69.07	36.77	26.44	18.11	0.61	30.63	1.22	1.21
Pd/Pt	2.13	2.32	1.72	0.40	3.66	4.19	3.34	2.66	1.70	2.10	3.30	0.55	0.54
Cu/Pd	977.29	11686.21	23483.70	274193.86	9666.67	646.14	1193.37	6304.42	12248.18	10718.30	7400.27		

*Values quoted from McDonough and Sun (1995); [§](ng/g)=ppb.

Geophysical Research Institute, Hyderabad, India. International geochemical certified reference materials (CRM) from the US Geological Survey, the Canadian Geological Survey, the International Working Group, France and NGRI, India, were used to prepare calibration curves for major oxides. Some minor and trace elements including rare earth elements (REE) and PGE were determined by ICP-MS (PerkinElmer SCIEX ELANDRC-II) at NGRI, Hyderabad (Balaram and Rao 2003). The analysis of PGE and Au was carried out by following NiS-fire assay method with Te co-precipitation and ICP-MS analysis described by Balaram *et al.* (2006). Single isotopes were used for all elements; they were selected based on their abundance levels and the freedom from interferences from other elements usually present in rock samples. The detection limits of most of the elements including PGE were about 0.01 ng/ml, and the precision is better than 6% RSD for trace and REE, and is <10% RSD for PGE data.

Locations of analyzed samples are given in figure 1 and a brief petrographic note has been provided in table 4. MgO content of the samples varies from 10.60 to 2.02 and SiO₂ content ranges from 56.34 to 48.19 wt%. The wide variations of SiO₂ and MgO have been reflected in terms of both 'olivine' and 'quartz' normative characters of the rocks (tables 1 and 4). Another interesting point is the range of TiO₂ in the investigated rocks (TiO₂ ranging from 4.30 to 1.37 wt%). Based on TiO₂ (figure 2) content, the mafic rocks have been divided into two geochemical types, viz., low titanium (LT) type having TiO₂ < 2.00 wt% and high titanium (HT) type having TiO₂ > 2.00 wt%. The investigated samples show both LT and HT affinity (table 4). Table 4, however, reveals that the geochemical types (HT or LT) are irrespective of their field names, namely foliated and massive type of mafic rocks. In other words, massive dyke might have both HT and LT geochemical affinities (Farm and Leshar 1997; Korenaga and Kelemen 2000; Momme *et al.* 2006). The same thing is true for foliated type as well (table 4).

5. Results

5.1 Major, minor and trace elements

The major and minor oxides and trace element compositions (including REE and PGE contents) of the mafic rocks of east Khasi Hills are presented in tables 1–3. The accuracy of PGE data has been tested by analyzing international standards (CRM WMG-1 and CRM WRP-1) using same analytical set-up (table 5). The precision was assessed by analyzing three separate analyses of the CRM

Table 4. *A brief note on the Khasi mafic rocks.*

Sp. no.	Field name with structural mode	Mineral composition	CIPW classification	Mg#*	MgO (wt%)	SiO ₂ (wt%)	TiO ₂ (wt%)	Geochemical type
SH-11B	Massive dyke	Altered plagioclase, actinolite, relict pyroxene, biotite, opaque	Quartz normative	39	6.35	49.55	4.30	HT
SH-29	Foliated mafic	Actinolite, altered plagioclase, opx, biotite, opaque	Olivine normative	49	8.28	49.15	2.35	HT
SH-113	Contact between massive and foliated	Altered plagioclase, actinolite, biotite, opaque	Olivine normative	56	10.12	49.57	2.13	HT
SH-119	Massive dyke	Altered plagioclase, actinolite, biotite, sphene	Quartz normative	40	6.28	50.67	3.83	HT
SH-120	Massive dyke	Plagioclase (fresh and saussiritized), muscovite, amphibole, epidote, biotite	Quartz normative	40	6.58	49.28	2.55	HT
SH-13B	Massive dyke	Actinolite, altered plagioclase, opx, biotite, opaque	Quartz normative	22	3.32	52.03	1.81	LT
SH-26	Foliated mafic	Actinolite, altered plagioclase, opx, biotite, opaque	Olivine normative	52	9.61	48.19	1.41	LT
SH-59	Foliated mafic	Altered plagioclase, actinolite, carbonate, opaque	Quartz normative	18	2.02	56.34	1.37	LT
SH-116	Massive dyke	Plagioclase (fresh and saussiritized), muscovite, amphibole, epidote, biotite	Olivine normative	59	10.60	49.23	1.53	LT
SH-118	Massive dyke	Altered plagioclase, amphibole, biotite, relict pyroxene, sphene, opaque	Olivine normative	55	10.60	48.27	1.69	LT
SH-108C	Massive dyke	Plagioclase (fresh and saussiritized), quartz, muscovite, amphibole, epidote, biotite	Olivine normative	53	9.05	49.02	1.54	LT

HT: High TiO₂ (>2 wt%) mafic types; LT: Low TiO₂ (<2 wt%) mafic types, also see figure 2.
 *Mg# = $[\text{MgO}/(\text{MgO}+\text{FeO})] \times 100$.

WMG-1; the values were found to be <10% RSD. The investigated mafic rocks of east Khasi Hills are characterized by relatively low MgO (2.02–10.60 wt%), low Fe₂O₃ (2.65–4.12 wt%) and moderate Al₂O₃ (~10.79–15.10 wt%), low to intermediate SiO₂ (48.19–56.34 wt%) and variable TiO₂ (1.37–4.30 wt%). Na₂O and K₂O contents of the analyzed rocks show a spectrum of 2.06–4.35 wt% and 0.75–2.96 wt%. The mafic rocks have a relatively lower range of Ni from 0.35 to 18.37 ppm, while Cu content ranges from 21.06 to 482.31 ppm. Σ PGE of these mafic rocks, in general, have a range from 923.90 to 4818.23 ppb (with the exception of two samples having higher Σ PGE, to the tune of ~10,000 ppb).

In order to understand the geochemical variation, several oxides and trace elements were plotted against respective MgO wt% (figure 3a–d). TiO₂ shows, in general, a negative relation with MgO (figure 3a). Moreover, as discussed earlier,

Figure 2. TiO₂ vs. MgO diagram showing the distribution of analyzed plots into high Ti field (marked A) and low Ti field (marked B). Major oxides are in wt%.

this diagram forms an important basis for classifying the mafic rocks into high TiO₂ (>2 wt%) and low TiO₂ (<2 wt%) mafic types (table 4) (figure 2). SiO₂ (wt%) shows a declining trend with rising MgO (wt%) (figure 3b) while CaO (wt%) and Ni (ppm) show a positive trend with MgO (figure 3c and d). Figure 3(e) shows Σ PGE vs. Fe₂O₃ plot where a broad positive trend is indicated which suggests primary magmatic character. Plots of Cu vs. Ni and Pd vs. Ni show distinct negative trends (figure 3f and g) indicating role of magmatic differentiation.

The chondrite-normalized REE patterns of the mafic rocks have been shown in figure 4(a) with a generalized characteristic flat pattern for both LREE and HREE. Samples have a negative Sm anomaly; but none of the samples have positive Eu anomaly which suggests that there was no role of plagioclase fractionation. The negative Sm anomaly can be attributed to retention of garnet in the restite during mantle melting as it had earlier been discussed by Ray *et al.* (2013). They have categorically shown that during the production of the mafic magma, garnet was held in the source region during low degree of mantle melting. As the parent melt was generated in a ‘garnet removed’ scenario, the investigated Khasi mafic rocks show positive Sm anomaly. The flat HREE patterns indicate that garnet peridotite mantle was not the sole source of melting to generate the parent magma and possibly this also suggests melting above the garnet stability field. Primordial mantle normalized multi-element diagram (figure 4b) shows distinct peaks at Rb, Th, La and highly marked trough at Nb. The negative Nb anomaly suggests subduction zone magmatic regime (Sheraton *et al.* 1990; Zhao *et al.* 1995). In other parts of the world (as for example in Fosdik mountain, Antarctica), melting of the mantle at the continental margin arc-setting has given rise to abundant mafic intrusives (Satio *et al.* 2013). Interestingly, those mafic rocks bear very sharp negative Nb anomaly similar to our present study.

Table 5. Analytical data of geochemical standards WPR-1 and WMG-1. WPR-1 was used as calibration standard and WMG-1 was analyzed as an unknown to check accuracy (Balaram *et al.* 2013).

Element	Mass no.	Unit	WPR-1		WMG-1	
			Certified value	ICP-MS obtained value	Certified value	ICP-MS obtained value
Ru	101	ng/g	21.6	22.343 ± 2	27.6	35 ± 2
Rh	103	ng/g	13.4	13.067 ± 1	25.6	26 ± 1.5
Pd	105	ng/g	235.0	233.934 ± 10	307.8	382 ± 18
Os	192	ng/g	13.3	13.097 ± 1.2	14.6	NA
Ir	193	ng/g	13.5	13.671 ± 1.5	44.5	46 ± 2
Pt	195	ng/g	285.0	284.216 ± 15	892.0	861 ± 41
Au	197	ng/g	42.2	41.683 ± 3	82.4	102 ± 5

Note. (ng/g) = ppb.

Figure 3. Chemical variation diagrams: (a–c) Plots of major oxides against MgO; (d) plot of trace element (Ni) against MgO; (e) plot of total PGE [PGE(T)] against Fe₂O₃; (f) and (g) represent plots of Cu *vs.* Ni and Pd *vs.* Ni, respectively. Major oxides are in wt%. Cu and Ni values are in µg/g (ppm). PGE(T) and Pd values in ng/g (ppb).

Figure 4. (a) Chondrite-normalized REE patterns for the mafic rocks of east Khasi Hills (normalizing values of chondrite after Nakamura 1974). (b) Primitive mantle-normalized multi-element diagram for the Khasi mafics (primitive mantle data after Sun and Mc Donough 1989).

5.2 PGE distribution patterns in mafic rocks of east Khasi Hills

The mafic rocks of east Khasi Hills show Σ PGE concentrations from 923.90 to 4813.23 ppb (table 3) (with the exception of two samples having higher Σ PGE to the tune of $\sim 10,000$ ppb). Their Ir (0.28–0.97 ppb with a single exception where Ir = 25.00 ppb), Ru (3.94–8.99 ppb), Rh (1.52–4.62 ppb), Pt (4.39–16.38 ppb), Pd (1.76–37.30 ppb), and Au (105.8–394.8 ppb) display relatively wide variations. The Ni/Cu ratios of the mafic rocks (table 2) are found to be very low (0.002–0.87), which suggest that the mafic rocks do not have any affinity towards well-defined geological fields like ‘Chromitites’, ‘Flood basalts’, ‘Layered intrusions’, ‘Cu rich sulphides’, ‘Ophiolite komatiites’, etc. (Barnes et al. 1988).

Chondrite-normalized PGE plots (figure 5a) for the mafic rocks show a smooth pattern (Naldrett et al. 1979), similar to that found for rock-chondrite pattern (figure 4a). These PGE patterns usually provide useful clues about

Figure 5. (a) Chondrite-normalized PGE trends of mafic rocks of east Khasi Hills (normalizing values of chondrite after Mc Donough and Sun 1995). (b) Primitive mantle-normalized multi-element PGE trends for the mafic rocks of east Khasi Hills (normalizing values of mantle after Mc Donough and Sun 1995).

the fertile mantle, tectono-magmatic environments, fractionation-contamination history and fluid sulphide-silicate melt interactions during magmatic evolution (Barnes et al. 1985; Zhou et al. 2004a, b; Mondal et al. 2007; Alapieti et al. 2008). The PGE trends (figure 5a) of these mafic rocks suggest relative enrichment of Palladium group PGE (PPGE) (Rh, Pt, Pd) compared to Iridium group PGE (IPGE) (Ir and Ru). The rock/primitive mantle PGE trends (figure 5b) also show an enrichment of PPGE in comparison to that of IPGE.

6. Discussion

Siderophile (iron loving) elements are valuable geochemical tools because they have the potential to trace the mantle petrogenetic processes such as degree of batch melting of cylindrical column and an ambient melting regime (Momme et al. 2006; Woodland et al. 2002). Momme et al. (2002) showed that Pd, Cu, and La contents of both

high titanium (HT) and low titanium (LT) mafic types of flood basalt provinces of eastern Greenland increase with differentiation and they were of the opinion that even though most differentiated magmas of the HT type represent ~60% fractional crystallization, these magmas did not reach S-saturation. In order to test the variabilities of concentration of Cu, Pd, and La of the mafic rocks of east Khasi Hills, their respective concentrations were plotted with respect to Mg# values (figure 6); Cu, Pd, and La show a general trend of scatter with very feeble tendency of increment with advent of differentiation (that is with fall of Mg#), a trend that was advocated by Momme *et al.* (2002), for mafic rocks of east Greenland. In a general mantle melting model, it is assumed that the mantle contains 250 ppm S, the primary magma S-solubility is 1000 ppm S (Mathez 1976) and that the mantle melts 1% per kb decompression (Langmuir *et al.* 1992).

Modelling of PGE in magmas during mantle batch melting of cylindrical column has traditionally been based on batch melting of a columnar (cylindrical) melting regime (Keyas 1995; Barnes and Maier 1999). This model assumes that the mantle source melts uniformly in the entire melting regime and, as a consequence, these magmas extract all the sulphide hosted PGE from the mantle source once sulphide is exhausted. Therefore, it produces magmas with relatively high PGE concentration in high F (degree of melting) melts. In the columnar model, the mantle sulphide component is used up at $F \sim 25\%$ and Cu–Pd–Pt reached their maximum concentration at this stage. Batch melting of cylindrical column beyond ~25% only dilutes the concentration of these chalcophile elements. Ir concentration on the other hand, is also hosted by non-sulphide mantle phases and the compatible behaviour leads to steady incremental concentration during progressive batch melting of cylindrical column even beyond 25%. The Cu/Pd ratio of the melts formed by <25% batch melting of cylindrical column is >100,000 because Pd is much more efficiently retained in the residual mantle phase. When F exceeds 25%, Cu/Pd drops to the mantle value (around 6000).

The triangular melting regime (TMR) model is thought to be an appropriate analogue to melting beneath spreading ridges (Langmuir *et al.* 1992; Momme *et al.* 2003) and it assumes near fractional melting in 1% melting step (Rekhamper *et al.* 1999; Momme *et al.* 2003). The TMR assumes perfect corner flow (Langmuir *et al.* 1992) (where initial melting takes place when the mantle crosses the solidus and as long as the mantle upwells vertically). The degree of batch melting of cylindrical column increases with vertical displacement (following the general principles of Langmuir *et al.*

Figure 6. Plots of Cu, Pd and La against Mg#. Fields of HTS (high Ti-suite) and LTS (low Ti-suite) are taken from Momme *et al.* (2006). Both the HTS and LTS samples show increasing concentrations of Cu, Pd and La with decreasing Mg# (that is with advent of differentiation). Solid circle represents high Ti type and solid diamond represents low Ti type. Cu and La values are in $\mu\text{g/g}$ (ppm). Pd values in ng/g (ppb).

1992); low degree melts form in the distal and lowest parts of the TMR. Such low F magmas are S-saturated at source with low PGE concentration and high Cu/Pd greater than 100,000. Thus it is evident that the melting process is broadly controlled by CMR (cylindrical) with degree of batch melting of cylindrical column by and large greater

Figure 7. (a–c) Scatter diagram of Sm vs. La, Cu vs. La and Pd vs. La. F refers to mean degree of melting. CMR: columnar melting regime, TMR: triangular melting regime. Fractional crystallization modelling (10–60%) of a suitable high Ti-suite primary magma is shown in all diagrams (Momme *et al.* 2006). Cu, Sm and La values are in $\mu\text{g/g}$ (ppm). Pd values in ng/g (ppb).

Figure 8. Cu/Pd vs. La/Sm plot for mafic rocks of east Khasi Hills and mantle melting models. The triangular portion represents most high Ti-suite approximated by triangular melting regime (F~6%) (F means degree of melting). The square portion represents the low Ti-suite formed from a columnar melting regime (F~19–20%). This diagram is efficient to discriminate between magmas formed in different melting regimes (Momme *et al.* 2006).

than ~25%. However, Cu/Pd of some sample (SH 119) (table 3) indicates batch melting of cylindrical column even less than ~25%.

In order to further understand the nature of melting regime (CM or TM) and degree of batch melting of cylindrical column, the investigated mafic rocks (both HT and LT type) have been plotted in Sm vs. La, Cu vs. La and Pd vs. La diagrams (figure 7a–c). These diagrams include fields for CMR and TMR as well as fields for mafic rocks of eastern Greenland (Momme *et al.* 2006). Interestingly, all these diagrams (figure 7) indicate involvement of columnar melting regime with relatively higher degrees of melting (~20%). Therefore, combining evidences obtained from concentration of Cu, PGE and REE, it may be safely concluded that the parent mafic magma originated by high degree of melting (~20% to ~25%). Figure 8 depicts plots of Cu/Pd vs. La/Sm and this particularly helps to constrain nature of mantle melting. The triangular field corresponds to triangular melting regime (TMR) which has been generated by F ~ 6% equilibrium batch melting. The square field corresponds to the field of columnar melting regime (CMR) which has been produced by F ~ 20% equilibrium batch melting. The plots for investigated rocks (for both HT and LT types) are clearly discriminated to have been formed by CMR. Mungall and Brenan (2013) have shown that mid oceanic ridge basalts (MORB) are the products of pooled low and high degree fractional melt. A significant control on PGE fractionation in mantle

Figure 9. (a) Plots of mafic rocks in ϵ_{Nd} vs. $^{87}Sr/^{86}Sr$ ratio diagram basalt from various tectonic settings (after Hofmann 1997) are shown. Here DM=depleted mantle, FOZO=focal zone mantle, EMI and EMII=enriched mantle sources, HIMU=high source, UC=upper continental crust, OIB=oceanic island basalts, OPB=oceanic plateau basalts, NMORB=normal oceanic ridge basalts. UC: $\epsilon_{Nd} = -22$; $^{87}Sr/^{86}Sr = 0.725$. The composition of the upper continental crust is marked. (b) $f_{Sm/Nd}$ vs. $\epsilon_{Nd}(750 \text{ Ma})$ diagram, showing the isotopic evolution of the source of the study area (after Shirey and Hanson 1986) (solid square: massive type of mafic rocks, solid triangle: foliated type of mafic rocks).

derived magmas is exerted by residual alloy or PGE minerals in their source. Within-plate picrites are pooled products of larger degrees of fractional melting in columnar melting regimes. In case of MORB-genesis at low pressure, the mantle residual to batch melting of cylindrical column retains the signature of primitive mantle, inter-element ratios and PGE abundances until sulphide has been completely dissolved but then evolves to extremely high Pt/Pd and low Pd/Ir because Pt and Ir alloys form in the restite.

Naldrett (2009), on regional review of different PGE deposits of the world, identified several well marked petrotectonic settings which are broadly

‘intracratonic’, ‘intracratonic rift’, ‘rifted continental margin’, ‘triple junction related rift’, ‘craton boundary with volcano plutonic rocks’ and ‘orogenic’. Thus, the characteristic PGE behaviours of the presently investigated mafic rocks of east Khasi Hills can be typically classified as ‘orogenic (discordant) type’.

Ray *et al.* (2013), in a previous publication based on ϵ_{Nd} vs. $^{87}Sr/^{86}Sr$ suggested that the mafic rocks of the present study have an enriched mantle affinity and they have a co-magmatic lineage (figure 9a and b). Further, the parent melts were originated from an enriched mantle source. The overall Rb–Sr and Sm–Nd isotopic compositions

Figure 10. Schematic diagram illustrating the generation of mafic rocks of east Khasi Hills at a continental margin arc setting (data taken from Ray *et al.* 2013).

marked by strongly positive ε_{Sr} and negative ε_{Nd} strongly favour an enriched source mantle. The melting behaviour of mantle in orogenic setting is sensitively dependent on H_2O content and has been determined experimentally up to 40 kb for H_2O saturated conditions (6% H_2O). High degree of melting under H_2O -saturated condition characteristically yield magnesian, quartz-normative basaltic andesite to quartz tholeiite magmas (Green 1973) similar to the mafic rock found during the present investigation. Moreover, the degree of mantle melting is positively and linearly correlated with the proportion of H_2O . In fact, incremental water content in the source mantle depresses its solidus and may produce arc-like basalt (Stolper and Newman 1994; Ulmer 2001). In the present scenario (which entails involvement of columnar melting regime), addition of H_2O rich components, which might have been derived from fluids from the subducting slab is in conformity with the slab dehydration and wedge melting milieu (Ray *et al.* 2013). These investigated mafic rocks of east Khasi Hills were generated through slab-dehydration, wedge-melting and assimilation-fractional crystallization process at a continental margin arc setting (figure 10). Continental arc related Proterozoic mafic rocks are now being widely reported from China showing negative Nb and Ta anomalies (Zhou *et al.* 2002, 2004a, b). It is believed that, in the generation of such mafic rocks, magmatism at convergent plate setting is mainly responsible rather than upwelling mantle plume.

7. Conclusions

- The mafic rocks of east Khasi Hills of the Meghalaya plateau, northeastern India, occur as an intrusive body, which cut across the Shillong group of rocks.
- The investigated mafic rocks (on the basis of petrography) can be divided into ‘massive’ and ‘foliated type’. On the basis of geochemistry, these can be divided into high-titanium (HT) and low-titanium (LT) types.
- REE and PGE characters clearly indicate role of magmatic differentiation. The PGE behaviours suggest generation of parent magma at a columnar melting regime with batch melting (~25%) of cylindrical columns. These mafic rocks can be best described as ‘orogenic discordance type’ on the basis of PGE-modelling.
- The parent magma has enriched mantle affinity, controlled by slab-dehydration, wedge-melting and assimilation-fractional crystallization at a continental margin arc setting.

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