

Research Article

Different Origins of the Fractionation of Platinum-Group Elements in Raobazhai and Bixiling Mafic-Ultramafic Rocks from the Dabie Orogen, Central China

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Concentrations of the platinum group elements (PGEs), including Ir, Ru, Rh, Pt, and Pd, have been determined for both Raobazhai and Bixiling mafic-ultramafic rocks from the Dabie Orogen by fire assay method. Geochemical compositions suggest that the Raobazhai mafic-ultramafic rocks represent mantle residues after variable degrees of partial melting. They show consistent PGE patterns, in which the IPGEs (i.e., Ir and Ru) are strongly enriched over the PPGEs (i.e., Pt and Pd). Both REE and PGE data of the Raobazhai mafic-ultramafic rocks suggest that they have interacted with slab-derived melts during subduction and/or exhumation. The Bixiling ultramafic rocks were produced through fractional crystallization and cumulation from magmas, which led to the fractionated PGE patterns. During fractional crystallization, Pd is in nonsulfide phases, whereas both Ir and Ru must be compatible in some mantle phases. We suggest that the PGE budgets of the ultramafic rocks could be fractionated by interaction with slab-derived melts and fractional crystallization processes.

1. Introduction

The platinum group elements (PGEs), including Os, Ir, Ru, Rh, Pt, and Pd, are strongly siderophile and chalcophile elements. They have similar geochemical behaviors during magmatic processes. Traditionally, the PGEs are subdivided into two groups, the compatible IPGEs (Os, Ir, and Ru) and the incompatible PPGEs (Rh, Pd, and Pt) [1]. It has been suggested that the IPGEs are refractory and tend to be retained in the mantle peridotites during partial melting [2]. In contrast, the PPGEs are concentrated in the base metal sulphides (e.g., pentlandite, chalcopyrite), which are released to the melts along with the molten sulfide melts [2]. Because of their unique geochemical characteristics, the PGEs can be used to identify the magma sources and unravel the complex

petrogenetic processes, such as partial melting, melt percolation, and metasomatism in the mantle [1]. Mafic-ultramafic rocks have lower REE contents but higher PGE contents than other rocks, so the PGEs have advantages in studying their petrogenetic processes [1, 3–7].

In this study, we present the PGE data of both Raobazhai and Bixiling mafic-ultramafic rocks from Dabie Orogen, central China, to discuss their fractionation behaviours during magma evolution. The mechanisms of differentiation between these elements will be examined below, taking into account the geochemical affinities of the PGE and their partition in the mineral phases. The results also demonstrate that the PGEs can provide important information on the genesis of magmas.

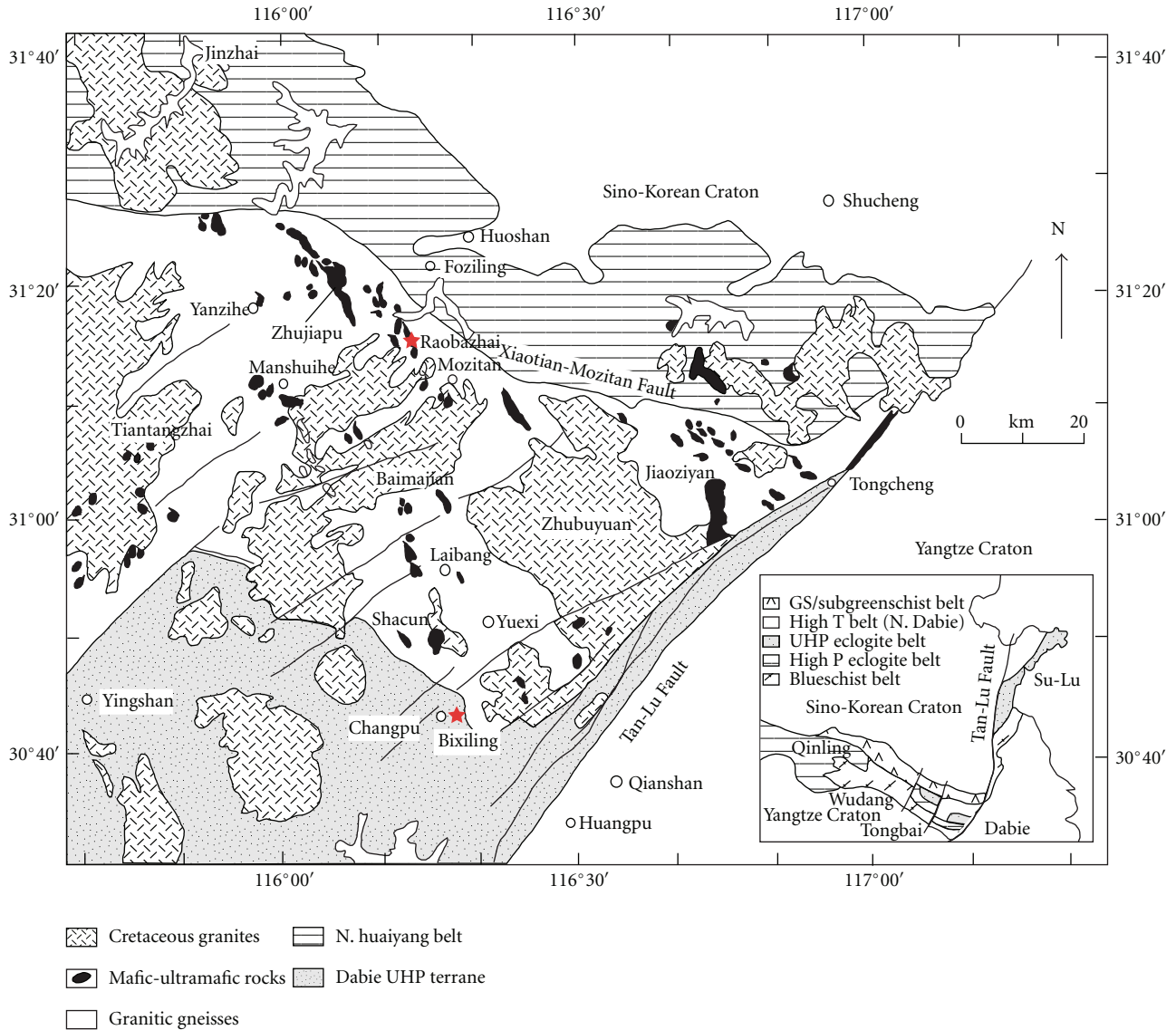


FIGURE 1: Simplified geological map of the Dabie Complex [8]. Sampling localities are roughly indicated by the names of Raobazhai and Bixiling.

2. Geological Background and Occurrence

The Dabie Orogen is the eastern segment of the Qinling-Dabie Orogen, which was formed by the continental collision between the Yangtze Craton and North China Craton (Figure 1). It has been subdivided, from north to south, into five main tectonic zones by several large-scale EW-trending faults [8, 10, 11].

The Raobazhai ultramafic massif is outcropped in the North Dabie high-temperature and ultra-high-pressure (HT/UHP) granulite-facies zone. It is located at ca 5 km south of the Xiaotian-Mozitan Fault (Figure 1), which is a major strike-slip fault along the eastern part of the Qinling-Tongbai-Dabie orogenic belt that might have witnessed the early evolutions of this orogenic belt [13]. Previous studies have suggested that the Raobazhai massif is a sheet-like peridotitic slice, which is in fault contact with the surrounding

amphibolite facies orthogneisses [14–16]. Migmatization can be locally observed in field. The long dimension of the massif is subparallel to the strike of the Xiaotian-Mozitan Fault and the regional foliation. The Raobazhai ultramafic body mainly consists of spinel harzburgites, with minor dunites and lherzolites [16]. They are all highly deformed and metamorphosed. Previous petrographic, geochemical, and thermobarometric studies have suggested that they represent a tectonic slice of the subcontinental lithospheric mantle [16–18]. Five representative samples have been selected in this study.

The Bixiling Complex is the largest (~1.5 km²) coesite-bearing mafic-ultramafic body in the Dabie Orogen, which occurs as a tectonic block that is enclosed within the foliated quartzofeldspathic gneisses in the eastern part of the Dabie UHP terrane (Figure 1). It consists predominantly of banded

eclogites and about 20 elongated lenses of garnet-bearing ultramafic rocks, for example, garnet peridotites, garnet pyroxenites, and wehrlites, which range from 50 to 300 m in length and from 5 to 50 m in width [19]. The contact between eclogite and ultramafic rocks is gradational. Field relationships and petrological evidence indicate a cumulate origin of the mafic-ultramafic rocks [19]. Therefore, the diverse rock types are considered, at least to a first approximation, as magmatically cogenetic [20]. The selected samples include three nattier blue eclogites (garnet, omphacite, kyanite, phengite, and rutile), two greenish black eclogites (garnet, omphacite, rutile, and quartz), and two garnet peridotites (olivine, orthopyroxene, clinopyroxene and garnet).

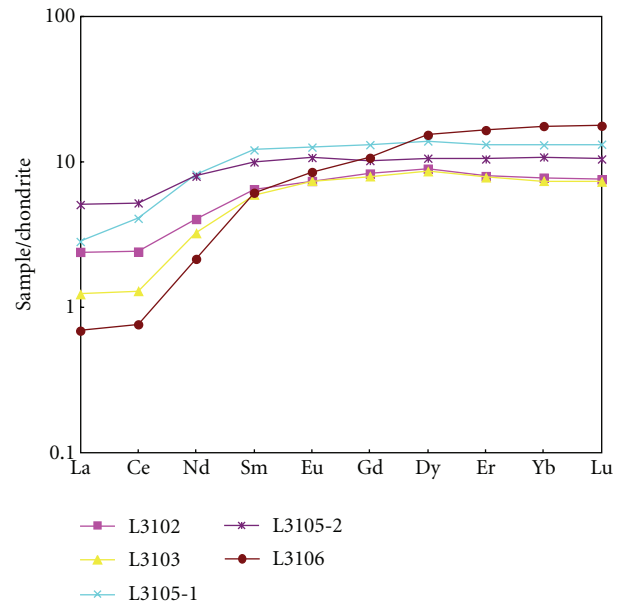
3. Materials and Methods

Samples were ground to 200 mesh powders using an agate mill. Whole-rock major elements were determined by X-ray fluorescence spectrometry (XRF) using a Phillips PW 2400 sequential XRF instrument at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). The analytical precision is better than $\pm 2\%$ for major oxides. Bulk-rock rare earth elements (REE) were analyzed on the Plasma PQ2 inductively coupled plasma mass spectrometry (ICP-MS) at IGGCAS. Replicate analyses of a monitor sample suggest that the reproducibility for the REE analysis is better than 3.5%.

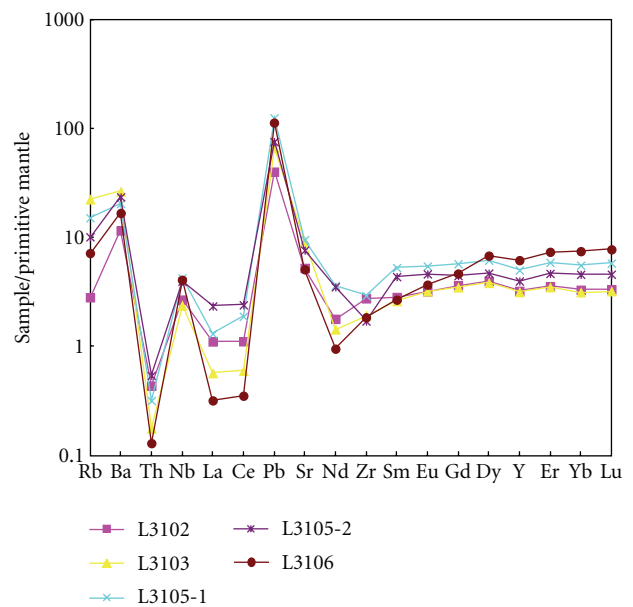
Whole-rock PGE contents were analyzed by fire assay (FA) method and measured on a Plasma PQ2 ICP-MS at IGGCAS. About 15 g sample powder, together with 20 g $\text{Na}_2\text{B}_4\text{O}_7$, 10 g Na_2CO_3 , 2 g Ni, 2 g S, and some SiO_2 , was fused in a fire-clay crucible at 1150°C for 2 hours. Then, the crucible was broken and a sulphide bead was recovered. The bead was dissolved in a Teflon beaker using 15 mL HCl. After the bead disintegrated into powder, 2 mL Te and 4 mL SnCl_2 were added into the solution. The solution was heated to become clear and then was filtered to collect the insoluble residue. The residue was cleaned and transferred into a Teflon beaker containing 2.5 mL aqua regia. Once the solution became clear, appropriate amounts of Re and Cd spike solutions were then added to the mixture, which was diluted with 50 mL H_2O for TJA Pro Excel inductively coupled plasma mass spectrometry (ICP-MS) determination. The detection limits, which are defined as average blank plus three standard deviations, for Ir, Ru, Rh, Pt and Pd were 0.002, 0.0086, 0.0048, 0.082, and 0.043 ppb, respectively. The PGE contents of most samples are higher than the detection limits, whereas both Ir and Ru contents of some samples are close to their detection limits. Replicate analyses of standard WPR-1 have respectively given values of 13.6 ppb Ir, 9.7 ppb Ru, 13.7 ppb Rh, 257 ppb Pt and 248 ppb Pd. The average element concentrations of replicate analyses of WPR-1 are within 10% of the certified value except Ir which is 13% lower.

4. Results

4.1. Raobazhai Mafic-Ultramafic Rocks. The major-, trace-elements and PGE concentration data of the Raobazhai



(a)



(b)

FIGURE 2: Chondrite-normalized REE patterns (a) and spider patterns (b) of Raobazhai mafic-ultramafic rocks (chondrite and primitive mantle values are from [9]).

mafic-ultramafic rocks are given in Table 1. The Raobazhai samples show consistent REE patterns (Figure 2(a)), that is, flat HREE patterns but variable depletion in LREE. Similar results have been reported in a previous study on the Raobazhai peridotites [9]. The REE are incompatible elements during partial melting of mantle peridotites; removal of basaltic components tend to decrease the REE contents of the mantle peridotites. In comparison, the LREE are more incompatible within mantle minerals than the HREE; therefore, the residual peridotites are depleted in LREE

TABLE 1: Major elements (wt%), trace elements (ppm), and PGE (ppb) concentration of Raobazhai and Bixiling mafic-ultramafic rocks.

Location sample	Raobazhai mafic-ultramafic rocks						Bixiling mafic-ultramafic rocks						
	L3102	L3103	L3105-1	L3105-2	L3106	L2906	L2907	L2912	L2908	L2909	L2910	L2911	L2911P
SiO ₂	46.81	47.99	46.23	45.64	44.72	50.65	50.66	46.88	42.96	42.97	42.11	38.34	38.42
TiO ₂	0.60	0.77	1.39	0.79	1.19	0.77	0.77	2.69	2.05	2.08	0.25	0.35	0.35
Al ₂ O ₃	13.94	11.94	13.33	14.11	15.02	16.64	16.09	13.95	13.57	13.84	8.85	6.59	6.61
Fe ₂ O ₃	12.99	11.21	12.35	12.87	14.82	9.31	9.34	18.83	20.89	20.63	14.3	15.76	15.91
MnO	11.00	11.53	10.45	10.83	9.46	0.15	0.15	0.24	0.14	0.14	0.2	0.21	0.2
MgO	0.23	0.18	0.20	0.21	0.28	7.47	7.76	5.49	7.08	7	24.65	28.78	28.71
CaO	11.72	12.20	12.04	11.48	11.50	11.92	12.01	9.26	12.02	11.99	5.33	3.08	3.07
Na ₂ O	2.11	2.11	2.13	2.28	1.82	2.1	2.21	2.37	1.23	1.22	0.21	0.32	0.31
K ₂ O	0.06	0.40	0.24	0.20	0.04	0.24	0.19	0.03	0.01	0.02	0.01	0.05	0.05
P ₂ O ₅	0.05	0.01	0.09	0.08	0.08	0.05	0.08	0.15	0.02	0.01	0.04	0.13	0.13
LOI	0.48	1.55	1.05	1.16	0.38	0.39	0.17	0.15	0.02	0.01	3.56	4.79	4.89
Total	99.99	99.90	99.49	99.64	99.32	99.7	99.42	99.24	99.39	99.48	99.51	98.4	98.66
Sc	42	44	49	46	56	40	39	50	55	57	15	12	11
V	257	326	347	272	318	225	232	389	911	918	99	116	102
Cr	1744	1258	1112	995	851	400	661	1			2673	7448	7313
Co	45	46	55	56	46	41	42	45	93	82	118	146	142
Ni	185	224	223	240	99	72	79	6	12	10	802	1062	1012
Cu	14	145	53	96	82	97	97	177	63	62	80	29	27
Zn	51	60	75	75	61	53	55	109	88	94	80	101	97
Ga	11	12	14	12	12	14	13	18	18	18	6	7	6
Rb	1.8	14.1	9.6	6.4	4.5	6.1	4.3	1.5	0.4	0.6	0.4	1.4	1.4
Sr	110	195	201	161	107	345	230	70	75	66	89	122	123
Y	15	14	23	18	28	10	10	19	7	7	5	5	5
Zr	31	22	33	19	21	7	10	17	11	12	11	14	13
Nb	1.9	1.7	3.0	2.8	2.9	0.5	0.5	0.1		0.1	0.3	0.6	0.6
Cs	0.6	0.5	0.6	1.0	0.9	0.4	0.3	0.1		0.1	0.3	0.2	0.2
Ba	81	184	143	164	117	87	74	27	11	17	14	36	48
La	0.8	0.4	0.9	1.6	0.2	3.1	2.1	3.2	0.3	0.3	1.7	4.6	4.2
Ce	2.0	1.1	3.3	4.3	0.6	7.1	3.8	10.2	0.8	0.8	4.3	9.7	8.6
Pr	0.4	0.3	0.8	0.8	0.2	1.2	0.6	1.7	0.2	0.2	0.8	1.4	1.2
Nd	2.4	1.9	4.9	4.8	1.3	5.8	2.7	9.2	1.4	1.4	3.6	6	5.5
Sm	1.26	1.15	2.34	1.93	1.19	1.54	0.91	2.55	0.93	0.98	0.95	1.23	1.16
Eu	0.54	0.54	0.91	0.78	0.62	0.66	0.46	1.09	0.43	0.45	0.32	0.37	0.37
Gd	2.16	2.07	3.41	2.65	2.77	1.76	1.42	3.34	1.24	1.28	0.9	1.15	1.09
Tb	0.43	0.41	0.66	0.52	0.65	0.32	0.29	0.59	0.22	0.24	0.15	0.18	0.17
Dy	2.9	2.8	4.5	3.5	5.0	2.1	2.1	3.9	1.5	1.6	1	1.1	1
Ho	0.6	0.6	0.9	0.7	1.1	0.4	0.4	0.8	0.3	0.3	0.2	0.2	0.2
Er	1.7	1.7	2.8	2.2	3.5	1.3	1.3	2.2	0.9	0.9	0.6	0.6	0.6
Tm	0.2	0.2	0.4	0.3	0.6	0.2	0.2	0.3	0.1	0.1	0.1	0.1	0.1
Yb	1.6	1.5	2.7	2.3	3.7	1.2	1.2	2.1	0.8	0.8	0.6	0.6	0.6
Lu	0.25	0.24	0.43	0.34	0.57	0.18	0.19	0.31	0.12	0.12	0.1	0.09	0.1
Hf	0.92	0.83	1.19	0.64	0.78	0.24	0.31	0.54	0.43	0.47	0.29	0.41	0.39

TABLE 1: Continued.

Location	Raobazhai mafic-ultramafic rocks				Nattier blue eclogite				Bixiling mafic-ultramafic rocks Greenish black eclogite				Garnet peridotite		
Ta	0.209	0.08	0.14	0.17	0.147	0.031	0.029	0.002	0.001	0.003	0.021	0.037	0.086		
Pb	7.4	12.2	23.0	13.9	20.8	2.7	0.9	9.7	2	1.3	2.5	7.7	7.8		
Th	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.6	0.2	0.2	0.2	0.3	0.3		
U	0.02	0.01	0.05	0.06	0.02	0.06	0.04	0.17	0.08	0.08	0.05	0.1	0.1		
Ir	0.153	0.060	0.257	0.180	0.360	—	0.003	—	—	—	0.837	1.18	0.52		
Ru	0.487	0.297	0.367	0.520	0.513	0.003	—	0.007	—	0.03	0.723	1.76	1.357		
Rh	0.237	0.327	0.447	0.343	0.633	0.108	0.083	0.002	0.109	0.142	0.665	0.648	0.422		
Pt	3.86	8.77	9.71	7.65	14.33	0.34	0.20	0.08	0.16	0.29	12.00	3.40	3.75		
Pd	4.86	31.98	4.44	7.69	23.38	0.47	0.03	0.16	0.09	0.50	7.42	8.67	8.34		

(—): lower than the limits of detection.

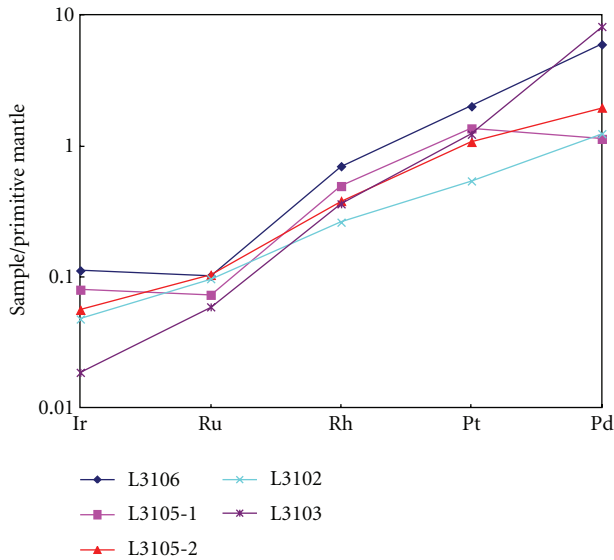
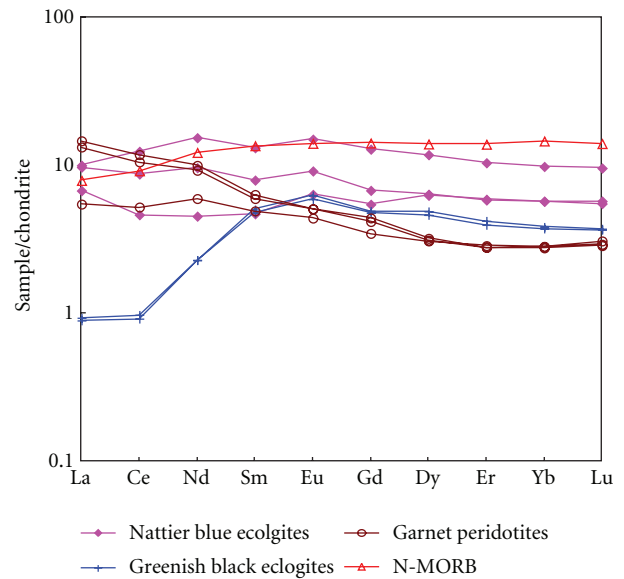


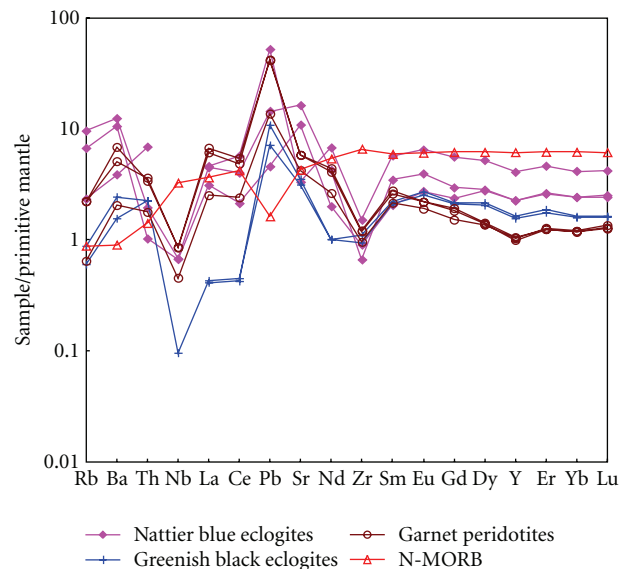
FIGURE 3: Primitive mantle-normalized PGE abundances for the Raobazhai mafic-ultramafic rocks (Normalizing values are after [1]).

relative to the HREE [21]. The Raobazhai peridotites are ubiquitously depleted in LREE, which suggest that they represent mantle residues after variable degrees of partial melting. In the (primitive mantle)-PM-normalized trace element diagram (Figure 2(b)), most Raobazhai samples show variable enrichment in LILE (e.g., Sr, Ba, and Rb). In particular, both Rb and Ba have concentrations ten times higher than those of the primitive mantle. The enrichment of LILE is an important feature of the Raobazhai mafic-ultramafic rocks. It has been suggested that enrichment of Rb and Ba in mantle peridotites could result from subduction-related metasomatism [21]. Zhi et al. [18] also concluded that the enrichment of LILE shown by the Raobazhai ultramafic rocks might be probably related to the slab-released fluids.

The total PGE contents of the Raobazhai mafic-ultramafic rocks range from 9.6 to 41.4 ppb, with an average of 24.4 ppb, which are higher than the estimated values of the primitive mantle (20.1 ppb) but similar to the Alpine-type orogenic peridotites, for example, Ronda (17.5–39.5 ppb) and the Beni Bousera (17.2–32.5 ppb) [22]. All Raobazhai mafic-ultramafic rocks display consistent and pronounced positive PGE patterns (Figure 3); they are strongly enriched in PPGEs (e.g., Pt and Pd) over IPGEs (e.g., Ir and Ru). Their Pd/Ir ratios vary from 17 to 65. Both Ir and Ru show good positive correlations with Ni, which suggest they behave as compatible elements during partial melting [23, 24]. In contrast, both Pt and Pd behave as incompatible elements. Therefore, the concentrations of Ir and Ru increase in the residual peridotites along with the melt extraction, whereas melts are enriched in both Pd and Pt relative to Ir and Ru. This suggests that the residual mantle peridotites should enrich in IPGEs over PPGEs, which is in contrast to the PGEs patterns shown by the Raobazhai mafic-ultramafic rocks. Therefore, the PGE budgets of the Raobazhai peridotites have been affected by processes other than partial melting.



(a)



(b)

FIGURE 4: Chondrite-normalized REE patterns (a) and spider patterns (b) of Bixiling mafic-ultramafic rocks (Chondrite, Primitive mantle, and N-MORB values are from [9]).

4.2. Bixiling Eclogites and Peridotites. Both REE and PGE data for five eclogites and two garnet peridotites from Bixiling are given in Table 1, and their distribution patterns are shown in Figures 4 and 5. All eclogites show remarkable positive Eu anomalies, suggesting that they were originally transformed from rocks with cumulated plagioclase. Three nattier blue eclogites selected in this study have quiet similar REE patterns with variable enrichment in LREE (Figure 4(a)), which are consistent with results reported in a previous study [20]. Compared to the normal mid-ocean ridge basalts (N-MORB), the Bixiling nattierblue eclogites have relatively low HREE contents and are slightly enriched in LREE.

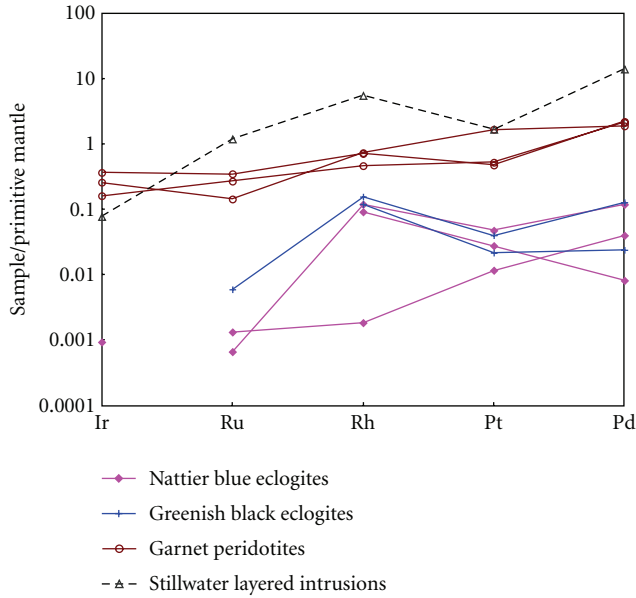


FIGURE 5: Primitive mantle-normalized PGE abundances for the Bixiling mafic-ultramafic rocks (Normalizing values are after [1]).

This suggests that they were not originally metamorphosed from N-MORB [20]. In contrast, the greenish black eclogites have lower REE contents and are strongly depleted in LREE (Figure 4(a)). This may be because the LREEs are incompatible in olivine, pyroxene, and garnet, but rich in liquid phase during the differentiation process, which make cumulation conglomerate facies that were formed by fractional crystallization have a relative depletion in LREE, and their HREE abundance also different from N-MORB. Compared to the eclogites, the garnet peridotites have lower HREE contents. They are variably enriched in LREE, which are also differed from both garnet peridotites entrained in kimberlites and Alpine-type orogenic peridotites [25]. The patterns suggest that these two garnet peridotites represent a more advanced crystal cumulation [20]. In the trace-element diagram (Figure 4(b)), both garnet peridotites and eclogites show pronounced negative Zr and Nb anomalies. Depletion of Zr has been suggested to be an indigenous feature of the upper mantle origin. The negative Nb anomaly is an important fingerprint of subduction-related magmas and continental crust. Based on Sr-Nd isotopes of the Bixiling eclogites and garnet peridotites, Chavagnac and Jahn [20] suggested that the Bixiling magmas were contaminated, probably by lower-crustal granulites that are depleted in LILE. The contamination did not significantly modify the Sr isotopes, but could result in lowering in ϵNd values and negative Nb anomaly as observed [20]. A previous study on oxygen isotopic compositions of silicate minerals in the Bixiling eclogites and garnet peridotites has suggested that the original magmas were derived from the upper mantle but probably contaminated by small amounts of crustal rocks during their differentiation processes [26].

The Bixiling mafic-ultramafic rocks display PGE patterns increasing from IPGEs to PPGEs (Figure 5), which

are different from that the mantle wedge xenoliths from Kamchatka [27] but very similar to the PGE patterns shown by the Stillwater layered intrusions [3]. The total PGE contents of garnet peridotites range from 14.39 ppb to 21.65 ppb. They have high Pd/Ir ratios up to 10 that are remarkably higher than that of the primitive mantle. It has been suggested that the typical mantle xenoliths and Alpine-type orogenic peridotites have flat PGE patterns, in which the PGEs are not fractionated [3]. Furthermore, partial melting would lead to depletion of PPGEs over IPGEs in the mantle residues, which should display flat to negative PGE patterns [3, 22, 28, 29]. Therefore, we suggest that the Bixiling garnet peridotites are refractory mantle residues after melt extraction but represent fractional crystallization products of mantle-derived melts, which is also supported by both trace-element and isotope compositions as discussed above.

The PGE patterns of both nattier blue eclogites and greenish black eclogites are distinguished from each other due to their very low contents of Ir and Ru, which are even lower than their detection limits. The Bixiling eclogites have low total contents of PGEs, which range from 0.25 ppb to 0.96 ppb. They display fractionated PGE patterns, which increase from IPGEs to PPGEs. This implies that they represent the late-stage products of magmatic differentiation. The PGE patterns of the Bixiling mafic-ultramafic rocks vary with the lithologies. The PGE content systematically decreases from the garnet peridotites to the eclogites, which show positive correlations with the MgO contents. Along with the magmatic differentiation, variations in PPGEs (i.e., Pt and Pd) are more limited than those observed for IPGEs (i.e., Ir and Ru). This suggests that the IPGEs are compatible during fractional crystallization and controlled by phases (e.g., metal alloys, chromite, olivine, or clinopyroxene) other than low-temperature sulphides [7].

5. Discussion

Although it has been suggested that the PGEs can be mobilized and fractionated by secondary post-magmatic events, such as hydrothermal alteration or weathering [30], it has been widely accepted that the PGEs are immobile under near-surface conditions. For example, Rehkämper et al. [31] suggested that the PGE budgets of abyssal peridotites have not been significantly disturbed by low-temperature alteration ($<150^\circ\text{C}$). Furthermore, it has also been suggested that the PGEs are immobile during serpentinization ($<600^\circ\text{C}$) processes, for which is commonly taken place under very reducing conditions [31, 32]. Büchl et al. [33] demonstrated that the PGEs are also significantly fractionated by hydrothermal fluids. Therefore, the fractionated PGE patterns observed in the Raobazhai peridotites cannot be ascribed to any secondary process; their PGE patterns reflect the magmatic processes occurred in the mantle, such as partial melting and melt percolation. The Raobazhai peridotites display enrichment in IPGEs over PPGEs, which is in stark contrast to the predicated PGE patterns of residual mantle peridotites. Hence, we believe that their PGE budgets have been affected by other processes than partial melting.

Recently, various studies have shown that the PGE budgets of mantle peridotites could be significantly disturbed by metasomatic processes, including melt/fluid infiltration and percolation [34–40]. Unlike hydrous fluids, slab-derived melts are capable of carrying HFSE (e.g., Zr, Hf, Nb and Ta) at some instances [41–43]. The mantle wedge could achieve such distinct geochemical signatures through extensive interaction with slab-derived melts [27]. It has also been suggested that slab-derived melts could fractionate the IPGEs from the PPGEs [27]. The positive relationship between Pt/Pd ratio and Hf concentration shown by the Raobazhai mafic-ultramafic rocks indicates that they have been metasomatized by slab-derived melts. Occurrence of hydrous mineral in Raobazhai mafic-ultramafic rocks also supports that they have been interacted with hydrous melts during subduction and/or exhumation [44]. Segregation of secondary sulfides from the volatile-rich melts into the mantle peridotites could increase their Pd abundances [34]. Enrichment of PPGEs over IPGEs in the Raobazhai peridotites could be interpreted by addition of secondary sulfides. In conclusion, both PGE and trace-elements data suggest that the Raobazhai mafic-ultramafic rocks have been metasomatized by slab-derived melts.

The partition coefficient of Cu between sulfide and silicate melts ($D^{\text{sulfide/silicate}}$) has been experimentally determined to be 900–1400, which is 3000–90000 for Pd [45]. The covariation between Cu and Pd is a useful indicator for sulphide fractionation. Because Cu is much less chalcophile than Pd, the Cu/Pd ratio should increase if sulphide is fractionated from a magma. In the Bixiling garnet peridotites and eclogites, The Cu/Pd ratio of the Bixiling garnet peridotites varies from 10^3 to 10^4 , whereas it ranges from 10^5 to 10^7 for the Bixiling eclogites. As shown in the Cu/Pd versus Pd diagram (Figure 6), the Cu/Pd ratios of the garnet peridotites are close to the mantle values, which suggests that they have not experienced sulphide segregation prior to their emplacement [12]. If sulfide segregation had occurred in the Bixiling garnet peridotites, then their Cu/Pd ratios should be greater than the normal mantle values because Pd is preferentially partitioning into sulfide liquid relative to Cu. The PGE patterns of the Bixiling eclogites are consistent with sulfide segregation from these samples. That is, the Cu/Pd ratio becomes elevated along with the increase of fractional crystallization.

Sulfide segregation is an inevitable process during fractional crystallization [7]. Fractional crystallization tend to decrease the FeO content in the residual magma, which might result in S saturation and thus formation of immiscible sulfide liquids [46]. The Bixiling garnet peridotites and eclogites were formed along with fractional crystallization, during which the S contents of the magmas became saturated to segregate sulfides. Removal of sulfides would lead to depletion of Pd in the residual magmas and increase in Cu/Pd ratio (Figure 6).

The Bixiling mafic-ultramafic rocks display a positive correlation between Ru and Pd, indicating that both elements are partitioning into the same kind of sulfides. The PGE data of the Bixiling mafic-ultramafic rocks suggest that

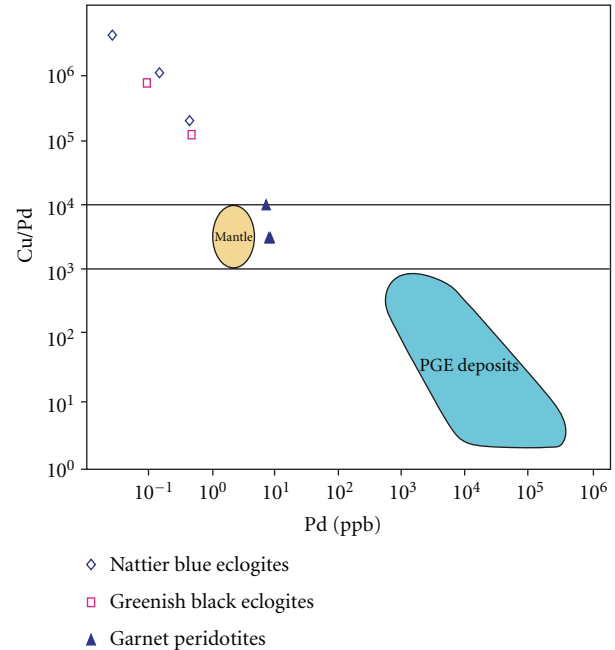


FIGURE 6: Plots of Cu/Pd ratios versus Pd for Bixiling mafic-ultramafic rocks (filled fields are after [12]).

the PGEs can be fractionated during magma differentiation. Both Ir and Ru are compatible in a nonsulfide phase, in which Pd is incompatible. Both petrological and geochemical studies have suggested that olivine [47, 48], spinel or chromite [49, 50], and refractory alloys [51, 52] are the most likely candidates [7]. However, modeling calculations have shown that neither olivine nor clinopyroxene can significantly fractionate the PGEs [7]. It has been suggested that the PGEs are not incorporated into the lattice of chromites but concentrated within tiny inclusions, such as sulfides or alloys. Therefore, chromites themselves are not able to fractionate the PGEs [52]. Keays [2] has suggested that both Ir and Os exist as Os-Ir alloys in the upper mantle. These tiny alloys can be physically segregated into the magmas during partial melting. They can be trapped within the crystallized silicate (e.g., olivine) and oxide (e.g., chromite) minerals, which results in the fractionation of the IPGEs from the PPGEs. Tredoux et al. [53] has also suggested that the PGEs and other nonlithophile elements could be aggregated together as clusters in silicate magmas. Theoretically, the IPGEs (i.e., Os and Ir) are more likely to form clusters than the PPGEs (i.e., Rh and Pd) [53]. Therefore, we explain the enrichment of IPGEs rather than PPGEs in the Bixiling mafic-ultramafic rocks as entrainment of such clusters in these samples. The PGE alloys have been rarely reported in mantle peridotites, which could be due to their extremely small sizes. Microinclusions of Os, Ir, and Pt have been identified in Merensky sulfides, which support the occurrence of PGEs as polymetallic clusters in silicates [54]. However, future studies are still needed to investigate the PGE-rich phases in the mantle.

6. Conclusions

On the basis of the geochemical compositions of both Raobazhai and Bixiling mafic-ultramafic rocks, in particular PGE data, we can draw the following primary conclusions:

- (1) The Raobazhai mafic-ultramafic rocks show consistent PGE patterns, in which the PPGes (e.g., Pt and Pd) are strongly enriched over the IPGEs (e.g., Ir and Ru). Such patterns are in stark contrast to those displayed by refractory mantle residues after melt extraction, in which the IPGEs are enriched over the PPGes. This indicates that the PGE budgets of the Raobazhai mafic-ultramafic rocks have been affected by processes other than partial melting. Both REE and PGE data support that the Raobazhai mafic-ultramafic rocks have interacted with slab-derived melts during subduction and/or exhumation.
- (2) The Bixiling mafic-ultramafic rocks were formed through fractional crystallization and cumulation from magmas. The PGE patterns shown by the Bixiling mafic-ultramafic rocks were produced by the magmatic differentiation processes, during which fractional crystallization of silicate minerals and segregation of immiscible sulfide liquids are involved. The fractionated PGE patterns of the Bixiling mafic-ultramafic rocks reflect that Pd is incompatible in the nonsulfide phases, whereas both Ir and Ru are compatible in some mantle phases.

Acknowledgments

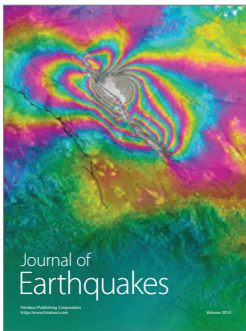
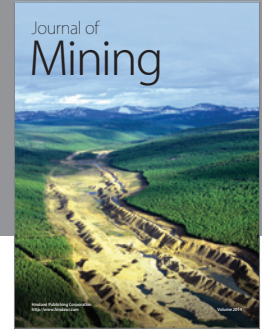
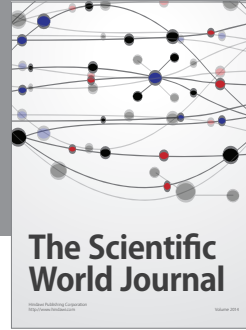
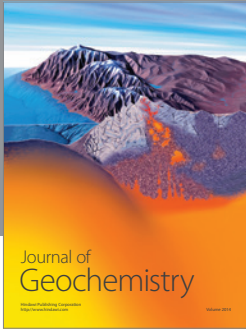
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