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The platinum-group element geochemistry of chromitites and silicate rocks from Swat, northwestern Pakistan

MOHAMMAD ARIF[1] & CHARLIE J. MOON[2]

[1]Department of Geology, Peshawar University, Peshawar, Pakistan

[2]Department of Geology, Leicester University, Leicester LE1 7RH, UK

ABSTRACT: *The concentrations of the platinum-group elements (PGE) and Au were determined in a limited number of samples which represent chromitites, altered ultramafic and mafic rocks of the Swat valley ophiolite. The PGE characteristics of the chromitites mostly conform to the trend exhibited by the podiform chromitites. However, being sulphide-poor and containing Cr-rich chromite, the Pd content of one of the samples is anomalously high compared to similar chromitites from other areas. This enrichment in Pd is probably caused by a localized hydrothermal activity. The Ir content of the chromite-poor, altered ultramafic rocks is remarkably uniform (4 ppb) and close to the values in mantle materials but their Pd (10 ± 3.7 ppb) and Au (5 ± 3.5 ppb) abundances are distinctly higher than the latter. These features of PGE and Au concentration of the host ultramafic rocks are consistent with an origin involving partial melting followed by hydrothermal alteration.*

INTRODUCTION

There are indications from elsewhere that ultramafic rocks, especially chromitites, of ophiolite complexes may contain platinum-group elements (PGE) in concentrations of economic significance. For example, the results of a reconnaissance work by Miller et al. (1991) show gold and PGE enrichment in the Jijal mafic-ultramafic complex. Although rocks of the Jijal complex exhibit layering, their geological setting is almost identical to that of the presently investigated ones. Locally, the variably altered ultramafic rocks of the Swat valley ophiolite are invaded by hydrothermal fluid(s) producing ubiquitous quartz veins which contain fuchsite, tourmaline and/ or emerald. The quartz-fuchsite veins in the Archean Abitibi greenstone belt of Canada carry high grade gold mineralization (Moritz et al., 1990). Furthermore, the occurrence of As-rich phases (maucherite and gersdorffite) in some of the studied rocks indicates their enrichment in As—a geochemical signature for Au and PGE mineralization (Boyle & Jonasson, 1973; Arif, 1994). Besides, the relative abundance of PGE (especially the Pd/Ir ratio) may serve as a useful petrogenetic indicator in identifying the nature of magmatic (fractional crystallization and partial melting) processes (Barnes & Picard, 1993). Due to these reasons, the Au and PGE contents of selected samples, representing different lithologies of the Swat valley ophiolite, have been determined and discussed.

SAMPLES AND METHODS

The platinum-group element and gold contents of nine samples (including three chromitites, four serpentinized peridotites, and one sample each of carbonated ultramafite and gabbro) were determined. The sample were collected from different occurrences of the ophiolite (see Table 1; Fig. 1).

The analyses were carried out by using nickel sulphide fire assay and ICP-MS at Genalysis Laboratory Services Pty. Ltd., Maddington, Western Australia. The recovery of the six PGEs is usually extremely good. However, the recovery rates for Au are not so good. The errors during the ICP-MS analysis are of the order of ±5 %. The analysis of the international reference material (SARM-7), performed by Prichard and Lord (1990), indicates a fairly high degree of accuracy of the method employed.

RESULTS

The contents of noble metals, i.e. the platinum group elements (PGE) and gold, are listed in Table 1 and displayed graphically in Figure 2. The PGE contents of ultramafic rocks, especially chromitites, seem to be related to the composition of their chrome spinel (Page et al., 1982a, b; Bacuta et al., 1990; Konstantopoulou & Economou-Eliopoulos, 1991). In order to explore such a possibility, the components of chrome spinel which are believed to be important in terms of PGE concentration are also given in Table 1.

The overall range of the different platinum group elements in the samples of chromitites are (ppb): Os = 26-36, Ir = 28-32, Ru = 72-94, Pd = <2-26 and Pt = <2-10. The concentration of Rh is the same in all the three samples (11 ppb). Although Pd and Pt are negligible (<2ppb each) in two of the chromitite samples (S5 and S21), the third one (Sp5) contains substantial amounts of these two elements (26 & 10 ppb, respectively) as well as Au (15 ppb). On the other hand, the Pd-, Pt-free chromitites have relatively high Os and Ru contents.

The ranges of different PGEs in the chromite-poor, altered ultramafic rocks are as follows (all in ppb): Os = 2-8, Ir = 4 in all the samples, Ru = 10-16, Rh = 1-3, Pd = 6-14, and Pt = 4-12. The concentration of Au ranges from <5 to 10 ppb. Pt (4 ppb) and Ru (2 ppb) are the only detectable PGEs in the sample of gabbro.

A plot of chondrite (C1)-normalized PGE concentrations in the studied samples of chromitites is shown in Figure 2a. These chondrite (values in Naldrett & Duke, 1980)-normalized patterns have been compared with the range exhibited by chromitites from stratiform (Bushveld and Stillwater) and ophiolite complexes. The chondrite-normalized values of PGE in the altered ultramafic rocks and the sample of gabbro are illustrated in Figure 2b.

The relationships of the PGEs with each other as well as with Ni and Cu contents (important indicator elements for PGE concentration; see Prichard & Lord, 1990) in the rocks were also studied (Fig. 2c-h). The values of Os and Ru in chromitites are positively correlated. Similarly, the concentrations of Pd and Pt in the altered ultramafic rocks show a sympathetic relationship. However, neither the compatible (Os, Ir, Ru) nor the relatively less compatible (Rh, Pd, Pt) PGEs show any relationship with either Ni or Cu concentration in the studied samples. It is most probably because the majority of the PGEs occur as discrete platinum-group metal sulphide, arsenide, or alloy phases, rather than in specific structural sites in the oxides and silicates. Besides, the lack of correlation between PGE concentration with the 'indicator' minerals could, in part, be due to the fact that the available data are too scarce and inadequate to yield a meaningful variational trend.

DISCUSSION

The geochemical behaviour of PGE is controlled by three main processes: partial melting, fractional crystallization and alteration (cf. Barnes et

TABLE 1. BULK-ROCK PLANTINUM ELEMENT AND GOLD CONCENTRATIONS (PPB) AND COMPOSITION OF CHROME SPINEL

Sample Type[1]	S5 Chr	S21 Chr	Sp5 Chr	B27 Gab	B31 SPdt	L1 Spdt	L28 Spdt	M9 CUM	Sp10 Spdt
Os	36	32	26	<2	8	8	2	6	6
Ir	32	28	30	<2	4	4	4	4	4
Ru	94	86	72	2	16	14	12	10	12
Rh	11	11	11	<1	2	3	2	1	2
Pd	<2	<2	26	<2	14	12	12	6	6
Pt	<2	<2	10	4	12	12	8	4	8
Au	5	<5	15	<5	10	5	<5	5	5
ΣPGE	173	157	175	6	56	53	40	31	38
Ir/Au	6.4	—	2.0	—	0.4	0.8	—	0.8	0.8
Pd/Ir	—	—	0.3	—	3.0	3.0	2.0	0.1	2.0
Ni ppm	1684	1398	1755	206	2295	2028	1770	2363	1814
Cu ppm	18	12.9	23.5	200	6.9	4.1	21	11.6	16.7
Average composition of chrome spinel									
[2]Cr #	71.8	71.1	90.5	n. a.	55.4	52.3	n. a.	85.4	n. a.
[3]Mgt #	68.6	36.4	38.2	n. a.	56.2	57.3	n. a.	4.4	n. a.
[4]TiO_2	0.16	0.16	0.43	n. a.	0.05	0.13	n. a.	0.22	n. a.

[1] Chr = chromitites; S5 and S21 represent the two pods of chromitite in the Barkotkai village, and Sp5 is from the Spin Obo area. Gab = a gabbroic rock from the Barkotkai area. SPdt = chromite-poor sepentinized peridotites; L1 and L28 are from the south of the Lilaunai village, B31 represents the serpentinized rocks of the Barkotkai village and Sp10 represents the rock south of the Kuh village.

CUM = a carbonated ultramafic rock, mainly consisting of magnesite + quartz, from the Mingora emerald mines area; [2] Cr # = 100 x Cr/(Cr + Al); [3] Mg # = 100 x Mg/(Mg + Fe^{2+}); [4] weight percent; n. a. = not analysed because chrome spinel grains have been completely altered to ferritchromite.

al., 1985). Ir is known to behave as a highly compatible element in magmatic processes (partial melting and fractional crystallization). This behaviour of Ir is generally attributed to (1) its high melting point and (2) its accommodation in the structure of olivine (Ross & Keays, 1979; Crocket, 1979). The lack of a positive correlation between Ni and the compatible PGEs in the

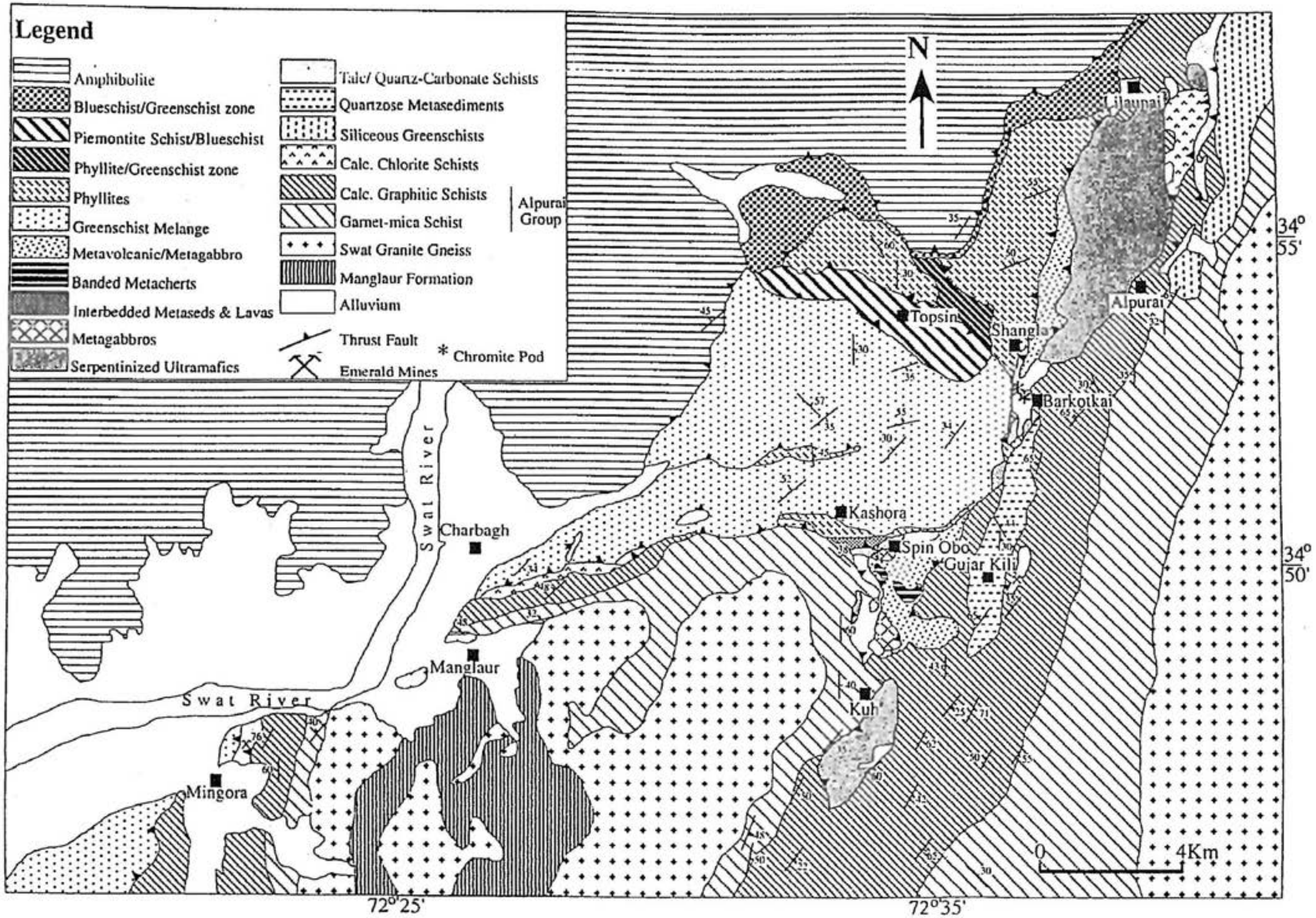

Fig. 1. Geological map of the Mingora-Lilaunai area, Swat, northwestern Pakistan (modified after Kazmi et al., 1984).

investigated samples does not support the second possibility (see also, for example, Mitchell & Keays, 1981; Barnes et al., 1985). Therefore, it appears that Ir occurs as minute refractory metal particles in the studied samples (see also Mitchell & Keays, 1981).

Being the least compatible PGE, Pd behaves opposite to Ir in magmatic processes. The contrast in compatibility between Ir and Pd is confirmed by the recently calculated bulk partition coefficients of the PGEs (6, 2, 0.6 and 0.2 for Ir, Rh, Pt and Pd, respectively) (Barnes & Picard, 1993). Also, whereas the reverse is true for Pd, Ir is believed to be the most resistant to alteration and least mobile among the noble metals in hydrothermal and other fluids (see Prichard & Lord, 1990).

The geochemical behaviour of Pt (as well as Au) is believed to be similar to that of Pd whilst Os and Ru appear to behave more like Ir. That is why the noble metals are treated as two separate subgroups: Os-Ir-Ru (refractory and compatible) and Pt-Pd-Au (less refractory and, therefore, relatively incompatible). The relative total concentration of these two subgroups of the noble metals serves as a distinguishing criterion between the two types of chromite deposits; i.e. stratiform chromite (chromitites occurring in layered intrusions) and podiform chromite (chromitites from ophiolite complexes).

Except a few rare cases (e.g. Shetland ophiolite) (Prichard et al., 1986), Ru followed by Os and Ir (the refractory PGEs) are reported to be the most abundant PGEs in podiform chromitites from most ophiolite complexes, whereas Pt, Pd (and Rh) dominate the concentrations of PGE in stratiform chromitites. That is why the conventional chondrite-normalized PGE patterns of podiform chromitites show a negative slope and that of stratiform chromitites exhibit positive slope (Fig. 2a).

The PGE contents and, therefore, the chondrite-normalized patterns of two of the chromitites studied are similar to podiform chromitites. The chondrite-normalized pattern of the third sample (Sp5) is different because of anomalously high concentration of Pd. In addition, the Pt and Au concentrations in Sp5 are distinctly higher than in the other two chromitites from the study area.

The relative abundance of the different PGEs in one of the chromitites from the study area is in accord with the Acoje chromitites where high Pd, Pt contents are also found to be associated with high-Cr chromitites (Bacuta et al., 1990). The general range in Cr # (60 to 80) of chromite in the Pd and Pt-enriched chromitites suggests that the other two chromitites from the study area should also contain high concentrations of Pd and Pt. It should, however, be noted that the Pt and Pd concentrations in the Acoje chromitites are rather high and are associated with interstitial base metal sulphides. In contrast, chromitite Sp5 with anomalously high Pd, Pt and Au contents does not contain any base metal sulphides. The Pd and Au concentrations in Sp5 are higher than in virtually all the previously reported sulphide-poor chromitites from ophiolite complexes (see Fig. 2a). Therefore, it is very hard to explain this anomaly in terms of any magmatic processes. Alternatively, it is suggested that the enrichment is probably a result of hydrothermal alteration.

The Ir concentration in the altered, chromite-poor ultramafic rocks of the present investigation is uniform (4 ppb) and close to the values in mantle materials (ultramafic nodules of spinel lherzolite composition) (4.2 ppb, Morgan & Wandless, 1979; 3.4 ppb, Jagoutz et al., 1979; 3.6 ppb, Mitchell & Keays, 1981). However, the amounts of Pd (6-14 ppb) and Au (5-10 ppb) in the studied samples are higher than the average abundances of these metals in ultramafic nodules

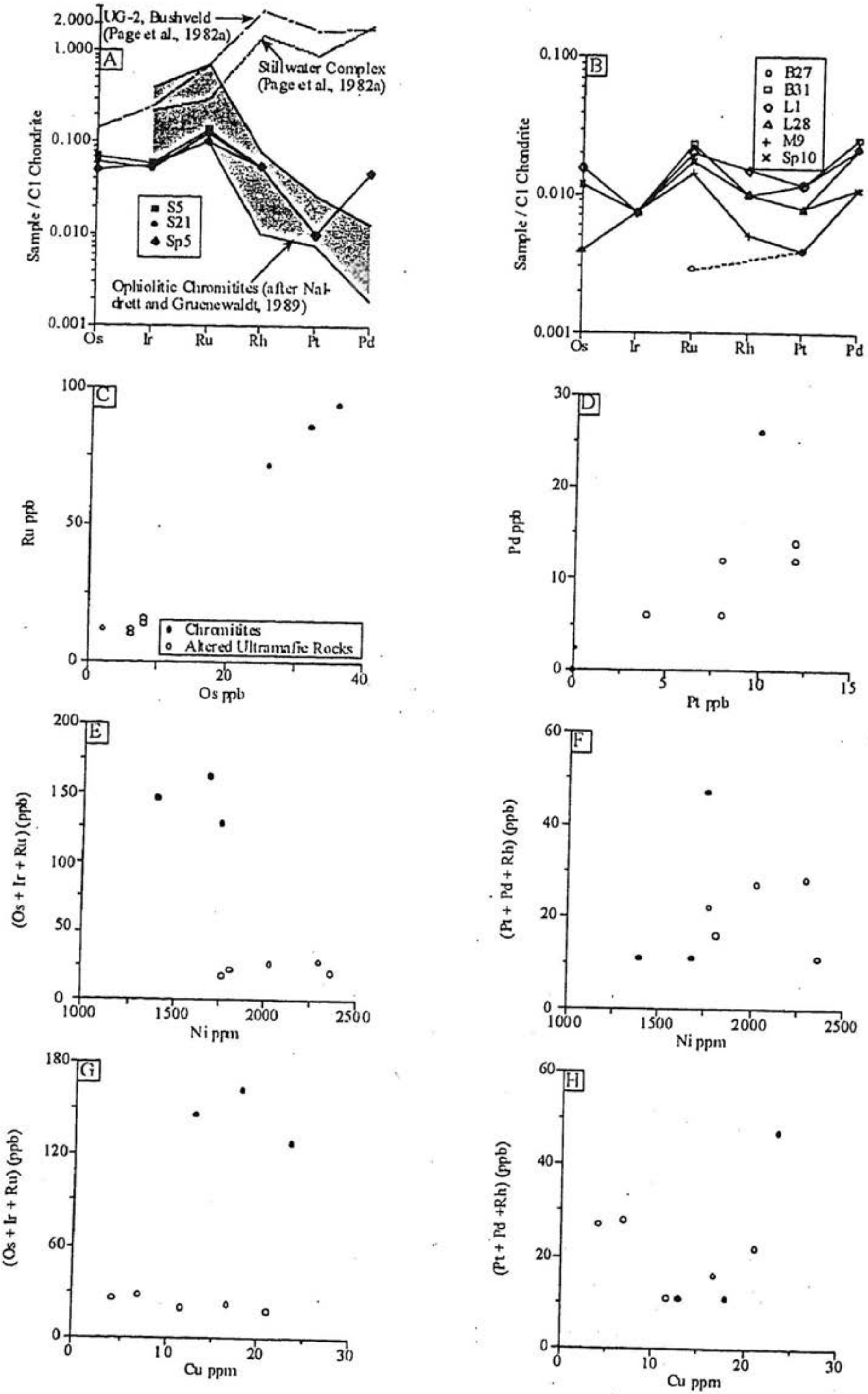
A
UG-2, Bushveld (Page et al., 1982a)
Stillwater Complex (Page et al., 1982a)
Ophiolitic Chromitites (after Naldrett and Gruenewaldt, 1989)
S5
S21
Sp5
Sample / C1 Chondrite
2.000
1.000
0.100
0.010
0.001
Os
Ir
Ru
Rh
Pt
Pd
B
B27
B31
L1
L28
M9
Sp10
Sample / C1 Chondrite
0.100
0.010
0.001
Os
Ir
Ru
Rh
Pt
Pd
C
Chromitites
Altered Ultramafic Rocks
Ru ppb
Os ppb
100
50
0
0
20
40
D
Pd ppb
Pt ppb
30
20
10
0
0
5
10
15
E
(Os + Ir + Ru) (ppb)
Ni ppm
200
150
100
50
0
1000
1500
2000
2500
F
(Pt + Pd + Rh) (ppb)
Ni ppm
60
40
20
0
1000
1500
2000
2500
G
(Os + Ir + Ru) (ppb)
Cu ppm
180
120
60
0
0
10
20
30
H
(Pt + Pd +Rh) (ppb)
Cu ppm
60
40
20
0
0
10
20
30

Fig. 2

(4.47 ppb & 4.47 ppb, respectively; Morgan et al., 1981; 4.0 ppb & 0.6 ppb, respectively, Mitchell & Keays, 1981). This comparison suggests that the PGE characteristics of the studied rocks most probably originated due to the process of partial melting followed by hydrothermal alteration. The former is indicated by the Ir content which is uniform and closely approximates the value in ultramafic nodules, whereas the effect of the latter process is shown by the enrichment in Pd and Au contents. Such an interpretation is also conformable with major and trace element geochemistry of the rocks (see Arif, 1994). The alternative explanation invoking magmatic differentiation is excluded because, had the rocks been cumulate, one would expect much lower Ir and higher Pd contents than what have been found (see the PGE data on differentiated rocks from ophiolite complexes in Barnes et al., 1985; Oshin & Crocket, 1986). As for the chromitite Sp5, the Pd and Au-enrichment of the investigated ultramafic rocks is most probably caused by hydrothermal alteration.

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Fig. 2. Platinum-group element compositions and their relationship with Ni and Cu contents of chromitites and chromite-poor ultramafic rocks. The plotted data are listed in Table 1. The legend, shown in C, also applies to the other diagrams.

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