

# **Platinum-group Elements in Rocks from the Voikar-Syninsky Ophiolite Complex, Polar Urals, U.S.S.R.**

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Analyses of platinum-group elements (PGE) in rocks collected from the Voikar-Syninsky ophiolite in the Polar Urals suggest that the distribution and geochemistry of PGE in this Paleozoic ophiolite are similar to those in Mesozoic ophiolites from elsewhere. Chondrite-normalized PGE patterns for chromitite, the tectonite unit, and ultramafic and mafic cumulate unit have negative slopes. These results are similar to those found for chromitites from other ophiolites; stratiform chromitites show positive slopes. If the magmas that form both types of chromitite originate from similar mantle source material with respect to PGE content, the processes involved must be quite different. However, the distinct chondrite-normalized PGE patterns may reflect differing source materials.

### INTRODUCTION

The Voilar-Syninsky ophiolite complex, which lies west of the city of Salekhard in the Polar Urals, U.S.S.R., is an exceptionally well exposed and well preserved ophiolite complex of Paleozoic age. The complex is about 300 km long and 50 to 80 km wide  $(Fig. 1);$  it is only moderately serpentinized, is extensively glaciated, and is largely free of vegetation. The area was examined in 10 traverses by participants in

an ophiolite conference sponsored by Project 39 of the International Geological Correlation Program in August ]978 (Bogdanov, Morgan, and Page, 1979), during which time samples were collected from the ultramafic tectonite, ultramafic and mafie cumulates, gabbros, and dike rocks in order to investigate the distribution of PGE (platinum-group elements) in the complex. The purposes of this investigation were (1) to document the abundances of PGE in the different parts of an ophiolite, (2) to define the distribution of the PGE with



Fig. I. Geologic sketch map of the Voikar-Syninsky ophiolite complex showing generalized sample locations. Modified from Efimov and others (1978) and Knipper (1979). Stars are sample locations

respect to minor and trace elements, and (3) to compare the PGE geochemistry of a Paleozoic ophiolite with that of Mesozoic ophiolites from various parts of the world.

#### GEOLOGIC SETTING AND SAMPLE LOCATION

The generalized geology of the Voikar-Syninsky massif consists of thrust slices. From the northwest to southeast they consist of Ordovician to Devonian flyschoid and pleagic sediments, the ophiolite complex, tonalite and diorite, and Silurian and Devonian island-arc sequences, thrust northwestward over an Eocambrian to Paleozoic platform sequence (Fig. I). The fly-

schoid and pelagic sediments occur in an imbricate thrust zone in which there are some sedimentary rocks of Upper Mississippian age that contain ophiolite detritus (Bogdanov, Morgan, and Page, 1979). At the eastern margin of the massif, gabbro and diabase dike complexes are intruded and hornfelsed by tonalite that is older than Middle Devonian (K-Ar ages of 375 m.y.; Bogdanov, Morgan, and Page, 1979). Knipper (1979) reported K-Ar ages of 400, 410, 420, and 470 m.y. for gabbroic rocks of the ophiolite. Reviews of the geology, petrology, mineralogy, and structure of the Voikar-Syninsky massif are contained in Efimov and others (1978) and in Sobolev and Dobretsov (1977). More directly focused on the Voikar-Syninsky ophiolite complex are reports by Savel'yev and Savel'yeva (1977) and



Savel'yeva and Stephanov (1980). The descriptions that follow are based on these references and observations made during the field conference.

Several monoclinal thrust sheets with differing structural and metamorph-locally sheared, recrystallized, and

ic histories make up the ophiolite complex. The westernmost sheet contains metagabbro interlayered with metaclinopyroxenite, metawehrlite, and metadunite that have been isoclinally folded,

metamorphosed up to amphibolite grade. The western boundary of this sheet is marked by a fault zone that dips to the southeast and contains slices of basalt, gabbro, tuff, and minor ultramafic rocks metamorphosed to the blueschist and greenschist facies. The eastern boundary is also a southeast-dipping thrust zone that emplaced ultramamfic tectonite over the metagabbro unit. The harzburgite sheet is estimated to be between 4 and 6 km thick (Efimov and others, 1978). Dunite occurs in irregular masses within the harzburgite and is associated with podiform chromitite occurrences. Deformed dunite-harzburgite layering within the central part of the complex defines a broad synform (Savel' yev and Savel'yeva, 1977). Numerous dikes and veins composed of dunite, orthopyroxenite, clinopyroxenite, and websterite cut the harzburgite mass. The eastern contact of the harzburgite is locally a fault but at other places appears to be an unconformity overlain by well-developed, repetitive cumulus sequences of dunite, wehrlite, pyroxenite, and gabbro. The development of slump structures and crossbedding in the layered gabbro and oikocrysts of clinopyroxene in the dunite are evidence that processes similar to those in stratiform intrusions contributed to the development of these layers. Gabbro becomes the dominant rock type in the upper part of the unit and near the top becomes deformed and metamorphosed to amphibolite intruded by dike complexes of diabases. Locally dikes intrude each other and have chilled margins against the dike country rock. Coarsegrained hornblende gabbros and plagiogranite form dikes and irregular pods in the gabbro-diabase dike complex. The eastern margin of the gabbro-diabase dike complex is intruded by the younger tonalite and diorite.

Samples of the ophiolite were collected during I0 traverses described by Efimov and others (1978); general locations are shown in Fig. I. Sample descriptions and some details of the relations between samples are given in Table I. Most of the samples were grab samples, apparently representative of the outcrops traversed, that weighed several kilograms.

ANALYTICAL TECHNIQUES AND RESULTS

Analytical information for palladium, platinum, rhodium, iridium, ruthenium, silver, gold, cobalt, chromium, copper, molybdenum, nickel, lead, tin, vanadium, and zinc are included in Table I. The samples are grouped in the following broad categories: dike complex, gabbroic units, ultramafic and mafic cumulates, and ultramafic tectonite and associated dikes. Individual rock names are based on thin section examination. Platinum, palladium, and rhodium analyses of all samples were performed by a fire-assay-atomic absorption described by Page, Myers and others (1980) and Simon and others (1978) which has detection limits of  $0.2$ ,  $1.0$ ,  $0.1$  ppb for Pd, Pt, and Rh, respectively. Some of the samples were also analyzed for palladium, platinum, and rhodium by the method described by Haffty and Riley (1968) using a fire-assay preconcentration step described by Haffty, Riley, and Goss (1977). Palladium, platinum, and rhodium by this method have detection limits of 4, 10, and 5 ppb, respectively. After the fire-assay preconcentration step, iridium and ruthenium were analyzed by the method of Haffty, Haubert, and Page (1980). Detection limits for iridium and ruthenium are 20 and I00 ppb, respectively. The other elements were analyzed by H.J. Calbert and W.B. Crandell by a computerized emission spectrographic technique for silicate rocks for which the relative standard deviation for each reported concentration is plus 50 percent and minus 33 percent.

## INTERPRETATION OF THE ANALYTICAL INFORMATION

Within a partially dismembered ophiolite such as the Voikar-Syninsky complex (s. Fig. I), one of the major problems is to be able to place the rocks into an overall stratigraphic sequence in order to examine geochemical trends or patterns with respect to stratigraphic position. We collected some

groups of samples for which we were able to determine the stratigraphic sequence. These include samples sequences 7PU78 to 12PU78, 13PU78 to 17PU78, and 49PU78 to 53PU78. While we have determined the stratigraphy within a group of samples, the field relations did not allow us to determine the relative stratigraphic positions between groups. Because of this difficulty, the data in Table 1 are treated in a general way based on the general sequence: ultramafic tectonite, ultramafic and mafic cumulates, gabbroic units, and dike complex. The highest PGE concentrations in the tectonite unit are Pd, 17 parts per billion (ppb); Pt, 19 ppb; Rh, 5.7 ppb; Ir, 54 ppb; and Ru, 240 ppb. The maximum PGE contents in the ultramafic and mafic cumulates are slightly higher and are Pd, 50 ppb; Pt, 51 ppb; Rh, 48 ppb; Ir, 85 ppb; and Ru, 250 ppb. Maximum PGE contents in the gabbroic and dike units are lower than those in the ultramafic and mafic cumulates. In the gabbroic unit, the largest PGE concentrations found are Pd, 29 ppb; Pt, 24 ppb; Rh, 1.0 ppb; and Ru, 140 ppb.

Arithmetic averages for the PGE values and for other selected elements are different from unit to unit (Table I); however, examination of the large standard deviations for most of the elements implies that often the differences between the averages for adjacent units are not significant. For example, differences in arithmetic averages for Co between the dike complex and gabbroic units are not significant at a 95-percent confidence level but are significant between gabhroic units and tectonite and associated dike units. The apparent trends of decreasing average concentrations of Co, Cr, Ni, and V and increasing Cu upward in the complex appear to fit differentiation processes. Changes in the PGE content over more limited stratigraphic intervals are not as regular, and definition of trends or patterns is hampered by lack of even more sensitive analytical methods.

Correlations between the PGE and other elements for all of the rocks as a group, for the larger stratigraphic units, and for individual rock types

were done by calculating Spearman-rank correlation coefficients and testing their significance. Although there are many interelement correlations with coefficients greater than 0.5 and confidence levels of greater than 95 percent, there are very few correlations of this nature involving the PGE's. Correlations observed include Pt negatively with Yb (-0.68) in a data set of all rocks, negatively with Y  $(-0.50)$  and Na  $(-0.66)$  in gabbros, and positively with Zr (+0.69) in chromitites; Pd positively with Pt (0.58) in all rocks, with Mn (0.61) in tectonite unit, with Cr (0.65) in gabbros, and with Pt (0.74) in dunite and chromitite; and Rh negatively with Si (-0.69) in tectonites, negatively with Ni  $(-0.65)$  and positively with Fe  $(0.60)$ , Ti  $(0.66)$ , and Nb  $(0.65)$  in chromitite. The correlation coefficients are given in parentheses. The relatively few correlations detected between PGE and other elements that occur in the silicate and oxide minerals suggests that processes which affect silicate and oxides phases affect the PGE differently.

Concentrations of the PGE in individual rock samples and average concentrations for each unit (Table I), except for the poorly sampled dike complex, were normalized with respect to chondrite concentrations. Data for all of the chromitites were also averaged and calculated as chondrite normalized PGE rations. Chondrite concentrations used in normalizing are Pd, 1,200 ppb; Pt, 1,500 ppb; Rh, 200 ppb; Ru, l,O00 ppb; and Ir, 500 ppb, which are the average values given by McBryde (1972). Figures 2, 3 and 4 show ehondrite normalized PGE for individual rocks from the tectonite, ultramafic and mafic cumulate, and gabbroic units, respectively. For many of the samples, the patterns formed by the normalized PGE values are incomplete either because there was not enough sample available for the Ir and Ru analysis or because Ir and Ru were below the levels of detection of the analytical technique used. Nevertheless, there are four groups or types of patterns reflected in the plots of individual rocks; (I) approximately flat patterns, that is



Table 1.—-Analyses of the PCE and selected metallic elements for rocks and averages and standard deviations for selected elements for units from the Voikar-Syninsky ophiclite, Polar Urals, U.S.S.R.<br>[Analysts: Philip J. Aru





Fig. 2. Chondrite-normalized PGE ratios for individual rock samples from the ultramafic tectonite unit. A. Chromitite. B. Dunite. C. Harzburgite. D. Wehrlite and clinopyroxenite

the chondrite normalized ratios for Pd, Pt, and Rh have essentially the same value, (2) hump-shaped patterns, that is the chondrite normalized ratio for Pt is larger than that for Pd or Rh, (3) positively sloping patterns, and (4) negatively sloping patterns. Within the tectonite unit (Fig. 2), the chondrite normalized patterns for individual rocks are either approximately flat or negatively sloping except for wehrlite, clinopyroxenite, and duniteorthopyroxenite dikes. Samples from interlayered dunite and harzburgite tectonite yield approximately flat patterns; negatively sloping patterns are most common from samples of chromitite, harzburgite with abundant chromite, and cross-cutting dunites containing chromite. In general, within the ultramafic and mafic cumulate unit (Fig. 3), samples of chromitite display negatively sloped patterns, and interlayered dunite, wehrlite, and clinopyroxenite show positively sloping patterns, with a few exceptions of both flat and humpshaped patterns shown by various rock types. Chondrite normalized patterns for individual samples of the gabbroic unit (Fig. 4) are more difficult to characterize because of the large portion of less than detectable contents

of PGE in a number of samples (Table I). If the "less-than" contents are treated as maximum chondrite normalized ratios, then hump-shaped, positively and negatively sloping patterns are shown by individual gabbroic rocks.

Average concentrations for the units in the ophiolite (Table 2) yield negatively sloping chondrite normalized patterns (Fig. 5). The patterns for ultramafic tectonite and associated dikes, ultramafic and mafic cumulates, and the chromitites have negative slopes and show more depletion in platinum and palladium than in iridium and ruthenium compared to chondrites. These patterns are similar to those obtained for chromitites in tectonite and from near the base of the cumulates in the Samail ophiolite, Oman (Page and others, 1979). The gabbroic unit of the Voikar-Syninsky ophiolite complex appears to have a different pattern from the rest of the ophiolite. Although the patterns of chondrite-normalized Ir, Ru, and Rh for the gabbroic unit are similar to those of other units, the pattern of Pt and Pd are quite different. The positive trend for the Rh, Pt, and Pd end of this pattern is similar to those obtained from stratiform cumulate sequences (Page, von Gruenewaldt, Aruseavage,

 $0,1$ 

quently for Pt, but the chondrite normalized ratios for these elements form approximately flat patterns within the area A of Figure 6. Some of the analyzed xenoliths have been assumed to represent undepleted pristine mantle. Comparison of chondrite-normalized patterns of xenoliths with those from the Voikar-Syninsky ophiolite suggest that the approximately flat patterns originating



Fig. 4. Chondrite-normalized PGE ratios for individual rock samples from the gabbroic unit



Fig. 3. Chondrite-normalized PGE ratios for individual rock samples from the ultramafic and mafic cumulate unit

and Haffty, 1982). The simplification (Fig. 6) of the patterns of chondrite normalizd PGE ratios from Figures 2, 3, and 4 is composed of areas containing the four most common patterns and compares these areas with the area within which chondrite normalizd PGE ratios of ultramafic xenoliths from basalts and kimberlites occur based on the data of Morgan and Wandless (1979), Jagoutz and others (1979), and Morgan and others (1980). Most of the xenoliths have been analyzed for Os, Ir, Pd, and less fre-

temperatures that were trapped as inclusions in the chromite crystals, whereas the depletion in the chromitites of Pt and Pd might reflect that these elements remained concentrated in the magma that escaped from the immediate system. Minerals containing Os, Ir, and Ru have been identified within chromitite from other ophiolite complexes (Constantinides and others, 1980; Z. Johan, written commun., 1980; H. Stockman, oral commun., 1980). The positively sloping patterns of chondrite normalized ratios of interlayered dunite,

 $\swarrow$  c \ 0.1 \ \ \ 0.05 \ , where  $\Lambda$ \ /~'...'~z/j,4 IJJ CHONDR 0.01 Z L  $\mathbf \mu$ 0.005 o © w<br>A Р 0.001 0.0005 *\ /"*  V..- 0.0001 **I I I OS Ir Ru Rh Pt Pd I I I**  ELEMENT

Fig. 6. Cartoon-like plot of chondritenormalized PGE patterns as areas for each characteristic pattern, discussed in the text

for the ultramafic tectonite, ultramafic ophiolite complex. Arrows indicate maxi-

from dunite and harzburgite tectonites, area B in Figure 6, may also represent undepleted mantle with respect to the PGE. The negatively sloping chondrite normalized PGE patterns derived from mainly chromitites occur in area C. Such patterns represent an enrichment of Ir and Ru and depletion in Pt and Pd with respect to ultramafic xenoliths. If the chromitite represents the early formed crystallization products from a magma passing through the lower part of the ophiolite in a manner similar to that proposed by Cassard and others (1981), then the enrichment relative to xenoliths of Ir and Ru and potentially Os could be due to the crystallization of Os-Ir-Ru alloys or sulfides at high

Fig. 5. Chondrite-normalized PGE ratios and mafic cumulates, gabbroic, and dike complex units of the Voikar-Syninsky mum ratios

 $\begin{array}{c} 0.5 \\ - \end{array}$ 0.1 CHONDRITE • ULTRAMAFIC AND MAFIC CUMULATES 0.05 U<br>U ROCK<br>X 0,01 ው<br>ደ ULTAMAFIC GABBROIC UNIT \* 0.005 **TECTONITE** : ,, ! : **HROMITITE** 0.001 Os Ir Ru Rh Pt Pd ELEMENT

wehrlite, and clinopyroxenite of the ultramafic and mafic cumulate unit fall in area D of Fig. 6, as do some of the patterns from the gabbroic unit. An enrichment in Pt and Pd with respect to ultramafic xenoliths is indicated



Fig. 7. Comparison of chondrite-normalized PGE patterns of chromitite in ophiolite and stratiform complexes with the pattern for chromitite from the Voikar-Syninsky ophiolite complex

by this pattern and might be the result of concentration of Pt and Pd in an immiscible sulfide melt that could accumulate in these rocks.

COMPARISON OF PGE DATA WITH OTHER **OPHIOLITES** 

Studies by Page, Pallister and others (1979) on the Samail ophiolite, Oman; Page, Cassard, and Haffty (1982) on the Massif du Sud and Tiebaghi Massif ophiolites, New Caledonia; Page, Haffty, Ahmad (1980) on ophiolites in Pakistan and Page, Engin, and Haffty (1980) on ophiolites in Turkey have established that chondrite-normalized PGE in chromitites from these Mesozoic ophiolites have negatively sloping patterns when plotted (Fig. 7). The chromitites from the Voikar-Syninsky ophiolite have a similar pattern. Thus, all ophioliteassociated chromitites so far examined have patterns with slopes opposite to those shown by chromitites in stratiform complexes.

If magmas that form both chromitite in both ophiolites and stratiform complexes originate from mantle material with similar PGE concentrations and ratios, then the processes, either partial melting of mantle material, concentration within the complexes, or both, involved are different, which is the hypothesis favored in this report. It is most likely that PGE patterns represent the percentage or portion of mantle material melted to produce the original melts. However, if the normalized PGE patterns represent source materials that are different, it should be possible, by examining chondrite-normalized PGE patterns, to map mantle compositions as characterized by PGE contents.

#### CONCLUSIONS

The PGE geochemistry and chondritenormalized PGE patterns of chromitites in Paleozoic and Mesozoic ophiolite complexes are similar, suggesting that chondrite-normalized PGE patterns may be used to identify ophiolites where they occur in a highly dismembered manner. The gabbroic unit of the Voikar-Syninsky ophiolite appears to have a different PGE geochemistry from the tectonite and ultramafic and mafic cumulate units, possibly suggesting that they differentiated and accumulated by processes similar to those by which gabbroic rocks in stratiform complexes form.

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