

# **Summary information about platinum-group elements and other trace metals in greenstones of the Wrangellia terrane and the Gravina belt, southeastern Alaska**

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# **SUMMARY INFORMATION ABOUT PLATINUM-GROUP ELEMENTS, COPPER, NICKEL, AND CHROMIUM IN GREENSTONES OF THE WRANGELLIA TERRANE AND GRAVINA BELT, SOUTHEASTERN ALASKA**

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## **ABSTRACT**

Platinum-group elements (PGE), Cu, Ni, and Cr concentrations have been determined for 134 samples of greenstone and other metavolcanic rocks of the upper Paleozoic and Triassic Wrangellia terrane and of the Upper Jurassic and Cretaceous terrane-overlap assemblage of the Gravina belt in the western part of the Coast Mountains between the Chilkat Peninsula and northern Admiralty Island and the results are summarized here. The elemental concentrations and ratios of the Gravina belt rocks are compared with corresponding data from the Alaskan-type mafic-ultramafic intrusions to test previously published hypotheses regarding their parent magmas. Finally, we speculate about the magmatic and other processes that led to the relative concentrations of the above-listed elements in these rock units.

This study is limited by the sampling and analytical methods used, by the elements selected, and by the lack of data pertinent to all of the processes that may have affected the original magmas; nevertheless it accomplishes three specific purposes: (1) it summarizes an original and comprehensive set of PGE, Cu, Ni, and Cr data for these units for the first time; (2) it compares summarized Douglas Island Volcanics data with those of the Alaskan-type mafic-ultramafic complexes, and suggests a new preliminary hypothesis regarding the parent magmas of the latter; and (3) it speculates about the magmatic and other processes that led to some regular, albeit loose, grouping of the data for the different units. This last purpose is controversial because it is especially fraught with uncertainties.

The rocks analyzed from the Wrangellia terrane include greenstone of Late Triassic age on Chilkat Peninsula near Haines and the Gastineau Volcanics of late Paleozoic to Late Triassic age near Juneau. The PGE-Ni-Cr concentrations and concentration ratios for these rocks supplement previous trace-element studies and may serve to further differentiate these rocks from those of Cretaceous age.

The previous trace-element studies showed that the Wrangellia tholeiitic basalt metavolcanic units and the Cretaceous-age Douglas Island Volcanics alkalic basalt units erupted in different tectonic settings and have different elemental concentrations and ratios. Our new studies, like the previous ones, are of potential value to mineral explorationists and others attempting to establish the presence or absence of Triassic metavolcanic units; this question is important because the Triassic rocks locally contain volcanogenic-massive-sulfide deposits .

Rocks analyzed from the Gravina belt principally belong to the Lower Cretaceous Douglas Island Volcanics exposed near Juneau. These latter rocks previously have been proposed to be the extrusive equivalent of magmas that formed Lower Cretaceous (118-100 Ma) Alaskan-type mafic and ultramafic intrusions, but our data do not support this interpretation. Instead, our study suggests that mafic dikes and plugs emplaced into the Douglas Island Volcanics either during a late stage of M1 (~120 Ma) low-grade regional metamorphism or possibly during the same time as the M2 contact metamorphism that marks the aureoles of the Alaskan-type intrusions, are the parents of those intrusions.

According to our data, the metavolcanic rocks of both the Wrangellia terrane and the Gravina assemblage are characterized by dominance of Pd over Pt as shown by mean Pd/Pt ratios of 2.30 and 1.61, respectively, for the lower and upper parts of the Wrangellia terrane, and of 1.82 for the Gravina belt. Average Pt/(Pt+Pd) ratios are about the same (0.3-0.4) for all the metavolcanic units; they are significantly lower than values (0.5-1.0) for the Pt-dominant Alaskan-type intrusions. The mean total PGE concentrations of samples of the Douglas Island Volcanics and equivalents [16 parts per billion (ppb)] and of associated dike rocks (10 ppb), however, are much lower than for Alaskan-type intrusions (generally 75-100 ppb). Dikes in the Douglas Island Volcanics are Pt dominant, with mean Pd/Pt of 0.74 and Pt/(Pt+Pd) of 0.58; these values are similar to those in some of the Alaskan-type bodies, suggesting that the late dikes may represent their parental magmas, instead of the parents of the extrusive rocks of the Douglas Island Volcanics. All of these analytical values and calculated ratios are subject to significant uncertainty.



The Cu, Ni, and Cr variations are complex; overall, the average Cu concentration of the units shows a general increase with increasing Pd but no systematic variation with Pt. In volcanic rocks of the Gravina belt of the Juneau area, Cu shows positive covariation with Pd and lacks systematic covariation with Pt. In contrast, in rocks of the Wrangellia terrane, Cu has a general overall increase with both increasing Pd and Pt. Neither Ni or Cr show covariation with Pt and Pd in all units. It should be noted that, in comparison with the Gravina assemblage rocks from the Juneau area, inferences regarding the Cu, Ni, and Cr concentrations of the metavolcanic rocks of both the Wrangellia terrane and the Gravina assemblage in the Ketchikan and Petersburg areas are limited by the small sample population for those areas.

## INTRODUCTION

This report summarizes platinum-group element (PGE), Cu, Ni, and Cr concentrations in 134 samples of upper Paleozoic and Mesozoic volcanic rocks from southeastern Alaska. The PGE's analyzed are Pt, Pd, Rh, Ru, and Ir. This study is part of a long-term study of the volcanogenic history of southeastern Alaska (Brew, 1968; Ford and Brew, 1978, 1987, 1988, 1993). The complete data set is in the files of co-author A.B. Ford.

The primary purpose of the report is to summarize the new data on the PGE, Cu, Ni, and Cr content of the volcanic rocks. The secondary purpose is to compare the Douglas Island Volcanics PGE data with those of the Alaskan-type complexes; this topic is of interest because of uncertainty about the parent magma of the Alaskan-type complexes and because the Douglas Island Volcanics have been suggested to be the extrusive equivalent of the Alaskan-type complexes. The third purpose is to speculate on the processes that led to the concentrations now present in the different geologic units; this purpose is similar to that of Ely and others (1998) in their study of Ontong Java Plateau basalts. The fourth purpose is to explore the possibility that PGE and other data may be used to differentiate the Wrangellia metavolcanic rocks, which locally contain volcanogenic massive sulfide deposits, from the Gravina belt metavolcanics, which generally do not.

Samples are principally from (1) the Wrangellia terrane of northern southeastern Alaska; it consists of two parts: (a) an upper Paleozoic and Triassic(?) and Upper Triassic lower and upper parts of the Gastineau Volcanics of Ford and Brew (1993) and (b) the Upper Triassic metabasalt of the Chilkat Peninsula and northern Admiralty Island; and (2) the Douglas Island Volcanics of Early Cretaceous age (Lathram and others, 1965). The Wrangellia rocks were assigned to the Taku terrane by Berg and others (1978), but have since been recognized on paleontological and chemical evidence to belong to Wrangellia (Ford and Brew, 1993). The Douglas Island Volcanics are part of the Upper Jurassic and Lower Cretaceous Gravina terrane-overlap assemblage that forms a discontinuous belt extending throughout southeastern Alaska (Berg and others, 1972; Brew and Ford, 1985; Brew and Karl, 1988a, b; McClelland and others, 1991; Cohen, 1992; Cohen and Lundberg, 1994). The Gravina belt is used in this paper as defined in Brew and Ford (1985).

Areas sampled for the study are shown in figure 1. Samples of mafic dikes and plugs that intrude the Douglas Island Volcanics on the Glass Peninsula of northeastern Admiralty Island and a small number of samples of metavolcanic rocks from southern parts of the Gravina belt in the Ketchikan and Petersburg areas are also included in the study. These dikes and plugs are included in the study because of the possibility that they represent the parental magma of Alaskan-type intrusions (Murray, 1972; Irvine, 1974; Loney and Himmelberg, 1992; Himmelberg and Loney, 1995).

The typical augite-porphyritic volcanic rocks of the Gravina belt are spatially related (Murray, 1972; Irvine, 1974; Brew and Ford, 1985) to a linear belt of distinctive, dominantly ultramafic intrusive bodies termed "Alaskan-type" (Irvine, 1973, 1974; Himmelberg and Loney, 1995). The bodies are scattered in a well-defined belt along the west side of the Coast mountains in southeastern Alaska (Taylor and Noble, 1960; Taylor, 1967; Murray, 1972; Clark and Greenwood, 1972; Irvine, 1974; Brew and Ford, 1985; Loney and Himmelberg, 1992). Himmelberg and Loney (1995) provided a comprehensive review and synthesis of the occurrence, petrology, and tectonic setting of these ultramafic and mafic intrusions. They also provided new trace-element data for three of the bodies, but PGE's were not analyzed in their study.

Most of the Alaskan-type bodies were originally mapped and briefly described by Buddington and Chapin (1929) and have been subsequently studied by the workers listed above. As summarized by Himmelberg and Loney (1995), K-Ar, Ar-Ar, and Pb-U zircon age determinations on rocks from the different Alaskan-type bodies have yielded Aptian (118 Ma, Meen and others, 1991) and Albian (110-100 Ma, Lanphere and Eberlein, 1966; 111-108 Ma, Saleeby, 1992) radiometric ages, using the time scale of Harland and others (1990). Alaskan-type complexes of other ages are also reported, such as the Salt Chuck intrusion and others of early Paleozoic age in southern southeastern Alaska (Loney and Himmelberg, 1992; Brew, 1996) and bodies of Late Triassic to Early Jurassic age in a belt in British Columbia about 350 km east and northeast of southeastern Alaska (Nixon and Hammack, 1991).

A cogenetic relation between some of the Alaskan-type intrusions and Lower Cretaceous Douglas Island Volcanics of the Gravina belt near Juneau was suggested by Murray (1972) and Irvine (1973, 1974) from compositional similarities of clinopyroxene in the volcanic and ultramafic rocks. Low-grade metamorphosed augite-rich volcanic flow and fragmental rocks, called “augite melaphyre” in early studies (Knopf, 1912), are the dominant lithologies of the Douglas Island Volcanics near Juneau and are common in other parts of the belt. As noted above, volcanic rocks of this unit conceivably represent the parent magma or are derived from the same parent magma as the mafic-ultramafic Alaskan-type intrusions (Irvine, 1974), but the absence of chilled margins that could represent parental magmas precludes identification of original magma types (Irvine, 1973, 1974; Loney and Himmelberg, 1992; Himmelberg and Loney, 1995). Page and others (1977) summarized evidence for a cogenetic relation of the intrusions with metavolcanic rocks of the Gravina belt near Ketchikan, and provided supporting evidence from their study of PGE comparisons. A cogenetic relation with volcanic rocks is also implied by suggestions that Alaskan-type intrusions formed in subvolcanic conduits or magma chambers (Irvine, 1974; Himmelberg and Loney, 1995). A parental magma may be represented by mafic dikes associated with one of the older Alaskan-type bodies, the Salt Chuck intrusion (Loney and Himmelberg, 1992; Himmelberg and Loney, 1995). Interestingly, very disparate types of original magma compositions have been suggested for the Alaskan-type bodies; they include ultramafic (Taylor and Noble, 1960; Noble and Taylor, 1960), olivine-rich tholeiite (Murray, 1972), island-arc tholeiite (Meen, 1991); alkaline basalt (Irvine, 1973); and subalkaline hydrous olivine basalt (Himmelberg and Loney, 1995).

## METHODS AND LIMITATIONS

As noted above, the primary purpose of this report is to summarize the results of an investigation of PGE, Cu, Ni, and Cr characteristics of metavolcanic rocks of the Wrangellia terrane and the Gravina overlap assemblage in northern southeastern Alaska. The sampling and analytical methods used necessarily affect the result and are therefore described here. There are also important limitations related to the complexity of the processes that lead to PGE variation in igneous rocks.

Most of the samples were collected during the course of regional geologic mapping and many are the same ones whose trace elements were reported on by Ford and Brew (1978, 1987, 1988, 1993). A few others were from the collections of G.R. Himmelberg and R.A. Loney of the U.S. Geological Survey; those samples were collected during detailed mapping of selected Alaskan-type bodies.

Standard U.S Geological Survey analytical methods were used for all elements. The major limitations on our primary purpose of summarizing the PGE characteristics of Gravina belt and Wrangellia volcanic rocks are: (1) the use of PGE data obtained by both the analytical methods of Meier and others (1991, 1996) and those of Haffty and Riley (1968) for the Gravina belt rocks; the latter method has higher lower detection limits than the former; (2) the probable, but unevaluated inhomogeneity (also known as "nugget effect"), in samples with low PGE concentrations, such as those in this study; and (3) the unevaluated effects of metamorphism and alteration. Regarding point (1): it should be noted that all earlier published studies of rocks from the Gravina belt (Page and others, 1977; Ford and Brew, 1978) used the less sensitive method of Haffty and Riley (1968). The Cu, Ni, and Cr values were determined with the methods described by Lichte and others (1987) and King (1996). Table 1 presents the lower limits of determination and the analytical uncertainties for all of the analytical methods used. We urge the reader to keep all the uncertainties listed above in mind when evaluating the discussions and various figures that follow.



The secondary purpose of this study is to compare the PGE characteristics of the Gravina belt volcanic rocks with those of the Alaskan-type intrusions. As with the PGE, Cu, Ni, and Cr characteristics described above, the comparison is limited by the three factors described above and also by: (4) the low amount of PGE- and other trace-element information available for most Alaskan-type intrusions; and (5) the lack of isotopic dating of the Gravina belt volcanic and dike rocks. Otherwise our approach to this purpose is a straightforward comparison of summarized analytical results and of calculated ratios.

In the figures supporting this secondary purpose, we have chosen not to include correlation coefficients in the various x-y plots of the different elements. This is for two reasons: (1) all of the plots obviously have large to extreme scatter; and (2) many of the samples lack values for one of the elements plotted, and calculation of coefficients is meaningless for those samples and truncating them from the remaining samples would, in our opinion, be misleading. We have also chosen not to attach any analytical plus or minus values to the individual data points; this is because they would unnecessarily complicate the diagrams. There are some large overlaps when these analytical uncertainties are plotted on the individual diagrams and we believe that the individual reader can evaluate the diagrams better by seeing the points and keeping in mind the analytical uncertainties for each element as given in table 1. Regardless of all these limitations, we believe that the data, ratios, and comparisons thereof support a new preliminary and different suggestion regarding the origin of the Alaskan-type intrusion magmas. Nevertheless, we again urge the reader to keep these limitations and uncertainties in mind when evaluating the discussions and various figures that follow.

Our third purpose is the most controversial and has attracted an undue amount of attention from our numerous reviewers; that purpose is to both speculate on the processes that led to the apparently different concentrations of these elements in the different geologic units and to explore the possibility that PGE and other data may be used to differentiate the Wrangellia metavolcanic rocks, which locally contain volcanogenic massive sulfide deposits, from the Gravina belt metavolcanics, which generally do not.

We are aware that (other than the study of Ely and others, 1998) variations in Pt and Pd ratios have not been used to infer petrologic processes or as a petrogenetic tracer because there are too many factors that affect Pd/Pt and thus make a unique interpretation almost impossible (M. Zientek, U.S. Geological Survey, written comm., 1998). Contrary to the views of at least one of our reviewers, we believe that the roles of these elements are still uncertain in magmas and volcanic rocks. We discuss these factors below, and we contend that the relatively consistent relations in our results require an interpretation similar to our speculations or some other similar alternative.

### **PREVIOUS STUDIES OF PGE IN THE VOLCANIC ROCKS**

Platinum-group elements had not been determined in previous studies of the volcanic rocks of the Wrangellia terrane in this area (Davis and Plafker, 1985; Ford and Brew, 1993; Gehrels and Barker, 1993) prior to this study.

PGE determinations of the Douglas Island Volcanics in the northern part of the Gravina belt showed a slight dominance of Pd over Pt (Pd /Pt, 1.61) in an early study (Ford and Brew, 1978) that used the fire assay-emission spectrographic analytical method of Haffty and Riley (1968) . Pd was detected above the lower limit of determination in 27 of 28 samples and was at the lower limit of determination in the one remaining sample; the concentration ranged from 4 ppb to 19 ppb. In the same study, Pt was detected above the lower limit of determination (10 ppb) in 69 percent of samples, and Rh was not detected above its lower limit of determination (5 ppb) in any samples. The same method (Haffty and Riley, 1968) was used for the PGE analyses in the study of Page and others (1977) of metavolcanic rocks in the Ketchikan part of the Gravina belt. That study reported Pt as determinable in only 17.5 percent of samples and Pd in 60 percent, and Rh, as in the Douglas Island Volcanics study, was not determinable in any samples. The methods used in the current study and the new results indicate that the older analytical methods and the associated results were severely limited.

## DESCRIPTION OF THE ROCK UNITS

The principal units of this study consist of greenstone and greenschist derived from basalt of upper Paleozoic, Triassic, Late Jurassic, and of Lower Cretaceous age (Ford and Brew, 1987, 1988, 1993; Gehrels and Barker, 1993).

The Wrangellia terrane rocks included in this study are: (1) upper Paleozoic and Triassic rocks of the Gastineau Volcanics near Juneau (Ford and Brew, 1993) and (2) the Upper Triassic metabasalt unit on the Chilkat Peninsula (Davis and Plafker, 1985; Plafker and others, 1989). Ford and Brew (1993) defined the Wrangellia terrane in the vicinity of Juneau to contain both the upper Paleozoic and Triassic(?) as well as Upper Triassic rocks, as found in other parts of the terrane. Gehrels and Barker (1993) included these same rocks in their Taku terrane, although they recognized the geochemical similarities with rocks of the Wrangellia terrane of other areas. Our samples of the Wrangellia terrane are the same as those of Ford and Brew (1993) but also include an additional 18 samples of volcanic rocks of the Upper Triassic Hyd Formation (Loney, 1964) on northern Admiralty Island, which we consider to be part of the Wrangellia terrane.

The Wrangellia terrane extends as a long, narrow and discontinuous belt along the western edge of the Coast Mountains from the Chilkat Peninsula (Plafker and others, 1989) southward beyond Tracy Arm (Ford and Brew, 1993; Brew and Ford, 1994). It also is found on Admiralty Island (as the Hyd Formation) and elsewhere in southeastern Alaska (Ford and Brew, 1993) and areas to the south of Alaska (Barker and others, 1989). The age and correlation of the rocks, the extent of the terrane, and the tectonic setting of volcanism were discussed by Ford and Brew (1993). Metabasalts of the upper Paleozoic and Triassic(?) lower part of the terrane are tholeiitic in composition (Ford and Brew, 1993), as are those of its Upper Triassic part (Davis and Plafker, 1985; Barker and others, 1989; Ford and Brew, 1993; Gehrels and Barker, 1993). Both parts lack trace-element signatures of subduction-zone volcanism and are inferred to have formed in an intra-oceanic volcanic setting with little crustal involvement (Ford and Brew, 1993). Major- and trace-element differences, however, suggest that the two parts formed in somewhat different environments (Ford and Brew, 1993).

One hypothesis that explains the difference is that all of the Upper Triassic volcanics are part of a single, short-lived, flood-basalt eruptive event (Richards and others, 1991; D.A. Brew, unpub. report) whereas the upper Paleozoic and Triassic(?) volcanics were formed as part of an interoceanic arc.

The Douglas Island Volcanics of the Juneau and Admiralty Island areas typically consist of relict-augite-bearing greenstone and greenschist derived from basaltic flows. The Douglas Island Volcanics include the Bridget Cove Volcanics of Irvine (1973) and the Brothers Volcanics of Loney (1964), which form the upper part of the Upper Jurassic and Lower Cretaceous Gravina belt section (Cohen, 1992; Cohen and Lundberg, 1994). The Douglas Island Volcanics are inferred to be of Late Jurassic and Early Cretaceous age, as discussed below.

Volcanic rocks of the Gravina belt extend south from near Juneau to the vicinities of Petersburg and Ketchikan (Berg and others, 1972; Page and others, 1977; Brew and others, 1984; Brew and Karl, 1988a, b; McClelland and others, 1991; Cohen, 1992; Cohen and Lundberg, 1994). Andesitic compositions were reported for the belt by Berg and others (1972), but all other workers have reported only basaltic compositions of alkalic and calc-alkalic character in areas near Juneau (Irvine, 1973; Ford and Brew, 1987, 1988) and in central parts of the belt (McClelland and others, 1991). Although McClelland and others (1991) state that compositions are basaltic to andesitic they do not provide data indicating occurrence of andesite, except possibly for one sample of the Brothers Volcanics ( $\text{SiO}_2$ , 54.7 percent). No systematic compositional differences are recognized along the length of the belt. However, given the possibility that there may be significant variations in the age of volcanism (with that in the Juneau area probably Early Cretaceous to mid-Cretaceous, and that in southern areas of the belt near Ketchikan probably Late Jurassic (Rubin and Saleeby, 1992) and possibly as old as Middle Jurassic (Berg and others, 1972)), and in the substrates through which the magmas ascended, along-belt compositional differences may well be present.

The age of the Gravina belt rocks has an important bearing on interpretations regarding the age and emplacement of the Alaskan-type mafic-ultramafic intrusions. As background, the unfossiliferous Douglas Island Volcanics are part of the Stephens Passage Group of Lathram and others (1965); the Group also includes the dominantly sedimentary Seymour Canal Formation. Numerous fossil collections by Loney (1964) established a Late Jurassic and Early Cretaceous age for the Seymour Canal Formation (Brew and Ford, 1985; Cohen, 1992; Cohen and Lundberg, 1994). The Douglas Island Volcanics overlie and intertongue at their base with the upper part of the Seymour Canal Formation on Admiralty Island (Lathram and others, 1965), thus indicating an Early Cretaceous age for its lower part. A mid-Cretaceous age was assigned to the volcanic rocks on Douglas Island based on fossils found in an interlayer of metasedimentary rocks in greenstone close to the contact of the volcanics with the Seymour Canal Formation (Ford and Brew, 1973).

The fossils, of *Inoceramus*, were reported to be of probable Hauterivian to Cenomanian age by D.L. Jones (U.S. Geological Survey, written comm., 1971), but on reexamination they are reported to be early Turonian (early Late Cretaceous) by J.W. Haggart (Geological Survey of Canada, oral comm., 1998). The *Inoceramus*-bearing rocks are probably an intertongue of the Seymour Canal Formation in the Douglas Island Volcanics, such as described on Admiralty Island (Lathram and others, 1965).

Thus, from paleontologic evidence, the volcanic rocks of the Juneau area of the Gravina belt are inferred to be Late Jurassic to Early or early Late Cretaceous in age (time scale of Harland and others, 1990). Elsewhere in the belt, volcanic rocks are inferred to be Albian in age at one locality and Late Jurassic and Early Cretaceous in others (Brew and others, 1984; Brew and Karl, 1988a, b; McClelland and others, 1991).

We studied mafic dikes and plugs that cut the Douglas Island Volcanics on the Glass Peninsula of northeastern Admiralty Island. Mafic sills as well as dikes occur widely in the Seymour Canal Formation (McClelland and others, 1991; Cohen and Lundberg, 1994) and sills would be expected in the volcanic rocks also, but none have been recognized.



The dikes and plugs consist of greenstone, commonly with abundant, euhedral, megascopic inclusions of clinopyroxene (augite?) in a groundmass metamorphic mineral assemblage of the pumpellyite-actinolite facies near the transition to the lower greenschist facies (chlorite+albite+epidote,  $\pm$ actinolite  $\pm$ pumpellyite), similar to that of the Douglas Island Volcanics (Himmelberg and others, 1994). Although of the same metamorphic grade as the rocks they intrude, the dikes lack the penetrative deformation recorded by the well-developed foliation of the host greenstone and greenschist. The relations suggest that the dikes were emplaced during a late, post-kinematic, stage of the M1 (~120-Ma) metamorphic event that affected the Douglas Island Volcanics or at the same time as the M2 event that produced the aureoles of the Alaskan-type intrusions (Brew and others, 1989; Himmelberg and others, 1995).

### **COPPER, NICKEL, AND CHROMIUM CONCENTRATIONS**

A summary of Cu, Ni, and Cr data and related ratios of the rocks sampled in this study is given in table 2. Inferences regarding the rocks of the Gravina belt in the Ketchikan and Petersburg areas are limited by the small sample population for those areas (G-KE, G-PE; table 2). The Cu, Ni, and Cr variations are complex and should be evaluated with the analytical uncertainties in mind (see table 1). Overall, the average Cu concentration of the units shows a general increase with increasing Pd but no systematic variation with Pt (fig. 2A). Specifically, in volcanic rocks of the Gravina belt of the Juneau area (G-JU, fig. 2B) copper shows positive covariation with Pd and lacks systematic covariation with Pt. In contrast, in rocks of the Wrangellia terrane (fig. 2C, D), Cu has a general overall increase with both increasing Pd and Pt. Finally, neither Ni or Cr show covariation with Pt and Pd in all units (plots not shown).

Copper sulfides are associated with the Pd-rich ores of the Alaskan-type Salt Chuck intrusion (Keays and Campbell, 1981; Watkinson and Melling, 1992), which is of Paleozoic age (Brew, 1996). Sulfides are well known to be PGE collectors during magmatic crystallization (Naldrett and Duke, 1980; Campbell and others, 1983; Barnes and others, 1985; Barnes, 1990). Only traces of sulfide minerals are found in the volcanic rocks we sampled; this suggests (but does not prove) that there may not have been sulfur saturation like that associated with the PGE crystallization found in plutonic-crystallization environments as described by Campbell and others (1983), Barnes (1990), and Keays and Campbell (1981); or of sulfur saturation at the time of eruption of basaltic magmas originating from little depleted source regions as described by Hamlyn and Keays (1986). It is possible that the magma was sulfur-saturated at some stage, but that the saturation did not persist to the final eruptive or intrusive phases (M. Zientek, U.S. Geological Survey, written comm., 1998). If Cu occurs in a sulfide phase in the volcanic rocks, then the positive Pd covariation with Cu could imply the association of Pd with that phase also; as noted above, however, such a relation does not occur for Pt (fig 2A) and the main Pd mineralization at Salt Chuck is not associated with sulfides. Covariations also might suggest a sulfide-phase occurrence for Pd but not Pt in the Douglas Island Volcanics and for both Pd and Pt in the Wrangellia terrane (fig. 2B-D). However, these nonsystematic variations suggest to us that the Pd and Pt in the volcanic rocks may not be associated with a sulfide phase.

Ni and Cr contents are strongly intercorrelated in all of the volcanic rock units, but there is little intercorrelation of Ni and Cr with Cu or with Pd (plots not shown). The compatible elements Ni and Cr were probably in part fractionated into early cumulates of source magmas of the volcanic rocks.

Trace- and major-element chemical characteristics have been used to distinguish greenstones and greenschists of various ages that are otherwise difficult to separate on field appearance alone (Ford and Brew, 1988; 1993). Our study suggests some additional trace-element characteristics that might be used for discriminating those units with similar field aspect. The volcanic rocks of the Gravina belt of the Juneau area show little difference from those of the Wrangellia terrane in mean Cu and Ni contents, but they show slightly higher Cr content and slightly lower Ni/Cu and Cu/Pt ratios (G-JU, W-U, W-L; table 2).

The dikes and their Douglas Island Volcanics host rocks are greenstones with generally similar mineralogy and close similarity in field appearance; however, the significantly lower Cu and higher Ni and Cr and much higher Cu/Pt in the mafic intrusive dike rocks may provide signatures that distinguish them from the extrusive rocks. (G-JUd, G-JU; table 2). Similar characteristics should also discriminate sills, if present.

### **PLATINUM-GROUP-ELEMENT (PGE) CONCENTRATIONS**

The percentage of samples with PGE concentrations above the lower limit of determination varies greatly for the different rock units and for the different PGE's, depending in part on the analytical method used and in part on the differences in the lower limits of determination (table 1). Gottfried and Froelich (1988) consider differences of more than 20 percent in Pd and Pt concentrations to be geochemically significant variations; such differences are greater than or about the same as could exist between two samples (table 1). Fifty percent of samples from all units contain more than 5 to 6 ppb Pt, and twice that much or more for Pd (except for the dike rocks; see median concentrations, table 3). Gravina-belt volcanic rocks (G-JU, G-KE, G-PE, table 3) and the Upper Triassic basalts of the Wrangellia terrane (W-U, table 3), in particular, show the highest percentage of Pd values at or above the limit of determination, and the dike rocks the lowest (G-JUd, table 3). Percentages of samples with Rh and Ru at or above the lower limits of determination are variable and generally low, except for Rh of Gravina-belt rocks of the Petersburg area (83 percent, table 3). Iridium contents are mostly below the lower limit of determination. Incidentally, it is not known from this study which minerals contain the platinum-group elements (PGE's).

We speculate that the previously discussed variations in Pt and Pd in relation to Cu, Ni, and Cr in the volcanic rocks may represent different fractionation stages, or phases, of parent magmas. They, in turn, may reflect possible variations in bulk distribution coefficients for Pt and Pd in mineral hosts in earlier fractionation (Gottfried and others, 1990) or other concentration, fractionation, or crystallization processes. Copper, a relatively incompatible element, is retained in magmas until later crystallization stages when, under appropriate conditions, it precipitates in a sulfide melt (Barnes and others, 1988). In the Salt Chuck intrusion, for example, PGE's dominated by Pd accumulated along with Cu sulfides by fractional crystallization and formed later sulfide- and Pd-rich gabbroic cumulates (Loney and Himmelberg, 1992).

Fractionation sequences have not been identified within any of the volcanic units. Platinum-group elements fractionate in the order  $Os < Ir < Ru < Rh < Pt < Pd$  according to Barnes and others (1985) and Fryer and Greenough (1992). We speculate that early fractionation from source magmas (Barnes and others, 1985) may account for the low contents of Ir, Ru, and Rh in the volcanic rocks of this study. Palladium, with a probable bulk distribution coefficient of less than one during silicate fractionation, is retained in the magma until a late crystallization stage (Gottfried and others, 1990). Figure 2B suggests that the Douglas Island Volcanics may conceivably represent a magma stage after fractionation of much Pt relative to Pd; this is not indicated for rocks of the Wrangellia terrane (fig. 2C, D).

Prior PGE studies of Gravina-belt volcanic rocks of the Ketchikan area (Page and others, 1977) indicated dominance of Pt over Pd (average Pt/Pd, 1.37). This conclusion is interpreted here as the result of using qualified data obtained by an earlier analytical method that had both high lower limits of determination and much different limits for Pt and Pd (Pt, <10 ppb; Pd, <4 ppb; Haffty and Riley, 1968). Averages for Pt and Pd and Pt/Pd ratios were calculated only from values above the lower limits of determination; values below those limits were not used (Page and others, 1977). This severely affected that study's results because 60 percent of samples had determinable amounts of Pd but only 17.5 percent contained determinable Pt. Thus many pairs with determined Pd values but Pt <10 ppb were not used in calculating the average Pt/Pd (Page and others, 1977).

As discussed previously in the section on "Methods and Limitations", the more recently available analytical methods that have lower lower limits of determination for both Pt and Pd (0.5 ppb; Meier and others, 1991; table 3) gave strikingly different PGE values for the Gravina-belt volcanic rocks in our study. Although our two samples from the Ketchikan area admittedly do not adequately characterize PGE concentrations for this part of the belt, they show Pd rather than Pt dominance (mean Pd/Pt, 1.34, G-KE, table 3). Six samples from the Petersburg area of the central part of the Gravina belt show a much higher dominance of Pd (mean Pd/Pt, 3.60, G-PE, table 3), and samples from the Juneau and Admiralty Island areas of northern parts of the belt also show strong Pd dominance (mean Pd/Pt, 1.82, G-JU, table 3). Our study thus shows that the extrusive rocks of the Gravina belt overall are characterized by Pd rather than Pt dominance. The dike rocks in the Douglas Island Volcanics, on the other hand, are Pt dominant (Pt/Pd, 1.39, G-JUd, table 3).

We also examined the relation between PGE and MgO because decreasing MgO is taken as an index of increasing crystallization stage in mafic magmas (Fryer and Greenough, 1992; Wyborn, 1992). The Douglas Island Volcanics near Juneau as a whole have a large range in MgO (about 3 to 19 percent; fig. 3B). Different parts of the unit (Ford and Brew, 1988) have appreciable ranges in average content of MgO (7.2 to 9.0 percent) and of total alkalis ( $K_2O+Na_2O$ , 3.8 to 5.0 percent) in the high-MgO alkali basalts (Ford and Brew, 1988; Wilson, 1989). Figure 3A shows the variation in average MgO with Pd and Pt concentrations in units of this study and the wide MgO range for different parts of the Gravina belt. Pd and, to a lesser degree, Pt, show a general decrease with decreasing MgO in the Douglas Island Volcanics (fig. 3B); this suggests a possible decrease in crystallization stage of the erupting magmas (Fryer and Greenough, 1992; Wyborn, 1992).

Wyborn (1992) reported that Pt is highest in the most magnesian volcanic rocks and that Pd is more abundant in more fractionated low-magnesian rocks. The relations shown in figure 3B are interpreted to suggest that Pd, and possibly Pt, are concentrated in later, lower magnesian rocks of the Douglas Island Volcanics. Volcanic rocks of the upper part of the Wrangellia terrane have a range of MgO content (about 3 to 12 percent); somewhat less than that of the Douglas Island Volcanics. In contrast to the Douglas Island, the Wrangellia terrane shows little covariation of Pt or Pd with MgO (fig. 3 C).



Histograms of Pd and Pt concentrations in rocks of the Gravina belt near Juneau and in the rocks of the upper and lower parts of the Wrangellia terrane are shown in figure 4. Rocks of the Gravina belt of the Juneau area show a central bimodal distribution for Pd (fig. 4A), which is unlike the marked negative skewed distributions (fig. 4B, C) for rocks of the Wrangellia terrane. Platinum distributions of all units are negatively skewed (fig. 4). We do not have any explanation for these features.

The spread of Pd values in the metavolcanic rocks of the Juneau part of the Gravina belt (fig. 4A) is nearly as broad as that of rocks of the Ketchikan area of the belt (<4 to 24 ppb) and they encompass the spread of values known in most large basalt provinces as described by Page and others (1977). Ranges in Pd values are even wider for metavolcanic rocks of the Wrangellia terrane (fig. 4B, C). Mean Pd concentrations of units (table 2) are generally similar to those in average flood basalt (10 ppb; Campbell and others, 1983) and are much higher than in midocean-ridge (~1.0 ppb, Crocket and Teruta, 1977; ~1.0 ppb, Campbell and others, 1983; < 0.1-6.3 ppb, Barnes and others, 1985) and ocean-island basalts (1.6 ppb, Barnes and others, 1985). Mean Pt and Pd concentrations are generally similar to those of ophiolitic Mg-rich basalt (Pt, 9.2 ppb, Pd, 9.7 ppb, Crocket, 1981). The presence of pillows in units we have studied (Ford and Brew, 1993) indicates subaqueous eruption of the basalts, but the Pd contents are so much higher than those reported by Crocket and Teruta (1977) to be due to Pd leaching by seawater-basalt reactions that it appears that such leaching did not take place in the samples in our study.

Ternary variation diagrams (not shown here) depicting relative concentrations of Pd, Pt, and Rh indicate that the principal variation in all the rocks in this study is between Pt and Pd, with generally negligible Rh variation and very low Rh concentrations; this relation includes the volcanic rocks of the Gravina belt in the Ketchikan area as well as of Alaskan-type mafic and ultramafic intrusions of southeastern Alaska (Page and others, 1977; Clark and Greenwood, 1972; Czamanske and others, 1981; Loney and Himmelberg, 1992). A large percentage of Rh values is below the lower limits of determination (table 3), as was reported for rocks of the Gravina belt of the Ketchikan area (Page and others, 1977), and thus the generally negligible Rh variation probably has limited significance.

The volcanic units of different ages in this study show closely similar chondrite-normalized PGE patterns (fig. 5). Chondrite (C-1, Naldrett, 1981) rather than mantle values are used here for normalization in order to allow direct comparison with those on other published diagrams of Alaskan-type bodies and other mafic plutonic rocks (Leblanc, 1991; Loney and Himmelberg, 1992). We are aware that Barnes and others (1988) instead recommend normalization with mantle values to show relations with that probable PGE source. The PGE sequence in figure 5 reverses Pt and Pd in the recommended order by melting point (Barnes and others, 1988) to allow direct comparison with published diagrams (Loney and Himmelberg, 1992) created by the same computer program (Wheatley and Rock (1988) as that used in our study. If PGE characteristics reflect mantle sources (Fryer and Greenough, 1992; Leblanc, 1991; Barnes and others, 1988), then the close similarity in normalized patterns (fig. 5) for these volcanic units with their differences in age and tectonic setting (Ford and Brew, 1987, 1988, 1993) seems to us to be a fairly remarkable feature and suggests that the processes that control PGE distribution at the deepest crustal levels override these differences. Recall that other evidence indicates that the generation of the melts for these units involved ocean-floor, ocean-island, flood-basalt, and subduction-related volcanism of late Paleozoic to Early Cretaceous age.

Platinum-group elements are fractionated according to order of decreasing melting point according to Fryer and Greenough (1992) but concentrations in the source rock during partial melting and the mechanisms of alteration, partial melting, crystal fractionation, and sulfide liquid-silicate liquid fractionation by which the whole process takes place are difficult to evaluate (Barnes and others, 1985; M. Zientek, U.S. Geological Survey, written comm., 1998). Platinum-group-element fractionation of mantle melts is strongly influenced by the nature of the source region and timing of sulfur saturation (Hamlyn and Keays, 1986). Our study does not aspire to explain those mechanisms, further, we believe that PGE concentration data are incapable of revealing the actual complexities of the fractionation process. Nevertheless, we speculate that the extraction of volcanic magmas at different crystallization stages of parent magmas may be one possible explanation of the PGE variations in rocks of this study. Differences between variations of Pt and Pd in the Douglas Island Volcanics (fig. 2B) might be accounted for by Pt fractionation in source magma prior to eruption according with the fractionation sequence  $Pt < Pd$  (Barnes and others, 1985; Gottfried and others, 1990).

The Wrangellia terrane flood basalts, on the other hand, do not have such Pt and Pd variations (fig. 2C, D); this could be argued to result from the rapid eruption of those magmas from lower crustal levels without the opportunity for such fractionation to occur.

### COMPARISONS WITH ALASKAN-TYPE INTRUSIONS

Mafic-ultramafic intrusions termed "Alaskan type" are reported from many parts of the world and are of widely varying age (Himmelberg and others, 1986; Himmelberg and Loney, 1995). Those principally of Cretaceous age in southeastern Alaska are used for comparison with the metavolcanic rocks of this study. As noted earlier, with few exceptions, the PGE data for the Alaskan-type bodies in southeastern Alaska (Clark and Greenwood, 1972, Loney and Himmelberg, 1992) were obtained using analytical methods with relatively high lower limits of determination, as were those in early studies of Gravina-belt rocks (Page and others, 1977; Ford and Brew, 1987). Also as discussed previously, the contradictory results obtained from data derived from different analytical methods and truncated at different lower determination limits makes use of aggregated data for comparisons questionable. The Alaskan-type intrusions are reported to have dominance of Pt over Pd, as shown by an average  $Pt/(Pt + Pd)$  of 0.59 (Loney and Himmelberg, 1992). However, in that report Loney and Himmelberg (1992) incorporated the Pt and Pd "averages" of Clark and Greenwood (1972) that were probably (although not stated clearly in their report) calculated from censored data.

The metavolcanic rocks of the Gravina belt in our study show dominance of Pd over Pt by a mean  $Pt/(Pt+Pd)$  of 0.33 (range, 0.26-0.43, table 3). The Pt and Pd averages for these Gravina-belt rocks were calculated from values above lower determination limits using data from both older and current analytical methods (table 3). In contrast to the rocks of extrusive origin, mafic dikes that cut the Douglas Island Volcanics have mean  $Pt/(Pt+Pd)$  of 0.58, showing their Pt dominance over Pd (table 3) and with about the same ratio as for Alaskan-type bodies (0.59, Loney and Himmelberg, 1992). The  $Pt/(Pt+Pd)$  ratios of rocks of the Gravina belt are very similar to those for the upper and lower parts of the Wrangellia terrane in the Juneau area (table 3).

Average  $Pt/(Pt+Pd)$  and  $Cu/(Cu+Ni)$  values for both units plot closely together in Loney and Himmelberg's (1992) diagram of figure 6. That figure compares those ratios with ratios of mafic and ultramafic rocks of southeastern Alaska and elsewhere; it also shows that such data are lacking for effective comparison of the volcanic rocks with most of the Alaskan-type intrusions in southeastern Alaska.

Loney and Himmelberg's (1992) chondrite-normalized multi-element plots (not shown here) for Alaskan-type bodies generally show Pd highs relative to Pt, except for Union Bay ultramafic rocks, and similar relations are shown for the volcanic units of our study (fig. 5). A major dissimilarity between rocks of the Gravina belt and Alaskan-type intrusions is that levels of PGE abundances are generally almost an order of magnitude lower in the volcanic rocks, based on data dominantly for ultramafic cumulates (Clark and Greenwood, 1972; Loney and Himmelberg, 1992). The mafic parts of the Alaskan-type intrusions are probably fractionates of ultramafic parts of the bodies (Himmelberg and Loney, 1995) and would be expected to be more similar to the Gravina-belt volcanic rocks than would be the ultramafic cumulates, but few PGE data that would allow comparison are available for the mafic parts of the Alaskan-type intrusions. A single gabbro sample from the Union Bay intrusion shows much closer comparison in Pd and Pt with the volcanic rocks than with the ultramafic rocks of the body (UM-UBgab, fig. 6B). More data for the mafic parts of Alaskan-type bodies are obviously needed in order to compare them with the volcanic rocks.

The Cretaceous volcanic rocks of our study show a dominance of Pd over Pt, in contrast to Pt dominance as reported for approximately coeval Alaskan-type intrusions (Loney and Himmelberg, 1992). The associated dike rocks, in contrast to the volcanic rocks, also show Pt dominance by their mean values for  $Pt/Pd$ , of 1.39, and for  $Pt/(Pt+Pd)$ , of 0.58 (G-JUd, table 3). Those values are nearly the same as for Alaskan-type intrusions (Loney and Himmelberg, 1992). Rare-earth element (REE) data also show differences between the volcanic rocks and the intrusions. Both mafic and ultramafic rocks of Alaskan-type bodies show flat chondrite-normalized REE patterns (Himmelberg and Loney, 1995) that are very unlike those of the Douglas Island Volcanics, which show comparatively strong enrichment in light REEs (Ford and Brew, 1988).



The REE and PGE comparisons thus argue against the previously suggested genetic tie between volcanic rocks of the Gravina belt and the Alaskan-type intrusions. Rare-earth-element data, however, are not available for the dike rocks.

Dike rocks associated with another Alaskan-type body are considered to be representative of a parental magma (Salt Chuck intrusion; Loney and Himmelberg, 1992). The dikes in the Douglas Island Volcanics, though not dated, were probably involved in either the ~110-Ma (M1) metamorphic event (Brew and others, 1989) that affected the Douglas Island Volcanics; however, the absence of penetrative deformation suggests that the dikes were emplaced during the time of the post-kinematic M2 metamorphism, although they clearly are not part of any of the aureoles formed by that metamorphism. It should be noted that at least two of the Alaskan-type bodies also show an involvement in deformation associated with M1 metamorphism (Himmelberg and Loney, 1995).

## SUMMARY

There are problems associated with our data because of different analytical techniques and analytical uncertainties; nevertheless, we judge our interpretations as strongly suggestive, although not conclusive. Metabasalts of the upper Paleozoic and Triassic Wrangellia terrane and of the Lower Cretaceous part of the Gravina belt in the Juneau area show few differences in Pt, Pd, and Rh contents. The Gravina-belt rocks near Juneau, which have high-Mg, alkalic basalt composition, are higher in Cr (mean, 266 ppm) and Ni (mean, 95 ppm) concentrations and have much lower Ni/Cu, Ni/Pd, and Cu/Pt ratios than do the tholeiitic composition basalts of the Wrangellia terrane (Cr, 210-246 ppm; Ni, 46-61 ppm, table 2). The mineral hosts of the PGEs are not known, but positive Pd and Cu covariations may be interpreted to suggest that Pd occurs in sulfides in the volcanic rocks and perhaps Pt may also in some units. Differences between covariations for Cu and MgO with Pd and Pt in the volcanic units may reflect differences in fractionation stages represented.



Intuitively, mantle source regions of the magmas (and PGE's; Fryer and Greenough, 1992) of the nonsubduction-related flood basalts of the Wrangellia terrane and of the post-accretionary, arc- and subduction-related Gravina terrane-overlap belt (Ford and Brew, 1987, 1988, 1993) are probably different ; the units are of widely different ages; and the source regions could be expected to differ greatly. The generally close similarity in PGE characteristics of these diverse and seemingly unrelated suites of mafic volcanic rocks is to us remarkable and calls for further comparisons with other suites of volcanic rocks.

Geographic PGE variations seem to exist in the volcanic rocks along the Gravina belt, but they are poorly defined with the small amount of modern data available for these rocks. The present study shows that the metavolcanic rocks of northern areas of the Gravina-belt are Pd rather than Pt dominant as reported from previous studies, and our data suggest that the belt as a whole shows Pd dominance. Mechanisms that can account for variations in PGE's (Barnes and others, 1985) have not been evaluated in this study.

The mean Pd concentrations of metabasalts of the Douglas Island Volcanics and the Wrangellia terrane are nearly the same as in average flood basalt (10 ppb) and high-Mg basalt of ophiolites (9 to 10 ppb) and much higher than that of about 1.0 ppb in ocean-ridge and ocean-island basalt. Thus, geochemical signatures of midocean-ridge, within-plate, or ocean-island tholeiite for Upper Triassic basalt of the Wrangellia terrane reported from earlier trace-element studies of these rocks and their tectonic-discriminant diagrams ( Ford and Brew, 1987, 1988, 1993) are inconsistent with results of our present study.

Nevertheless, the Early Cretaceous age of both the Douglas Island Volcanics of the Gravina belt and of many of the mafic-ultramafic Alaskan-type bodies is consistent with their previously suggested cogenetic relationship. Also, (1) the generally much lower PGE concentrations of the Gravina-belt volcanic rocks as compared with the Alaskan-type bodies is exactly what would be expected in comparisons between mafic rocks and ultramafic cumulates; and (2) the Gravina belt is a volcanic province characterized by Pd/Pt ratios that show Pd dominance; in contrast, the mafic-ultramafic Alaskan-type intrusions have reported ratios for these elements that show Pt dominance, this is compatible with a cumulate-extrusive  $Pt < Pd$  crystallization sequence. However, dikes in the Douglas Island Volcanics also show Pt dominance, with  $Pt/(Pt+Pd)$  of 0.58, which is about the same as the average for Alaskan-type intrusions. We interpret the dikes to better represent the parent magma for the intrusions than do the extrusive rocks.

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**Table 1.** Lower limits of determination and uncertainties for elements analyzed for by different methods and reported in tables 2 and 3.

<u>Element</u>	<u>Lower limit of determination</u>	<u>Analytical uncertainty</u>
Cu <sup>1</sup>	10 ppm (2 ppm)	+/- 5-10 % at these levels of concentration
Ni <sup>1</sup>	10 ppm (2 ppm)	+/- 5-10 % at these levels of concentration
Cr <sup>1</sup>	20 ppm (20 ppm)	+/- 5-10 % at these levels of concentration
PGE <sup>2</sup>		
Pt	1.5 ppb	+/- 10-15 % at these levels of concentration
Pd	1.5 ppb	+/- 10-15 % at these levels of concentration
Rh	0.5 ppb	+/- 10-15 % at these levels of concentration
Ru	0.5 ppb	+/- 10-15 % at these levels of concentration
Ir	0.5 ppb	+/- 10-15 % at these levels of concentration
PGE <sup>3</sup>		
Pt	10 ppb (10 ppb)	+/- 10-15 % at these levels of concentration
Pd	4 ppb (1 ppb)	+/- 10-15 % at these levels of concentration
Rh	5 ppb (2 ppb)	+/- 10-15 % at these levels of concentration

<sup>1</sup>Analysis by energy-dispersive X-ray fluorescence (EDXRF) spectrometry (Johnson and King, 1987; King, 1996); lower limits of determination from King (1996, p. 229); lower limits of determination in parentheses from Baedeker (1987, p. 3); analytical uncertainty from King (1996, p. 232).

<sup>2</sup>Analysis by ICP-mass spectrometry (ICPS) (Meier and others, 1991, 1996); lower limits of determination from Meier and others (1996, p. 159); analytical uncertainty from Meier and others (1996, p. 163-164).

<sup>3</sup>Analysis by fire-assay and emission-spectrographic method of Hafty and Riley (1968); lower limits of determination from Hafty and Riley (1968, p. 111); lower limits of determination in parentheses from Baedeker (1987, p. 3); analytical uncertainty judged to be like that of Meier and others (1996, p. 163-164).

TABLE 2. Summary of Cu, Ni, and Cr determinations and ratios for samples of mafic metavolcanic rocks of the Gravina belt and Wrangellia terrane of southeastern Alaska.

(In parts per million (ppm))<sup>1</sup>. See Table 1 for lower limits of determination.]

Unit <sup>2</sup>	Number of analyzed samples	Cu mean	Cu st.dev	Cu range	Ni mean	Ni st.dev	Ni range	Cr mean	Cr st.dev	Cr range	Ni/Cu mean	Ni/Pd (X 10 <sup>-3</sup> ) mean <sup>3</sup>	Cu/Pt (X 10 <sup>-3</sup> ) mean <sup>3</sup>	Pd/Cu (X 10 <sup>-3</sup> ) mean <sup>3</sup>
G-JU	47	98	35	13-190	95	98	5-400	266	271	<20-1300	1.1	7.8 (46)	7.4 (47)	0.11 ( )
G-JUd	7	71	30	<10-100	114	56	<10-188	375	165	<20-590	1.8	21.5 (4)	33.8 (5)	0.05 ( )
G-KE	2	86	—	82-90	48	—	44-52	188	—	80-295	.6	7.5 (2)	17.1 (2)	0.09 ( )
G-PE	6	116	27	78-158	54	40	<10-98	144	99	<20-255	.4	3.0 (5)	28.5 (5)	0.12 ( )
W-U	44	93	84	5-390	102	61	20-330	246	189	<20-780	3.1	22.4 (40)	15.2 (28)	0.18 ( )
W-L	23	112	77	24-220	91	46	30-250	210	135	<20-470	2.2	5.4 (13)	27.6 (15)	0.07 ( )

<sup>1</sup> Analysis by energy-dispersive X-ray fluorescence spectrometry (Johnson and King, 1987).

<sup>2</sup> G-JU, Gravina belt, Juneau-area Cretaceous Douglas Island Volcanics and Seymour Canal Formation; G-JUd, dikes in G-JU unit; G-KE, Gravina belt, Ketchikan area;

G-PE, Gravina belt, Petersburg area; W-U, Upper Triassic metabasalt of Wrangellia terrane; W-L, upper Paleozoic and Triassic(?) metabasalt of lower part of

Wrangellia terrane (lower part of Gashineau Volcanics, see text). Areas shown on fig. 1.

<sup>3</sup> PGE data from table 23 based on unqualified determinations (number of unqualified determinations in parentheses).

TABLE 3. Summary of platinum-group element concentrations and ratios determined for samples of mafic metavolcanic rocks of the Gravina belt and the Wrangellia terrane of southeastern Alaska

[In parts per billion (ppb). See Table 1 for lower limits of determination.]

Unit <sup>3</sup>	Number of analyzed samples, total and (Pt+Pd+Rh only) <sup>2</sup>	Number of samples at or below determinable limits	Percent of samples with determinable values	Median concentrations of Pt, Pd, Rh, Ru, Ir	Mean <sup>4</sup> concentrations of Pt, Pd, Rh, Ru, Ir	Mean <sup>4</sup> ΣPGE	Median ΣPGE	Mean <sup>4</sup> Pt/Pd	Mean <sup>4</sup> Pt/(Pt+Pd)	Mean <sup>4</sup> Pd/Pt	Mean <sup>4</sup> Pd/Rh
G-JU	69 (24)	20, 1, 60, 61, 68	71, 100, 13, 12, 1	5, 10, 0, 0, 0	6, 10, .1, 0, 0	16 (47)	15	.64 (47)	.31 (47)	1.56 (47)	15.0 (7)
G-JUD	8 (1)	2, 3, 8, 8, 8	75, 62, 0, 0, 0	6, 5, 0, 0, 0	6, 7, 0, 0, 0	10 (4)	10	1.39 (4)	.58 (4)	.72 (4)	—(0)
G-KE	2	0, 0, 2, 2, 2	100, 100, 0, 0, 0	—	6, 8, 0, 0, 0	13 (3)	—	.76 (3)	.43 (3)	1.32 (3)	—(0)
G-PE	6	1, 1, 1, 4, 6	83, 83, 83, 33, 0	6, 17, 1, 1, 0	6, 17, 1, 1, 0	20 (5)	22	.37 (5)	.26 (5)	2.70 (5)	23.3 (5)
W-U	44 (15)	16, 3, 33, 36, 44	64, 93, 25, 18, 0	5, 10, 0, 0, 0	6, 11, .2, .2, 0	17 (28)	13	.74 (28)	.40 (28)	1.635 (28)	27.5 (11)
W-L	23 (2)	8, 9, 19, 14, 23	65, 61, 17, 39, 0	6, 13, 0, 0, 0	5, 11, .1, .3, 0	16 (15)	21	.45 (15)	.37 (15)	2.22 (15)	38.3 (4)

<sup>1</sup> Analysis by ICP-mass spectrometry (Meier and others, 1991).

<sup>2</sup> Analysis, Pt, Pd, and Rh only, by fire-assay and emission-spectrographic method of Haffty and Riley (1968).

<sup>3</sup> Units as in table 2.

<sup>4</sup> Calculated from unqualified determinations of PGE. Number of unqualified determinations in parentheses.

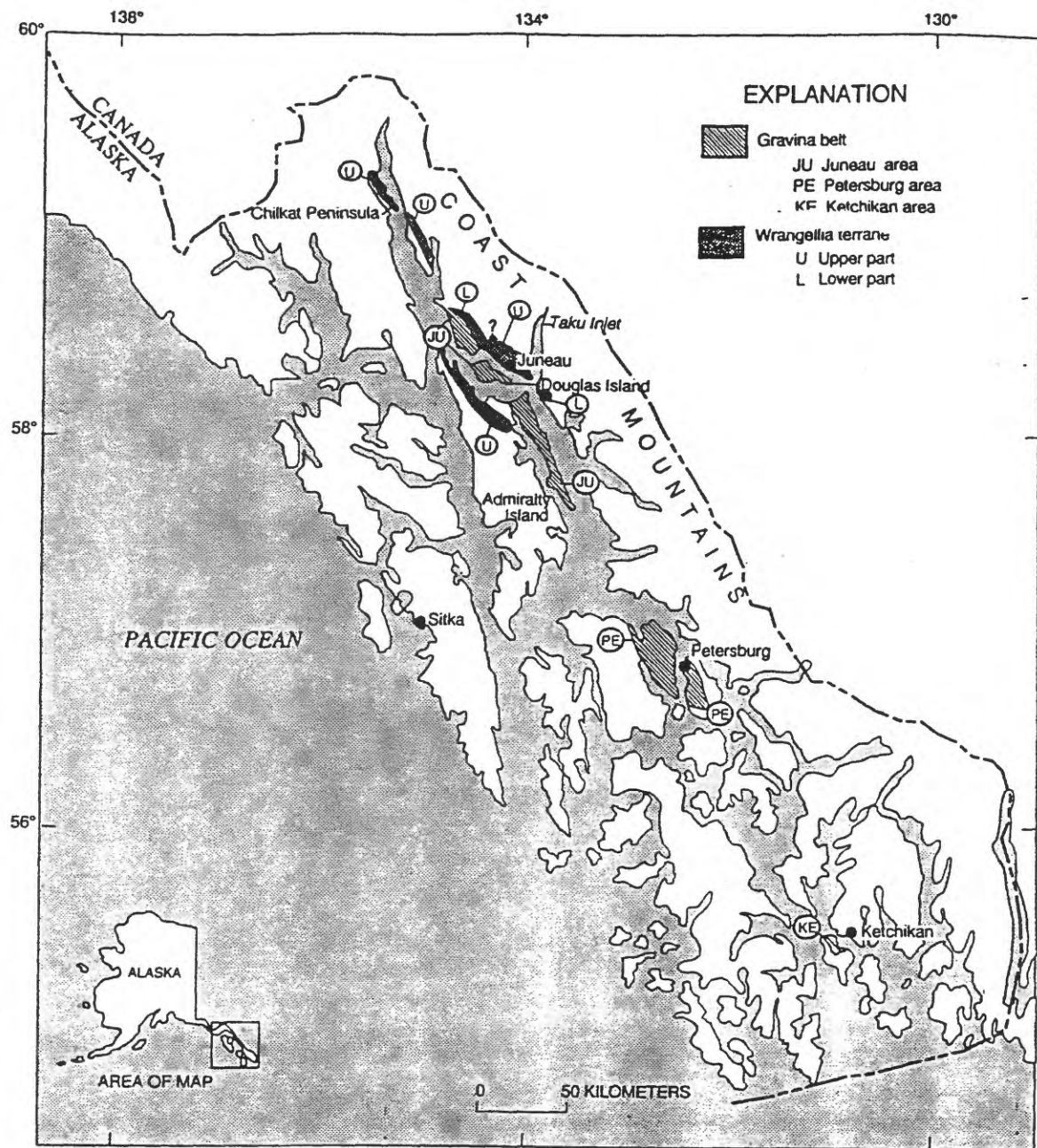


Figure 1. Index map of southeastern Alaska, showing areas of Gravina belt rocks (JU, PE, KE) and of Wrangellia terrane rocks: upper part (Triassic, U) and lower part (upper Paleozoic(?), Triassic(?), L) sampled in this study. Patterns show areas of samples. Extent of units not shown (see Ford and Brew, 1993).



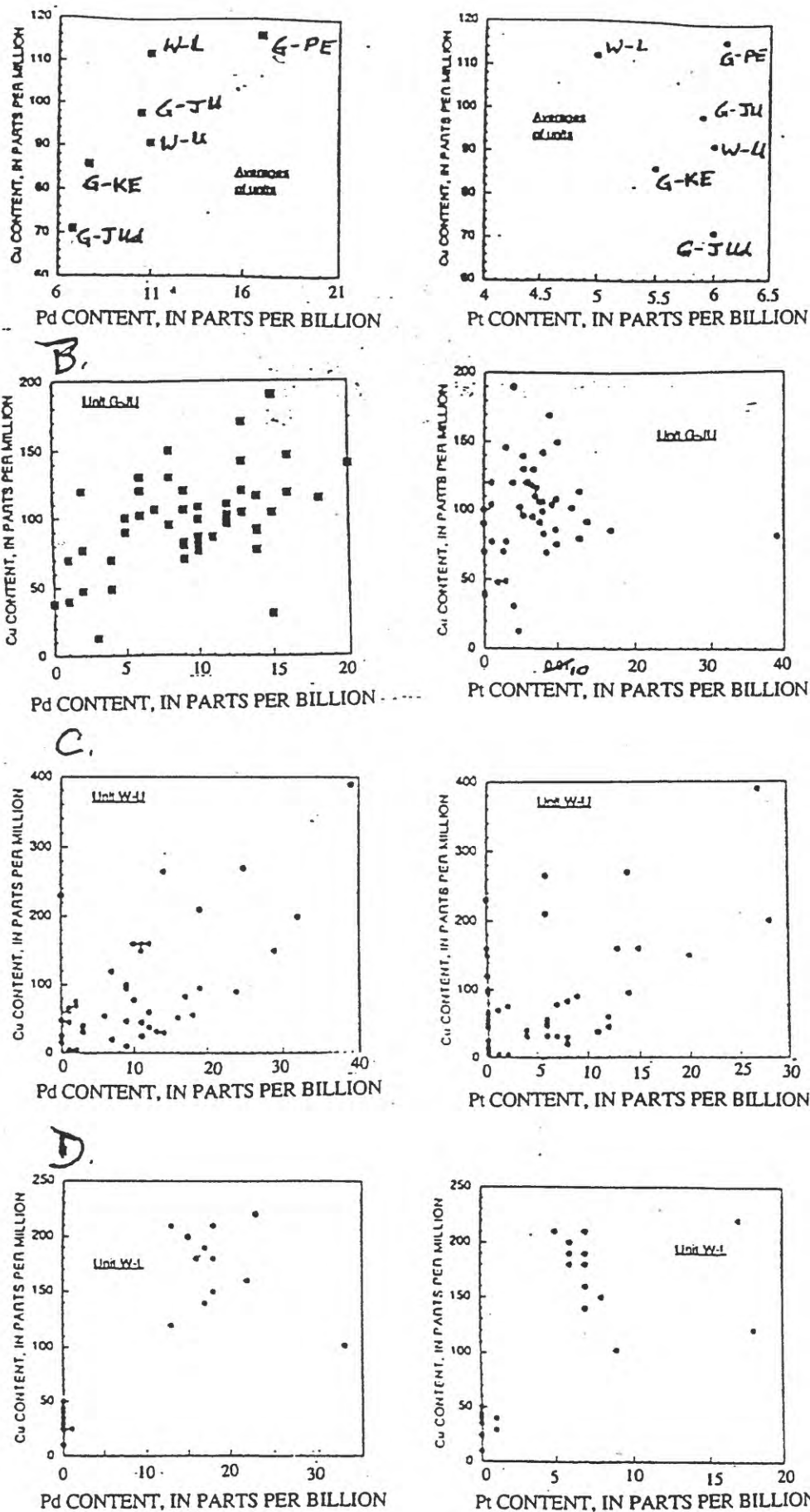
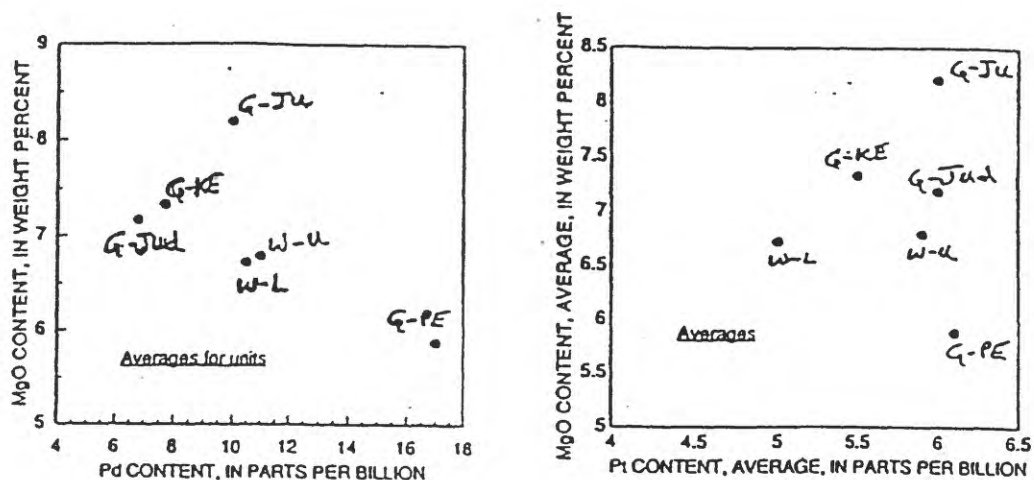
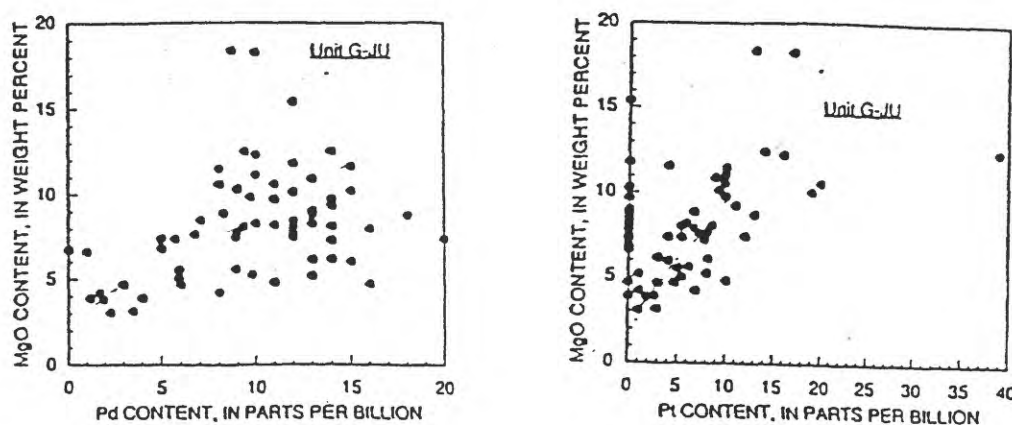


Figure 2. Variations of Pd and Pt with Cu concentrations in metavolcanic units of this study: A., averages of all units (table 2); B., Gravina belt of the Juneau area (G-JU); C., upper part of Wrangellia terrane (W-U); D., lower part of Wrangellia terrane (W-L).

A.



B.



C.

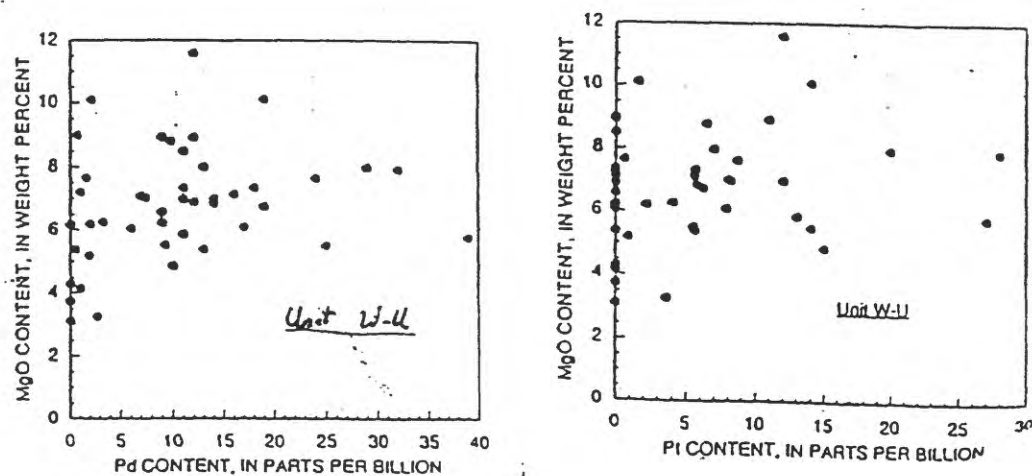


Figure 3. Variations of Pd and Pt with MgO concentrations in metavolcanic units of this study. A., averages of all units (table 3). B., Gravina belt of the Juneau area (G-JU); C., Upper Triassic part of Wrangellia terrane (W-U). MgO contents from A.B. Ford (Unpub. data).

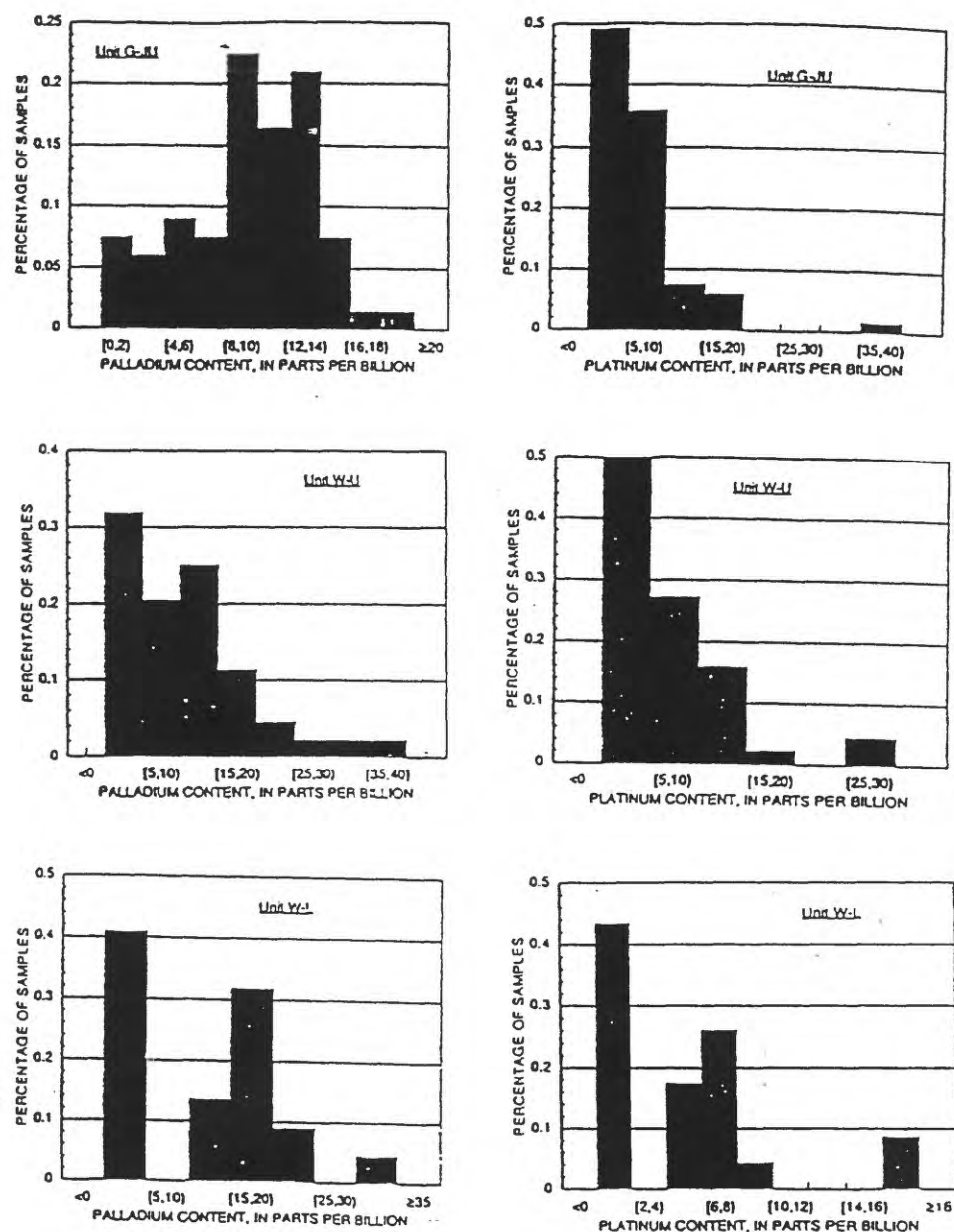


Figure 4. Histograms showing distribution of percentages of samples in 2 ppb intervals of Pd and Pt contents in metavolcanic rocks of A., the Gravina belt of the Juneau area (G-JU); and B., the upper (W-U) and C., the lower parts (W-L) of the Wrangellia terrane. (See table 3 for number of samples).

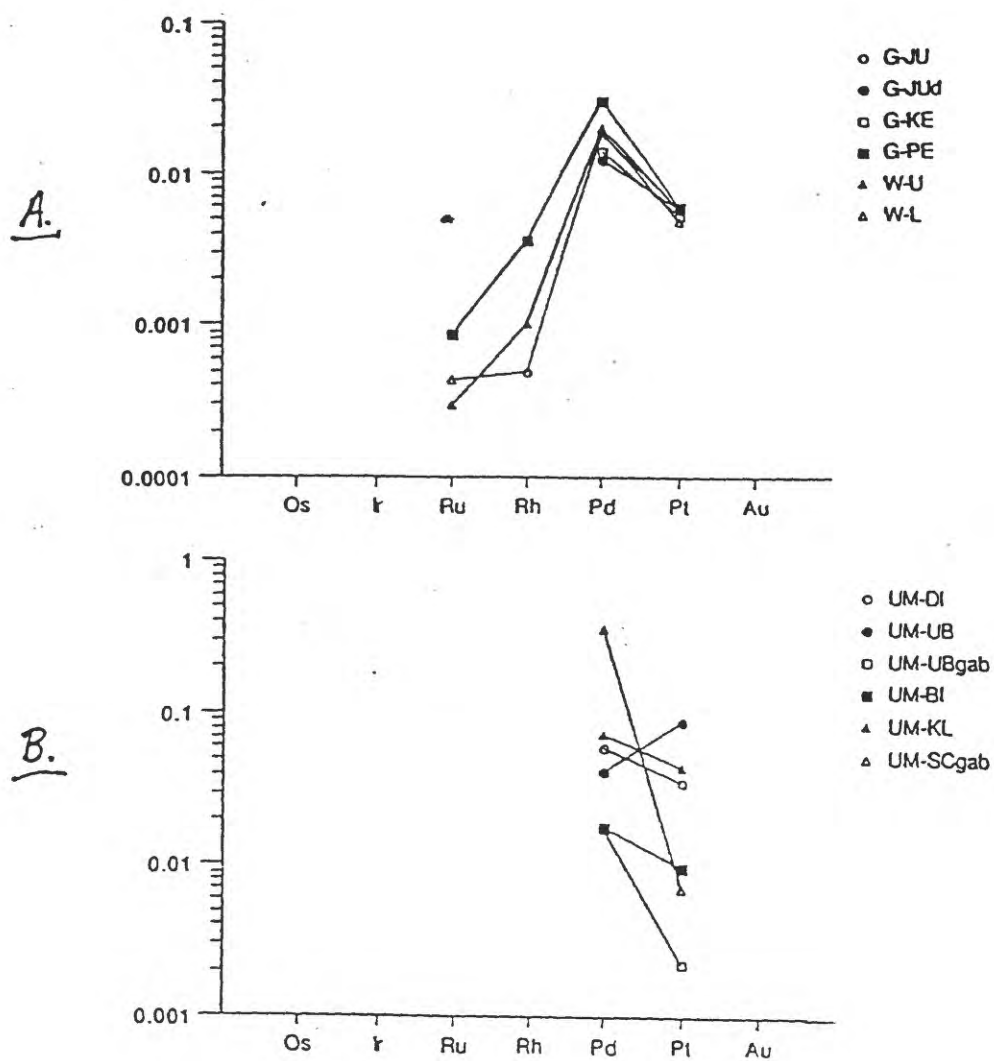


Figure 5. Chondrite-normalized PGE diagram comparing metavolcanic rocks of southeastern Alaska. Prepared by computer program of Wheatley and Rock (1988). Chondrite (C-1) normalizing values of Naldrett (1981). Letter symbols are as in table 2.

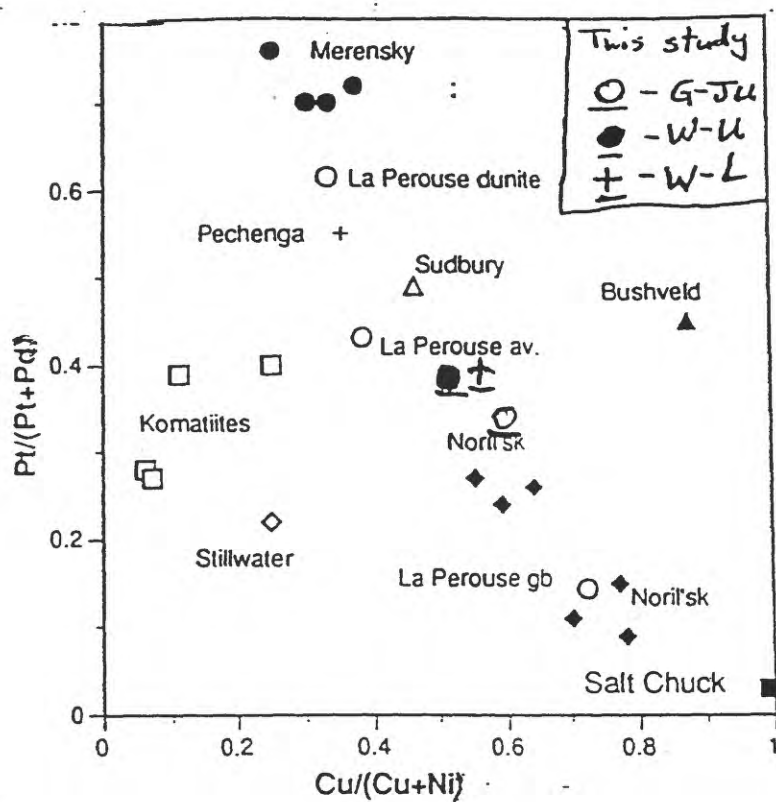


Figure 6. Variation between  $Pt/(Pt+Pd)$  and  $Cu/(Cu+Ni)$  in metavolcanic units of this study compared with Alaskan-type intrusions and other mafic igneous rocks of Loney and Himmelberg (1992). G-JU, Gravina belt of Juneau area; W-U, upper part of Wrangellia terrane; W-L, lower part of Wrangellia terrane.