THE GEOCHEMISTRY OF Pd, Os, Ir AND Au IN THE MOUNT ALBERT PLUTON

THE GEOCHEMISTRY OF Pd, Os, Ir AND Au IN THE MOUNT ALBERT ULTRAMAFIC PLUTON, QUEBEC

By

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Title: The Geochemistry of Pd, Os, Ir and Au in the Mount Albert Ultramafic Pluton, Quebec

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Scope and Contents: A neutron activation analysis procedure for the simultaneous determination of Au, Pd, and Ir, and separate determination of Os is described. The procedure has been applied to the determination of these metals in the Mount Albert ultramafic pluton. A review of previous geological studies on the pluton mainly by MacGregor is presented.

A total of 20 samples, including 5 fresh dunites and peridotites, 8 serpentinized equivalents, 4 disseminated chrome spinels, 1 clinopyroxenite, and 2 massive chromites, were analyzed. The results are compared with other terrestrial materials and meteorites. A correlation matrix for the analyzed metals was calculated, and compared with that obtained by Keays for precious metal values for Cu-Ni sulfides from the Strathcona Mine, Sudbury. The origin of the alpine type ultramafics is discussed in terms of precious metal abundances and trends in the pluton. The fractionation of the metals between the residual magma and primary crystals, between accessory chrome spinel and whole rock, between deuteric massive chromite and whole rocks and finally, variations produced by serpentinization, are discussed.

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TABLE OF CONTENTS

TABLE OF CONTENTS (continued) Page

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

A neutron activation analysis procedure for the simultaneous determination of Au, Pd and Ir, and separate determination of Os is described and applied to the determination of these metals in the Mount Albert ultramafic pluton, Quebec.

The Mount Albert is an alpine-type ultramafic body whose petrography, geology and geochemistry has been discussed in some detail by MacGregor (1962, 1964). It consists mainly of serpentinized dunite and peridotite. However, it is distinguished by the presence of an eastern lobe which is essentially unserpentinized. In addition to ferromagnesians, two varieties of spinel including disseminated accessory chrome spinel and massive, discordant chromite veins or schlieren are important mineralogical constituents.

Twenty samples were analyzed including 5 fresh dunites and peridotites, 8 serpentinized equivalents, 4 disseminated chrome spinels, 1 clinopyroxenite, and 2 massive chromite.

The concentrations (in p. p. b.) of average fresh ultramafics and their serpentinized equivalents are:

	Pd	Os	Ir	Au
Fresh rocks	7.7	7.2	2.5	0.99
Serpentinized rocks	10	6.6	2.2	2.4

The pluton was intruded as a nearly solid mass of olivine and some orthopyroxene with about 15 weight per cent melt. A small concentration of the precious metals, a factor of 2 to 3, in the melt relative to crystalline phases appears to have occurred. The disseminated chrome spinel and massive chromite appear to concentrate the precious metals. In particular, Os and Ir content of the massive chromite is approximately 10 times that of fresh or serpentinized whole rocks.

There is little change in average precious metal content with serpentinization. Pd shows a slight increase, and Ir and Os slight decreases in concentration with degree of serpentinization. Only Au appears significant to be enriched in serpentinized rocks where a two-fold increase occurs. The variation in precious metal content of all four metals increase when the rocks are serpentinized.

When normalized to chondrite meteorites, the precious metal data give fractionation trends similar to that of average chondrite. These trends are compatible with a model in which alpine ultramafics are regarded as residua from the partial melting of parental material of approximately chondritic composition.

CHAPTER 1

INTRODUCTION

The principal studies on the geochemistry of the precious metals are largely restricted to those materials with part per million precious metal contents including iron meteorites, the metal phase of chondrite, and ore deposits. The abundances of the precious metals in ordinary terrestrial materials are still very limited. Our knowledge of their geochemical behaviour, particularly as regards fractionation in igneous rock forming processes are still more or less hypothetical. Although recent works of Vincent and Crocket (1960a, b), De Grazia and Haskin (1964), Baedecker and Ehmann (1965), Razin (1965), Crocket and Skippen (1966), Morgan and Lovering (1967), Barker and Anders (1968), etc. cast some light on their geochemistry, much of the available data are largely for gold. Data on other precious metals, are for samples of widely scattered geographic distribution and their systematic geochemical behaviour in specific rock types has not been studied in any detail. An exception is the extensive and systematic study of the Strathcona Mine, Sudbury for Pd, Ir and Au by Keays (1967), and for Os and Ru by Hsieh (1967) which made important contribution to our understanding of the fractionation of precious metals associated with magmatic Cu-Ni sulfide deposits. With this type of study in mind, it was decided to conduct systematic study of Au, Pd, Ir and Os in the Mount Albert ultramafic pluton.

The geology, petrology, mineralogy, and geochemistry of the Mount Albert pluton has been extensively studied by many workers, particularly McGerrigle (1953, 54) and McGregor (1962, 64). Their conclusions on the origin of the pluton and its mode of emplacement have been generally accepted. A neutron activation procedure described by Crocket et al. (1968, in press) for analysis of Ru, Pd, Os, Ir, Pt and Au was used. Because of competing reactions and detection problems, and interference problems with U^{235} fission products, Pt and Ru were not included in the analytical scheme. Four metals, Pd, Os, Ir and Au, were analyzed on twenty samples including fresh ultramafics, serpentinized rocks, clinopyroxene, disseminated chrome spinel, and massive chromite.

The data permit an evaluation of the fractionation of these metals between major mineral phases in the pluton, a comparison of these metal fractionation trends in an alpine peridotite with trends for basaltic rocks and meteorites, a consideration of the effect of serpentinization on redistribution of previous metals and finally, a consideration of the fractionation of these metals in the residuum of this rock body represented by massive chromite schelerin.

Neutron activation analysis possesses some advantages over most other analytical techniques for this type of study. In particular, it has sufficiently high sensitivity to adequately detect many precious metals in the p. p. b. range common in this rock type. Further problems of reagent contamination are minimized and quantitative analytical procedures are not required. The simultaneous determination of a group of elements in the same sample is also advantageous,as it minimizes problems of sample inhomogeneity which may be very serious particularly when a comparison of geochemical trends of two or more elements is required.

CHAPTER 2

GENERAL GEOLOGY

2-1. General Statement

The geology, petrology and geochemistry of the Mount Albert ultramafic pluton and its contact metamorphic aureole are the subject of M.Sc. and Ph.D. theses by I. D. MacGregor (1962, 1964). The regional geology in the vicinity of Mount Albert has been discussed by McGerrigle (1953, 1954). The outline below is taken principally from the work of MacGregor.

The pluton (Fig. 2-1) is one of the chain of small ultramafic bodies that extends irregularly for more than 2,000 miles along the Appalachian axis of eastern North America from North Carolina to Newfoundland. Two smaller satellite dunitic plutons, Mount South, and Mount Paul, occur within 7 miles of Mount Albert. Besides the larger bodies, small pods and lenses of highly sheared serpentine have been found along the fault marking the south contact of the Shickshock group. They are shown in Fig. 2-2. The Mount Albert pluton has been intruded into the metavolcanic rocks of the Shickshock group. While the northern circumference of the semicircular mass contacts concordantly in strike with the surrounding Shickshock rocks, the

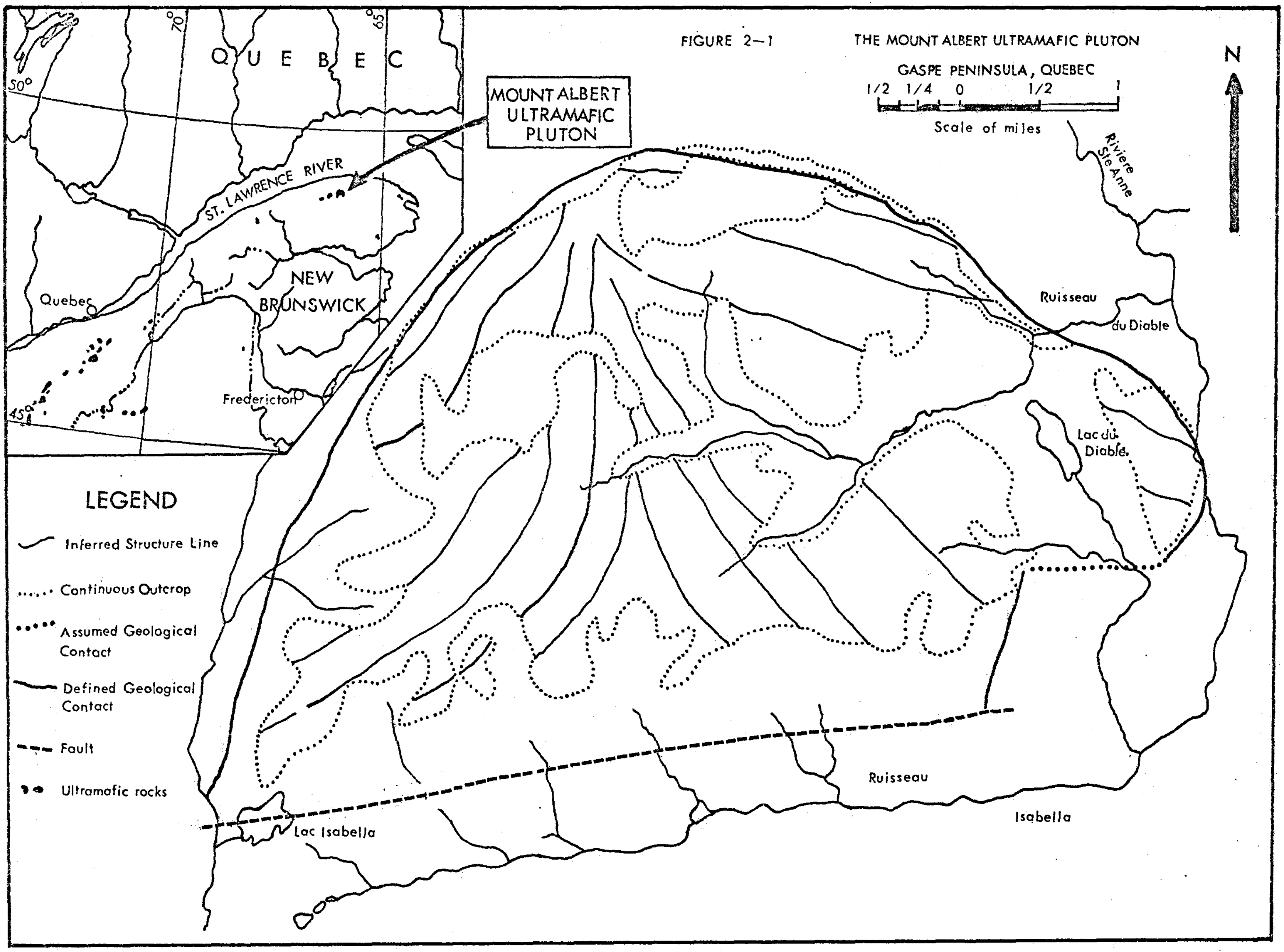

FIGURE 2—1 THE MOUNT ALBERT ULTRAMAFIC PLUTON

GASPE PENINSULA, QUEBEC

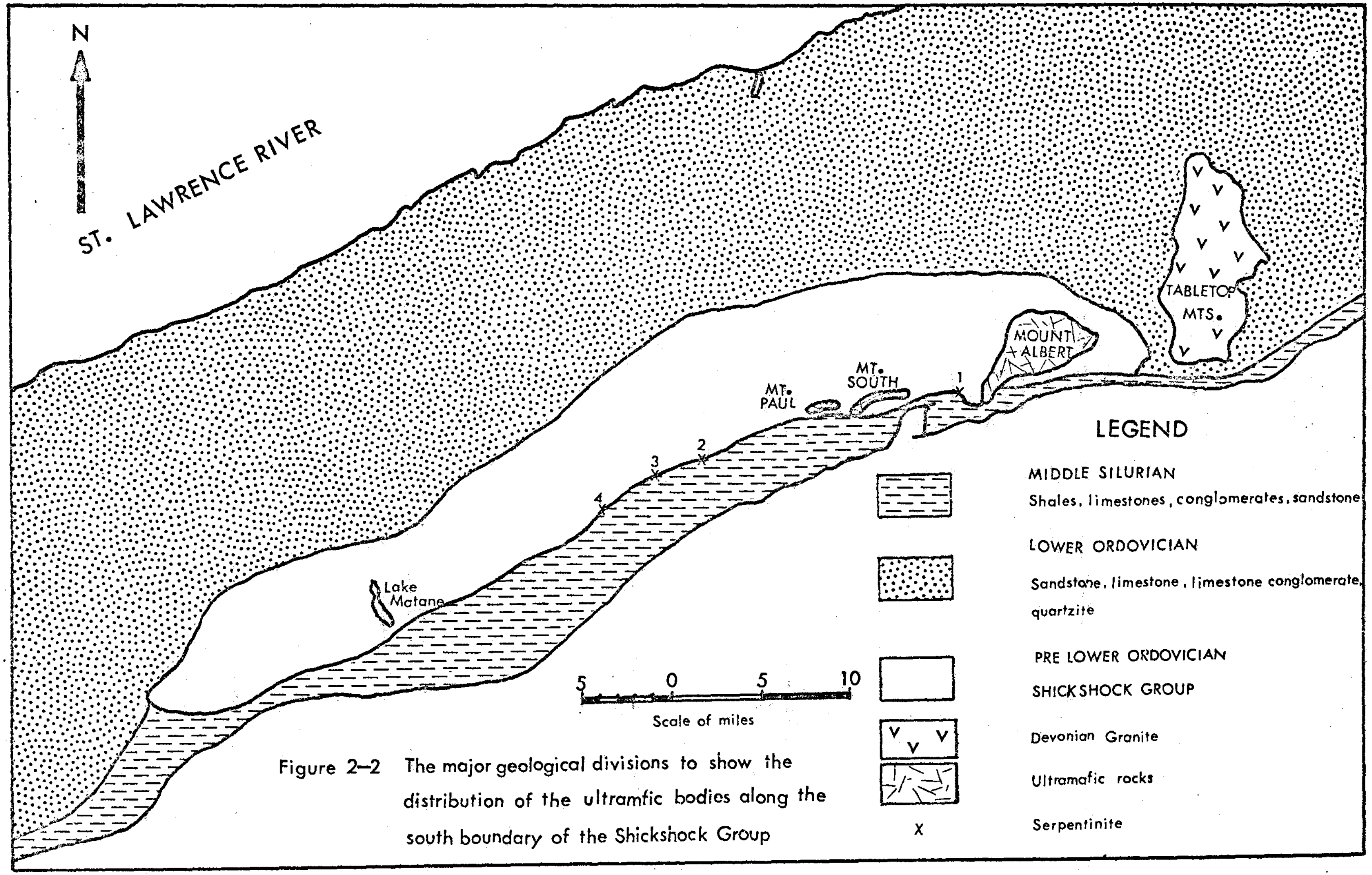

Figure 2–2 The major geological divisions to show the distribution of the ultramfic bodies along the south boundary of the Shickshock Group

southern margin is in fault contact with them.

The pluton is composed mainly of dunite and peridotite with minor pyroxenite and chromitite bands. A striking feature is its well developed thermal aureole which is less obvious around other ultramafic bodies of the type. Aureole rocks range from greenschist through epidote amphibolite to garnetiferous hornblende-pyroxene granulite at the contact. The maximum width of the contact aureole may reach 10, 000 feet. There is little variation in the bulk chemical composition of the country rock. Changes in mineral composition appear to be the result of recrystallization under a high temperature gradient away from the pluton rather than metasomatism.

As a result of varying degrees of serpentinization the pluton has a central core of less serpentinized rocks surrounded by a more serpentinized rim along most of the northern circumference with the exception of the eastern lobe near Lac du Diable which is nearly free of this alteration.

2-2. Country Rocks

The country rocks are shown in Fig. 2-2. The Shickshock group is composed predominantly of chlorite-epidote-albite-amphibole schists with minor arkose, quartzite, siliceous schist and a few limy beds. The original rocks are interpreted as intermediate to basic volcanic rocks with minor sedimentary layers. The northern margin of the Shickshock group has been variously interpreted as a fault, an unconformity and a gradational sequence from the Lower Ordovician rocks to the north. All writers agree that the southern boundary is in fault contact with Silurian sedimentary rocks. A gradual increase in metamorphic grade from north to south across the Shickshock belt was recognized by Mattinson (1958). The metasedimentary rocks increase in grade from chlorite-muscovite schist on the north through chlorite-biotite schist to biotite-sodic plagioclase-quartz rocks on the south. The metavolcanic rocks pass from massive medium to fine-grained volcanic rocks on the north to hard dark green amphibole schists on the south. The fault zone seen along the southern contact of the Shickshock group has been operative over a long period of time and is related to a major zone of crustal weakness responsible for the extrusion of the Shickshock volcanic rocks and the intrusion of the Mount Albert pluton and other ultramafic bodies.

The rocks to the south of the Shickshock group are primarily unmetamorphosed sediments of Silurian and Devonian age. They consist of limy shales and sandstones, limestones and occasional bands of limestone conglomerate. These beds occur as a southward dipping series with the oldest against the Shickshock group.

2-3. The Mount Albert Ultramafic Pluton

a) Rock types and mineralogy

Peridotite and dunite are the most abundant rock types composing the Mount Albert pluton.* They occur in distinct layers commonly with sharp contacts. The major mineral components are a forsterite olivine (Fo 90-91) with lesser amounts of orthopyroxene and accessory clinopyroxene and chrome spinel. Clinopyroxene occurs as thin lamellae in orthopyroxene parallel to (100) or occupies interstitial positions between olivine grains. Two varieties of chrome spinels including a red subhedral chrome-rich type commonly occurring as pods or schilerin and a brown anhedral interstitial chrome-poor type are found. All the chrome spinels are subject to intense alteration and commonly associated with kammererite. Talc and tremolite are found as minor alteration products mainly from pyroxenes.

Occasionally, orthopyroxene forms thin layered mass in the dunites and peridotites. Talc and tremolite are commonly found in these rocks.

In a few isolated localities, chromatites have been found occurring as discordant veins or schilieren up to 60 feet in length. They are coarse grained, composed primarily of chromite with minor chlorite, and accessory diopside and tremolite.

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* Orthopyroxene-forsterite rocks are termed peridotite if their modal percentage of orthopyroxene exceeds 10%.

Clinopyroxenite may also be found as small discordant veins. It consists predominantly of clinopyroxene with broad lamellae of orthopyroxene and may represent a crystal differentiate of a lighter phase.

b) Mode of emplacement and serpentinization

The steeply dipping primary igneous layering and the geometrical similarity of the laying to experimental patterns produced by Esher and Keunen (1928-30) suggest that the Mount Albert pluton has been emplaced as a diapiric structure resembling a salt dome. The intrusive mechanism was probably related to deep faulting. The ultramafic material rose along the fault plane due to a release of pressure and eventually developed into an irregular diapiric structure.

The age of the intrusion varies from Pre-Ordovician to Pre-Silurian according to the geological relations. K-A dating on rocks of the contact metamorphic aureole yielded a lower Ordovician age of 495 m. y. (Lowdon et al., 1963) which is probably the best estimate of the time of intrusion into the crust.

The peridotite was intruded as a crystal mush composed largely of olivine crystals with about 15 per cent interstitial liquid. The water content of the liquid phase was less than 3 per cent at the time of emplacement. As indicated by the exsolution of clino- and orthopyroxene and the heat balance between the intrusion and the contact metamorphism, the intrusion temperatures are estimated at approximately 1100°C. Clino- and orthopyroxene appear to have crystallized after crystallization of most of the olivine. Their intense mylonitic texture, occurrence of larger cataclastic grains of orthopyroxenes in a groundmass of finely comminuted olivine crystals, bent cleavages and wavy extinction of enstatite suggest that they grew under Massive stress. Chrome spinel is late magmatic crystallization after the major silicates. The mylonitized textures developed gradually as the intrusive became charged with crystals and moved as a nearly solid mass from its initial intrusion site to its present position. The course of crystallization and chemical composition of the primary minerals, particularly chrome spinel were strongly affected by the water vapour content. The massive varieties of chrome spinel are thought to be hydrothermal and their crystallization occurred immediately prior to serpentinization.

As the temperature dropped to 500°C and below the primary minerals were serpentinized producing serpentine, talc and tremolite. At the same time, the chrome spinels were altered to a magnetic and a non-magnetic variety. Kammererite is characteristically associated with this alteration and only occasionally are flakes seen away from the altered chromites. Serpentinization may have operated continuously until later weathering processes became important.

The lack of correlation of serpentinization with either composition of primary silicate minerals and content of minor elements, suggests that the serpentinization process was essentially an addition of water without transfer or addition of other elements.

CHAPTER 3

EXPERIMENTAL METHOD

3-1. Sample Preparation

a) Whole rock

About one hundred grams of each rock sample was crushed with hammer and mall to 1" ~ 1-1/2" chips. These were loaded into a steel percussion mortar, previously cleaned with brush and air blast, and crushed further to about 1/4" in size. Finally, the sample was pulverized for 20 minutes in a carbid ball mill. The resulting powder was passed through 200 mesh silk bolting cloth. Material retained on the cloth was returned to the mill, mixed with new crushed chips and pulverized again. The procedure was repeated until all sample passed 200 mesh. The last sample material on the cloth was treated for another 20 minutes. The powders were stored in polyethylene bottles.

Approximately 100 mg of each sample was weighed into a 2 mm O. D. x 1.5 mm I. D. labelled quartz ampoule and capped with a polyethylene plug.

b) Chrome spinel

About a hundred grams of each dunite or peridotite with chrome spinel content greater than 1% was crushed and pulverized as described above. The 100 ~ 200 mesh size fraction was separated by sieving with silk bolting cloth. The fines were removed by washing with distilled water and the sample dried with acetone and infrared heat.

Magnetite was first removed with a hand magnet. The powder was then run through a Franz magnetic separator at 30° forward inclination, 20° ~ 30° tilt at 0.5 ~ 0.6 amperes. A 70% chrome spinel concentrate was collected on the magnetic side after repeating this procedure twice.

This concentrate was then run through at the same forward inclination, but a tilt at 10° or less and a current at 0.35 amperes. The chrome spinel was separated from other contaminants, mainly olivine, collecting at the non-magnetic side. This procedure was repeated five times until a 95% or better chrome spinel concentrate was obtained.

Some 70 mg of the concentrate were weighed into a labelled quartz ampoule and sealed with a polyethylene plug.

3-2. Analytical Procedure

a) Introduction

A comprehensive neutron activation chemical procedure for analysis of Ru, Pd, Os, Ir, Pt and Au has been described by Crocket et al. (1968, in press). The procedure used in this study employs selected parts of the above comprehensive procedure with necessary modification introduced as required. The activation procedure involves comparison of the induced radioactivity generated in the analysis element in the sample with the produced in a standard irradiated simultaneously with the sample. Silicate samples are initially processed by high temperature alkali fusion which serves both to dissolve the analysis element and to effect mixing and equilibration with milligram amounts of non-radioactive carrier. Separation and radiochemical purification of the analysis element radioactivity is obtained by ion exchange, distillation and solvent extraction procedures. The final purified radiation from sample and standard are measured by either differential gamma spectroscopy or by gross beta radiation counting. In this study Pd, Ir and Au were determined simultaneously and Os was analysed in separate irradiations.

b) Standard solution preparation

Solutions of each metal were prepared from Johnson, Matthey "Specpure" gold foil, palladium sponge, ammonium chloriridate, and ammonium chlorosmate. Gold, palladium and iridium were combined into a single solution. Osmium was prepared separately. About 400 mg of gold foil, 100 mg of palladium sponge, and 400 mg of iridium salt were weighed on a 5-place "Mettler" balance, transferred to 100 ml beakers, covered with watch glasses, and dissolved in aqua regia at low heat on a hot plate. The solutions were then evaporated to dryness, and converted to chlorides by two digestions of 1 ml conc. HCl.

The chlorosalts were dissolved in 1 N HCl, transferred to 100 ml volumetric flasks and diluted to 100 ml with 1 N HCl. By further dilution and combination of appropriate aliquots of these three precious metal solutions, a final flux monitor standard solution containing 0.020804 μg Au/ml, 0.32975 μg Pd/ml, and 0.04474 μg Ir/ml was prepared.

Three 1 ml aliquots of this solution were pipetted with a calibrated 1 ml pipette into weighing bottles, and the density determined.

An osmium standard containing 1.153 μg Os/ml was prepared by the same procedure.

Au, Pd and Ir irradiation standards were prepared by introducing about 30 mg of the standard solution into a weighed 3 mm O. D. x 2 mm I. D. quartz ampoule. The ampoule was constricted in the middle and the liquid introduced with a polyethylene capillary pipette. Any drops of solution adhering to the inner walls of the ampoule near the open end which might be lost in sealing the ampoule were carefully wiped off with tissue paper. The ampoule plus solution were weighed immediately taking the first balance reading only. The ampoule was then sealed with a hydrogen-oxygen flame.

Tubing of the same size was used in preparing osmium standard ampoules, but the constriction was omitted. Solutions were introduced into the ampoules with capillary polyethylene pipettes and any solution left on the walls was wiped out. After weighing, about 50 mg of Al_2O_3 powder was added to absorb the solution. The ampoules were then put in a drying oven at 65°C, dried overnight, and sealed with polyethylene plugs.

c) Carrier solution preparation

Carrier solutions containing approximately 20 mg Au/ml, 5 mg Pd/ml, and 2.5 mg Ir/ml, were prepared from the concentrated salt solutions used to make up standards. For osmium, about 15 mg of ammonium chlorosmate was weighed directly into the crucibles, and used as carrier.

d) Analytical procedures for Au, Pd and Ir

A flow chart of the procedure for Au, Pd and Ir is shown in Fig. 3-1 and the details of the procedure follow below.

i) For the samples pipette 20, 5 and 10 mg of Au, Pd and Ir carrier solutions respectively into clean crucibles and for the standards into 50 ml beakers. The former are evaporated to dryness under an infrared heat lamp while the latter are covered with watch glasses and held for processing with the standard solutions.

Clean the outside of the irradiated[1] ampoule with acetone-wetted paper tissue, dry off the polyethylene plug and carefully empty the irradiated powder into the crucibles. If the plug will not come out, scratch the ampoule with a file and break into the crucible. This operation is done in a clean enamel tray, behind two inches of lead bricks.

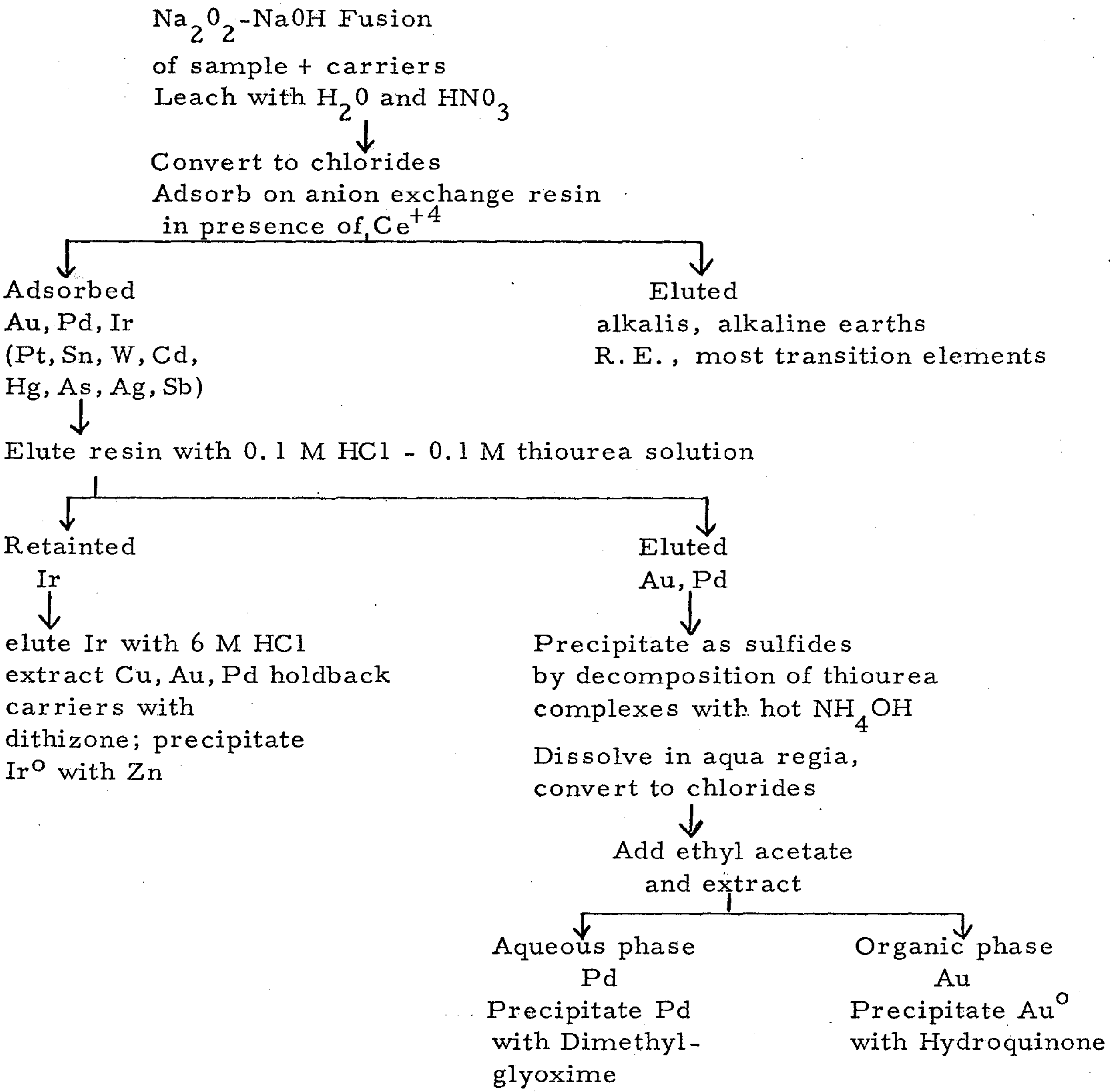

Figure 3-1. Generalized flow chart for Au, Pd and Ir Analysis

ii) To each crucible add 1 gm of Na_2O_2 to cover the irradiated sample powder and 0.5 gms NaOH (6 pellets). Turn off fume hood air current and fuse in a Meeker flame for three minutes at low heat to prevent splattering. Increase the flame until the bottom of the crucible is bright cherry red and heat for another seven minutes. Swirl twice during this operation at four and seven minute intervals. Cool for five minutes.

iii) Slowly add 4 to 5 ml of distilled water and then 20 ml of conc. HNO_3. After strong effervescence ceases, transfer as quantitatively as possible to a 400 ml beaker. Add a few ml of 2M HCl to the crucible, scrub thoroughly with a rubber policeman, and transfer to the beaker. Repeat. Heat nearly to boiling on a hot plate for 10 to 15 minutes, add 10 ml of conc. HCl and evaporate to incipient dryness with the aid of an infrared lamp and an air-stream. Add 10 ml aqua regia, cover with a ribbed watch glass, and stew for 10 minutes. Take to dryness, add a second 10 ml of aqua regia, and again evaporate to dryness. Treat twice with 5 ml aliquots of conc. HCl to convert to chlorides. In order to reach incipient dryness, decrease the temperature of the hot plate and allow the heat of the lamp and the air stream to dry the salts until evolution of HCl fumes ceases.

Dissolve the salts in approximately 30 ml of 0.5 M HCl containing 0.004 moles of ceric ion per ml of solution. (Prepare by dissolving 3.288 gm of $(NH_4)_2Ce(N0_3)_6$ in 30.0 ml of 0.5 M HCl and add 5 ml of this solution to every 245 ml of 0.5 M HCl).

iv) Filter the solution through a Whatman No. 41 paper onto an anion exchange column pretreated immediately prior to the introduction of the sample solution with 50 ml of 0.5 M HCl containing 0.004 moles ceric ion/ml. Rinse the beaker and filter paper with a few ml of 0.5 M HCl. Allow the sample solution to pass through the resin bed at the rate of 1 ml/min.[2] Discard the effluent to radioactive liquid waste. Wash column by putting 120 ml of 0.5 M HCl through at a rate of 2 ml/min and again discard effluent to radioactive waste.

Elute Au and Pd with 120 ml of 0.1 M thiourea in 0.1 M HCl[3] into a clean 400 ml beaker. Wash the column free of thiourea with 2 to 3 ml of distilled water and add to the main thiourea solution.

Add 30 ml of conc. NH_40H to the thiourea solution, place on a hot place, and evaporate to about 90 ml[4] to precipitate Au and Pd sulfides.

Elute Ir with 120 ml of 6 M HCl into a clean 400 ml beaker and evaporate the solution to 1 to 2 ml.

v) After the solution Au-Pd has been evaporated to 90 ml, transfer the precipitate and solution to two 50 ml centrifuge tubes and centrifuge. Combine the sulfide precipitates, wash once with distilled water and ethanol, and dissolve in 1 ml of aqua regia by gently heating in an electrical Bunsen heater. Convert to chlorides by two digestions in conc. HCl. Take Au and Pd up in 20 ml of 2 M HCl. Transfer to a 125 ml separatory funnel, add 20 ml of ethyl acetate and shake for 2 minutes to extract Au into the organic phase. Transfer the aqueous phase to a fresh 125 ml separatory funnel, add 5 ml of ethyl acetate and extract. Transfer the aqueous phase containing Pd chlorides to a 50 ml centrifuge tube and add the organic to the previous ethyl acetate fraction. Transfer acetate fractions to a 100 ml beaker, add an equal volume of 2 M HCl and warm gently on a hot plate until the Au chloride transfers to the aqueous phase and the acetate has evaporated. Finally, heat strongly for about 5 minutes to drive off all residual acetate.

Transfer the Au solution to a 50 ml centrifuge tube. Precipitate Au with 0.5 gm of hydroquinone, centrifuge, discard the supernatant, wash twice with 25% ethanol. Dissolve Au in aqua regia, convert to chlorides and repeat the hydroquinone precipitation. Wash twice with 25% ethanol and finally once with 10 ml ethanol. Plate Au out in a weighed aluminum planchet and dry with infrared heat.

Add 10 ml of 1.5% dimethylglyoxime solution to the Pd chloride solution to precipitate Pd-dimethylglyoximate. Centrifuge, decant the supernatant, wash twice with 25% ethanol. Add 1 ml aqua regia, convert to chlorides and repeat the precipitation. Wash as before, plate out on a weighed aluminum planchet and dry with infrared heat.

When dealing with chrome spinel samples, some other purification steps must be introduced to eliminate Cr contamination. The procedure is discussed in Appendix A.

vi) Take up the evaporated Ir solution in distilled water making the solution 0.5M in HCl. Transfer to a separatory funnel and add 20 ml of 0.001% dithizone in chloroform. Shake for 1 minute to extract the dithizonates of Cu, Ag, Au and other metals. Repeat the extraction until no discoloration of the dithizone solution occurs. Flush out all traces of dithizone with pure chloroform. Transfer into a 100 ml beaker, place on a hot plate, and evaporate to dryness. Treat with aqua regia, and conc. HCl and take up in 2 M HCl.

Place on hot plate, heat to near boiling, and precipitate Ir with Zn. Dissolve excess Zn with conc. HCl. Centrifuge, transfer to 100 ml beaker, boil with aqua regia for a few minutes. Transfer to a centrifuge tube, spin,decant the supernatant, wash twice with 25% ethanol and once with 10 ml ethanol. Then plate out on a weighed aluminum planchet and dry with infrared heat.

vii) Standards - Immerse the standard ampoule for 10 minutes in 20 ml of aqua regia containing 1 drop each of Au, Pd and Ir carrier. Remove, rinse with H_2O, and wipe with acetone sprayed paper tissue. Repeat to remove any absorbed radioactivity.

Gently warm the tip of the ampoule to drive all liquid down to the bottom of the ampoule. Cool in ice water or dry ice, acetone for 10 minutes, scratch and break at the constriction into the carrier solution. Transfer the standard liquid into the carrier solution with the aid of a capillary tube. Cover with a watch glass, place on a hot plate, and heat gently for 20 minutes to promote the interchange of the carrier and standard solution.

With the aid of a capillary pipette, flush all traces of the irradiated standard solution from the ampoule with 2 M HCl. Keep the volume under 25 ml. Transfer the standard to a separatory funnel, add an equal volume of ethyl acetate, and extract Au as in the sample procedure.

Precipitate Pd as in sample procedure but transfer the supernatant containing Ir to a 100 ml beaker. Filter through a Whatman 41 paper into a new 100 ml beaker. Warm on a hot plate, add 10 ml of 10% $NaBrO_3$ or enough to keep the color dark red, add NaOH to pH 6 to 7 to precipitate $Ir(OH)_4$ or IrO_2-$2H_2O$.

Transfer to a centrifuge tube, spin, wash once with distilled water, and dissolve $Ir(OH)_4$ in 1 ml of aqua regia. Convert to chlorides with two treatments of conc. HCl. Take up in 2 M HCl, heat to near boiling point and precipitate Ir with Zn as in the sample procedure.

e) Analytical procedure for Os

i) Open the sample ampoule, empty the irradiated powder into a crucible containing a weighed amount of ammonium chlorosmate powder carrier*, cover the irradiated powder with 1 gm Na_2O_2 and 6 NaOH pellets, and fuse in a Meeker flame as in the Au-Pd-Ir procedure.

Dissolve the fusion cake with 25 ml of H_2O, transfer into a 100 ml beaker and scrub the crucible 3 times with distilled water and a rubber policeman.

ii) The major Os separation is by distillation. The apparatus is the same as that used by Hsieh (1967) and includes a 250 ml reaction bulb with a thermometer, a spray guard and trap bulb to reduce contamination, a cooling jacket to condense water vapor, and a receiver tube to collect distilled OsO_4. Joints are sealed and lubricated with 50% H_2SO_4.

Circulate cold water through the cooling jacket. Add 30 ml of 3 M NaOH to the receiver tube and place in an ice bath. Pass air through the system, at a rate of about 2 bubbles per second. Check for leaks at the joints,[5] and add 30 ml distilled water to the trap bulb.

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* A few samples were processed using ammonium chlorosmate in 1M HCl solution as carrier. In this procedure about 8 mg of Os was pipetted into a crucible and dried with infrared heat.

Transfer the solution from the fusion step into the distillation bulb, add 20 ml of 50% H_2SO_4, and 10 ml of 30% H_2O_2. Heat with a small Bunsen burner to bring the temperature to 85°C to 90°C.[6]

Add 30% H_2O_2 from a thistle tube, drop by drop, continuously throughout the distillation to ensure that undecomposed H_2O_2 is present during the entire distillation. Distil OsO_4 for about 30 minutes. After 20 minutes, heat the liquid in the trap bulb to boiling, to distil absorbed OsO_4.

iii) Transfer the chilled sodium osmate solution to a 125 ml separatory funnel. Acidify with 10 ml of chilled H_2SO_4,[7] and immediately contact with 30 ml of CCl_4. Shake the mixture for 2 minutes to extract OsO_4 into the organic phase. Transfer and back extract the OsO_4 by contacting with 30 ml of NaOH. Transfer the aqueous phase to a 50 ml centrifuge tube and centrifuge to ensure complete removal of CCl_4. Transfer the aqueous phase to a 150 ml beaker, add 20 ml of conc. HCl, warm on a hot plate, cover with a watch glass, and precipitate Os with Zn. Dissolve excess Zn with conc. HCl. Warm the Os metal in 6 M HCl for 10 minutes to remove any Zn carried down with the Os precipitate. Wash twice with 25% ethanol, once with ethanol, plate out in vycor planchet, and dry under infrared heat.

iv) Standard - Carefully open the ampoule and quickly transfer the contents into the carrier solution (15 mg of chlorosmate in 10 ml 3 M HCl). Rinse the ampoule several times with distilled water. Add 2 ml of ethanol to reduce Os^{+8} to Os^{+6}. Make the solution alkaline by adding 4 ml of 9 M NaOH and evporate gently to dryness on a warm hot plate under a heat lamp. Fuse with Na_2O_2-NaOH as for the samples.

The distillation apparatus for the standard is essentially the same as for the samples. After distillation, acidify the sodium osmate with conc. HCl, warm on a hot plate and precipitate Os with Zn.

Notes to the Analytical Procedure

1. For Au, Pd and Ir packets of 4 samples and 3 standards were sealed in aluminum radiation cans and irradiated for 24 hours. For Os packets of 8 samples and 3 standards were irradiated for 72 hours. The average neutron flux was approximately $1x10^{13}$ neutrons/cm^2/sec.
2. The ion exchange columns are made up with 1.75x0.8 cm of chromatographic grade Rexyn 201(Cl) resin. They are pre-treated with 120 ml of 0.5 M HCl before use.
3. This step also effects reduction of Ir^{4+} to Ir^{3+}. The reduced Ir, which is only weakly adsorbed in strong HCl medium, can subsequently be eluted with 6 M HCl.

4. Excessive evaporation of the thiourea results in dissolution of the sulphides.

5. OsO_4 is a colorless and very poisonous gas which is particularly hazardous to the eyes.

6. Control the reaction rate by adjusting the acidity. Add 50% more H_2SO_4 if the reaction goes too fast.

7. The H_2SO_4 should be added as rapidly as possible to avoid hydrolysis of Os at the neutral point.

3-3. Counting and Calculations

a) Equipment description

A Nuclear Chicago beta counting system, which includes a scaler-timer, an automatic sample changer, a gas flow Geiger-Mueller counting tube with coincidence shielding and a paper-tape printer, was used for beta counting. The system had an average background of 2.0 c.p.m. Machine drift was monitored by three uranyl acetate standards, which were fixed on copper planchets by spraying with a heavy coat of transparent commercial varnish.

For gamma counting, a Nuclear-Chicago gamma counting system utilizing a well-type 2" x 1-3/4 NaI(Tl) scintillation detector, an analog to digital converter, a 1600 channel memory, and a teletype paper and punched tape print out, was used throughout the research. Background was checked two or three times in every counting period. Machine drift was monitored by the 0.662 MeV photopeak of a ^{137}Cs standard and occasionally the 1.173 MeV and 1.332 MeV photopeaks of ^{60}Co.

b) Counting

i) Gold

Gold contents in five of the thirteen experiments were determined by gross beta counting. To minimize errors due to self-absorption from difference in particle size and geometrical distribution, the lumpy gold particles precipitated with hydroquinone were first broken to smaller size with a capillary pipette and plated out evenly on the counting planchet. The samples and the standards were put side by side and sprayed for 5 seconds with a transparent commercial varnish. Activity from ^{199}Au, which is produced from $^{198}\mathrm{Pt}(n,\gamma)\mathrm{Pt}^{199} \xrightarrow{\beta^-} {}^{199}\mathrm{Au}$ is not significant. (A Pt/Au ratio of more than 4:1 would introduce an error of only 1 per cent according to Vincent and Crocket, 1960a). The beta decay curves were followed for several half-lives. If long-lifed radio-contaminants were recognized, the curve was followed for a longer period so that the contaminants could be subtracted.

Other gold values were determined by gamma-counting the 0.412 MeV photopeak of ^{198}Au.

ii) Palladium

All of the palladium contents were determined by gross beta counting. The palladium dimethylglyoximate was plated out and dried on the planchet as an even thin film. No self-absorption problems were encountered.

A possible competing reaction which could cause interference is ^{235}U(n, f)Pd^{112}, Pd^{109}

Interference in Pd determination from ^{235}U fission products was determined experimentally by Crocket and Skippen (1966) who found that a U/Pd ratio of 180 causes a 1 per cent interference. The U content in ultramafic rocks and chromite as reported by Adams et al. (1955) are always less than 30 ppb. Thus U/Pd ratios of 30 to 3 may be expected for the Mount Albert rocks and no significant interference from U fission is probable.

iii) Iridium

Neutron activation produces two major iridium radioisotopes, a 74 day ^{192}Ir and a 19-hour ^{194}Ir. Both emit gamma as well as beta radiation. The decay curves were followed for 4 to 5 months, and their half-lives determined. The energy spectra were calibrated against 0.662 MeV photopeak of ^{137}Cs and compared with the spectra given by

Heath (1964) to detect any radiochemical contaminants. The area under 0.316 MeV gamma photopeak of 74 day ^{192}Ir was integrated and used to determine the Ir content.

iv) Osmium

Gross beta counting of 15 day ^{191}Os and 32-hour ^{193}Os were used to determine the Os content. Theoretically, these two nuclides can be produced not only from stable ^{190}Os and ^{192}Os, but also by fast neutron reaction on Pt and Ir. According to Hsieh (1967) for samples of approximately equal amounts of Os, Pt and Ir, the interference from Pt and Ir may be ignored. Except for long lived contamination, no further corrections were made.

v) Calculation

Knowing the total activity from either gross beta or differential gamma counting, the chemical yield of both sample and standard, the weight of sample irradiated, and the concentration of the metal in the standard, the metal content in the sample can be calculated according to the following equation:

$$C = \frac{m}{w} \cdot \frac{a_o \cdot Y}{A_o \cdot y} \times 10^9 .$$

where

m = weight of the metal in the standard

w = weight of the sample irradiated

a_o = activity of sample at time t_o

A_o = activity of standard at time t_o

y = chemical yield of the sample

Y = chemical yield of the standard

and C = metal content in p.p.b.

All values were checked by computer calculation with a programme prepared by Mr. J D. McDougall.

CHAPTER 4

GEOCHEMISTRY

4-1. Occurrence and abundance in meteorites and terrestrial materials

Pd, Ir and Os are members of group VIII in the periodic table. The platinum metals are strongly siderophilic occurring as pure metals and alloys, but also somewhat chalcophilic and combine with sulfur, tellurium and arsenic. In the presence of coexisting metal and sulfide phases, they enter the former preferentially. In the case of coexisting sulfides and silicates, they are concentrated in the sulfide.

Au belongs to group IB in the periodic table, but geochemically it differs sharply from the rest of elements of the group. With reference to its terrestrial manner of occurrence, Au is found predominantly as the native metal or alloy and as selenides and tellurides. In its dominant occurrence as the metal Au very much resembles the siderophilic platinum metals.

Pd, Os, Ir and Au are extremely rare in both terrestrial materials and the universe as a whole. In meteorites they concentrate in the irons, and in the iron-nickel metal of chondrites. Their covalent bonding character and high ionization potential probably prevent them from easily substituting in the more ionic silicate structures and hence they probably concentrated in residual fluids or late magmatic differentiates. Hydrothermal deposits of gold are well known but no economic pegmatitic or hydrothermal deposits of Ir, Os and Pd are found. Economic concentrations of these metals are restricted to mafic and ultramafic rocks instead.

Abundances in meteorites and terrestrial materials, determined mainly by radioactivation analysis, are summarized in Tables 4-1 and 4-2. Extensive determinations of Au were performed by Shcherbakov and Perezhogin (1964) who found mafic and ultramafic rocks to be generally higher in Au than acid and intermediate rocks. As indicated by the analyses of DeGrazia and Haskin (1964), the spread of Au concentrations over a wide variety of rock types was fairly narrow, between 0.6 and 44 p.p.b. They estimates a crustal abundance to be ~ 2.5 p.p.b. which is about one hundredth of the value of the average chondrite.

The very limited data suggest that Pd is more enriched in mafic and ultramafic rocks relative to acid rocks than Au. Contrasting distribution patterns were observed in oceanic and continental basalts by Crocket and Skippen (1966). The former were characterized by rather uniform Pd content whereas the latter exhibited large variations (see Table 4-1). It was suggested that regional variation in Pd content of the source material might be responsible for the larger variation in continental basalts. Their contents in marine sediments are quite uniform and their values are higher than oceanic basalt. Whether this indicates an accretion of cosmic material requires further investigation.

Ir and Os are highly depleted in terrestrial material relative to iron and chondritic materials, particularly in some sedimentary rocks and deep sea sediments. The data suggest an upper limit of 1.4 p.p.b. for the metals in sediments.

Table 4-1. Previous determinations of the metals in terrestrial materials (p.p.b.)

Metal	Ultramafic rocks	Mafic Rocks	Felsic Rocks	Sediments & Sedimentary Rocks	Reference
Au	6.6(2)[1]	-	-	-	Vincent & Crocket (1960b)
	9.4(27)	8.7(33)	3.2(33)	3.6(39)[2]	Shcherbakov & Perezhogin (1964)
	-	-	-	3.2(6)[3]	"
	-	2.6(15)	2.4(12)	4.7(12)[4]	DeGrazia & Haskin (1964)
	-	-	-	12(7)[5]	"
	-	-	-	2.4(27)[6]	McDougall (1968)
	8.9	6.8	3.0	4.0	Average
Pd	11.8	1.9(10), 8.5(10)[8]	1.6(4)[9]	-	Crocket & Skippen (1966)
	-	0.45-29.4(13)[10]	-	-	"
	-	-	-	3.1(27)[6]	McDougall (1968)
Ir	-	0.30(2)[11]	0.045(2)[9]	-	Keays (1967)
	-	-	-	0.012-1.4(6)[12]	Baedecker & Ehmann(1965)
	-	-	-	$<$ 0.1(26)[13]	McDougall (1968)
	-	-	-	0.057-0.56(19)[14]	Barker & Anders (1968)

Table 4-1. (continued)

Os	-	0. 30(5)[11]	0. 056(5)[9]	-	Keays (1967)
	-	-	-	0. 06-0. 45(6)[15]	Lovering & Morgan(1964)
	5.6(2)[16]	-	-	-	Lovering & Morgan(1967)
	-	-	-	0. 047-0. 343(13)[14]	Barker & Anders (1968)

1. The number in the parenthesis indicates number of analyses.

2. Shales and sandstones.

3. Limestones and marbles.

4. Calculated according to the ratio, 82% shale, 12% sandstone and 6% limestone, in sedimentary rock suggested by Leith and Mead (1915).

5. Pelagic clays.

6. 3 Antarctic, 14 East Pacific Rise, 9 Arctic near-shore sediments and 1 Pacific Calcareous ooze.

7. A dunite from Mount Albert intrusion, Gaspé, P. Q. and a pyroxenite from Thetford district, P. Q.

8. Average of oceanic basalts, and average continental basalt.

9. G-1, Standard granite from Westerly, Rhode Island.

10. Continental plateau-building and orogenic basaltic rocks.

11. W-1, Standard diabase from Centerville, Virginia.

12. Pacific ocean and Argentine basin cores.

13. Same as note 6. but without Pacific Calcareous ooze.

14. Five cores from the central Pacific ocean.

15. Sandstone, Wilpena Pound, South Australia, shale, Etheridge Creek, A. C. T., Australia & Pyritiferous shale, Captain's Flat Railway State, N. S. W.

16. A peridotite from Snowy Mts., N. S. W., Australia and a peridotite from Cazadero Quad., California, U. S. A.

Table 4-2. Previous determinations of the metals in meteorites (p.p.m.)

Type of Material[1]	Au[2]	Pd[3]	Ir	Os
Chondrites:				
Ce	0.37	1.5	0.22	0.71
CH	0.24	1.1	0.48	0.86
CL	0.17	0.82	0.38	0.64
CHL		1.5		0.73
Cc	0.17	0.84	0.59	0.60
All chondrites	0.24	1.15	0.42	0.71
Irons:				
Ogg	1.44	3.1	4.4	
Og	1.18	3.65	3.9	3.3
Om	1.22	3.8	4.8	6.2
Of	1.25	4.2	1.5	2.3
Off	1.25	5.4	0.45	
Brecciated Octahedrites	0.94	2.8		
All octahedrites	1.22	3.82	3.53	4.75
H	0.86	2.1	8.8	8.4
D	1.35	9.7	7.1	16.2

1. From Prior and Hey (1953).
2. Au of chondrites was from Baedecker & Ehmann (1965).
   Au of irons was from Fouché & Smales (1966).
3. Pd, Ir and Os were calculated from all of the previous data by Crocket (1968, in press).

4-2. Abundance and distribution of the metals in the Mount Albert pluton

Samples were collected from a number of localities in the eastern part of the Mount Albert pluton by Drs. J.H. Crocket and R.H. McNutt. The sample locations are shown in Fig. 4-1.

A total of 16 samples were analyzed for all four precious metals. Seven were run either 4 or 5 times each, three were run in duplicate, and the remainder are single analyses. Accessory chrome spinel was separated from four samples in which the mineral exceeded 1 per cent. Of these four,MA8A was run in quadruplicate with the exception of Os, and the rest were run as single analyses only. All results are presented in Tab. 4-4. Values determined in different irradiation are separated by semicolons. For example, considering the Au data for MA3, values of 0.51 and 0.21 p.p.b. were obtained in one irradiation, 0.81 p.p.b. in a second irradiation, and finally, 0.77 and 0.76 p.p.b. in a third irradiation. Average values for the major rock types are given in Tab. 4-5, and a comparison of the precious metal contents of accessory chrome spinel, parent whole rock and massive chrome spinel are listed in Tab. 4-6.

The errors included in Table 4-4 are standard deviations for single determinations and coefficients of variation. Although some analyses show quite satisfactory precision particularly for duplicate

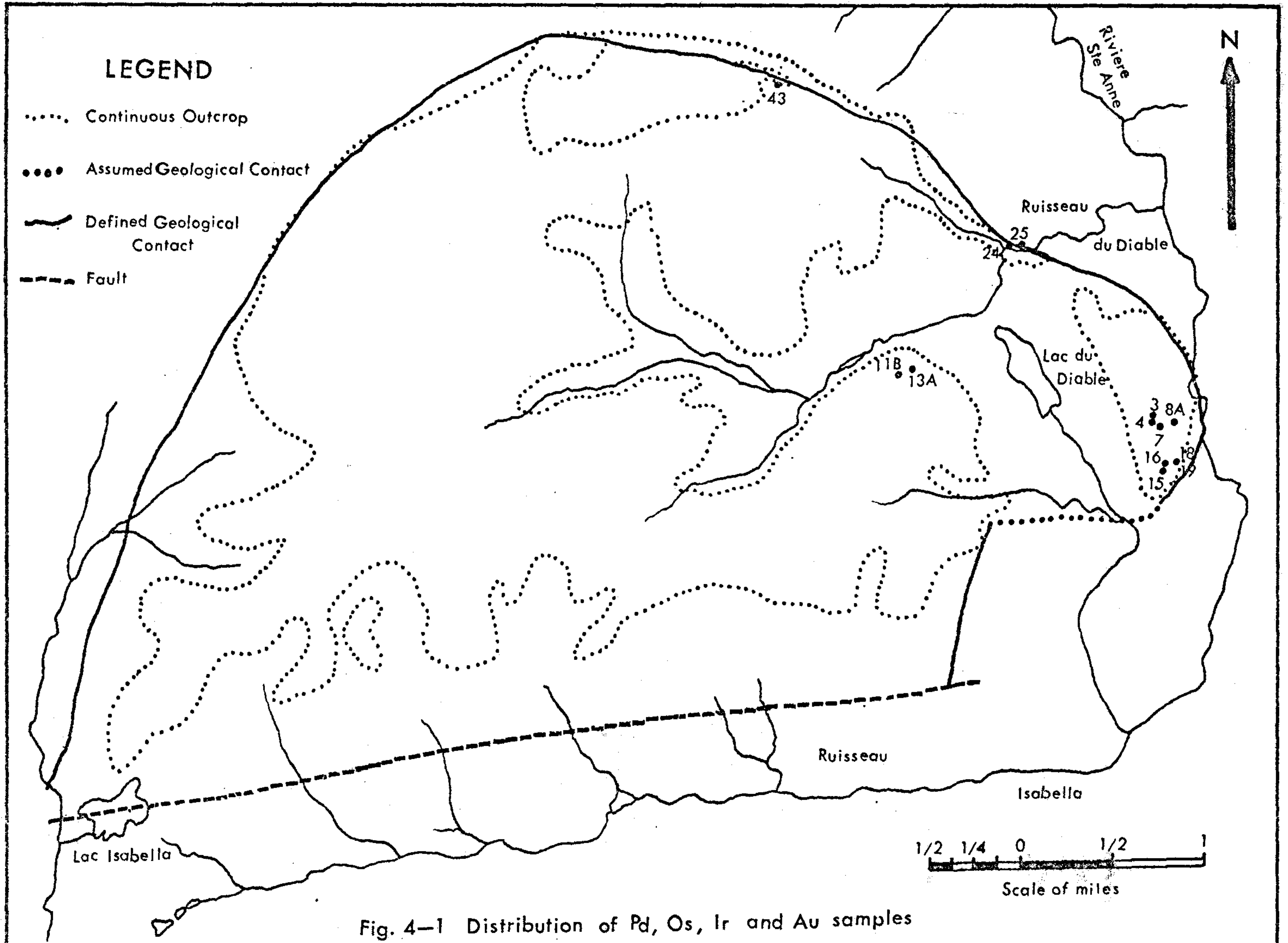

Fig. 4—1 Distribution of Pd, Os, Ir and Au samples in the Mount Albert pluton

analysis from a single irradiation, many samples do not yield results of high precision. It is of interest to compare the precision obtained in this study with that reported by Crocket *et al.* (1968) for the determination of Pd, Ir and Au in the granite and diabase rock standards G-1 and W-1. This is presented in Table 4-3 where coefficients of variation based on standard deviations of average values are compared. For the Mount Albert rocks the average of the coefficient of variation for sample with 4 or more determinations including MA3, 7, 11B, 13A, 8A; clinopyroxenite; chromite sample 100 and 100A are tabulated.

Table 4-3. Comparison of coefficients of variation for the determination of Pd, Ir and Au in Mount Albert rocks, G-1 and W-1

Sample	Investigator	Pd (%)	Ir (%)	Au (%)
Mount Albert	This study	24	29	26
G-1	Crocket et al., 1968	17	18	27
W-1	Crocket et al., 1968	10	19	12

Note: Coefficients of variations are percentage standard deviations for average values, that is, with

$$\bar{\sigma}^2 = \left(\frac{\sum(x_i-\bar{x})^2}{n(n-1)}\right)$$

The data from Tab. 4-3 show that the precious errors for the Mount Albert rocks are about twice as high as those for W-1. For G-1 the error for Au is comparable with that for Mount Albert but those for Pd and Ir average some 35% higher. As very similar analytical methods were used in both studies, the higher errors found for the Mount Albert rocks are somewhat unexpected. A second line of evidence also suggests that smaller precision errors might have been expected. For most irradiations three standards were processed with each group of samples and were put through a similar chemical procedure to the samples. The most significant difference in procedure was that the standards were not mixed with carrier by an alkali fusion but simply by exchange in hot 2M HCl acid. For triplicate standards coefficients of variation seldom exceeded 5% and it seems reasonable to expect that the method is capable of precision of approximately this order of magnitude. It is therefore pertinent to briefly consider the most probable sources of error.

Analytical errors inherent in this type of activation procedure may result from:

1) Contamination from non-precious metal radioactivity.
2) Contamination precious metal activity accidentally introduced during sample preparation prior to irradiation or resulting from cross-contamination with standards.

3) Failure to equilibrate carrier and radioactive analysis element.

4) Sample inhomogeneity.

The first factor is quite improbable as a significant source of error because foreign contamination is easily identified by decay curve measurements and by differential gamma spectroscopy. Decay curves were taken on all beta entities (Pd and Os) and any contamination present was subtracted. The full gamma spectrum for Au and Ir was visually inspected for contaminants by comparison with standard spectrum. Only the photo peak radiation was counted.

The second factor is also considered an unlikely source of error although it cannot be entirely discounted. Cross contamination with standards is a possibility for Ir and Os only as Pd and Au radioactivities characterized by 13.5 and 64.5 hr. half lives decay to very low levels in the two week interim between irradiations. The usual practice of separating standard and sample glassware was followed. Further, it is to be noted that the maximum disagreement in replicates is a factor of 2 or 3 and that the precision errors for Ir, Pd and Au are all comparable, about 27%. Accidental pre-irradiation contamination would probably produce values which were extremely high and would not be expected to give rise to comparable precision errors for all these metals.

Failure to equilibrate the carrier and the activated analysis element would produce more or less the pattern of error found for replicates. However, one might expect the most insoluble metal, Ir, to be subject to far worse precision, which is not the case.

It is considered that sample inhomogeneity is a very probable source of poor agreement in replicate analyses. It has recently been demonstrated by Fritze and Robertson (1968,. personal communication and Final Program, Modern Trends in Activation Analysis, N. B. S. International Conference) that there is a good case for sample inhomogeneity in G-1 with respect to gold. They irradiated a powder sample of G-1 which was split into aliquots of equal weight following the irradiation. Analyses of these aliquots (~20 mg. each) yielded a precision comparable to that obtained for Au by Crocket et al. (1968). However, irradiation of a synthetic oxide mixture of comparable composition to G-1 doped uniformly by a dilute acid solution of Au, yield a precision of 2 to 3% on replicate analyses. They concluded that inhomogeneity in the rock powder sample was a probable explanation of this result.

If sample inhomogeneity is the cause of the relatively high precision errors for precious metals in the Mount Albert rocks, it follows that large samples must be irradiated, more thorough mixing procedure should be adopted or more replicates must be analysed if one wishes a reliable precious metal value for an individual hand specimen. However, the inhomogeneity itself is of interest in that it indicates some features of precious metal geochemistry in ultramafic rocks. In this case, it is suggested that solid solution of these metals in ferromagnesian silicates is minimal and that the bulk of the Pd, Ir, Os and Au occurs as discrete mineraloids, alloys or other particulate material along intergranular boundaries, fractures in mineral grains or lattice defects.

In comparing the Mount Albert data with precious metal values for corresponding rock types from other areas (Tab. 4-7) and bearing in mind that strong fractionation of Au within the intrusive is unlikely, it is obvious that the Mount Albert is depleted in Au relative to other ultramafic rocks. The gold content for other ultramafic rocks is at least three times that of the fresh rocks of Mount Albert.

Palladium in Mount Albert is comparable to available data for other ultramafic rocks. It is of interest to note the similarity in average Mount Albert Pd and the Pd content of an olivine nodule from Salt Lake Crater, Hawaii, interpreted by Kuno (1962) as of mantle origin. According to the present data, the previous single determination of Crocket & Skippen (1966) on dunite from this pluton is too low. Very high values found in serpentinite from Oberfranken, Germany (Tab. 4-7) and higher values found here in serpentinized rocks suggest that Pd is slightly concentrated in the serpentinization process.

Despite poor precision in replicate analysis, the Ir content is quite constant throughout all rock types including fresh and serpentinized dunite and peridotite, clinopyroxenite, and massive chromite. No other data from corresponding rock types are available for comparison. The Ir content of the Mount Albert is at least ten times higher than that of other non-ultramafic terrestrial rocks (Tab. 4-1).

Osmium shows consistent average values in various rock types similar to Ir and is comparable to determinations for other ultramafic rocks (Tab. 4-7).

Two duplicate analyses show that Pd is enriched in clinopyroxene by a factor of five relative to the fresh rocks. In both fresh and serpentinized rocks, Au and Pd tend to be enriched by approximately 3 times in accessory chrome spinel relative to the whole rock. Iridium and osmium are enriched in late massive chromite by a factor of 10, while Pd is depleted by approximately a factor of 10 (Tab. 4-6). Precious metals contents are quite uniform in fresh rocks, and show larger variations in serpentinized rocks as shown in Tab. 4-4 and 4-5.

Table 4-4. Analytical results of Mount Albert samples

		Au		Pd		Ir		Os	
		result	average	result	average	result	average	result	average
Fresh Rock	MA3 Peridotite	0.51,0.21;0.81; 0.77,0.76	0.61±0.25 (41%)	2.2,3.5;1.0; 2.7,2.7	2.4±0.9 (38%)	0.65,1.2;1.6; 6.5,2.7	2.5±2.4 (96%)	5.6, 3.6	4.6±1.5
	MA7 Peridotite	1.2,0.68;1.6; 1.7,1.8	1.4±0.4 (29%)	9.0,7.7;7.0; 8.5,6.3	7.7±1.1 (14%)	1.5,1.5;4.2; 3.4,4.2	3.0±1.4 (42%)	7.2, 6.6	6.9±0.4
	MA4 Peridotite	0.64		9.3		1.7		7.7	
	MA8A Dunite	1.2,1.2	1.2	8.0,8.5	8.3±0.3	3.4,2.5	3.0±0.6	5.1,3.1; 12	6.7±4.6 (69%)
	MA15 Peridotite	1.5,0.70	1.1±0.6	13, 8.3	11.0±3.6	2.8,2.3	2.5±1.0	10	
Serpentinized Rock	MA11B Serpentinite	0.80,0.78;0.50; 0.80,0.62	0.70±0.13 (19%)	2.0,1.6; 3.7,0.24	1.9±1.5 (79%)	0.9,2.5;4.0; 0.3,1.0	1.7±1.5 (88%)	3.3	
	MA13A Serpentinite	1.0,0.21; 0.67,0.31	0.54±0.34 (63%)	4.0,1.6; 0.56,1.0	1.8±1.5 (83%)	0.80,0.97;0.37; 5.4,1.0	1.7±2.2 (129%)	6.9,3.4	5.2±2.5
	MA43 Serpentinite	150,180	160±20	7.3,6.8	7.1±0.4	4.0,4.0	4.0	5.7	
	MA18 Serpentinite	3.4		9.7		3.4		3.2	

TABLE 4-4 continued

Serpentinized Rock	MA19 Serpentinite	2.3		25		1.7		1.9	
	MA24 Serpentinite	5.9		13		0.94		21	
	MA16 Serpentinite	0.83		2.9, 2.8	2.9±0.1	1.7, 4.1	2.9±1.7		
	MA25 Soapstone	2.9		22		1.7			
	MA8A Dunite	1.3, 5.9; 6.7, 4.8	4.7±2.4 (51%)	3.2, 2.7; 3.3, 4.2	3.4±0.6 (18%)	4.1, 4.2; 2.9, 3.1	3.6±0.7 (19%)	3.4	
Disseminated Chrome spinel	MA7 Peridotite	2.8		69		0.66			
	MA13A Serpentinite	2.6		5.7		1.1			
	MA15 Peridotite	2.6		18		12			
Clinopyroxenite		0.61, 2.3; 0.79, 0.74	1.1±0.8 (73%)	59, 18; 18, 47	36±21 (58%)	5.1, 4.4; 2.0, 2.0	3.4±1.6 (47%)		
Massive Chromite	100	1.9, 0.28; 0.22, 2.4	1.2±1.1 (92%)	0.44		25, 21; 32, 33	28±6 (21%)	55, 130	93±52
	100A	0.45, 0.24; 0.33, 0.82	0.46±0.25 (54%)	0.59, 0.35	0.47±0.17	31, 5.5; 21, 22	20±11 (55%)	99, 99	99

Table 4-5. Precious metals in different rock types of the pluton

Metal	No. of Samples	Content (p.p.b.)	
		Range	Average
Fresh Rocks			
Au	5	0.61-1.4	0.99±0.16
Pd	5	2.4 -11	7.7 ±1.4
Ir	5	1.7 -3.0	2.5 ±0.2
Os	5	4.6 -10	7.2 ±0.9
Serpentinized Rocks			
Au	7 (exclude MA43)	0.54-5.9	2.4 ±0.7
Pd	8	1.8 -25	10.0±3.1
Ir	8	0.94-4.0	2.2 ±0.4
Os	6	3.3 -21	6.6 ±2.9

Table 4-6. Precious metal content in whole rock and chrome spinel

Sample	Au		Pd		Ir		Os	
	Chrome spinel	Parent rock	Chrome spinel	Parent rock	Chrome spinel	Parent rock	Chrome spinel	Parent rock
MA8A dunite	4.7	1.2	3.4	8.3	3.6	3.0	3.4	6.7
MA7 peridotite	2.8	1.4	69	7.7	0.66	3.0		6.9
MA13A Serpentinite	2.6	0.54	5.7	1.8	1.1	1.7		5.2
MA15 Peridotite	2.6	1.1	18	11	12	2.5		10
Massive chromite	0.85		0.46		24		96	

Table 4-7. Comparison of the Mount Albert pluton data to other ultramafic rocks

Sample description	Content	Reference
GOLD		
Ultramafic rocks		
Altai-Sayan folded belt	9.4	Shcherbakov & Perezhogin (1964)
Serpentinite		
Kuznetsk Ala-Tau	4.3	"
Peridotite		
Eastern Sayan, Ospinskii massif	6.0	"
Serpentinite		
Transbaikal, Dzhida massif	3.7	"
Dunite, China	4.6	"
" "	31	"
" "	5.3	"
" Urals, Ray-12 massif	15	"
" " Solv'yeva	11	"
" Uktusskii massif	5.3	"
" Elizaveta massif	5.3	"
" Polar Urals, Sibsko-Vaykarskii massif	22	"
" Khatanga River Basin Gula intrusive	5.6	"
" Albania, Bulchiz massif	3.7	"
Alpine type dunite, Balsam N. Carolina	2.2	Vincent & Crocket (1960)
Autochthonous olivine cumulite average Rhum peridotite	11	
Ultramafic rocks	0.99	This work
Serpentinized rocks	2.37	"
PALLADIUM		
Dunite, Mt. Albert, Quebec, Canada 95% forsterite, 5% enstatite	1.3	Crocket & Skippen(1966)
Peridotite Nodule		
Salt Lake Crater, Hawaii	7.3	"
Peridotite, Montrose Point, N. Y.	8	Hagen (1954)

Table 4-7 (continued)

PALLADIUM (continued)		
Pyroxenite Approximately equal volumes of enstatite and diallage, partially serpentinized, Thetford district, Quebec	22.2	Crocket & Skippen(1966)
Serpentinite, highly altered rocks contain antigorite, brucite, magnetite, Leupoldsgrun(Munchberg gneisse), Oberfranken, Germany	300	Hahn-Weinheimer(1959)
Serpentinite Normal serpentinite from the Munchberg gneisse mass. Less altered than above sample	12	"
Harzburgite Bushveld Complex, South Africa	12	Hagen (1954)
ultramafic rocks	7.7	This work
Serpentinized rocks	10.3	"
IRIDIUM		
Ultramafic rocks	2.5	This work
Serpentinized rocks	2.2	"
OSMIUM		
Peridotite, Snowy Mts., N.S.W. Australia	5.3	Morgan & Lovering(1967)
Dunite, Twin Sisters, Washington U.S.A.	1.3	"
Peridotite, Cazadero Quad., California, U.S.A.	5.9	"
Ultramafic rocks	7.2	This work
Serpentinized rocks	6.6	"

4-3. Precious metal correlations

A correlation matrix for Pd, Au, Ir and Os was calculated using the 7040 computer. The correlation coefficients at the 95% confidence level are tabulated in Tab. 4-8. Those from Keays (1967) for the same metals for sulfide samples from the Strathcona Mine, Sudbury, are tabulated for comparison in Tab. 4-9.

Os and Ir are very strongly correlated. Weak negative correlations were found for Pd-Os and Pd-Ir, while Au-Pd, Au-Ir and Au-Os are not significantly correlated.

The negative correlations of Pd-Ir and Pd-Os are weak in both fresh and serpentinized rocks. The high Ir-Os correlation, 0.949, applies to all rock types, clinopyroxenite, and massive chromite. Similar correlations were found by Keays (1967) for precious metals in sulfide minerals from Strathcona in that Os-Ir showed a strong positive correlation, Pd-Os and Pd-Ir weak negative correlations and gold exhibited no significant correlation with a platinum metal. This strong geochemical coherence of Os and Ir in both the Mount Albert rocks and the Strathcona sulfides suggests considerable similarity of physio-chemical properties. Some physical constants for these metals are listed in Tab. 4-10. Although their chemical character during the emplacement and subsequent processes affecting the pluton is unknown, a consideration of their strong correlation and similarity in physio-chemical properties (Tab. 4-10) suggests that the bonding and other chemical properties of these two elements in this environment are similar.

Table 4-8. Correlation coefficient for Au, Pd, Ir and Os in Mount Albert pluton

	Au	Pd	Ir	Os
Au	1.000			
Pd	-0.072	1.000		
Ir	-0.040	-0.241	1.000	
Os	-0.118	-0.359	0.949	1.000

Table 4-9. Correlation coefficient for Au, Pd, Ir and Os in Strathcona samples (from Keays, 1967)

	Au	Pd	Ir	Os
Au	1.000			
Pd	0.051	1.000		
Ir	-0.030	-0.270	1.000	
Os	0.003	-0.262	0.761	1.000

Table 4-10. Some physio-chemical properties of Os and Ir

	Os	Ir
Metallic radius Å	1.35	1.35
Oxidation states		
Most common	IV, VI	III, IV
Highest	+8	+6
Specific gravity (20°C)	22.5	22.5
Electronegativity*	2.1	2.1
	1.52	1.55

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* Upper figure of each pair is that of Pauling (1951); lower figure is that of Little and Jones (1960).

CHAPTER 5

DISCUSSION

5-1. Origin of the metals in the Mount Albert pluton

Two major hypotheses have been proposed for the origin of alpine type ultramafic rocks. Lodochinikow (1933) and Hess (1933, 1938) postulated the existence of hydrous magnesian silicate melts possibly approaching serpentine in composition. This hypothesis was proved improbable on a basis of experimental work by Bowen and Tuttle (1949). Bowen (1928, 1949) suggested an olivine crystal cumulate formed by gravitational settling from a basaltic parent magma with entrapment of minor interstitial magma as the source of ultramafic rocks rather than a hydrous melt.

The Mount Albert peridotites were probably intruded as a crystal mush composed largely of suspended olivine crystals with about 15 per cent interstitial liquid according to MacGregor (1964). In accordance with Bowen's hypothesis, serpentinization is a post-intrusion phenomenon in which the water needed to induce the process is derived mainly from sediments or volcanics of the intruded geosynclinal pile. Such a source of water is certainly available at Mount Albert for serpentinization. However, Bowen's further contention that the olivine crystal mush accumulated by gravitational settling from a basaltic magma seems highly improbable when considering the metal contents found in this study, alkali element concentrations, and Sr^{87}/Sr^{86} ratios of alpine ultramafic rocks.

The Pd content of basalts and the Mount Albert rocks are comparable while Au shows slight depletion in latter with respect to basalts. These two metals do not present serious problems with the crystal settling hypothesis. However, the marked increase in Os and Ir contents of the Mount Albert rocks relative to basic rocks implies a strong fractionation of these metals into early olivines and pyroxenes crystallizing from basaltic magma. There is no evidence to support a strong fractionation of these metals in olivine or pyroxene.

The Na_20 and K_20 studies of the alpine ultramafics by Hamilton and Mountjoy (1965) show that the alpine ultramafics are depleted in Na_20 (0.004%) and K_20 (0.0034%) in comparison with basalt. The values of the former are only 1/600 to 1/200 of the later. Another Sr isotope study by Stueber and Murthy (1965) show that the alpine ultramafic rocks are high in initial Sr^{87}/Sr^{86} ratios, ranging from 0.705 to 0.715, while oceanic basalt are low, ranging from 0.702 to 0.705. Both Sr^{87}/Sr^{86}

ratios and the alkali element concentrations suggest that alpine ultramafic rock cannot be crystallization differentiates of basalt.

More recent models such as that of Clark and Ringwood (1964) regard the dunitic ultramafics as residues in the partial melting of a primitive undifferentiated material termed pyrolite (a pyroxene-olivine rock of one part of basalt to three parts of dunite) producing a melt fraction of basaltic composition. The composition of the primordial material has been debated by many investigators. Chondritic meteorites have been studied and evaluated from this point of view but most chondritic earth models are defective with respect to at least some aspect of their composition as possible source material. O'Hara and Mercy (1963) have discussed various ultramafic xenoliths as possible undifferentiated material and believe that only garnet peridotite from kimberlite represent unmodified mantle material.

Lack of precious metal abundance data on garnet peridotite prevents a discussion of this material as possible undifferentiated mantle material with respect to suitability for these metals. Acknowledging the problems with the chondritic models, some observations seen, however, appropriate. Precious metal data for acid rocks, basic rocks, Mount Albert rocks and average chondrite are compared in Fig. 5-1 in which data are normalized to abundances in ordinary chondrites.* The figure illustrates the marked difference in ultramafic precious metal trends and basic and acid rock trends, and also demonstrates that the normalized ultramafic trends are the most similar to the meteorite trends.

If material of chondritic compositionis subject to partial melting to produce an ultramafic residuum plus basaltic melt, it is apparent that the residuum is subjected to minimal fractionation of precious metals with respect to the parent. This may reflect concentration of these metals in some phase which is not melted or their general insolubility under the P_{0_2} and temperature prevailing in the region of partial melting. This is quite obvious for Ir and Os which are largely retained in the residuum. For Au and Pd, however, the fractionation between the melt and the residuum is not large and these contents in the Mount Albert and basic rocks are more or less of the same order of magnitude. The tendency for fractionation of the previous metals

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* The normalized values are $\frac{\text{Sample (p.p.b.)}}{\text{Chondrite (p.p.m.)} \times 10^{-3}}$

Chondrites contain about 1000 times the previous metal content of ultramafic rocks or ultramafic rock xenoliths with the bulk of these metals occurring in Fe-Ni particles. In chondrites the separation of this metal phase is incomplete due probably to the relatively small size of the chondrite parent bodies whereas in the larger earth the correspondingly greater gravitative attraction towards its center of mass has effected a far more complete separation although without marked fractionation of precious metals one with respect to the others.

between the melt and residuum probably depends on the melting point, oxidation state of the individual precious metal and P_{O_2} environment in the region of melting. Different melting points and oxidation states for Ir-Os and Au-Pd may be instrumental in effecting the observed fractionation trends.

5-2. Interpretation of behaviour of the metals during intrusion

It was concluded by MacGregor (1964) that the Mount Albert intrusion was emplaced as an essentially solid mass of olivine with minor interstitial liquid. Taking interstitial orthopyroxene, clinopyroxene and chrome spinel as representative of the liquid phase, a melt:crystal ratio of 15:85 was suggested. According to this suggestion, the partition of the metals between crystals and melt during intrusion may be interpreted by comparing their contents in disseminated chrome spinel, clinopyroxene and massive chromite with that in olivine plus orthopyroxene. Disseminated chrome spinel is considered late magmatic crystallizing after ollvine and at the same general period of ortho- and clinopyroxene. Average values for the precious metals in chrome spinels (Table 4-6) indicate that they are enriched in this mineral relative to the whole rock by a factor of 2 to 3. All the gold analyses, 3 of 4 Pd analyses and 2 of 4 Ir determinations show this trend. Thus, although

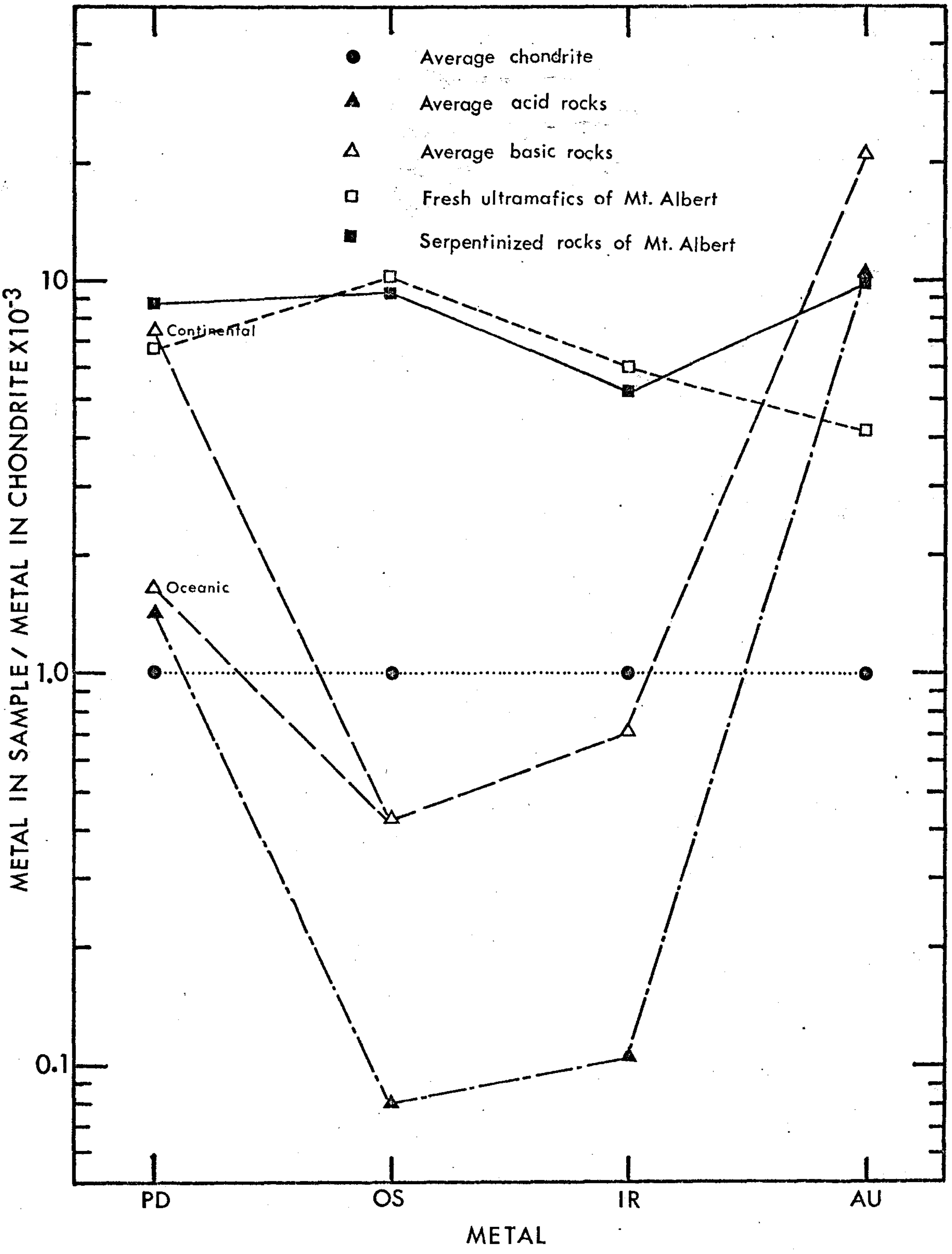

Fig. 5—1 The fractionation trends of the precious metals in meteorites and some terrestrial materials

there are some samples showing a reversal of trend, the chrome spinel indicates a slight enrichment of precious metals, particularly Au and Pd in the melt phase.

Clinopyroxene also gives information about the precious metal content of the liquid phase. Although the genetic relationship of clinopyroxenite to the pluton is somewhat uncertain, the mineral may represent, (1) a remelted phase from crystallized peridotite, (2) a reaction product of the peridotite and a more gabbroic phase above it, or simply (3) crystallization from the melt phase. The Pd content in clinopyroxene is 4 times that of the whole rock while Au and Ir are slightly enriched relative to the whole rocks.

The fractionation trends for the precious metals in the whole rock, clinopyroxene, massive and disseminated chromite are presented in Figure 5-2 which shows that disseminated chrome spinel and clinopyroxenite have the same general trend. This trend contrasts strongly with that for the massive chromite and moderately so with the whole rock trend, particularly with respect to Pd and Os. This suggests that both clinopyroxene and disseminated chrome spinel have shared some common genetic feature or process and may well reflect precious metal partition into the late melt phase. Although some uncertainty is generated by the small number of data and the inconsistencies in those data, it seems reasonable to conclude that precious metal values in disseminated chrome spinel and clinopyroxenite indicate a small concentration of these metals in the melt phase relative to crystalline olivine and orthopyroxene. Pd might be enriched in the liquid phase, due to either the rejection by the more ionic crystal structure of olivine or the incorporation of Pd from overlying basic volcanics. Chrome spinel is a good precious metal concentrator, but the large variations suggest that precious metals are not in solid solution in its crystal structure. The enrichment may be due to different kinds of surface chemical reactions related to chrome spinel and precious metal complexes which vary from place to place.

The massive chromite is quite distinct from the disseminated type. It is high in Cr_2O_3 and low in total Fe and CoO. Warshaw and Keith (1954) have shown that the system spinel-picrochromite may crystallize under hydrous conditions down to temperatures of 510°C. MacGregor (1962) believes that the massive chromites have formed during this late deuteric stage. Their concentration in structurally favourable areas suggests migration of the deuteric liquids.

The precious metal content of the massive chromite is also of considerable interest in that Os and Ir are strongly concentrated in it relative to either fresh or serpentinized rocks. Gold and Pd, however, show no enrichment in massive chromite. The reasons for this differentiation of precious metals is not obvious but the following factors may be pertinent.

Precious metal contents in the fresh rocks (Table 4-7) with the exception of one of the Pd values, vary by only a factor of 2. It is suggested that they may exist as neutral, uncharged atoms as suggested by Vincent and Crocket (1960), DeGrazia and Haskin (1963), Mantei and Brownlow (1967). The neutral atoms are incorporated into the crystal structure randomly, perhaps in lattice defects or other imperfections, but not by ionic substitution. There is no special affinity between these atoms and the silicate lattices, nor is there a strong partition between crystals and coexisting melt.

Inspection of the ionization potential data (Table 5-1) indicates that most of the iron in the initial liquid is in +2 state, as indicated by the Fe^{2+}/Fe^{3+} (≈ 25) for unserpentinized rocks. The only precious metal that could exist as an ion is Au^{+}. The probability that the other three metals exist in an ionic state is low because their stable oxidation states are higher (+2 for Pd and +4 for Os and Ir).

While the precious metals are probably largely in the neutral state during much of crystallization history of the intrusive, they may be in part oxidized in the final stages if the P_{0_2} of the melt rises. Again, considering stable valence state, Au and Pd should be the first to oxidize and probably form complex ions whereas Ir and Os would be most difficult to oxidize and would remain in a neutral state until an advanced stage of crystallization.

Keays (1968) argued that Au and Pd tend to form stronger complexes than Os and Ir with anionic donors, because they have more d-electrons, larger atomic radii, lower stable oxidation states, and high polarization properties. By this reasoning, the distribution of precious metals in different phases should be closely related to the volatile contents of coexisting melts or residual fluid.

It seems that Au and Pd are enriched a factor of 2 to 3 in disseminated chrome spinel, and perhaps clinopyroxene as well. This effect may have depleted these metals in the last residual deuteric liquid from which the massive chromite crystallized. Os and Ir, however, perhaps because of difficulty of oxidation, have not been so strongly fractionated into accessory chrome spinel and their concentration in the melt or residual liquid has increased as the volume of fluid phase gradually decreases. In spite of the strong concentrating effect of the massive chromite, their absolute contents are still very low in view of the small volume of these veins.

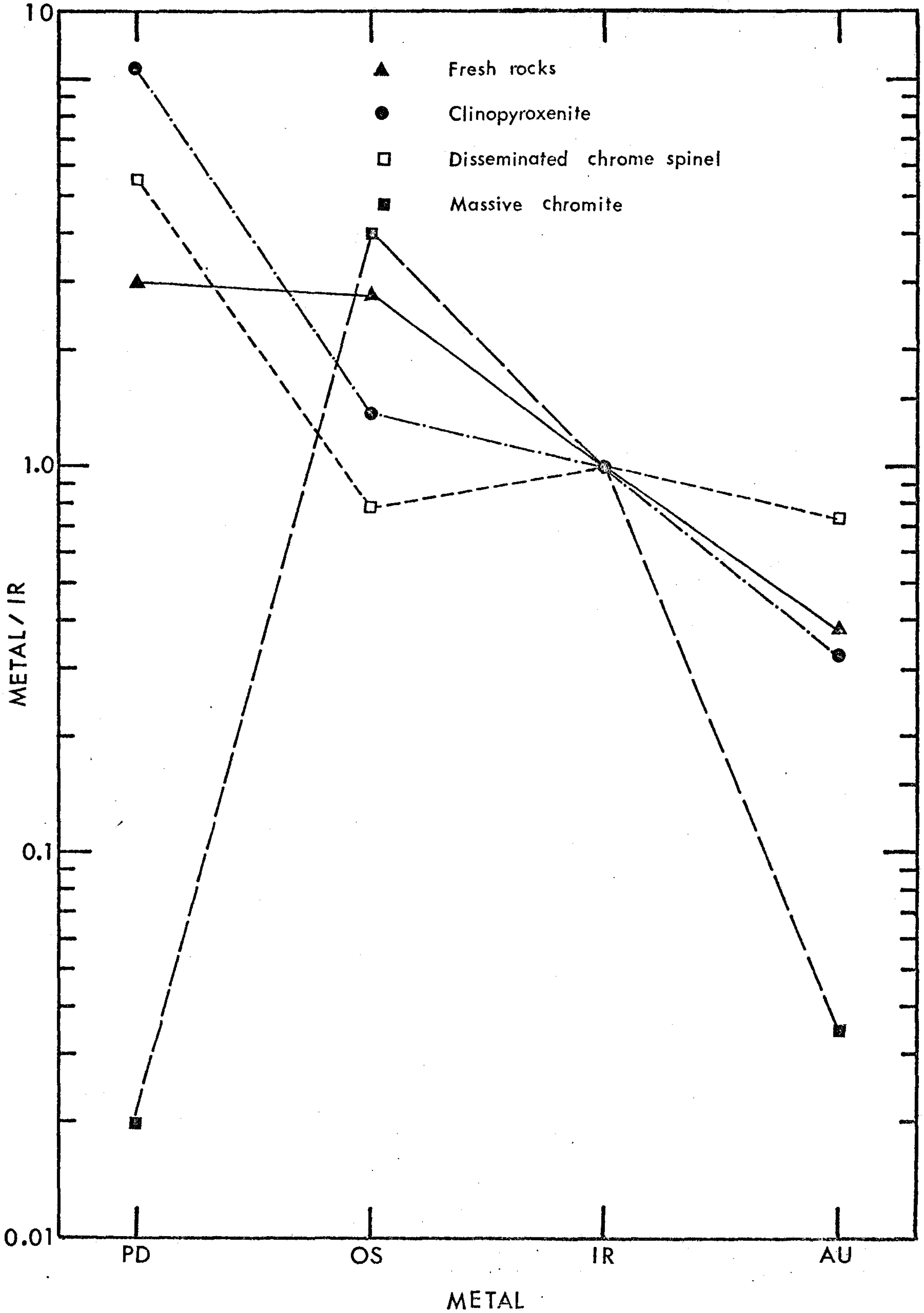

Fig. 5—2 The fractionation trends of the precious metals in Mount Albert

Table 5-1. Ionization potentials of the metals in electron volts (after Ahrens, 1964)

	I	II	III	IV	V
Fe	7.868	16.178	30.643	(56)	(79)
Pd	8.334	19.423	32.921	(49)	(66)
Os	8.732	(17)	-	-	-
Ir	9.1	-	-	-	-
Au	9.223	20.045	(29)	-	-

5-3. Interpretation of behaviour of the metals during serpentinization

From Bowen and Tuttle's (1949) experimental studies of the system $MgO-SiO_2-H_2O$, it is known that serpentine is unstable at temperatures higher than 500°C, no matter how high the water pressure. If SiO_2 is not present in significant amount, serpentinization does not occur until 400°C. In the case of Mount Albert, the SiO_2 is very low, and the process would be simply an addition of water.

According to MacGregor (1962) a slight dehydration of the aureole rocks occurred during metamorphism resulting from the migration of water into the intrusion. The water content of the pluton is expected to be less than that of the country rocks, which is approximately 3 weight per cent. The large amounts of water needed for serpentinization thus cannot be attributed to the contribution from country rocks in the immediate vicinity of the intrusive only. The addition of some water from deeper contact metamorphic zones and juvenile sources is highly probable and necessary.

The variation in precious metal content in serpentinized rocks is much greater than in fresh rocks as illustrated in Figs. 5-3, 5-4, 5-5 and 5-6 where average values for fresh and serpentinized rocks are represented by solid squares. The variance of all four metals increase when the rocks are serpentinized. Using average values for fresh and serpentinized rocks there is little change in average precious metal content with serpentinization. Pd shows a slight increase and Ir and Os slight decreases in concentration with degree of serpentinization. Only in the case of Au does it appear that serpentinization effects a significant redistribution of the metal which appears to be increased in concentration in serpentinized rocks by a factor of two. The increase may be apparent only due to insufficient number of data. However, if the intruded country rock includes much basalt, a prominent rock type in surface exposures, gold is the one metal which is significantly higher in basalt than in the Mount Albert rocks. Hence, addition of gold in waters extracted from intruded wall rocks is feasible.

In response to temperature and pressure gradients from the depth to the surface, and, at any single level, from center to periphery of the body, there is a tendency for water to migrate upward and outward thereby concentrating toward the top and sides of the intrusive. With decreasing temperature serpentinization of the primary silicates commences at approximately 500°C probably beginning from marginal areas. With serpentinization the water vapour of the environment decrease, and the tendency for continued upward and outward migration of water would persist. As the country rocks have been metamorphosed, they tend to become impermeable and act as a seal for water vapour.

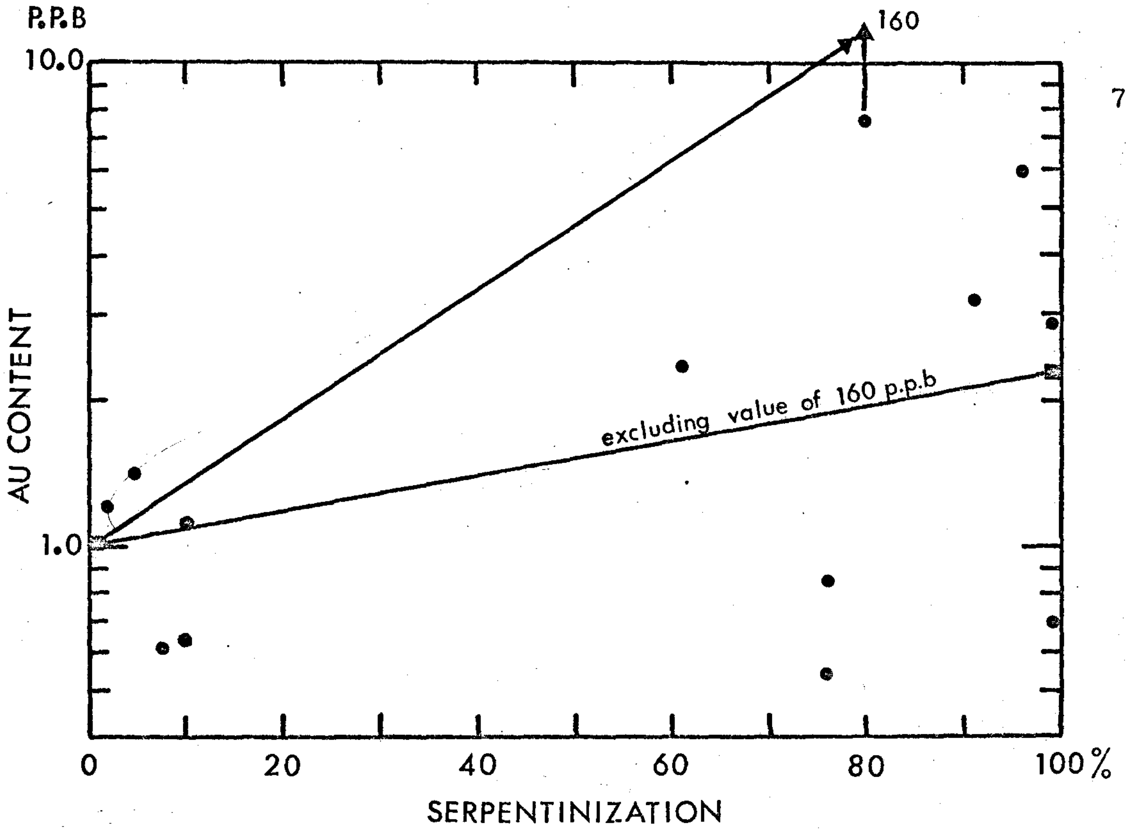

Fig. 5—3 Variation of Au content with serpentinization

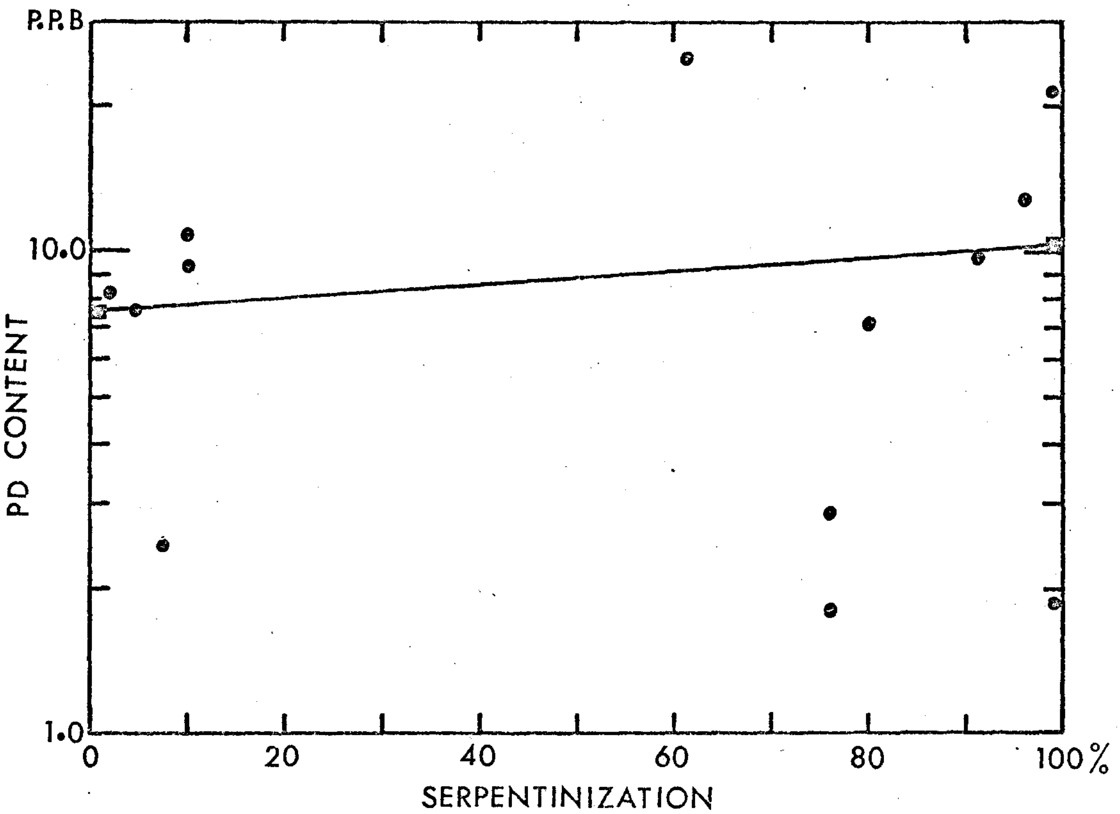

Fig. 5—4 Variation of Pd content with serpentinization

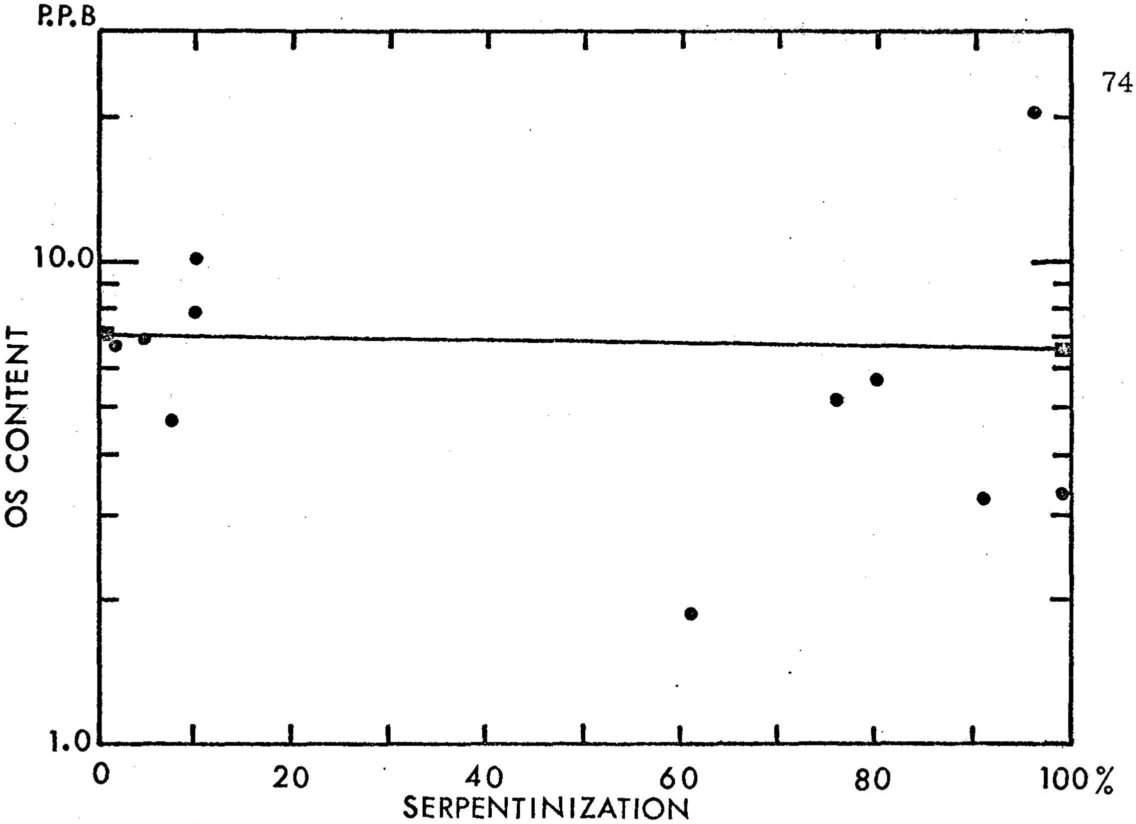

Fig. 5—5 Variation of Os content with serpentinization

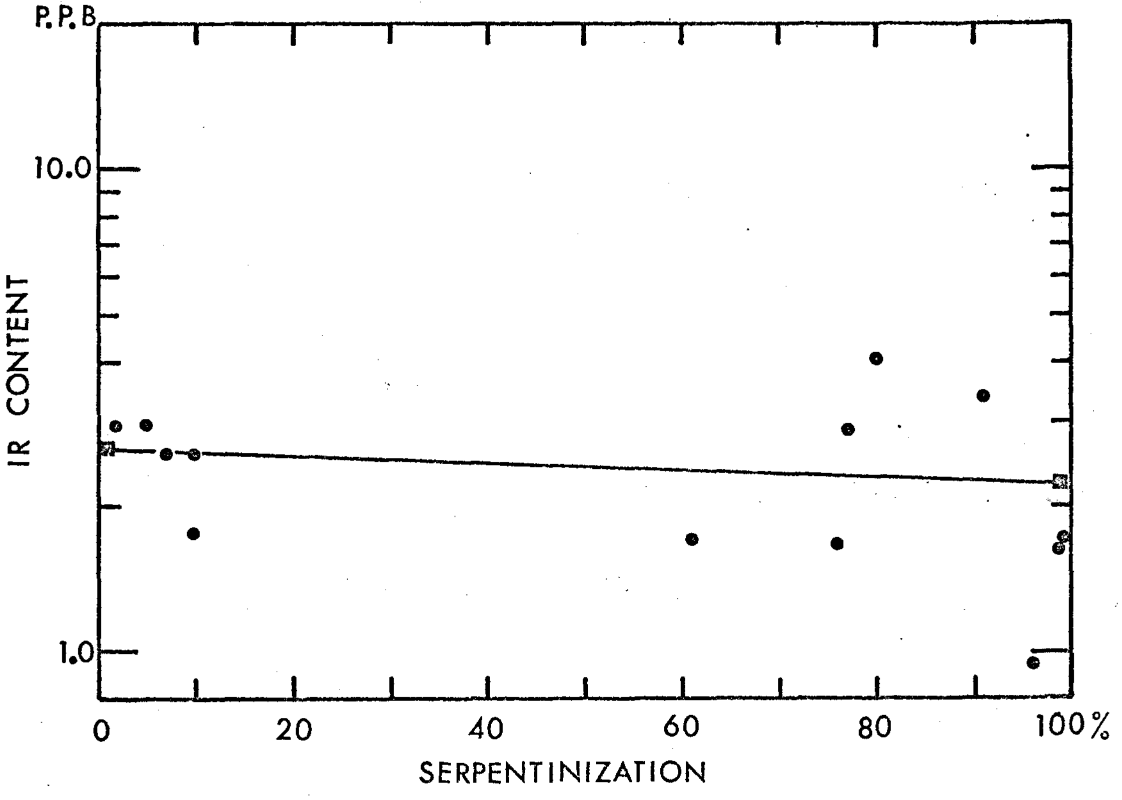

Fig. 5—6 Variation of Ir content with serpentinization

The sealing effect of the country rocks cause a marked increase of water immediately along the border of the intrusion.

As a consequence of the water migration, and attendant serpentinization of primary ferromagnesian silicates, the precious metals absorbed on the surface of these silicates or occupying lattice defects or in solid solution,may be transported from deep and central areas and redeposited along the border of the intrusive body if they are soluble in the aqueous fluid phase.

The solubility of precious metals in the aqueous fluid phase would be primarily dependent on three factors including: (1) their oxidation state prior to serpentinization, (2) the availability of anions in the fluid medium capable of forming stable precious metal complexes, (3) the P_{0_2} of the fluid medium. If the low temperature properties of the precious metals can be used as a guide, their greatest stability in an aqueous phase is achieved by complex ion formation with a wide variety of anions, particularly halogens. Although there are no data on the halogen content of Mount Albert rocks, it is obvious that only trace quantities would be needed to complex p. p. b. concentrations of precious metals. However, as most stable precious metal complexes involve +2 to +8 oxidation states, a P_{0_2} in the fluid medium high enough to stabilize these states would be required. In most cases oxidation from the zero valence state to some higher state would probably be required to bring the precious metals into solution. Au and Pd are apparently the two metals most readily carried in solution. Ir and Os are not sensitive to the leaching effect of serpentinizing aqueous solutions as their average contents are relatively uniform throughout the intrusive. The most stable oxidation states of these metals are +4 whereas Pd has a stable +2 state and Au a stable +1 state. The higher oxidation potential required to stabilize Ir and Os was perhaps not attained in the fluid medium.

The gradual leaching effect of the serpentinization process may cause the precious metal contents in the samples from central area to decrease. Sample 11B and 13A listed in Tab. 4-3 and plotted in Fig. 4-1 illustrate this feature. In marginal samples precious metals are in general higher than in the fresh rocks. An extremely high value of Au, 160 p.p.b., was obtained in one sample.

Local precious metal content increase could also be caused by the alteration of precious metal rich phases, such as chrome spinel, massive chromite, and/or clinopyroxene.

5-4. Conclusions

The Mount Albert pluton was intruded as a nearly solid mass of olivine with minor interstitial liquid, about 15 weight per cent. At the time of intrusion most of the olivine had crystallized, and the liquid phase was pyroxenic. The precious metals were slightly enriched in this melt phase possibly by a factor of 2 to 3. Higher Au and Pd contents in late magmatic chrome spinel are thought due to the reaction of the complex ions of these metals with chrome spinel.

Before the emplacement of the pluton the oxidation potential and volatile components were very low. At this stage all four metals probably existed as neutral atoms, as suggested by their uniform contents in the fresh rocks. After intrusion, due to crystallization and incorporation of some water and other volatile components from the country rocks, the residual melt gradually increased in P_{O_2} and possibly in content of anions. Precious metals, particularly Au and Pd, may have formed complex ions in the melt by the onset of chrome spinel crystallization. Reactions between chrome spinel and the complexes caused deposition on the surface of chrome spinel and some enrichment in this phase. Massive chromite formed during a late dueteric stage down to 510°C. When massive chromite started to crystallize, Au and Pd were already depleted in the melt. On the other hand, due to the increase in volatile contents and oxidation potential of the solution, Ir and Os may have been complexed or simply carried with the final solution phases and enriched on the surface of the massive chromite accordingly.

Below this temperature, the rocks underwent serpentinization on a large scale. Some precious metals were remobilized, particularly Au, and were taken into the solution, carried upward and outward, and concentrated around the marginal area of the pluton.

Au is the metal most sensitive to this effect and it shows apparent depletion in the central part of the pluton and enrichment around the marginal area. Pd was slightly effected by serpentinization and depleted in the central area but without enrichment around the marginal. Owing to its overall enrichment, some additional Au added from juvenile and deep source water is expected. Os and Ir are not sensitive to serpentinization and their only response is an increase in the variability of concentration in serpentinized rocks.

The country rocks functioned like a seal after metamorphism, and the pluton remained largely a closed system. Serpentinization only redistributed the precious metals, and except for Au, little increase or decrease has been observed.

The fractionation trend of the metals in the pluton are compatible with Clark and Ringwood's ultramafic mantle model. The selective melting of the mantle material possibly of chondritic composition to produce basaltic magma and dunite or peridotite residuum, could conceivably generate the observed precious metal fractionation trends in ultramafics and basalts.

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APPENDIX A

Analytical Procedure for Pd in Massive Chromite

With the general analytical procedures described on page 18 to 24, long-lived contamination was always found in ^{109}Pd extracted from massive chromite samples. Examination of the gamma spectrum suggested the contaminant was ^{51}Cr. The following modifications of the general procedure successfully eliminated this contamination.

1) Fuse the irradiated powder and Pd carrier with Na_20_2 + Na0H, dissolve in 25 ml of 6M $HN0_3$, and 5 ml conc. HCl, and evaporate to a volume of a few mls.

2) Add 5-10 mls. of 2M HCl, boil, and precipitate Pd with Zn. Dissolve precipitate in aqua regia and digest in two aliquots of conc. HCl to convert to chloride.

3) Prepare an ion exchange column, dissolve Pd chloride with 0.5M HCl - Ce^{4+} solution and filter the Pd solution onto the column.

4) Elute Pd with 120 ml of 0.1M thiourea in 0.1M HCl solution. Destroy thiourea with conc. NH_40H and heat to coagulate Pd as the sulfide.

5) Dissolve the sulfide in aqua regia and convert to chlorides. Take up in 20 ml of 2M HCl, make the solution alkaline with conc. NH_4OH and scavenge the solution with 0.02M $FeCl_3$ solution several times.

6) Evaporate the scavenged solution to dryness, treat with aqua regia, convert to chloride, and then follow the normal procedure.

APPENDIX B

Analytical Procedure and Counting Result of Ru

The determination of Ru by counting the ^{97}Ru and ^{103}Ru activities was attempted on duplicate peridotite samples. Os was also determined on these samples. The distillation of Ru was carried out in the same apparatus as Os, as follows:

1) After distillation of Os, continue heating until the decomposition of H_2O_2 is complete. Place a new receiver tube containing 30 ml of 3M NaOH in an ice bath.

2) When the solution has cooled to about 40°C, add 20 ml of 10% $NaBrO_3$ to the reaction flask and heat to 105°C to 110°C.

3) Distil RuO_4 for about 30 minutes. After 20 minutes, heat the liquid in the trap bulb to boiling to distil absorbed RuO_4 into the receiver tube.

4) Acidify the sodium ruthenate solution with 6 ml of conc. HCl and add 10 ml of ethanol to precipitate RuO_2.

5) Heat for 10 minutes to coagulate the precipitate, transfer the RuO_2 precipitate to a centrifuge tube and centrifuge. Wash twice with 1M NaOH, add 5 ml of conc. HCl and heat in an electrical bunsen until dissolved.

6) Dilute the solution to 30 ml with 1M HCl, transfer to 150 ml beaker and precipitate Ru^0 with Zn. Transfer to a pyrex vial and dry under infrared heat.

7) The Ru powder standard was prepared and processed the same way as Os down to the Na_20_2-Na0H fusion step. Both metals were always combined in one standard and processed at the same time. The distillation of the Ru standard was the same as for the samples, except that no trap bulb was included in the apparatus.

Ru was determined by counting appropriate photopeaks in the gamma spectrum including ^{97}Ru and ^{103}Ru produced by the following reactions:

$^{96}Ru(n,\gamma)Ru^{97}$ (T 1/2 = 2.9 days, γ photopeak = 0.22 MeV)

$^{102}Ru(n,\gamma)Ru^{103}$ (T 1/2 = 40 days, γ photopeak = 0.50 MeV)

A competing fission reaction also produced ^{103}Ru: $^{235}U(n,f)^{103}Ru$

Thus, the ^{103}Ru cannot be used as a measure of the (n,γ) process, and if fission product ^{103}Ru is present, its Compton radiation will contribute to the ^{97}Ru photopeak. However, no significant amount of fission product ^{103}Ru should be present in the standard (a pure Ru salt) and the ratio of ^{97}Ru to ^{103}Ru in the sample may be compared to that of the standard to confirm the absence of fission product Ru.

Hsieh (1967) determined Ru concentrations by using the 0.22 MeV photopeak of ^{97}Ru after subtracting the contribution from the Compton portion of ^{103}Ru spectrum and the background of the counter.

In the two duplicate samples analysed in this study, a gamma peak in the ^{97}Ru region of the spectrum was recognized in only one sample. However, the half-life of this radiation was approximately 30 days. Obviously, a significant contribution from the Compton radiation of ^{103}Ru seems probable. Assuming the Ru concentration was three times that of Os*, counting rates for the ^{97}Ru photopeak were calculated (in conjunction with the Ru standard). These counting rates were found to be only half of those actually obtained, implying that Ru fission contribution from ^{235}U is too high to permit Ru determination in these samples.

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* This factor is suggested by the Os/Ru in carbonaceous chondrites (Crocket _et al._, 1967) and in sulfide minerals (Hsieh, 1967).