No. 5

RUTHENIUM AND OSMIUM ABUNDANCES IN SULFIDES FROM THE SUDBURY ORES

ANALYSIS OF RUTHENIUM AND OSMIUM ABUNDANCES IN SULFIDE MINERALS FROM THE SUDBURY ORES, ONTARIO

By

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SCOPE AND CONTENTS: This work was undertaken to evaluate neutron activation analysis as a technique for simultaneous determination of Ru and Os in sulfide minerals by counting the γ radiation of ^{97}Ru and ^{103}Ru, and the β^- radiation of ^{191}Os and ^{193}Os. The samples studied were collected from the Strathcona and Frood-Stobie Cu-Ni sulfide deposits of Sudbury. Sulfide minerals, including pyrrhotite, chalcopyrite, pentlandite and cubanite were separated from samples including representatives of both ore grade and non-commercial material. The minerals were analysed for Ru and Os to determine their concentration ranges in these sulfides, the degree of geochemical coherence of the metals in sulfides from both high grade ore zones and weakly mineralized rocks and their distribution between coexisting sulfides.

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ABSTRACT

The neutron activation analysis has been used as a technique for simultaneous determination of Ru and Os in sulfide minerals by counting the γ radiation of ^{97}Ru and ^{103}Ru and the β^- radiation of ^{191}Os and ^{193}Os. The sensitivity of the method is approximately 10^{-9}gm per gm for Ru and 10^{-10}gm per gm for Os.

Thirty five specimens of sulfides, including pyrrhotite, chalcopyrite, pentlandite and cubanite from the Strathcona and Frood-Stobie deposits of the Sudbury district, Ontario, were analysed. The concentration of Ru was generally below 50 ppb and Os below 20 ppb. In the case of Ru, significant quantities of ^{103}Ru and ^{105}Ru were produced by ^{235}U fission and interfered seriously with use of these nuclides, which are both produced by n,γ on ruthenium for analytical purposes. The concentrations of Ru based on ^{97}Ru activity was generally used for Ru determination except when the ^{97}Ru was contaminated with other unknown radionuclides.

A very strong geochemical coherence between Os and Ru in sulfide mineral assemblages was observed. The Os fractionation between pyrrhotite and chalcopyrite indicates a slight preferential concentration of Os in the pyrrhotite, which is explained in terms of its crystal chemistry. The distributions of Ru and Os in Strathcona Mine also suggest two generalizations: (1) Both Os and Ru settled gravitatively in a body of fairly continuous sulfide liquid as either metallic particles or sulfide minerals concentrating toward the base of the hanging-wall breccia. (2) Ru and Os are higher in the sulfides of the hanging-wall breccia than in the footwall breccia ore zone, suggesting a possible different generation or source of sulfides in footwall breccia ore zone and hanging-wall ores.

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I. INTRODUCTION

1. Review of previous work

Ru and Os are the lightest members of the six platinum transitional elements of the second and third series respectively. They exhibit striking similarities in their chemical properties. Their geochemistries are poorly understood because most trace element analytical techniques, including optical spectrography, X-ray fluorescence and colourimetry are not sufficiently sensitive to accurately determine their concentrations in common rocks and minerals due to their extremely low abundances. Except for some data on minerals from ultrabasic rocks associated with ore deposits (Ruzin et al, 1965), we have virtually no data for these elements in any terrestrial materials. With respect to meteoritic materials which are probably enriched in Os and Ru by three orders of magnitude relative to terrestrial material, reliable Os and Ru analyses are available for approximately 20 and 35 meteorites respectively (mostly irons and ordinary chondrites).

The earliest attempts to study the geochemistry of these metals were those of I. and W. Noddack, and Goldschmidt and Peters (See Geochemistry, V.M. Goldschmidt, 1954). Both these investigators used spectrographic methods. The bulk of their data on Os and Ru are for iron meteorites and are tabulated in Table 1. Based on a comparison with modern data it is suggested that these early results tend to overestimate Os by factors of approximately 4 or 5 and Ru by factors of approximately 2 in iron meteorites.

Table 1 Ru and Os abundance in cosmic materials

Material	Numbers of sample	Ru(ppm)	Os(ppm)	Investigator	Year	Method
Iron meteorite		23.9	8.8	Noddack & Noddack	1930	Spectrography
"		19.3	19.3	"	1931a	"
"		9.0	3.9	"	1931b	"
"		10.6	7.6	" (See Goldschmidt,1954)	1934	"
"	2	10	> 3	Goldschmidt & Peters	1932	"
"	17	7	--	Hara & Sandell	1960	Absorption spectrophotometry
"	10	--	2.03	Herr et al.	1960	Neutron activation
"	6	--	6.6	Sen Gupta & Beamish	1963	Absorption spectrophotometry
"	24	6	---	Nichiporuk & Brown	1965	Spectrography
Chondrite	15	0.89	0.91	Bate & Huizenga	1963	Neutron activation
"	14	0.95	---	Hara & Sandell	1960	Absorption spectrophotometry
Achondrite	2	0.0029	0.0058	Bate & Huizenga	1963	Neutron activation
Troilite	2	5.8	---	Hara & Sandell	1960	Absorption spectrophotometry
"	2	0.032	0.0068	Bate & Huizenga	1963	Neutron activation
Tektite	1	---	0.00046	"	1963	"
"	10	---	0.0008	Lovering & Morgan	1964	"

The main modern studies on Os and Ru geochemistry in meteorites and tektites include the work of Herr et al.(1960), Hara and Sandell (1960), Bate and Huizenga (1963), Sen Gupta and Beamish (1963), Lovering and Morgan (1964), Morgan and Lovering (1964), Morgan (1965) and Nichiporuk and Brown (1965). The analytical methods used include spectrochemical, spectrophotometric and neutron activation. A summary of the data obtained by these workers is included in Table 1. For iron meteorites average Ru and Os concentrations of 6 to 7 and 2 ppm respectively have been obtained. The work of Nichiporuk and Brown and Bate and Huizenga has established that the bulk of these metals in chondrites are present in the metallic iron-nickel phase, and that their concentrations in the metal of chondrites is approximately the same as in the irons. Although much less data are available it appears likely that the achondrites are depleted by approximately a factor of 1,000 in both metals relative to the irons. Concentrations in troilite appear to be highly variable.

This highly siderphilic character of Os and Ru was recognized by Goldschmidt (1932) who later proposed (1937) that a strong partition of platinum metals between the earth's core and crust has occurred and is responsible for the extremely low concentrations of these metals in crustal rocks.

Data for Os and Ru in crustal rocks are virtually lacking. That which is available is tabulated in Table 2. It is obvious that discussion of their geochemistries in terrestrial rocks must be extremely speculative. Abundance estimates from various sources are tabulated in Table 3. The data in Table 2 (G-1, W-1, basalt, shale, sandstone) suggest that

Table 2 Ru and Os abundances in some terrestrial materials

Rocks or minerals	Locality	Ru(ppb)	Os(ppb)	Investigators	Year	Methods
Chromite	Geragen (Norwan)	500	---	Goldschmidt & Peters	1932b	Spectrography
	Mineral Hill (Penn, U.S.A.)	500				
Dunite with Chrome spinal	Urals (USSR)	500	800	Razin et al	1965	Spectrography
G-1	Rhode Is.	---	0.2	Bate & Huizenga	1963	Neutron activation
			0.056	Lovering & Morgan	1964	"
W-1	Virginia	---	0.46	Bate & Huizenga	1963	"
			0.26	Lovering & Morgan	1964	"
Basalt	Hawaii	---	0.30	Bate & Huizenga	1963	"
Dunite	---	---	1.14	"	"	"
Shale	A.C.T. (Australia)	---	0.46	Lovering & Morgan	1964	"
Qtz-rich sandstone	S.Australia	---	0.055	"	"	"

Table 3 Estimation of Ru and Os in the upper lithosphere

	Ru (ppm)	Os (ppm)
I and W Noddack (1930)	0.50	0.050
(1931)	0.018	0.030
(See Goldschmidt 1954) (1934)	0.020	0.010
G. Berg (1932)	0.040	0.040
V.M. Goldschmidt (1954)	> 0.0004	> 0.0004
Taylor (1964)	0.01	0.005

Goldschmidt's (1954) estimation is more accurate than the more recent estimates of Taylor (1964) whose values seem too high.

The association of precious metals with orthomagmatic Cu-Ni sulfide deposits is well known but here again published data on Os and Ru is lacking. One important factor is probably the difficulty in obtaining quantitative recovery of these metals in the fire assay procedures commonly used to concentrate the precious metals in sulfide samples, although modern methods such as the tin collection scheme of Faye (1965) have largely eliminated these problems. In view of the general need for precious metal data, particularly Os and Ru, in all types of terrestrial material and because of the high sensitivity of neutron activation for these elements and the relative lack of analytical problems as compared with some of the chemical methods, a study of Os, Ru distribution in some of the Sudbury Cu-Ni ores has been carried out.

2. Scope of the study

Various analytical procedures for determination of Os and / or Ru in meteorites and rocks by neutron activation analysis have been published by previous investigators, including Herr et al. (1960, 1961), Bate and Huizenga (1963), Lovering and Morgan (1964) and Morgan (1965). The analytical procedure developed was an adaptation of the activation method to the procedures of Westland and Beamish (1954, 1957) and involved separate distributions of Os and Ru as their tetroxides. Various steps for purification of base metals were used and the procedure was applied to the analysis of Fe-Cu-Ni sulfide minerals. Counting procedures involved measurement of the γ radiation of ^{97}Ru and

^{103}Ru, and the β^- radiation of ^{191}Os and ^{193}Os. The sensitivity of the method is approximately 10^{-9} gm per gm for Ru and 10^{-10} gm per gm for Os.

The samples studied were collected from two of the magmatic Cu-Ni sulfide deposits associated with the Sudbury Ni-irruptive, Ontario. Thirty-three specimens were taken from the Strathcona Mine on the north rim of the Irruptive and two from the Frood-Stobie deposit on the south rim. Sulfide minerals, including pyrrhotite, chalcopyrite and pentlandite were separated from the samples which included representatives of both ore grade and non-commercial material. In six cases coexisting sulfides were separated from the same sample. Ru and Os analyses were carried out to determine the average concentration in sulfides from both high grade ore zones and relatively weakly mineralized rocks, and to study the distribution of these metals between coexisting sulfides and within the various ore types at Strathcona.

II. OUTLINE OF THE GEOLOGY OF STRATHCONA MINE

The Strathcona Mine is located on the northern perimeter of the Sudbury basin approximately 20 miles northwest of Sudbury (Fig. 1). It is one of a number of deposits that occur close to the base of the Ni-irruptive. The rock types and mineralization of the Strathcona Mine have been described in some detail by Naldrett and Kullerud (1965, 1966). An outline of the geology based on their description follows.

1. Rock formations near the ore body.

A vertical geological cross section (21, 200E) through the Strathcona Mine (Fig. 2) is used to show the relationships of various rock types. It consists of two main rock groups including: (a) irruptive rocks (b) footwall rocks.

A. Irruptive rocks

Irruptive rocks consist of micropegmatite and norite. Only norite will be discussed here because of its close association with the ore deposits. On a basis of texture, mineralogy and age relationships, Naldrett and Kullerud (1967) recognize three different varities of noritic rocks including: (1) felsic norite, (2) mafic norite and (3) xenolithic norite. The felsic norite constitutes the main bulk of the noritic rocks of the Nickel-Irruptive proper whereas the mafic and xenolithic norites, which are collectively referred to as sub-layer rocks, are considered to be younger than the felsic norite. The xenolithic norite consists of two distinct facies depending on the abundance of xenoliths.

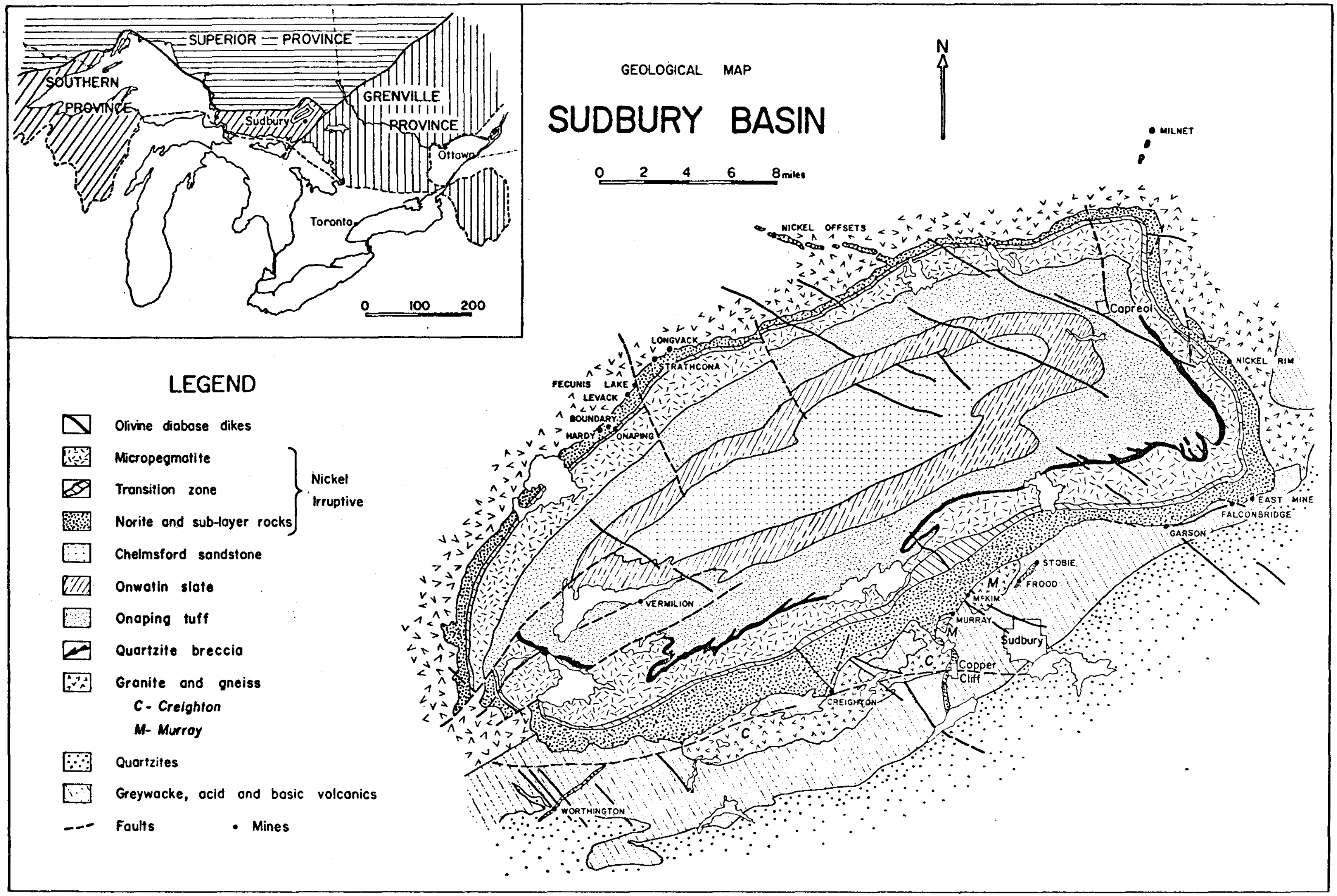
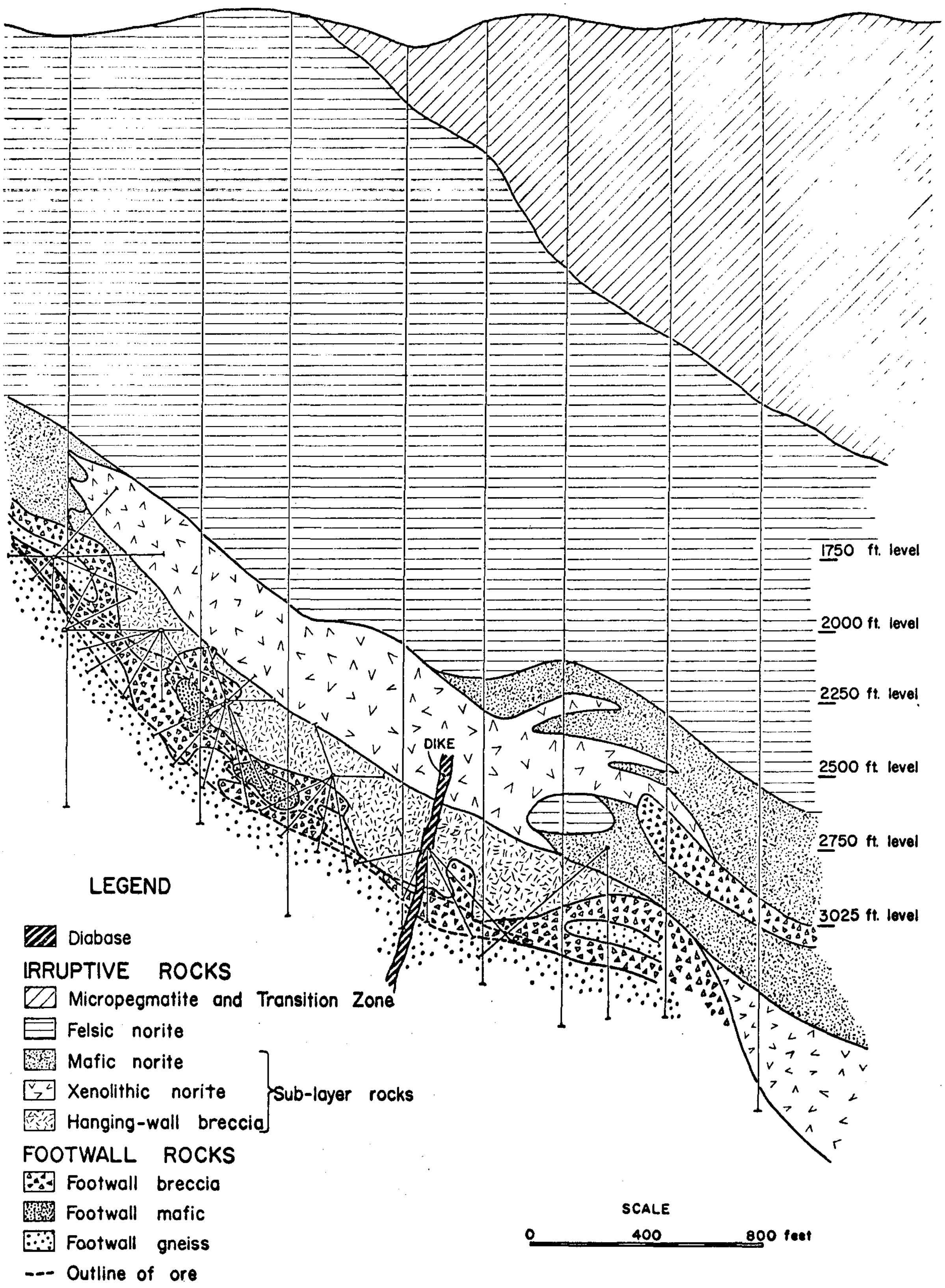


Fig. 1 Index map of Strathcona Mine and Frood-Stobie Mine, Sudbury, Ontario (After Hawley,1962)

Fig. 2 A vertical geological cross section (21,200E) through Strathcona Mine (After Naldrett and Kullerud, 1967)



If xenoliths exceed 30 volume percent the rock is referred to as hanging-wall breccia.

a) Felsic norite

Felsic norite is a coarse grained, holocrystalline granular rock with hypidiomorphic texture containing 50 to 70% plagioclase together with hypersthene, augite, potash feldspar and quartz. Some potash feldspar occurs in granophyric intergrowth with quartz. The original content of pyroxene varied between 20 and 45% of which 50 to 80% has been altered to anthophyllite, actinolite, chlorite and talc. This rock comprises the norite facies of the Nickel-Irruptive proper.

b) Mafic norite

Contacts clearly indicating the age relationship between the mafic norite and the overlying felsic norite have not been discovered in the mine workings. However, this contact has been observed in drill cores and is in part transitional over a few tens of feet and in part sharp. As felsic norite has been observed as xenoliths in mafic norite in drill cores, it is generally believed that the mafic norite is younger than the felsic.

Mafic norite is a medium to coarse grained holocrystalline granular rock, with a texture varying between hypidiomorphic and poikilitic. In general, mafic norite resembles felsic norite except for its colour in hand specimen, a higher proportion of mafic minerals, less uralitization of pyroxene and a tendency toward poikilitic fabric.

c) Xenolithic norite and hanging-wall breccia

Xenolithic norite is the youngest of the various types of norite rock and is most closely associated with the ore. It is a fine to medium grained holocrystalline rock with hypidiomorphic intergranular texture and contains xenoliths of ultrabasic to gabbroic rock. It is a plagioclase, hypersthene, augite rock in which the plagioclase is interstitial to the pyroxene and where the lineation of plagioclase laths suggests that much of it was crystalline at the time of intrusion. Quartz and potassic feldspar are approximately 1% or less. Both ortho- and clinopyroxene are abundant but less uralitized than in felsic norite.

Hanging-wall breccia is similar to xenolithic norite except for its increased proportion of xenoliths. This term is used when xenoliths exceed 30 volume percent. Xenoliths consist of olivine norite, pyroxenite, olivine pyroxenite and pyroxene peridotite. They are, therefore, rocks consisting of varying proportions of orthopyroxene, augite, olivine and plagioclase. In sulfide-rich portions of breccia, the proportion of pyroxene decreases as the sulfides increase while the proportion of plagioclase remains the same. Up to 5% of quartz is also present toward the base of this unit.

B. Footwall rocks

Two main units comprise the footwall rocks including the footwall breccia and footwall gneiss. The latter rock is the oldest in the area and is the rock into which the Ni-irruptive was intruded on the north rim. The footwall breccia is a cataclastic breccia produced by comminution of both footwall gneiss and the overlying Ni-irruptive particularly the hanging-wall breccia unit. It is the youngest of all the rock units present except for diabase dikes (see Fig. 2).

a) Footwall breccia

The contact of the footwall breccia with overlying hanging-wall breccia is sharp in some areas but difficult to distinguish megascopically in others. The texture and model composition of the footwall breccia are similar to those of footwall gneiss but very different from those of hanging-wall breccia. Footwall breccia is a fine grained, holocrystalline rock with xenoblastic, granular texture. It consists mainly of plagioclase, potash feldspar, quartz and mafic minerals. Carlsbad twinning is well-developed in plagioclase. Quartz is abundant ranging from 20 to 50%. Mafic minerals occur as clusters of anhedral grains and irregular aggregates of hydrous alteration products after pyroxene. From 3 to 8% apatite is also observed.

b) Footwall gneiss

Footwall gneiss is also a fine grained, holocrystalline rock with xenoblastic, granular texture. Its modal composition is similar to that of footwall breccia except that: (1) The breccia is much richer in apatite and potash feldspar than the gneiss; (2) The pyroxene of the breccia is much more altered than that of the gneiss; (3) No orthopyroxene has been observed in the gneiss, while minor amounts occur in the breccia.

2. Ore body

The ore within the Strathcona Mine can be classified into three types: hanging-wall ore, main-zone ore and deep-zone ore. The hanging-wall ore occurs as disseminations within the matrix of the hanging-wall breccia and to a lesser extent within the xenolithic and mafic norite. The sulfides, which occur interstitially to the silicates, show little, if any replacement of silicates and consist principally of pyrrhotite and pentlandite rather than pyrite as in felsic norite. These factors together with silicate-sulfide textures indicate that the hanging-wall ores were introduced as immiscible sulfide rich droplets in the younger noritic intrusions.

Most of the main-zone ore occurs within the footwall breccia as massive stringers and as fine disseminations in the matrix. The disseminated ore is restricted to footwall breccia with a somewhat high proportion of mafic fragments. The stringers are roughly parallel to the base of the overlying Ni-irruptive. Near the eastern end of the deposit, stringers of ore extend from the breccia zone along fractures into the footwall gneiss. This is referred to as the deep-zone ore. According to Naldrett and Kullerud, the main-zone ore in footwall breccia, as well as deep-zone ore in footwall gneiss, could not have settled directly from the norite because the footwall breccia is younger than any of the units of the Ni-irruptive. Rather, they suggest that these ores were either produced by remobilization and re-emplacement of sulfides that had previously settled out of the xenolithic and hanging-wall norite or that they were introduced separately as a magma or a high-temperature aqueous solution.

III. EXPERIMENTAL METHOD

1. Preparation of samples, standards and carriers

A. Samples:

The sulphide samples were prepared by R. R. Keays. A few grams of specimen were broken in a steel percussion mortar, washed with distilled water to remove the fines, and the 100-200 mesh size fraction separated by sieves utilizing silk bolting cloth. Pyrrhotite was first separated with a hand magnet. Chalcopyrite and pentlandite were then separated using the Frantz Isodynamic Separator. The sulfide concentrations were then powdered in an alumina ceramic ball mill to pass 200 mesh. Approximately 70 mg of sample, together with 30 mg of Al_2O_3*, were weighed into quartz ampoules for irradiation.

B. Standards:

Ru and Os standard solutions were prepared by dissolving Johnson-Matthey specpure grade ammonium aquochlororuthenate and ammonium chlorosmate in 3 N HCl. These solutions were diluted with 3 N HCl to approximately 3.8 µgm per ml of Ru and 1.1. µgm per ml of Os.

The actual Os and Ru contents of these salts were determined by reduction to the metals at 600°C under hydrogen. The results of replicate determinations are given in Table 4 and Table 5.

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* The concentrations of Os and Ru in Al_2O_3 were below the sensitivity limits of the activation method used.

Table 4 Ru in ammonium aquochlororuthenate

	Salt taken $(NH_4)_2(Ru(H_2O)Cl_5)$ (mg)	Ru theoretical 30.41% (mg)	Ru recovered (mg)	% difference	actual % Ru in salt
1	32.59	9.91	10.18	2.7	31.23
2	31.60	9.61	9.88	2.8	31.26
3	31.68	9.63	9.91	2.9	31.28
				Average	31.26

Table 5 Os in ammonium chlorosmate

	Salt taken $(NH_4)_2Os\ Cl_6$ (mg)	Os theoretical 43.32% (mg)	Os recovered (mg)	% difference	actual % Os in salt
1	22.70	9.83	9.62	2.2	42.38
2	24.55	10.63	10.39	2.4	43.32
3	23.99	10.39	10.13	2.5	42.23
				Average	42.31

A number of different methods of standard preparation were attempted. The most successful procedure proved to be the preparation of a powder standard made by adsorbing a dilute acid solution of Os and Ru on Al_2O_3 powder with subsequent evaporation to dryness. The powder standard was used for all experiments with sulphide minerals. Approximately 40-50 mg of standard solution of known specific gravity were weighed into quartz ampoules followed by 20-30 mg of Al_2O_3 powder to absorb the solution. The standards were then dried overnight in an oven at 80°C (Morgan 1963) and sealed with polyethylene plugs for irradiation.

Other types of standards were tried and discarded due to various experimental problems. They include the following:

(a) Polyethylene sheet standard

This standard was prepared by weighing a drop of standard onto a polyethylene sheet and evaporating to dryness under a heat lamp. The dried residue was covered by folding the sheet and heat sealing the edges. However, it was found that the polyethylene burst into flame during a subsequent fusion process, with consequent possible loss of Ru and Os before complete mixing with carrier in the molten alkali peroxide flux.

(b) Aluminum sheet standard

Aluminum sheet was used as backing material instead of polyethylene. The method proved to be unsuccessful as the aluminum was dissolved even by dilute HCl (0.1 N) during the final stages of evaporating the liquid under a heat lamp.

(c) Aluminum sheet sprayed with krylon

To prevent the dissolution of the aluminum sheet by HCl, it was first sprayed with krylon (a commercially available transparent varnish).

This preparation was also discarded because the krylon burst into flame during the fusion as in the case of polyethylene sheet.

(d) Dilute acidic Os-Ru solution

A dilute acidic Os-Ru solution was also tried as a standard. It was discarded because of explosive release of gas on opening. In this method, the concentration of HCl in the standard solution was diluted to 1 N. The standard solution was then weighed into a quartz ampoule and carefully sealed with a hydrogen flame before irradiation. It was found that, after three days of irradiation and two days of cooling, a high gas pressure was built up causing an explosion when the tube was opened. The pressure of the gas in this case was found to depend mostly on the concentration of HCl and the time of irradiation. The pressure decreased as the concentration of HCl and irradiation time decreased, and no explosions occurred for irradiations of 8 hours or less. This method can be used if the concentration of Ru and Os in the sample is higher, say, several hundred ppb, because the irradiation time can be decreased.

C. Carriers

Ru and Os carriers were made up by dissolving ammonium aquochloruthenate and ammonium chlorosmate in 1 N HCl and diluted to a concentration of 2.5 mg per ml each of Ru and Os with 1 N HCl.

2. Irradiation

Four samples including one in duplicate or six samples with two duplicates were irradiated together with two or three standards for three days in the McMaster Reactor at a neutron flux of about 1×10^{13} neutrons / cm^2/sec. The ampoules were sealed in an aluminum can for irradiation. After cooling for two days, chemical analyses was carried out in a filtered hood behind two inches of lead shielding.

3. Analytical procedure for Ru and Os

Ru and Os exhibit striking similarities in their chemical properties. In this procedure the separation and purification of these elements was achieved by utilizing the selective volatility of their tetroxides during distillation from H_2O_2-H_2SO_4 solution for Os and $NaBrO_3$-H_2SO_4 solution for Ru followed by extraction of OsO_4 into CCl_4 and precipitation of RuO_2 with ethanol. The purified elements were finally reduced to the metal by Zn, and chemical yields determined gravimetrically.

A. Mineral samples

a) Fusion

Prior to the irradiation, pipette 4 ml of carrier solution containing 2.5 mg / ml of both Ru and Os into Zr crucibles and evaporated to dryness under an infrared heat lamp. Mix the irradiated sample with approximately 10 times its weight of Na_2O_2-NaOH (flux mixture contains approximately 70% Na_2O_2). Then heat the crucible gently in a Meeker burner flame for about 4 minutes until the alkali flux is melted and finally at full heat for another 4 minutes. Swirl twice during the fusion to ensure that the sample is completely dissolved.

Dissolve the fusion cake in 25 ml of distilled water, transfer the solution to a 100 ml beaker, scrub the crucible with a rubber policeman and complete the transfer with 2 or 3 ml of H_2O.

b) Distillation of Os

The distillation method used was principally based on that of Westland and Beamish (1954, 1957). The apparatus (Fig. 3) included a spray guard and trap bulb to decrease contamination, particularly from Na and Cu.

Transfer the solution from the fusion step into a 250 ml distillation flask, add 30 ml of H_2O to the trap bulb and place 30 ml of 3 N NaOH in the receiver tube which is cooled in an ice bath. Bubble air through the apparatus at a rate of approximately 2 bubbles per second and put cold H_2O through the cooling jackets. Add 20 ml of 50% H_2SO_4 to the sample solution in the distillation bulb and 10 ml of 30% H_2O_2. Heat the bulb with a small bunsen burner to bring the temperature to about 90°C. Distil OsO_4 for approximately 30 minutes, adding H_2O_2 as needed to ensure that undecomposed H_2O_2 is always present.(1) Do not allow the reaction in the distillation flask to become too vigorous as this increases particulate carry-over.(2) After approximately 20 minutes, heat the liquid in the trap bulb to boiling to distil absorbed OsO_4.(3) During the addition of H_2O_2, the gas pressure in the apparatus increased and it was necessary to decrease the air flow to prevent the reaction from becoming too vigorous and the receiver solution from backing up. After completion of the Os distillation, store the distilled sodium osmate solution in an ice bath for further purification. Cool the distillation apparatus with the air stream still flowing to expel excess H_2O_2 in preparation for the Ru distillation.

c) Distillation of Ru

The distillation of Ru was carried out in the same apparatus. After excess H_2O_2 has been completely decomposed (4) and the solution cooled to about 40°C, oxidize Ru to RuO_4 by adding 20 ml of 10% $NaBrO_3$ to the distillation flask. Heat the flask to 90°~95°C and distil RuO_4 for approximately 30 minutes. After 20 minutes, heat the trap to boiling to remove absorbed RuO_4.(5) Store the 3 N NaOH solution containing the sodium ruthenate in an ice bath for further purification of Ru.

d) Purification of Os

Transfer the chilled sodium osmate solution to a 125 ml separatory funnel. Add 10 ml of chilled 50% H_2SO_4 to acidify the solution and immediately contact with 30 ml of CCl_4.(6) Shake the mixture for about 2 minutes to extract OsO_4 into the organic phase. Transfer the organic portion to a clean separatory funnel and back-extract the OsO_4 by contacting with 30 ml of 3 N NaOH. Transfer to a 50 ml centrifuge tube and centrifuge the aqueous phase to ensure complete removal of CCl_4. Transfer the aqueous phase to a 150 ml beaker, acidify with excess concentrated HCl and place on a hot plate. Heat to nearly boiling and add Zn metal powder to reduce Os to the metal.(7) Add a slight excess of Zn, cover the beaker with a watch glass and heat for 10 to 15 minutes. Dissolve excess Zn with conc. HCl. Centrifuge and decant the supernate. Purify the Os metal further by adding 6 N HCl and heating in an electrothermal bunsen heater for at least 5 minutes to remove any Zn carried down with the Os precipitate. Centrifuge, wash the precipitate twice with distilled water and once with ethanol. Slurry with ethanol, transfer to a vycor planchet and dry under a heat lamp. Count the gross radiation from the sample.

e) Purification of Ru

Transfer the sodium ruthenate from the distillation step to a centrifuge tube. Add 4 mg $CuCl_2$ solution as a hold-back carrier and acidify with about 6 ml of chilled concentrated HCl to precipitate Cu as $Cu(OH)_2$.(8) Centrifuge, transfer the supernate to a 100 ml beaker, and obtain a black, bulky precipitate of RuO_2 by the addition of 10 ml of 95% ethanol.(9) Heat for 10 minutes to coagulate the precipitate. Transfer the RuO_2 precipitate to a 50 ml centrifuge tube, centrifuge and wash once with warm distilled water. Dissolve in 3 ml conc. HCl by heating in an electrothermal bunsen heater. Transfer the Ru solution to a 150 ml beaker and bring the volume up to 30 ml by addition of 2 N HCl. Reduce to the metal with Zn, and finally remove excess Zn by heating with conc. HCl as in the case of Os.(10)

f) Reduction by hydrogen

Small amounts of Ru and Os oxides may be produced along with the metal in the reduction step. For the chemical yield determination, complete reduction to the metal in hydrogen is necessary. After counting the β^- and γ radioactivity of Os and Ru respectively, the samples were placed in a quartz tube in a cylindrical electric furnace, and reduced under hydrogen at 600°C for 30 minutes. After cooling in hydrogen and weighing, it was found that the loss of weight of Os ranged from 3 to 8% and Ru from 4 to 10%. The reduced weights were used for chemical yield determination.

B. Standard

The powder standard method was used for all experiments. The procedure follows that of Morgan (1963), except that the dilute acid solution of Os and Ru was absorbed on Al_2O_3 rather than silica.

Pipette 4 ml of carrier solution into a Zr crucible and add 1 ml of 95% ethanol. Carefully open the ampoule and quickly transfer the contents quantitatively into the carrier solution, rinsing the tube several times with distilled water. If some of the powder floats on the surface of the carrier liquid, wet with additional ethanol until all powder is immersed in the liquid. Make the solution alkaline by the addition of 2 ml of 3 N NaOH and evaporate to dryness on a warm hot plate under a heat lamp.

Fuse the standard salts with Na_2O_2-NaOH flux and distil as for the samples. The distillation of standards was the same as for mineral samples, except that no trap bulb was included in the distillation apparatus. After distillation, acidify the sodium ruthenate and sodium osmate by addition of excess conc. HCl. Take directly to a hot plate and reduce with Zn to the metal. Plate out and evaporate to dryness for counting in a vycor planchet. Finally reduce under hydrogen to remove any dioxides and weigh to establish the chemical yield.

Footnotes:

(1) During the distillation, Ru was reduced to the +4 state and remained in the flask while Os was oxidized to OsO_4. Undecomposed H_2O_2 must always be present to prevent oxidation and consequent partial distillation of Ru with Os at high temperature (Westland and Beamish 1954).

(2) It was found that the reaction rate could be adjusted by controlling acidity. If the reaction goes too fast, more 50% H_2SO_4 was added to decrease its intensity.

(3) Some OsO_4 is absorbed in the trap, the remainder passing through the receiver tube. The impurities in the air current were largely removed by the spray trap and the trap bulb.

(4) H_2O_2 causes the decomposition of $NaBrO_3$ to Br_2.

(5) Most of the RuO_4 was absorbed in the trap solution which should be heated for at least 10 minutes.

(6) The H_2SO_4 should be added rapidly to avoid hydrolysis of Os at the neutral point.

(7) The presence of CCl_4 will cause incomplete reduction of Os to the metal.

(8) Ru was not precipitated in this step.

(9) Neither Os nor Cu was reduced and precipitated by the ethanol in this step.

(10) Any Cu hold-back carrier present should also be dissolved in this step.

IV COUNTING PROCEDURES AND CALCULATIONS

The nuclear data for Ru and Os are listed in Table 6 and Table 7 respectively. The determination of Ru in this study is based on counting 2.9 day ^{97}Ru which has a sufficiently long half-life to permit convenient chemical processing of Ru in the laboratory and which is not produced by ^{235}U fission. Both ^{103}Ru and ^{105}Ru are subject to serious interference from ^{235}U fission and cannot be used unless the absence of a significant fission contribution can be demonstrated.

Os was determined by counting the activity of 15 day ^{191}Os and 32 hour ^{193}Os in all cases.

1. Ruthenium

A. γ radiation counting procedures

The final purified precipitates of standard and sample ruthenium metal were counted with a Baird-Atomic single channel gamma scintillation spectrometer which received pulses from a 1 3/4" x 2" well type NaI(Tl) crystal. A typical spectrum is plotted in Fig. 4 and shows the two dominant photopeaks of 0.22 MeV ^{97}Ru and 0.50 MeV ^{103}Ru. The Ru concentration was determined from 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.

B. Correction of the 0.22 MeV ^{97}Ru photopeak

Although ^{97}Ru is not a uranium fission product, its gamma spectrum is subject to interference from the Compton portion of any fission product

Table 6 Nuclear data for ruthenium

Naturally occurring isotope	Isotopic abundance atom %	Thermal neutron activation cross section barns	Radio nuclides formed by (n.γ) reactions			
			Radio-nuclide	Half-life	Mode of decay and radiation in MeV	Daughter nuclides
$^{96}\mathrm{Ru}$	5.51	0.2	$^{97}\mathrm{Ru}$	2.9 d	E.C.γ 0.22,0.11-0.57	$^{97m}\mathrm{Tc} \xrightarrow[t_{\frac{1}{2}}=91d]{\mathrm{I.T.}} {}^{97}\mathrm{Tc} \xrightarrow[t_{\frac{1}{2}}=2.6x10^{6}Y]{\mathrm{E.C.}} {}^{97}\mathrm{Mo}$
$^{102}\mathrm{Ru}$	31.61	1.4	$^{103}\mathrm{Ru}$	40 d	β^- 0.21,0.10,0.71 γ 0.50, 0.05-0.61	$^{103m}\mathrm{Rh} \xrightarrow[t_{\frac{1}{2}}=57]{\mathrm{I.T.}} {}^{103}\mathrm{Rh}$
$^{104}\mathrm{Ru}$	18. 58	0.48	$^{105}\mathrm{Ru}$	4.43 h	β^- 1.15, 1.08,1.87 γ 0.72 0.21-1.7	$^{105m}\mathrm{Rh} \xrightarrow[t_{\frac{1}{2}}=45sec]{\mathrm{I.T.}} {}^{105}\mathrm{Rh} \xrightarrow[t_{\frac{1}{2}}=36.5]{} {}^{105}\mathrm{Pd}$

Table 7 Nuclear data for Osmium

Naturally occurring isotope	Isotopic abundance atom %	Thermal neutron activation cross section barns	Radio nuclides formed by $(n.\gamma)$ reactions			Daughter nuclides
			Radio-nuclide	Half-life	Mode of decay and radiation in MeV	
^{184}Os	0.018	<200	^{195}Os	94 d	E.C. γ 0.65, 0.88 0.072-0.75	^{185}Re
^{189}Os	16.1	0.008	^{190m}Os	10 m	I.T. 0.04 γ 0.50, 0.62, 0.36 0.19	^{190}Os
^{190}Os	26.4	8.6	^{191m}Os	14 h	I.T. 0.014 0.074	^{191}Os
			^{191}Os	15 d	β^- 0.14 γ 0.042, 0.129	^{191m}Ir I.T. $t_{\frac{1}{2}}=4.85$ ^{191}Ir
^{192}Os	41.0	1.6	^{193}Os	32 h	β^- 1.13 γ 0.139, 0.073 0.107 - 0.56	^{193m}Ir I.T. $t_{\frac{1}{2}} = 12$ d ^{193}Ir

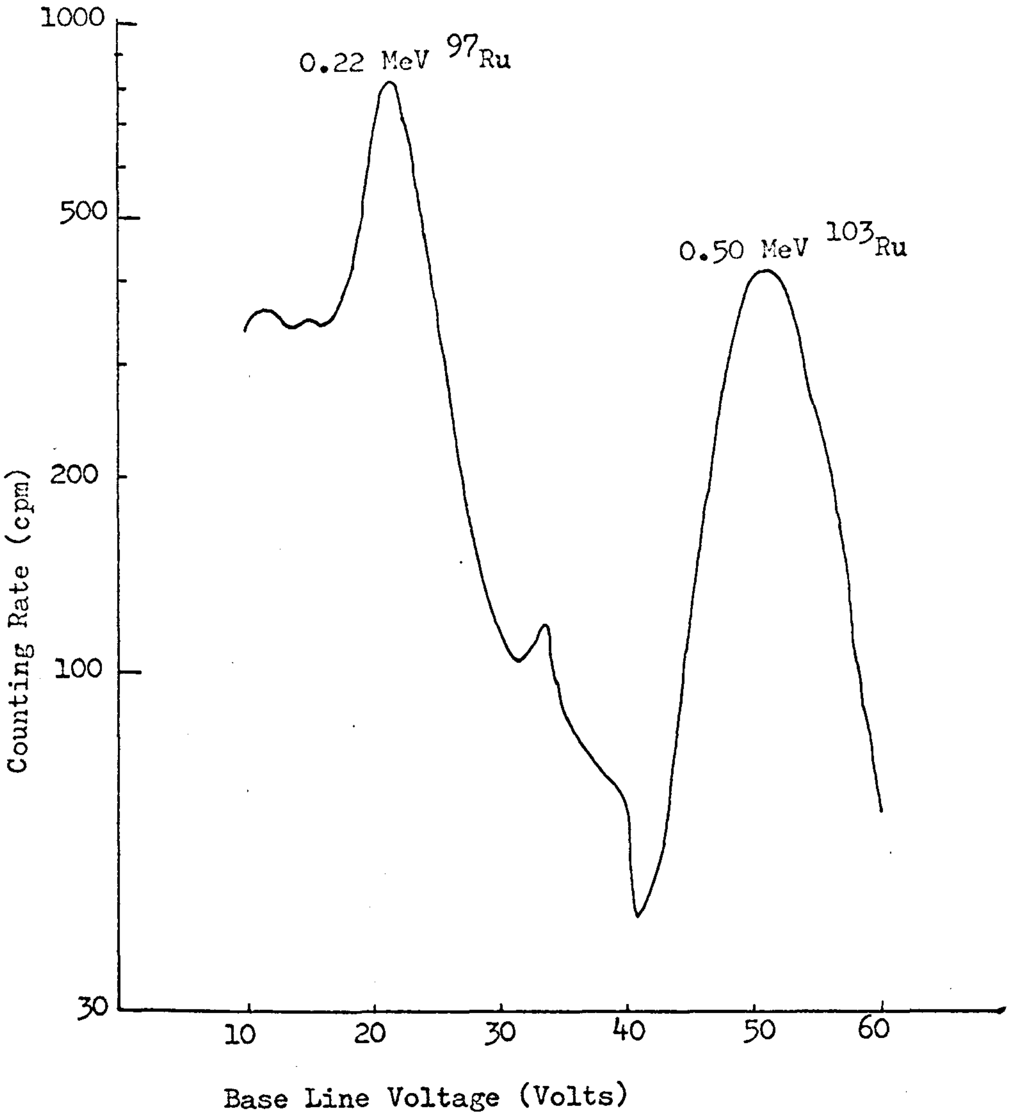

Fig.4 A typical spectrum of a mixture of ^{97}Ru and ^{103}Ru showing two dominant photopeaks at 0.22 MeV and 0.50 MeV respectively

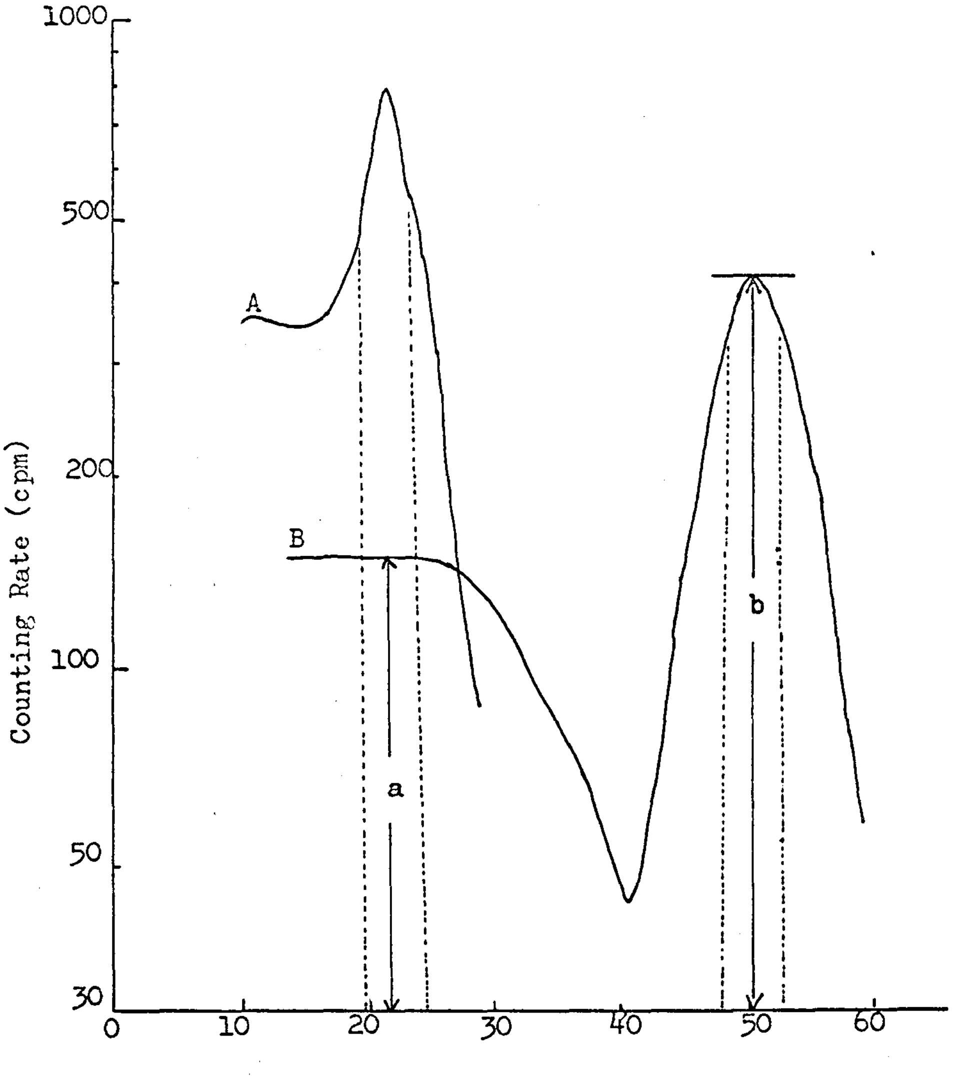

Fig. 5 Correction of the 0.22 MeV ^{97}Ru photopeak

A - Pure ^{97}Ru spectrum

B - Pure ^{103}Ru spectrum

a/b - Ratio of Compton to photopeak activities for ^{103}Ru where Compton region taken is that portion which coincides with the ^{97}Ru photopeak

^{103}Ru. Thus, a correction must be made for this contribution to the ^{97}Ru spectrum. The procedure used was the following. The ratio of activity under the ^{103}Ru photopeak (over a four volt interval) and that portion of the Compton region coincident with the ^{97}Ru photopeak (again over a four volt interval) was determined by counting the Ru standard at the appropriate base line voltage settings and window interval after the complete decay of ^{97}Ru. A value of 0.363 was obtained for the ratio of Compton to photopeak regions for the ^{103}Ru standard spectrum. The procedure is illustrated in Fig. 5.

Thus for this counter and the voltage intervals considered the activity from the pertinent Compton portion of the ^{103}Ru spectrum is 0.363 times that of the photopeak. By measuring the photopeak activity a correction for ^{103}Ru contribution to the ^{97}Ru spectrum was obtained.

The activity for the 0.22 MeV photopeak of ^{97}Ru at time t_o, which is the time used for calculation, is therefore, given by the following equation:

$$\begin{aligned} A_{t_o} &= \left[A_{t_1} - 0.363\,(B_{t_1} - C_B) - C_A\right] e^{\lambda_A(t_1 - t_o)} \\ &= \left[A_{t_1} - 0.363\,(B_{t_2} - C_B)e^{\lambda_B(t_2 - t_1)} - C_A\right] e^{\lambda_A(t_1 - t_o)} \end{aligned}$$

where ----------------(1)

A_{t_o} = The calculated value of 0.22 MeV photopeak activity of ^{97}Ru at time t_o.

A_{t_1} = The total count rate from the 0.22 MeV photopeak including the Compton effect from ^{103}Ru and background at time t_1 (voltage window = 4 volts)

0.363 = Compton effect constant.

B_{t_1} = The 0.50 MeV photopeak count rate of ^{103}Ru at time t_1. (voltage window = 4 volts)

B_{t_2} = The 0.50 MeV photopeak count rate of ^{103}Ru at time t_2.

C_A = The background under the 0.22 MeV photopeak of ^{97}Ru.

C_B = The background under the 0.50 MeV photopeak of ^{103}Ru.

λ_A = The decay constant of ^{97}Ru

λ_B = The decay constant of ^{103}Ru.

If $t_1 \rightarrow t_2$, the $e^{\lambda_B(t_2-t_1)} \rightarrow 1$ and equation (1) then can be rewritten as

$$A_{t_o} = \left[A_{t_1} - 0.363\,(B_{t_2} - C_B) - C_A\right] e^{\lambda_A(t_1-t_o)} \qquad \text{------------(2)}$$

This equation is generally sufficient for calculation.

C. Calculation of Ru concentration

After the correction of the activity of 0.22 MeV photopeak of ^{97}Ru in both standard and sample, the mass of Ru in the samples can be simply obtained from equation (3)

$$\frac{M}{m} = \frac{A_{t_o}/Y}{a_{t_o}/y}$$

or

$$M = m \cdot \frac{A_{t_o} \cdot y}{a_{t_o} \cdot Y} \qquad \text{------------------------------(3)}$$

where

M = Mass of Ru in sample

m = Mass of Ru in standard

A_{t_o} = Activity of sample at time t_o

a_{t_o} = Activity of standard at time t_o.

Y = Chemical yield of sample.

y = Chemical yield of standard.

Dividing M by the weight W of the sample irradiated, gives the ppb values as:

$$C = \frac{M}{W} = \frac{m}{W} \cdot \frac{A_{t_o} \cdot y}{a_{t_o} \cdot Y} \quad \text{------------------------} (4)$$

where M is in units of 10^{-9} gm, W is in gms and m in 10^{-9} gm.

The determination assumes a normal ^{97}Ru/Ru ratio in all samples and standards.

D. Statistical counting errors

For the low concentrations of Ru in some of the mineral samples analysed, the statistical counting errors were one of the most important sources of error. Coefficients of variation have been calculated for samples of varying Ru content and are presented in Table 8. They range from 2.4% to 54% for samples containing 172 and 3.0 ppb Ru respectively. Improved counting statistics could have been obtained in principal by taking larger counts on the low level samples although other factors limited the length of counting time which was practical. Thus, Ru determinations obtained from ^{97}Ru depended on the difference between the ^{97}Ru and ^{103}Ru counting rates, which is time dependent and which decreases with time. As the maximum difference was desirable for most accurate subtraction long counts (days) were not desirable. Furthermore, as four to eight samples are counted for each radiation, a considerable decay interval could lapse between samples if long counts were employed.

Table 8 Coefficient of Variation Computation

Ru (ppb)	T_{97} (60 min.)	T_{103} (60 min.)	σ^2_{S97}	σ^2_{S103}	σ^2_{b97}	σ^2_{b103}	σ^2_{Q}	σ_{Q}	C_{S97}	Coeff. of variation (%)
172	5434	4050	1.510	1.123	0.237	0.058	2.930	1.71	71.9	2.4
70	2246	1322	0.623	0.367	0.223	0.073	1.287	1.13	18.1	6.2
45	2766	1424	0.768	0.395	0.223	0.070	1.456	1.20	25.5	4.7
23	1809	1320	0.503	0.367	0.237	0.078	1.185	1.09	9.9	11
7.2	1233	756	0.343	0.210	0.250	0.075	0.878	0.93	2.7	34
3.0	845	287	0.235	0.080	0.207	0.063	0.585	0.76	1.4	54

Footnotes:

T_{97} - The total counts of the 0.22 MeV photopeak of ^{97}Ru including the Compton effect from ^{103}Ru.

T_{103} - The total counts of the 0.50 MeV photopeak of ^{103}Ru.

σ_{S97}, σ_{S103} - The standard deviation of count rate of the 0.22 MeV photopeak of ^{97}Ru and counting rate of the 0.50 MeV photopeak of ^{103}Ru respectively.

σ_{b97}, σ_{b103} - The standard deviation of counting rate of background corresponding to the 0.22 MeV photopeak of ^{97}Ru and the 0.50 MeV photopeak of ^{103}Ru respectively.

C_{S97} - Pure counting rate of the 0.22 MeV photopeak of ^{97}Ru.

The coefficient of variation was computed from the general equation of errors (Overman and Clark, 1960):

$$\sigma_Q^2 = (\frac{\partial Q}{\partial X})^2 \sigma_X^2 + (\frac{\partial Q}{\partial Y})\sigma_Y^2 + \ldots\ldots$$

Where Q = f (X, Y, ...) and X, Y etc are independent variables. Thus, for addition or subtraction (ie, for Q = X+Y or X - Y etc):

$$\sigma_Q = (\sigma_X^2 + \sigma_Y^2)^{\frac{1}{2}}$$

Where $\sigma_X^2 = \frac{Rx}{t}$ with Rx equal to the counting rate of X in counts per minute and t equal to the length of counting time in minutes (and similarly for σ_Y^2). The coefficient of variation is then 100 σ_Q / Cs_{97}, where Cs_{97} is counting rate of ^{97}Ru.

The results of computation for 6 samples which are shown in Table 8 suggest that statistical counting errors are reasonable for samples of 10 to 20 ppb Ru or greater. However, for samples of lower Ru content somewhat longer counting periods would probably have been desirable.

E. Interference from ^{235}U fission products

If Ru is determined by counting ^{103}Ru activity, radiation produced from the fission of ^{235}U may constitute serious contamination depending on the U/Ru ratio of the sample. A theoretical calculation has been adopted to estimate the extent of ^{235}U fission product interference in counting ^{103}Ru produced by the reaction ^{102}Ru (n,γ)^{103}Ru.

Assuming the ^{103}Ru activity induced by the reaction ^{235}U (n,f) ^{103}Ru is A_1 and ^{103}Ru produced by ^{102}Ru (n, γ) ^{103}Ru is A_2, after an irradiation for a period of time t_{ir} and decay for time t_d, then:

$$A_1 = \frac{0.72\%\ \mu gm\ U x N}{238.03 x 10^6}\ x\ f\ x\ \sigma_f\ x\ nv\ x\ (1-e^{\lambda t_{ir}})e^{-\lambda t_d} \text{ ---------(5)}$$

$$A_2 = \frac{31.6\%\ \mu gm\ Ru\ x\ N}{101.07 x 10^6}\ x\ \sigma_n\ x\ nv\ x\ (1-e^{\lambda t_{ir}})e^{-\lambda t_d} \text{ ---------(6)}$$

where

N = Avogadro's number

f = fission yield of ^{235}U = 1.6% (Katcoff, 1958).

σ_f = thermal neutron fission cross section -550 barns.

nv = neutron flux in neutrons/cm^2/sec.

λ = decay constant of ^{103}Ru.

σ_n = thermal neutron activation cross section = 1.4 barns

From equations (5) and (6), A_1/A_2 activity ratio can be computed as a function of U/Ru weight ratio, i.e.

$$A_1/A_2 = 0.06\ U/Ru \text{ ------------------------------------(7)}$$

Equation (7) expresses a linear relationship of the activity ratio of A_1/A_2 with regard to the weight ratio of U/Ru. Obviously, the extent of ^{235}U fission interference of counting ^{103}Ru activity produced by the reaction $^{102}Ru\ (n,\gamma)^{103}Ru$ is simply dependent on the ratio of U/Ru, i.e. high U/Ru ratio results high interference of counting ^{103}Ru activity produced by the reaction $^{102}Ru\ (n,\gamma)^{103}Ru$.

2. Osmium

A. β^- radiation counting

The β^- radiation from 15 day ^{191}Os and 32 hour ^{193}Os was counted with a Nuclear of Chicago low level coincidence - shielded gas flow geiger counter. Half-lives were determined for all samples. The parallel decay curves for the total activity of ^{191}Os and ^{193}Os on all mineral samples and duplicate standards, as shown in Fig. 6, indicate the excellent purity of osmium obtained in the chemical procedure. No correction of the raw counting data other than background subtraction was required except in a few cases in which less than 10 cpm were obtained from the sample and subtraction of small amounts of long-lived contamination were necessary.

For an irradiation of 3 days and a decay period of 3 days before counting, a counting rate of 16 cpm above background was obtained from 1 ppb Os in a 70 mg sample with 60% chemical yield (the typical sample weight irradiated and chemical yield obtained). The only practical method of establishing the degree of radiochemical purity of the osmium sources was half-life measurement. It is suggested that adequate sensitivity requires sufficient activity to follow the decay over three half-lives at counting rates which exceed the background by at least 50%. With a counter background of 1.5±0.3 cpm, a sensitivity limit of 0.5 ppb Os is suggested as the lower limit of detection.

B. Calculation of Os concentration

The Os concentration in the sample can be calculated from equation (4) knowing the total activity, weight of sample irradiated, concentration of Os in the standard, and the chemical yield of both sample and standard. No correction for self-absorption loss was applied in this work.

C. Competing reactions

Os radionuclides may be produced by fast neutron reaction on Pt and Ir according to the following nuclear reactions:

$$^{196}\mathrm{Pt}\ (n,\alpha)\ ^{193}\mathrm{Os} \text{ -----------------------------} (1)$$

$$^{194}\mathrm{Pt}\ (n,\alpha)\ ^{191}\mathrm{Os} \text{ -----------------------------} (2)$$

$$^{193}\mathrm{Ir}\ (n,p)\ ^{193}\mathrm{Os} \text{ -----------------------------} (3)$$

$$^{191}\mathrm{Ir}\ (n,p)\ ^{191}\mathrm{Os} \text{ -----------------------------} (4)$$

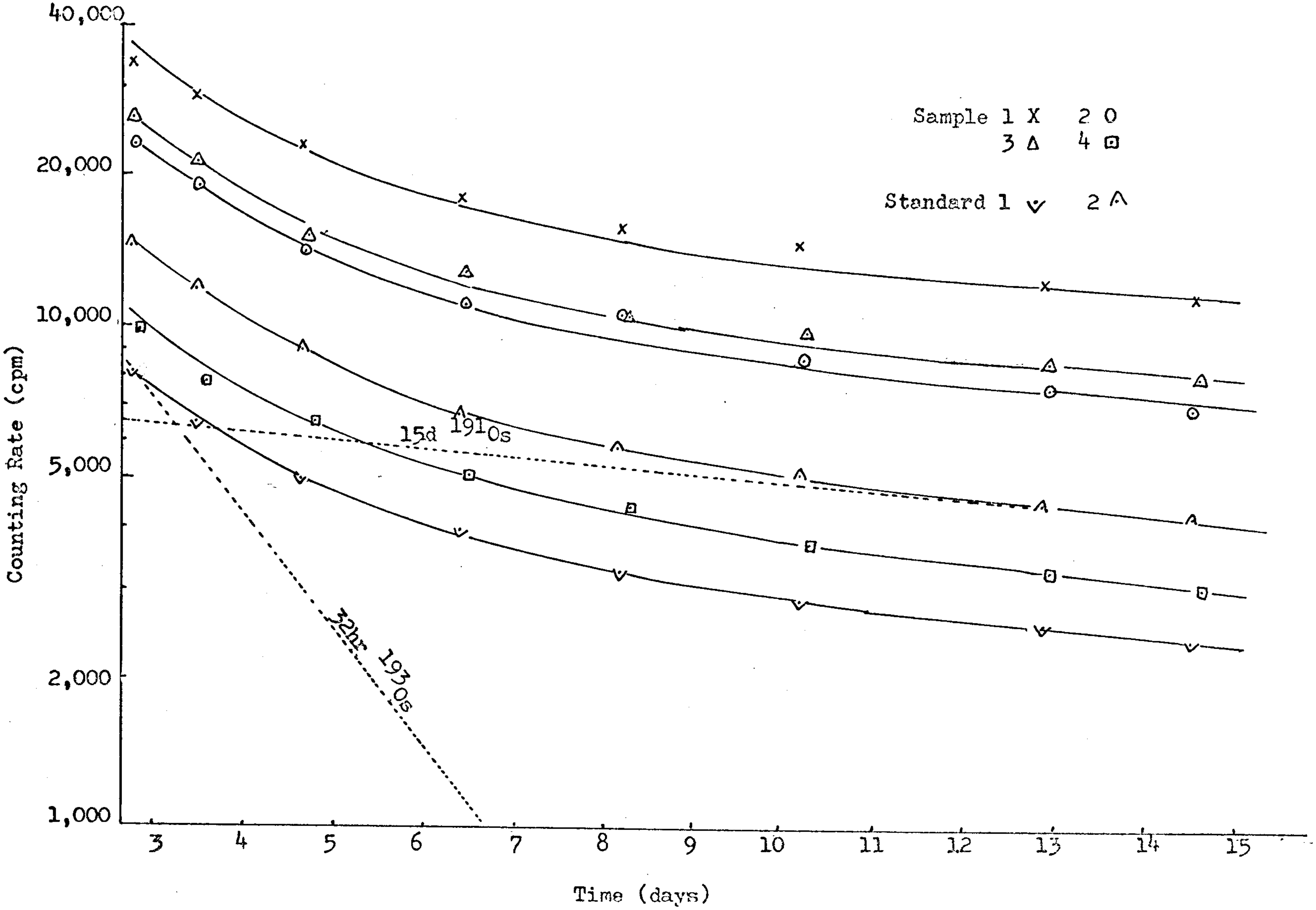

Fig. 6 The Parallel decay curves for the total activity of ^{191}Os and ^{193}Os on 4 sulfide samples and duplicate standards. Sample 1 and 3 are 10 times and samples 2 and 4 are 100 times the actual activities.

Note: time after the end of irradiation was 3 days

Os radionuclides produced by reactions (1) and (2) have been experimentally studied by Morris and Killick (1961). They showed that an average of 0.35 ppm Os was obtained for six 0.1 g samples of Pt using a thermal neutron flux of 1×10^{12} neutrons / cm^2 / sec with a corresponding fast neutron flux of 1.6×10^{11} neutrons / cm^2/sec. For samples of approximately equal Os and Pt content, the interference from Pt may therefore be ignored. The possible interference from the nuclear reactions involving Ir is also unimportant due to the low cross section of the reaction and low abundance of Ir in the sulfides (same order as Os).

V. RESULTS AND DISCUSSION

1. Determination of Os and Ru in G-1, W-1 and a sulfide matte standard

The concentrations of Ru and Os in a Cu-Ni sulfide matte standard provided by Falconbridge Nickel Laboratories were determined and the results are tabulated in Table 9 together with a comparison of data obtained on the same matte by Falconbridge Nickel Laboratories and Mineral Science Division, Department of Energy, Mines and Resources, Ottawa. The method used by the Falconbridge Laboratory was a wet chemical procedure involving an acid dissolution of the sample, concentration of precious metals by coprecipitation on copper followed by isolation of individual elements and determination by spectrophotometry. The Mineral Sciences Division procedure involved a fire assay tin collection concentration with subsequent determination of individual metals by colourimetric analysis. The determination of Os concentration in this work was made by counting the β^- radiation of ^{191}Os, while Ru was determined by counting β^- radiation of ^{103}Ru, the 0.50 MeV γ radiation of ^{103}Ru and 0.22 MeV γ radiation of ^{97}Ru. Both results of Os and Ru determination show good agreement with the data obtained by Falconbridge Nickel Laboratories and the Mineral Sciences Division Laboratory.

The comparison of Ru values obtained from γ counting of ^{97}Ru and ^{103}Ru in the Cu-Ni sulfide sample are tabulated in Table 10, which generally show a slight discrepancy with higher value for ^{103}Ru. This may be due to minor contamination of ^{103}Ru nuclide from U fission products.

Table 9 Os and Ru Analyses of a Cu-Ni Sulfide Matte provided by Falconbridge Nickel Laboratories

Metal	This work (ppm)	Nuclide and radiation counted	Falconbridge Nickel Laboratories	Mineral Sciences Division DMER, Ottawa
Ru	1.51	^{103}Ru, $^{-}$	1.44	1.41
	1.36			
	1.75			
	1.51			
	1.52 (1)	^{103}Ru 0.50 MeV γ		
	1.52	^{97}Ru 0.22 MeV γ		
	1.40			
	1.46			
	Average 1.50 ± 0.12			
Os	0.35	^{191}Os, β^{-}	N.D. (2)	0.3
	0.34			
	0.31			
	0.31			
	Average 0.33 ± 0.02			

(1) Data obtained by averaging the Ru values from ^{97}Ru and ^{103}Ru

(2) Not determined

Table 10 Comparison of Ru values (ppm) obtained from ^{97}Ru and ^{103}Ru in the Cu-Ni sulfide matte

^{97}Ru	^{103}Ru
1.51	1.54
1.50	1.54
1.44	1.37
1.44	1.47

Table 11 Os analyses of G-1 and W-1

Rock	Nuclide and radiation counted	This work, 1967	Morgan, 1965	Bate and Huizenga, 1963
G-1	^{191}Os, β^-	$\leq$0.076 $\leq$0.072 Average 0.074	0.065 ± 0.039 $\leq$ 0.048	0.20
W-1	^{191}Os, β^-	0.27 0.24 Average 0.25_5	0.226 ± 0.055	0.46

Because the discrepancy is small and falls within the region of experimental errors, the contamination of ^{103}Ru from U fission process was hence considered insignificant in the analyses of the Ru-rich (in the range of ppm) Ni-Cu sulfide matte. However, the contamination of ^{103}Ru nuclide from U fission process may become serious if the Ru concentration is as low as several tens of ppb as indicated by the analyses of sulfide minerals from the Sudbury ores.

The concentration of Os in G-1 and W-1 has also been determined and the results are tabulated in Table 11. An average Os value of 0.25 ppb in W-1 and $\leq$ 0.074 ppb in G-1 was obtained. These values are lower than those of Bate and Huizenga (1963) but in good agreement with Morgan's data (1965). The discrepancy of these data is possibly due to experimental error because of low concentration of Os in these rocks. The determination of Ru in G-1 and W-1, either by counting the β^- radiation of ^{103}Ru and ^{105}Ru or by counting the γ radiation of ^{97}Ru and ^{103}Ru, has not been achieved because of the low concentration of Ru in G-1 and W-1 and high concentration of U in these rocks with consequent significant contamination with Ru fission product nuclides.

2. Determination of sulfide minerals

The concentrations of Ru and Os in ppb in 20 pyrrhotite, 11 chalcopyrite, 3 pentlandite and 1 cubanite sample are given in Table 12, which shows that the concentration of Ru is generally below 50 ppb and Os below 20 ppb. The main technical and geochemical features of the data are discussed as follows:

A. The discrepancy of ^{97}Ru and ^{103}Ru data

Table 12 shows that the Ru concentrations based on ^{97}Ru are less

Table 12 Os and Ru contents of pyrrhotite, chalcopyrite, pentlandite and cubanite samples from the Strathcona and Frood Mines, Sudbury, Ontario.

McMaster(1) No.	Mine Level	Mine Location coordinates(2) North	East	Mineral	Description	Os (ppb)	^{97}Ru (ppb)	^{103}Ru (ppb)
27-1	2750	8970	21220	Po(3)	Disseminated sulfides in hanging-wall breccia	2.2	7.2	28
27-3	2750	9050	21280	Po	Disseminated sulfides in hanging-wall breccia	13	27	47
27-4	2750	9130	21340	Po	Disseminated sulfides in hanging-wall breccia	7.7	23	73
27-7	2750	9370	21520	Po	Disseminated sulfides in hanging-wall breccia	68	214	228
27-9	2750	9480	21615	Po	Disseminated sulfides in hanging-wall breccia	18, 18(4)	47, 41	56, 53
27-11	2750	9590	21680	Po	Main ore zone in footwall breccia	19	45	56
27-12	2750	9700	21680	Po	Main ore zone in footwall breccia	12, 11	30, 30	29, 30
27-13	2750	9750	21680	Po	Main ore zone in footwall breccia	0.68	4.3	10
27-13	2750	9750	21680	Cpy(5)	Main ore zone in footwall breccia	1.7,0.74	3.5	8.4
20-16	2000	DDH 20-20, 245'		Po	Main ore zone in footwall breccia	2.9	4.0	7.1
20-16	2000	DDH 20-20, 245'		Cpy	Main ore zone in footwall breccia	2.8	26	48
20-17	2000	DDH 20-3, 385'		Po	Deep ore zone in footwall gneiss	19	30	19
20-18	2000	DDH 20-14, 180'		Po	Main ore zone in footwall breccia	1.9	3.0	3.0
20-21	2000	10780	22200	Po	Disseminated sulfides in hanging-wall breccia	8.2	24	11
20-25	2000	10760	21900	Po	Disseminated sulfides in hanging-wall breccia	52	174	190
20-28	2000	10700	21600	Po	Disseminated sulfides in hanging-wall breccia	4.6	9.7	27
20-30	2000	10660	21400	Po	Disseminated sulfides in hanging-wall breccia	8.0	20	37
20-31	2000	10760	21300	Po	Disseminated sulfides in hanging-wall breccia	3.4	5.1	19
22-20	2250	DDH 22-2, 410'		Cpy	Deep ore zone in footwall gneiss	17, 19	27, 36	37, 31
22-20	2250	DDH 22-2, 410'		Po	Deep ore zone in footwall gneiss	38, 33	71, 75	65, 81
22-26	2250	10575	21475	Cpy	Main ore zone in footwall breccia	3.7	10	20
22-26	2250	10575	21475	Po	Main ore zone in footwall breccia	6.9	2.0	18

continued.......

Table 12 continued....

McMaster No.	Mine Level	Mine Location coordinates North East	Mineral	Description	Os (ppb)	^{97}Ru (ppb)	^{103}Ru (ppb)
22-28	2610	DDH 22-75, 365'	Cpy	Deep ore zone in footwall gneiss	2.7	23	17
22-29	2425	DDH 22-38, 180'	Cpy	Deep ore zone in footwall gneiss	4.7	16	13
25-11	2500	10350 21450	Cpy	Main ore zone in footwall breccia	5.3	9.1	6.7
25-11	2500	10350 21450	Po	Main ore zone in footwall breccia	6.4	4.2	3.7
25-14	2615	DDH 25-76, 170'	Cpy	Deep ore zone in footwall gneiss	4.7	5.5	5.1
25-15	2715	DDH 25-185,240'	Cpy	Deep ore zone in footwall gneiss	1.4	4.6	12
DDH 242L	2280)	Surface hole	Po	Main ore zone in footwall breccia	1.3	7.5	37
DDH 242L	2280)	with sample taken	Cpy	Main ore zone in footwall breccia	0.76	1.2	9.8
DDH 242L	2280)	at 2475 ft.	Pn(6)	Main ore zone in footwall breccia	2.9, 3.2	39	44
DDH 242L	2345)	Surface hole with	Cpy	Main ore zone in footwall breccia	3.7	20	11
DDH 242L	2345)	sample taken at 2540 ft.	Pn	Main ore zone in footwall breccia	1.6	5.2	15
F-18			Cub(7)		73, 63	6.3,3.8	8.3, 18
F-C			Pn		39	155, 139	143, 155

Footnotes

(1) The McMaster numbers refer to the Strathcona Mine samples except for those prefixed with F which are from the Frood Mine.

(2) For the Strathcona samples locations are given in terms of mine coordinates except in the case of drill core samples where the Strathcona Mine DDH (diamond drill hole) number and footage from the hole collar are given. In some cases the mine level of the sample differs from the level of the collar of the drill holes. Samples 20-16, 20-17 and 20-18 are horizontal holes and hence on the 2000 foot level. Samples 22-28, 22-29, 25-14 and 25-15 are inclined holes and the corresponding mine level footages are 2610, 2425, 2615 and 2715 feet respectively.

(3) Po - pyrrhotite

(4) Duplicate analyses

(5) Cpy - chalcopyrite

(6) Pn - pentlandite

(7) Cub - cubanite

Table 13 Estimation of U content in sulfide minerals from the Strathcona and Frood Mines, Sudbury, Ontario, by comparing the radioactivity of ^{97}Ru and ^{103}Ru

McMaster No	^{97}Ru(ppb)	^{103}Ru(ppb)	U(ppb)
27-1	7.2	28	345
27-3	27	47	330
27-4	23	73	830
27-7	214	228	230
27-9	44	54	170
27-11	45	56	180
27-12	30	30	---
27-13	4.3	10	95
27-13	3.5	8.4	80
20-16	4.0	7.1	50
20-16	26	48	370
20-17	30	19	---
20-18	3.0	3.0	---
20-21	24	11	---
20-25	172	190	300
20-28	9.7	27	290
20-30	20	37	280
20-31	5.1	19	230
22-20	31	34	50
22-20	73	73	---
22-26	10	20	170
22-26	2.0	18	270
22-28	23	17	---
22-29	16	13	---
25-11	9.1	6.7	---
25-11	4.2	3.7	---
25-14	5.5	5.1	---
25-15	4.6	12	120
DDH 242L (2280')	7.5	37	500
DDH 242L (2280')	1.2	9.8	140
DDH 242L (2280')	39	44	80
DDH 242L (2345')	20	11	---
DDH 242L (2345')	5.2	15	160
F-18	5	8.1	140
F-C	147	149	---

determined than those from ^{103}Ru in most cases. It is suggested that the higher Ru concentrations obtained by counting ^{103}Ru, are due to contamination from fission product Ru. In a few cases, samples yielded higher Ru contents from ^{97}Ru rather than from ^{103}Ru. This is probably due either to large statistical counting errors or contamination with radionuclides other than Ru in to 0.22 MeV region of the spectrum. In these cases, the concentration of Ru based on ^{103}Ru activity was chosen as the maximum value of Ru in the sample in question and is used in further discussions.

As indicated by equation (7) in the preceeding chapter on the comparison of the production factors of ^{103}Ru by the reactions ^{102}Ru(n,γ) ^{103}Ru and ^{235}U (n,f) ^{103}Ru, the U content of a sample may be estimated by assuming that the difference between ^{97}Ru and ^{103}Ru results can be attributed to fission products. Using sample 20-25 as an example, the Ru concentration based on ^{97}Ru activity is 172 ppb, and on ^{103}Ru is 190 ppb. If it is assumed that the n,γ ^{103}Ru = 172 ppb then the fission product ^{103}Ru is 190 - 172 = 18 ppb and the activity ratio A_1/A_2 = 18/172. From equation (7) A_1/A_2 = 0.06 U/Ru with Ru = 172 ppb, then U = (18/172) x 172 x 1 / 0.06 = 300 ppb. In general, if the assumption that the difference between ^{97}Ru and ^{103}Ru results is due to fission products is valid, the U contents in most of these sulfide minerals fall below 500 ppb, (Table 13).

B. Linear Correlation

All samples, except one cubanite which is abnormally high in Os compared to Ru, have been used to compute a linear correlation coefficient for the purpose of evaluating the degree of geochemical coherence between

Os and Ru in a sulfide mineral assemblage. If a high correlation coefficient is obtained, it may be useful in predicting the concentration of one element if the other is known, or in recognizing possible experimental error if an unusual result is observed.

Let $(X_1, Y_1), (X_2, Y_2) \ldots.(X_n, Y_n)$ denote n pairs of observed values of Os (X) and Ru (Y) that fit a simple linear model

$$Y_i = \alpha + \beta X_i + e_i \quad \text{--}(8)$$

where α is the intercept, β the slope and e_i is an unobservable random error of the ith Os-Ru pair with mean value $\mu = o$. Equation (8) can be rewritten as an estimate formula for Ru (Y)(denoted as $\hat{\mu} Y$), if we assume Os (X) is an observable variable that can be measured with negligible error.

$$\hat{\mu} Y = \alpha + \hat{\beta} X \quad \text{--}(9)$$

where the quantities β and α can be computed from equations (10) and (11) respectively.

$$\hat{\beta} = \frac{\Sigma(Y_i-\bar{Y})(X_i-\bar{X})}{\Sigma\,(X_i-\bar{X})^2} = \frac{\Sigma Y_i X_i-(\Sigma Y_i)(\Sigma X_i)/n}{\Sigma X_i^2-(\Sigma\, X_i^2)/n} = \frac{SSXY}{SSX^2} \quad \text{-----------}(10)$$

$$\hat{\alpha} = \bar{Y} - \hat{\beta}\,\bar{X} = (\Sigma\, Y_i - \hat{\beta}\,\Sigma\, X_i)/n \quad \text{---------------------------}(11)$$

Solving for $\hat{\beta}$ and $\hat{\alpha}$ from equations (10) and (11) and substituting in (9), we obtained the following functional relationship between Os (X) and Ru (Y) using all the data from Table 12 except that for sample F-18

$$\hat{\mu}\, Y = -\,3.926 + 3.069X \quad \text{------------------------------------}(12)$$

The maximum and minimum values of both α and β with 90% confidence limits are

$$2.794 < \beta < 3.344 \quad \text{--}(13)$$

$$-9.146 < \alpha < 1.295 \quad \text{--}(14)$$

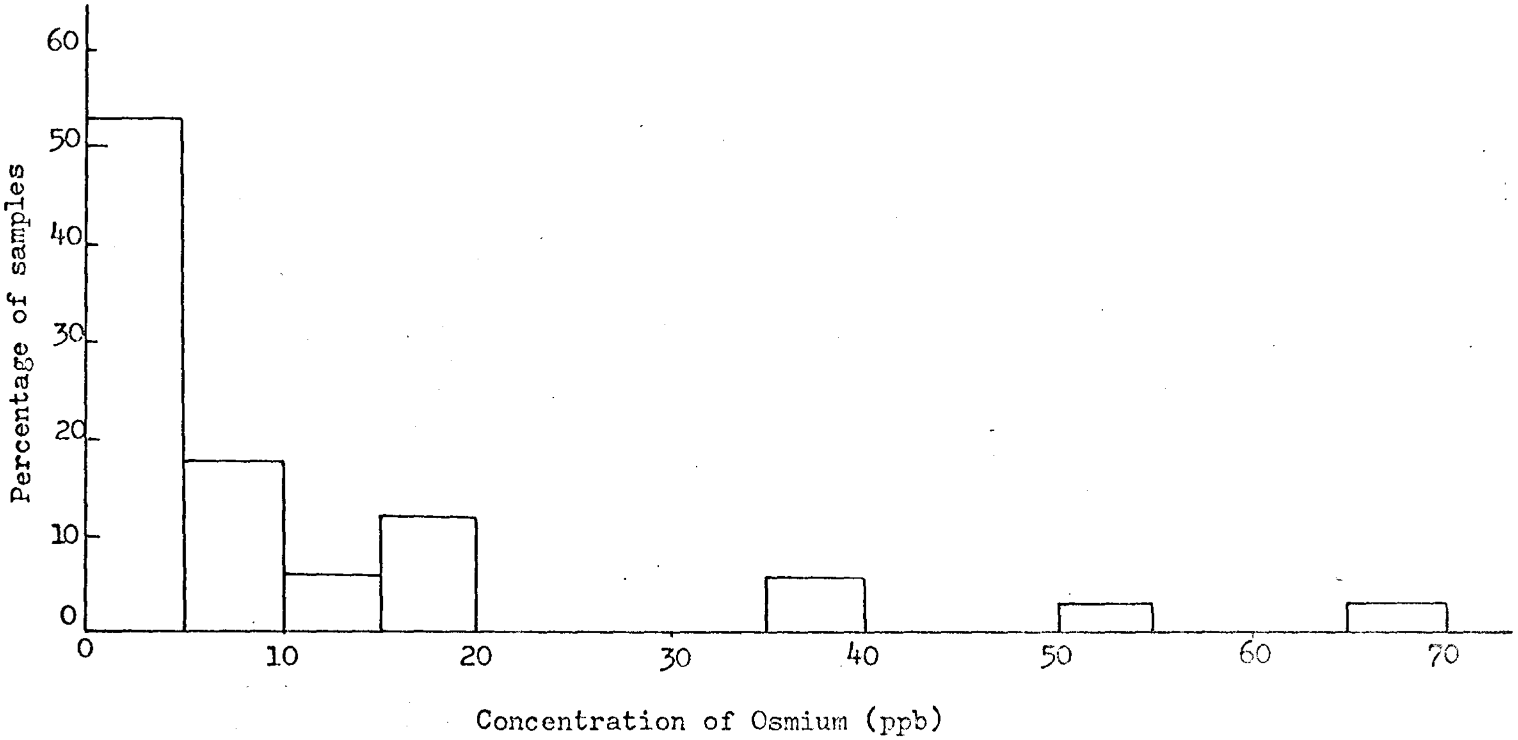

Fig. 7 Histogram showing the extremely high positive skewness of Cs in 34 sulfide samples

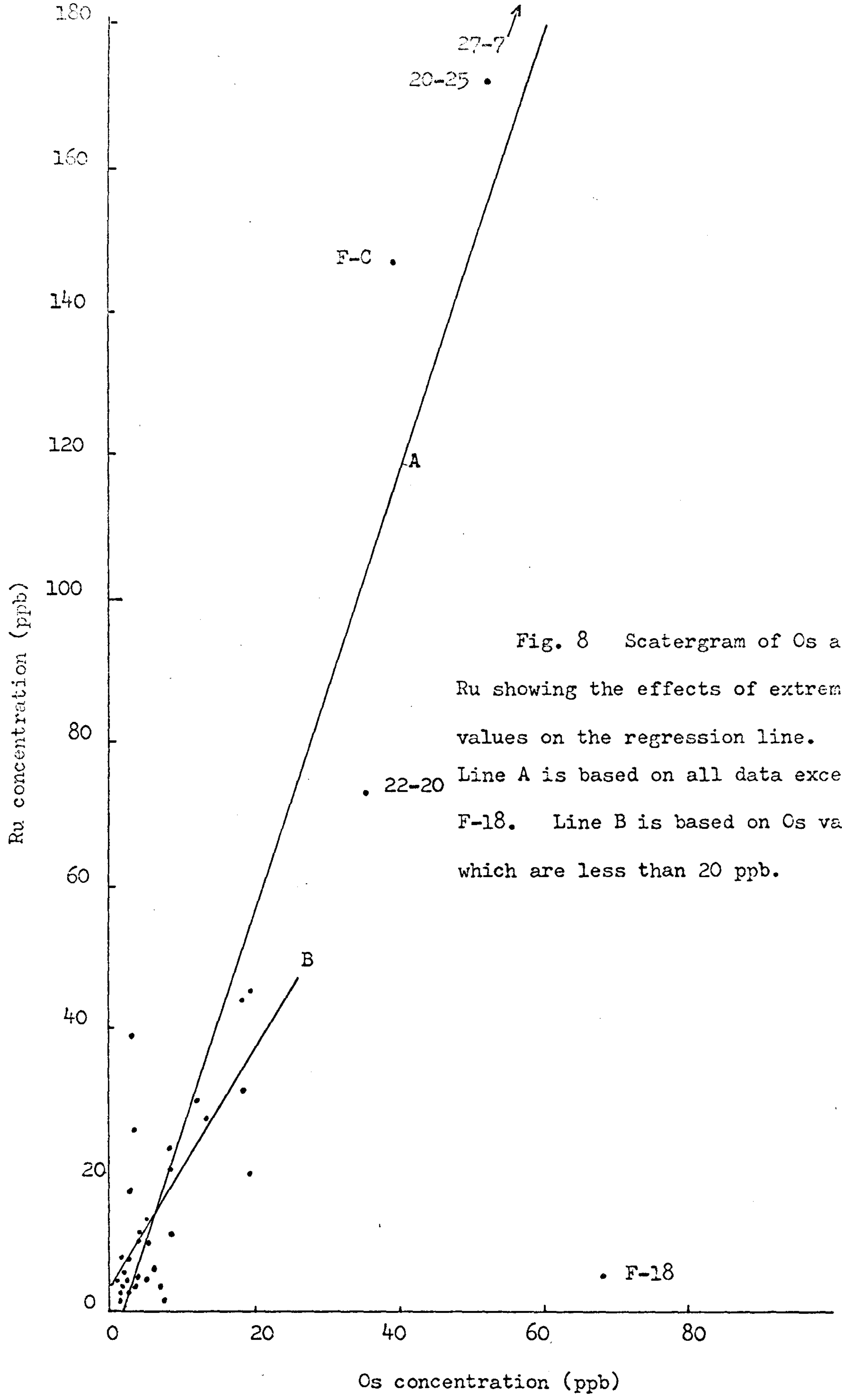

Fig. 8 Scatergram of Os and Ru showing the effects of extreme values on the regression line. Line A is based on all data except F-18. Line B is based on Os values which are less than 20 ppb.

The linear correlation coefficient r is an important parameter to express the "goodness" of Os(X) as a predictor for Ru(Y) in equation (12). Equation (15) is then used in order to see how "good" this line is as a predictor.

$$r = \frac{\Sigma X_i Y_i - \Sigma Y_i \Sigma X_i / n}{\sqrt{(\Sigma X_i^2 - (\Sigma X_i)^2/n \quad \Sigma Y_i^2 - (\Sigma Y_i^2)^2/n}}$$

$$= \frac{SSXY}{\sqrt{(SSX^2)\ (SSY^2)}} \quad \text{------------------------------------}(15)$$

A value of $r = 0.958$ is then obtained by using the same data from Table 12. Thus, the linear correlation coefficient is very high in this case. Because the data show an extremely high positive skewness (Fig.7), the computation is strong dominated by the four samples with high Os - Ru contents, including 27-7 (pyrrhotite), 20-25 (pyrrhotite), 22-20 (pyrrhotite) and F-C (pentlandite). It is desirable to recompute equations (9), (10), (11) and (15) excluding data for these four samples to obtain a relationship applicable to a sample suite of lower Os - Ru concentration. The computation results in the functional relationship below:

$$\mu Y = 4.442 + 1.613X \quad \text{--------------------------------------}(16)$$

$$r = 0.716$$

$$1.108 < \beta < 2.118$$

$$0.192 < \alpha < 8.692$$

The correlation coefficient r shows the correlation of Os and Ru is not as good as previously obtained, but still satisfactory for the prediction of Os and Ru when either of the two is known (Fig. 8). Explanation for high geochemical coherence of Os and Ru are considered below in section D.

C. Variation of Ru and Os concentrations in the Strathcona Mine

Sixteen samples of pyrrhotite from the 2000 and 2750 foot levels of the Strathcona Mine, were chosen for analysis to study the variation of Ru and Os concentrations in the footwall breccia ore zone, hanging-wall breccia and xenolithic norite. The samples from 2750 level were taken perpendicularly from xenolithic norite and hanging-wall breccia toward the footwall breccia ore zones (see Fig. 9), while the samples from 2000 level were taken generally along the strike of the footwall breccia ore zone as well as from the base of hanging-wall breccia (see Fig. 10).

The results are plotted in Fig. 9 and Fig. 10 which show clearly the abundances of Ru and Os in various rock and ore types of these two levels, and again in Fig. 11 in which the variation on the 2750 foot level along a traverse roughly perpendicular to the irruptive-country rock contact is shown. The data suggests the following generalizations:

(a) The Ru and Os concentrations in the hanging-wall breccia and xenolithic norite tend to increase toward the footwall breccia and main ore zone, but decrease in the main ore zone itself (2750 level: Fig. 9 and Fig. 11).

(b) On the 2000 foot level, the concentrations of Ru and Os are remarkable higher in the sulfides of the hanging-wall breccia than in the footwall breccia ore zone (Fig. 10 and Table 14).

To discuss the variation of Ru and Os contents in pyrrhotite, we shall consider them in the light of the hypothesis of ore forming processes at Strathcona as based on the discussions of Naldrett and

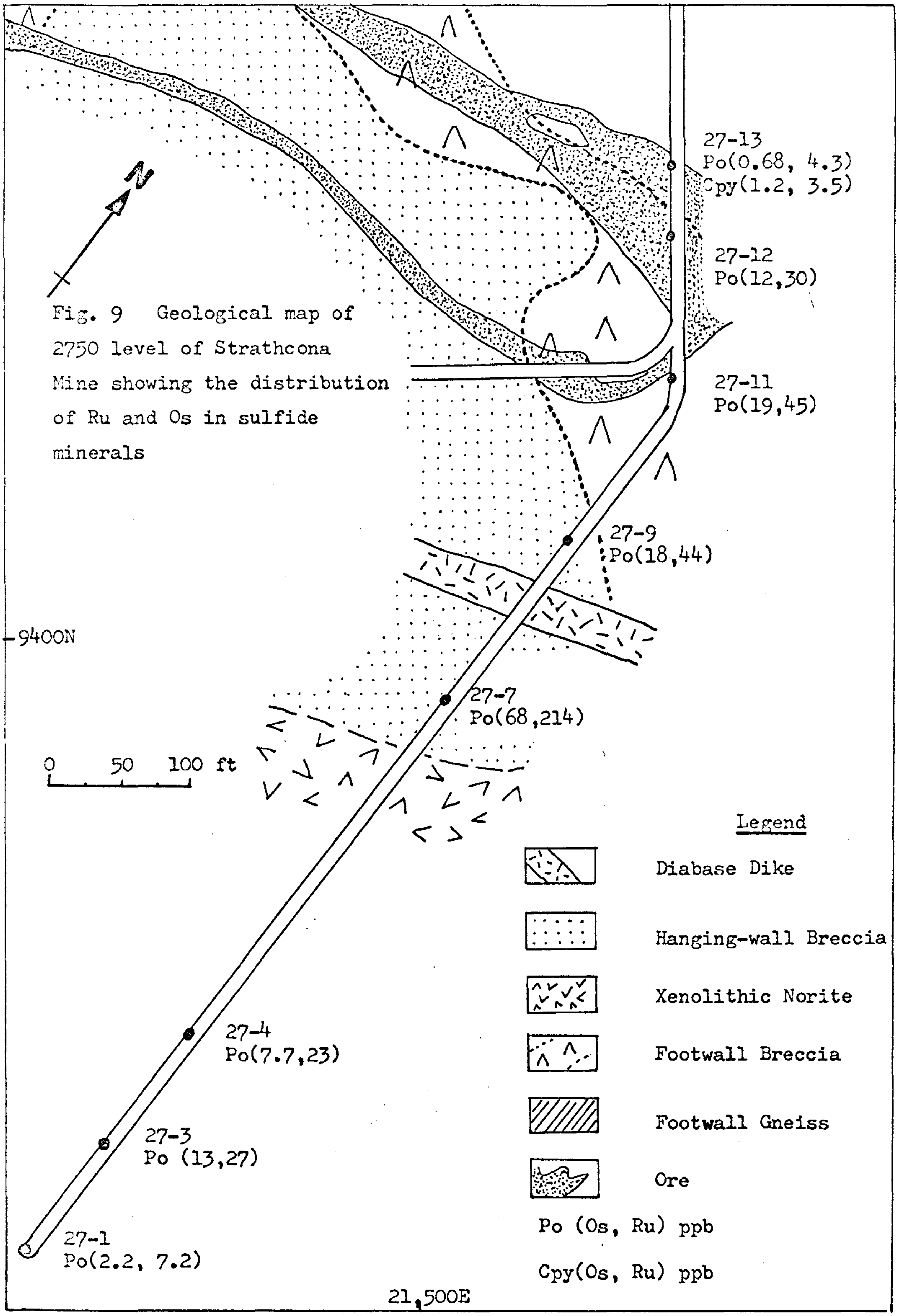

Fig. 9 Geological map of 2750 level of Strathcona Mine showing the distribution of Ru and Os in sulfide minerals

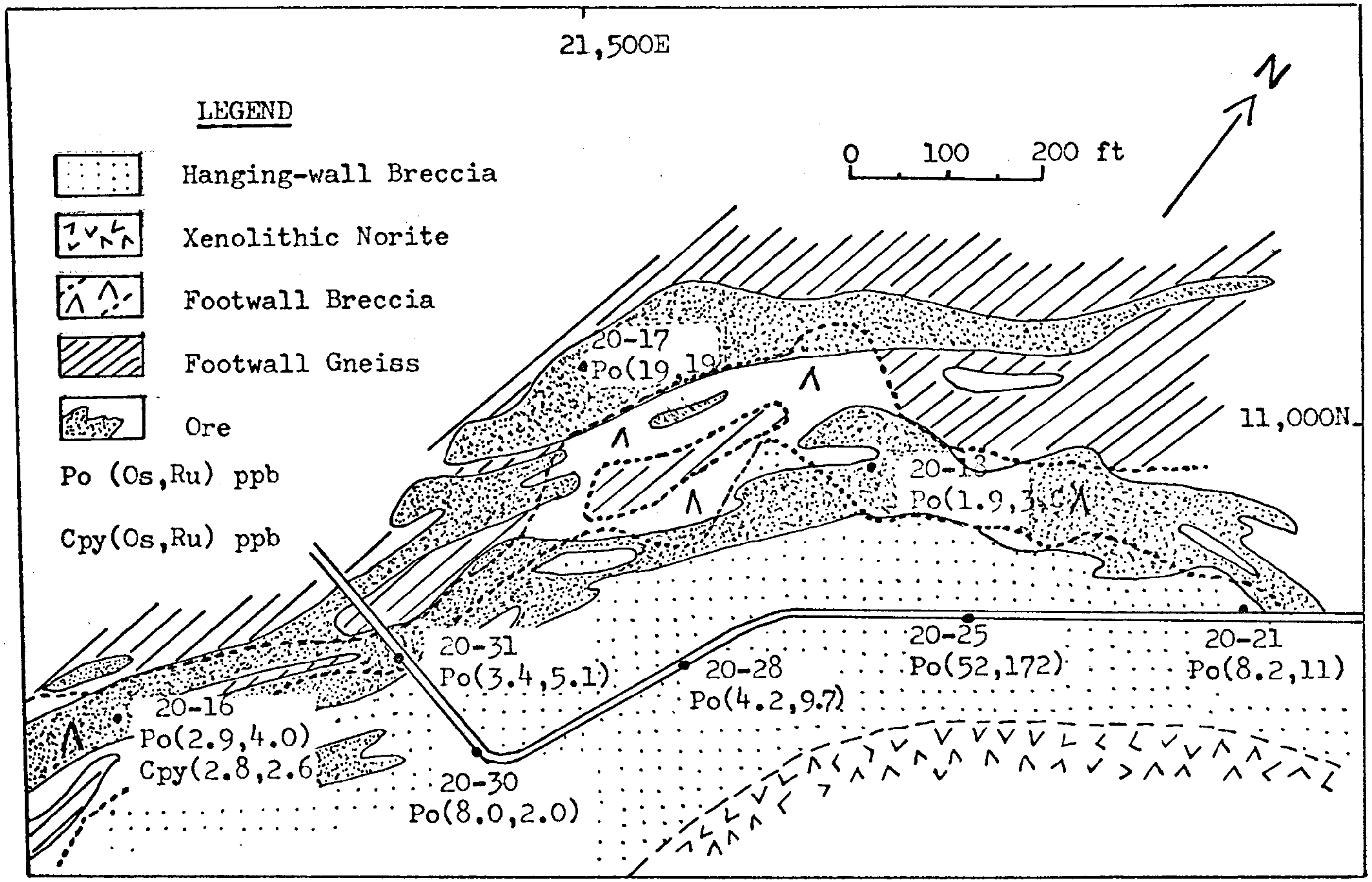

Fig. 10 Geological map of 2000 ft level of Strathcona Mine showing the distribution of Ru and Os in sulfide minerals

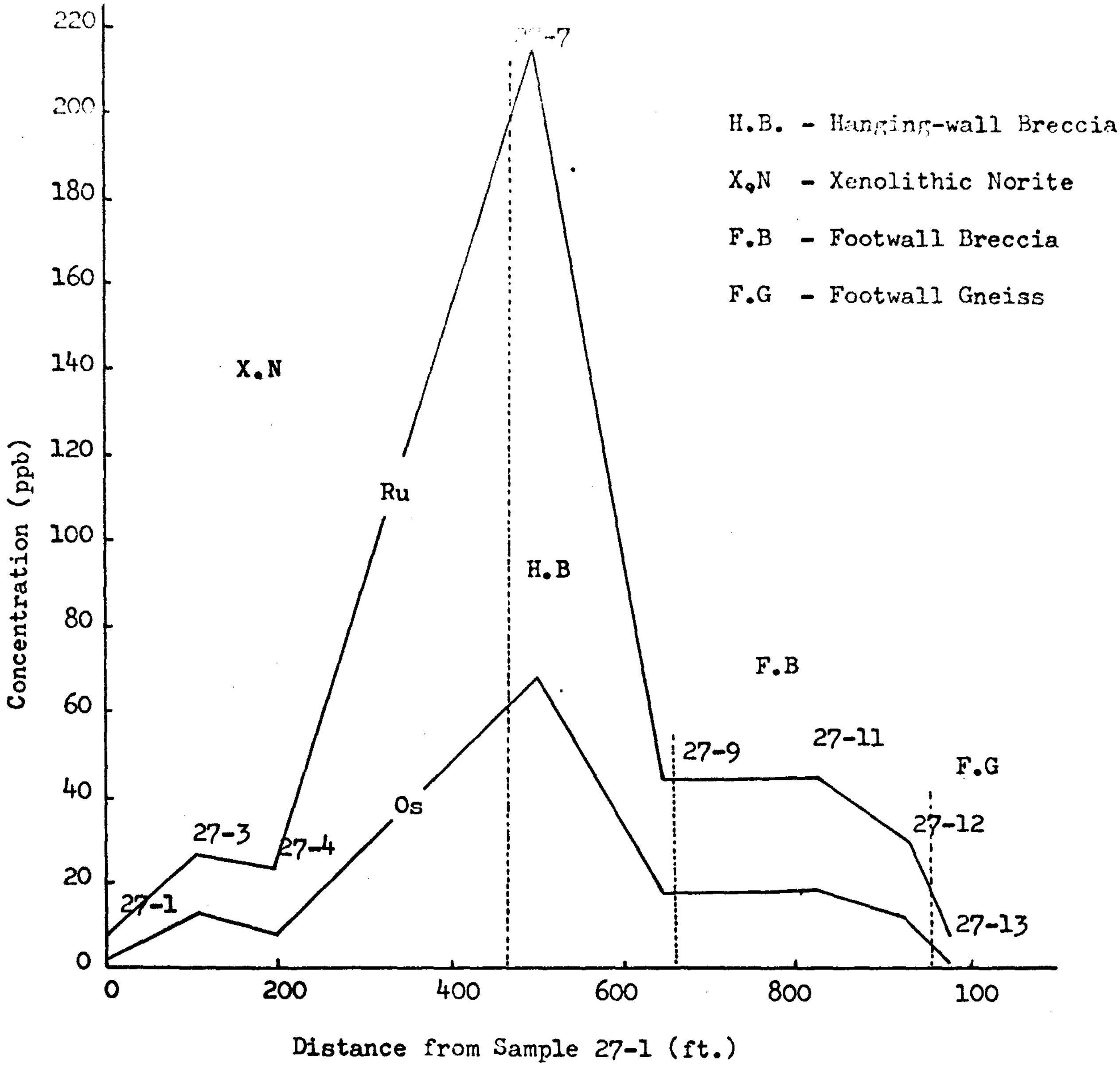

Fig. 11 The distribution of Ru and Os in pyrrhotite in 2750 foot level of the Strathcona Mine

Table 14 Comparison of Ru and Os concentrations in pyrrhotite from the footwall breccia ore zone and from hanging-wall breccia from the 2000 foot level, Strathcona Mine, Sudbury, Ontario

Footwall breccia ore zone			Hanging-wall breccia		
Sample No.	Os (ppb)	Ru (ppb)	Sample No.	Os	Ru
20-17	19	19	20-25	52	172
20-31	3.4	5.1	20-30	8.0	20
20-16	2.9	4.0	20-21	8.2	11
20-18	1.9	3.0	20-28	4.2	9.7
Average	6.8	7.8	Average	18.1	53.2

Kullerud (1965, 1966, 1967). Their main points concerning the genesis of the ore are the following:

(a) The sublayer rocks, including mafic norite, xenolithic norite and hanging-wall breccia, are regarded as intrusions which are younger than the Ni-irruptive proper, in particular younger than the felsic norite. The brecciation which produced the footwall breccia is considered to postdate the sublayer rocks.

(b) The sulfides of the hanging-wall breccia and xenolithic norite were introduced with the magma which produced these rock units as immiscible droplets of sulfur-rich liquid. The hypothesis that these sulfides represent in situ accumulation of an immiscible liquid from overlying felsic norite of the irruptive proper is discounted by Naldrett and Kullerud.

(c) The immiscible sulfur-rich liquid is considered to have initially precipitated magnetite and pyrrhotite solid solution containing Ni and Cu. Chalcopyrite exsolved from the pyrrhotite solid solution at some temperature below 400°C and pentlandite at a temperature below 300°C.

(d) The sulfides in the footwall breccia (main-zone ore) and footwall gneiss (deep-zone ore) were considered the result of either:

(1) remobilization and re-emplacement of sulfides from the hanging-wall breccia implying that all sulfides were introduced in a single episode, or

(2) the introduction of a second body of sulfide ore as ore melt or magma or a high temperature aqueous solution.

For the sulfides of the hanging-wall ore zones a magmatic origin is advocated by Naldrett and Kullerud. Supporting evidence includes lack of silicate-sulfide reactions (that is, silicates are not corroded or altered in contact with sulfides), ore-silicate texture and the intrusive nature of the sublayer rocks. The sulfides are introduced as immiscible liquids in the sublayer rock magma. As a marked increase in sulfide to silicate proportions occurs toward the base of the hanging-wall ore zone (which is the irruptive floor), settling of the dense sulfide liquid in the lighter silicate magma seems to have occurred. A fairly continuous sheet or pool of sulfide liquid probably existed at the base of the irruptive due to this process. The increase in Os and Ru content toward the base of the hanging-wall ore zone may be due to the gravitative settling of either Os and Ru minerals (possible sulfides) or metallic particles within this sulfur-rich fluid. As the hanging-wall ore is dominantly pyrrhotite, mineralogical fractionation does not appear to be a likely explanation of the Os-Ru distribution in the hanging wall ore zone. As for the origin of the main- and deep-zone ores, the low Ru and Os content in these ores as compared with those in the hanging-wall breccia (Table 14) seem to favour the introduction of a second body of sulfide ore rather than the remobilization and re-emplacement of sulfides from the hanging-wall breccia. It would seem that the higher Ru and Os contents characteristic of the hanging-wall ores might be expected in the sulfides of the footwall ore zones if these sulfides were remobilised from the base of irruptive rocks where the Ru and Os are most highly concentrated.

D. The fractionation of Ru and Os between pyrrhotite, chalcopyrite and pentlandite mineral pairs and the geochemical coherence of Os and Ru.

Fifteen samples from 7 localities in the Strathcona Mine have been analysed to study the paritition of Ru and Os between coexisting pyrrhotite, chalcopyrite and pentlandite. All data are summarized in Table 15 which shows Os to be slightly enriched in pyrrhotite relative to chalcopyrite. For six mineral pairs analysed, five show enrichment of Os in pyrrhotite. The average value of the ratio Os(po)/Os(cpy) is 1.4. The variation in Ru data for pyrrhotite - chalcopyrite pairs is considerably greater than for Os, with three samples showing depletion and three showing enrichment of Ru in pyrrhotite relative to chalcopyrite. Although the average value for the Ru(po)/Ru(cpy) ratio is 1.8, analyses of more samples would be required to establish that Ru is definitely enriched in pyrrhotite relative to chalcopyrite. However, as Ru and Os have been shown to exhibit strong geochemical coherence in a pyrrhotite sample suite (Fig.12), it may be expected that Ru would also be enriched in pyrrhotite relative to chalcopyrite if the Os enrichment in pyrrhotite is significant. No significant variation of Os has been found in pentlandite as compare to pyrrhotite or chalcopyrite. As for Ru, it seems to be enriched in pentlandite rather than chalcopyrite according to these limited data.

The slight concentration of Os and probably Ru in pyrrhotite is difficult to explain but the following suggestion is proposed. According to Naldrett and Kullerud (1967) the immiscible sulfide rich liquid was introduced at approximately 1000°C, initially crystallising magnetite and pyrrhotite solid solution with chalcopyrite exsolving from the pyrrhotite at a temperature less than 400°C. If this is corrected the formation of chalcopyrite is a completely subsolidus phenomenon (that is, all sulfide liquid was crystallised before the appearance of chalcopyrite). Hence,

Table 15 The distribution of Ru and Os in pyrrhotite, chalcopyrite and pentlandite mineral pairs

Sample number	Mineral	Os(ppb)	Po/Cpy	Ru(ppb)	Po/Cpy
20-16	Po	2.9	1.0	4.0	0.15
	Cpy	2.8		26	
22-20	Po	36	2.0	73	2.4
	Cpy	18		31	
22-26	Po	6.8	1.8	2.0	0.2
	Cpy	3.7		10	
25-11	Po	6.4	1.2	4.2	0.46
	Cpy	5.3		9.1	
27-13	Po	0.68	0.5	4.3	1.2
	Cpy	1.2		3.5	
DDH 242L2280'	Po	1.3	1.7	7.5	6.3
	Cpy	0.76		1.2	
	Pn	1.6		5.2	
DDH 242L2345'	Cpy	3.7		20	
	Pn	3.1		39	
Average			1.4		1.8

the fractionation of Os and Ru between chalcopyrite and pyrrhotite is probably dependent on processes involving reactions occurring in the solid state.

Assume that the precious metals are incorporated in the pyrrhotite at high temperature (~ 1000 - 900°C) and are present in the +4 valence state which is the most stable oxidation state of these elements. As they are then characterized by 6 fold coordination, it would seem that cation positions in the host minerals with the same coordination number might constitute the best sites for substitution of foreign ions. Chalcopyrite, exsolved from a pyrrhotitic host at 400°C or less, probably is not a favourable host for either Os or Ru as the cation sites are 4 fold coordination and as the phase is formed at a much lower temperature than the host and probably cannot tolerate many impurities. Also the lattice vacancies which characterize the pyrrhotite structure may increase its ability to accumulate foreign ions relative to chalcopyrite.

It should further be noted that it is not at all certain that these precious metals are in solid solution with sulfide minerals. They may crystallize as sulfides occurring in intergranular spaces between pyrrhotite grains. The sulfide laurite (Ru, Os)S_2 occurs in nature. Alternately the oxidation potential in the immiscible sulfide droplets may never be oxidizing enought to permit Os and Ru to reach the stable +4 valence state, and these elements may exist as the metal (or alloy with Ir). Again any marked fractionation between pyrrhotite and chalcopyrite would be unlikely.

The high degree of geochemical coherence of Os and Ru is perhaps related to either their chemical inertness or the fact that both have very stable quadrivalent oxidation states. Neither metal can, for example, be oxidized and dissolved at low temperatures by any single acid. Thus, depending on the oxidation potential of the magma both elements may exist as the metal (unchanged atoms) or, if they are oxidized to the quadrivalent state, their coordination with anions (probably sulfur) would be similar and would probably produce complexes of similar size and charge characteristics.

VI. SUMMARY

Neutron activation analysis was undertaken as a technique for simultaneous determination of Ru and Os in sulfide minerals. The separation and purification of these elements was achieved by utilizing the selective volatility of their tetroxides during distillation from H_2O_2-H_2SO_4 solution for Os and the $NaBrO_3$-H_2SO_4 for Ru followed by extraction of OsO_4 into CCl_4 and precipitation of RuO_4 into RuO_2 with ethanol. The purified elements were finally reduced to the metal by Zn as well as in H_2 and the resulting activities determined by counting the γ radiation of ^{97}Ru and ^{103}Ru and the β^- radiation of ^{191}Os and ^{193}Os. The sensitivity of the method is approximately 10^{-9}gm per gm for Ru and 10^{-10} gm per gm for Os.

Thirty five samples of sulfide minerals, including pyrrhotite, chalcopyrite, pentlandite and cubanite from Strathcona Mine and the Frood-Stobie deposit of the Sudbury area, Ontario were chosen for analysis to determine the Ru and Os concentrations in sulfides from both high grade ore zones and relatively weakly mineralized rocks as well as to study the fractionation of these metals between coexisting sulfides. The following generalizations were obtained based on observed data.

(1) The contamination of Ru radionuclides from U fission products is serious for the determination of Ru. A correction must be made for the contribution of the Compton effect of ^{103}Ru to the ^{97}Ru spectrum before the ^{97}Ru activity can be used for calculation of Ru concentration unless

the absence of a significant fission contribution from U can be demonstrated.

(2) The concentrations of both Ru and Os are very low; Ru is generally below 50 ppb and Os below 20 ppb, in the analysed sulfides.

(3) A strong geochemical coherence between Os and Ru was observed in the sulfide minerals. It may be useful in predicting the concentration of one element if the other is known or in recognizing the possible experimental error if an unusual result is obtained.

(4) Both Os and Ru settled gravitatively in a body of fairly continuous sulfide liquid as either metallic particles or sulfide minerals concentrating toward the base of the hanging-wall breccia. Ru and Os are higher in the sulfides of the hanging-wall breccia than in footwall breccia ore zone suggesting a possible different generation of sulfides in granite breccia ore zone from hanging-wall norite.

(5) The data show Os is slightly enriched in pyrrhotite over coexisting chalcopyrite. It may be expected that Ru has the same preference as Os if the Os enrichment in pyrrhotite is significant.

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