NEUTRON ACTIVATION DETERMINATION OF THE PRECIOUS METALS

A NEUTRON ACTIVATION ANALYSIS TECHNIQUE FOR DETERMINATION OF THE PRECIOUS METALS AND ITS APPLICATION TO A STUDY OF THEIR GEOCHEMISTRY

By

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SCOPE AND CONTENTS: A neutron activation analysis procedure for the simultaneous determination of Ru, Pd, Os, Ir, Pt and Au has been developed. It consists principally of distillation, anion exchange, solvent extraction and precipitation steps and was used to determine all of these metals in meteorites as well as Pd, Ir and Au in sulphide minerals from the Sudbury Nickel Irruptive. The accuracy of the method was checked against G-1 and W-1 and a sulphide standard. A literature survey of the geology of the Sudbury Nickel Irruptive and a description of the geology of the Strathcona mine are presented. A detailed description of the inorganic chemistry and its bearing on the geochemistry of the precious metals, with special reference to basic rocks is given. Analytical results for Pd, Ir and Au in a large number of pyrrhotite and chalcopyrite samples and a smaller number of sulphide and oxide minerals and an ultramafic xenolith are presented. Arsenic was determined in 15 of the sulphide samples and found to be highly correlated with Pd. The genesis of the Strathcona ores is discussed and the differential behaviour of the precious metals during fractionation of a sulphide-rich basic magma is described.

Seven carbonaceous and two enstatite chondrites were analysed and the data evaluated with respect to estimation of the cosmic abundances of these metals.

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ABSTRACT

A neutron activation analysis procedure for simultaneous determination of Ru, Pd, Os, Ir, Pt and Au in sulphides, meteorite, and silicate samples has been developed. ^{235}U fission interference precludes analysis of Ru and produces errors in uranium-rich rocks. Poor sensitivity is often a problem with the determination of Pt in terrestrial samples. Although the method can be used for analysis of all six metals, it is more convenient to determine Os and Ru separately. Os and Ru were determined in a concurrent study.

Results for the U.S.G.S. standards W-1 and G-1(in p.p.b.) are:

	Pd	Ir	Au
G-1	1.6 ± 0.3	0.044 ± 0.008	3.3 ± 0.9
W-1	11.5 ± 1.1	0.26 ± 0.05	5.8 ± 0.7

These data compare favourably with previous determinations, with the exception of Ir in W-1 for which the present value is considered more accurate. Analysis of a Cu-Ni sulphide matte for five platinum metals and Au yielded results within 6% of previous spectrophotometric and spectrographic determinations, except for Pt, for which the data were 18% higher.

The method was used principally to study the geochemistry of Pd, Ir and Au in the Strathcona and Frood deposits, Sudbury, Ontario. The data for Ir are the first for the distribution of this metal in the ores.

The metals are highly fractionated in the zoned Strathcona and Frood ores with the bulk of the Ir (and Os) concentrated in the earliest

pyrrhotite crystals whereas Pd, Au and Pt are concentrated in the last phases to crystallize from residual sulphur-rich liquids. In co-existing chalcopyrite and pyrrhotite, Pd and Au are always enriched in the former and Ir and Os in the latter. Relative to early, primary mineralization, Ir is depleted by a factor of 400 whereas Pd and Au are concentrated 50 and 20 times respectively in late stage mineralization. Pd is correlated with Ni and As. Ir is highly correlated with Os and Ru and has a strong inverse correlation with Pd.

The following order of mobility in a sulphur-rich magma was established:

$$\mathrm{Au} > \mathrm{Pd} > \mathrm{Pt} > \mathrm{Rh} > \mathrm{Ru} > \mathrm{Os} \geq \mathrm{Ir}$$

As a consequence of the very high mobility of Au, considerable amounts may have migrated away from both the Strathcona and Frood ore bodies in the residual aqueous phases that developed during fractional crystallization of the sulphide magmas.

The data support an hypothesis that the sulphides were injected with the noritic sub-layer rocks, settled to the floor of the Irruptive, and migrated into the granitic footwall, perhaps via thermal fractures effected by the presence of the hot, liquid sulphides. As the sulphide liquid migrated into the footwall, it crystallized with solid-liquid fractionation enriching the liquid in such metals as Ni, Cu, Pt, Pd and Au. This fractionation accounts for the Cu-Ni zoning previously explained by diffusion. The sulphides in the mafic norite and upper part of the xenolithic norite represent the original sulphide liquid, while the sulphides constituting the hanging-wall zone represent the first sulphide crystal separates.

As it can be demonstrated that the fugacity of sulphur was high enough to stabilize sulphide compounds or complexes, the following hypothesis for the detailed paragenesis of the metals is suggested: 1) the more insoluble metals, Os and Ir, either a) formed early discrete sulphides which coprecipitated with the first solids to separate, or b) were incorporated into the pyrrhotite solid solution. In the latter case exsolution at lower temperature would have been possible. 2) The more soluble metals, together with small amounts of Ir, Os and Ru formed complexes and accumulated in the residual phases to crystallize finally by combining with S and elements such as Bi, Te and Pb which had also accumulated in the volatile-rich liquids.

The analytical procedure was used to determine the precious metal content of seven carbonaceous and two enstatite chondrites. The results are given below in atomic abundances ($Si = 10^6$):

Chondrite Group	Ru	Pd	Os	Ir	Pt	Au
Carbonaceous	$1.84 \pm 0.09_6$	1.32±0.21	0.79±0.12	0.76±0.28	1.4±0.25	0.18±0.040
Enstatite	1.60±0.08	1.23±0.06	0.66±0.01	0.25±0.03	1.1±0.00	0.19±0.010

The carbonaceous chondrites have higher precious metal atomic abundances than either enstatite or olivine hypersthene chondrites, except for Au in enstatite chondrites. There is very little variation in the precious metal content of Types I, II and III carbonaceous chondrites. As no obvious mechanisms for fractionation of precious metals during condensation of meteoritic matter are apparent, their concentrations in carbonaceous chondrites should provide good estimates of their cosmic abundances.

CHAPTER I

INTRODUCTION

1. Introductory Statement

The precious metals are strongly siderophilic and chalcophilic elements, occurring predominantly as pure metals and alloys and to a much lesser extent combined with sulphur, tellurium, bismuth, and arsenic. For the most part the platinum metals are concentrated in the early stages of magmatic differentiation and are consequently most abundant in magmatic mafic and ultramafic bodies and associated ore deposits, especially of the chalcopyrite-pyrrhotite-pentlandite type. Gold, on the other hand is very often enriched in the residual solutions of magmas (especially granitic magmas) and is of low concentration in pyrrhotite-pentlandite ores associated with gabbroid magmas. Under certain conditions, the platinum metals are carried through the differentiation process and are likewise concentrated in the products of late hydrothermal solutions. The factors which control the distribution of the precious metals are inadequately known. As large quantities of the precious metals are associated with copper-nickel sulphides, much can be learned about the geochemistry of the metals by studying their behaviour during crystallization of a sulphide magma.

The problem undertaken in this research was a study of the distribution of the precious metals in the chalcopyrite-pyrrhotite-pentlandite ores of the Sudbury Irruptive. Little was known about the distribution of any of the metals, except that they are occasionally concentrated in late stage mineralization. The purpose of the study was to augment our knowledge of the geochemistry of the precious metals and to apply their distribution in the sulphides to the elucidation of the problem of the genesis of the Sudbury ores.

For most of the precious metals, there is a serious lack of reliable analytical data, particularly with regard to abundances in terrestrial materials. The only exception is Au where activation analyses of some 400 samples of igneous and sedimentary rocks have been reported. Determinations of noble metals in terrestrial rocks prior to the advent of neutron activation analysis cannot be accepted as reliable. As regards the reliability of activation analysis, Beamish _et al_. (1967) state:

"In many of the earlier activation methods the more unacceptable separatory procedures and reagents seem often to have been used. This deficiency is particularly evident in the analytical methods of iridium and ruthenium. On the other hand, in the more recent reports of activation methods, a number of new reagents for both the separation and determination of noble metals has been proposed and results for known separatory processes have been provided which indicate the advisability of re-examining some of the classical analytical methods".

In the last 15 years, the classical methods for separation and determination of the noble metals have been greatly improved, especially for determination on a microscale (see reviews by Beamish (1960, 1965, 1966) and papers by Westland and Beamish (1954, 1957). The use of ion exchange methods in analytical schemes for the noble metals by Kraus _et al_. (1954), Berman and McBryde (1958a, 1958b), and Cluett _et al_. (1955) has greatly improved the effectiveness of group separation of the noble metals from the major elements of many rocks and ores. Adaption of the improvements in the classical methods and new techniques such as ion exchange and solvent extraction have greatly improved the quality of activation analysis. In activation analysis of the noble metals, the use of ion exchange is the single most effective step in isolation of the noble metal activity from bulk sample radioactivity. Many reagents are now available which are specific for one or a small number of elements.

Many reliable activation methods have been described by the authors mentioned in this and the following section for determination of from 1 to 3 of the noble metals at a time. The Nuclear Science Series of the U.S. Atomic Energy Commission is an excellent series of monographs which outline in detail the radiochemistry of a large number of elements. The series includes monographs on Ir, Pt and Os by Leddicotte (1961a, b, and c), on Au by Emery and Leddicotte (1961), on Pd by Høgdahl (1961) and on Ru by Wyatt and Rickard (1961) respectively. A critical review of neutron activation and tracer methods for the determination of the noble metals has been written by Beamish et al. (1967).

A procedure capable of analysis of all or selected groups of these metals in a wide variety of materials is clearly advantageous with respect to rapidity of data accumulation, comparison of geochemical properties, and economy of sample. The analytical method described here relies principally on distillations, ion exchange and solvent extraction procedures with modifications introduced where warranted by the particular requirements or advantages of the radioactivation method. The procedure is applicable to analysis of many silicate rocks and minerals, meteorites and sulphides, particularly Cu-Fe-Ni varieties, and includes all the precious metals except Rh.

2. Activation Analysis of Precious Metals

Neutron activation analysis is a comparative method which is based on the fact that the amount of radioactivity induced in an element when irradiated is proportional to the amount of the element present and the neutron flux. The induced radioactivity of the analysis element is compared with the activity induced, under identical conditions, in a standard of known concentration. Sample and standard are irradiated side by side. After irradiation, a small amount of inactive analysis element is added to the irradiated material to serve as a carrier of the radioactive analysis element through a chemical separation procedure which serves to isolate the species of interest from the other radionuclides. The major advantages of the method are: 1) it is highly sensitive for many elements; 2) it is not necessary to obtain quantitative recovery of the analysis element, as the fraction of radioactive analysis element recovered is equal to the fraction of carrier recovered; and 3) the method is not sensitive to post-irradiation contamination from chemical reagents provided the mass of contaminant introduced is negligible in comparison to the mass of carrier.

Detailed accounts of neutron activation analysis may be found in Smales (1957), Reed (1959), Moorbath (1960), Mapper (1960), Winchester (1960) and Herr (1959).

All of the precious metals including Ru, Rh, Pd, Os, Ir, Pt and Au can be determined by neutron activation analysis in many natural materials. To evaluate various possible neutron induced reactions, the pertinent data have been tabulated in Table 1-1. Given are data on the isotopic abundance of the stable isotope, capture cross-section of these isotopes, radionuclide produced by (n,γ) reactions resulting from irradiation of the stable isotopes, and the half-lives of the radionuclides formed. Information is also provided for the mode of decay of the radionuclide along with the type and quantity of radiation emitted. If a radioactive daughter is produced by decay of a radionuclide, its half-life, mode of decay, and type and quantity of radiation are indicated.

A quantity called the production factor, P.F., was computed for irradiations of 19 hours and 1 week. This factor is a measure of the relative yields of the various reactions and is given by the following equations:

a) for direct products of n, γ reactions,

$$P.F. = \frac{\sigma\,\phi}{w}\,(1 - e^{-\lambda t_{ir}})$$

b) for direct products of n, f reactions,

$$P.F. = \frac{\sigma\,\phi}{w}\,Y(1 - e^{-\lambda t_{ir}})$$

c) for first daughter of n, γ or n, f products,

$$P.F. = \frac{\sigma\,\phi}{w}\,(1 - \frac{\lambda_3}{\lambda_3-\lambda_2}\,e^{-\lambda_2 t_{ir}} + \frac{\lambda_2}{\lambda_3-\lambda_2}\,e^{-\lambda_3 t_{ir}}$$

(if a fission product daughter is involved, multiply the right hand side of the last equation by Y) where

σ = thermal neutron capture cross-section (in barns)
ϕ = per cent atomic abundance
λ = decay constant
t_{ir} = irradiation time
w = physical atomic weight
Y = fractional chain fission yield.

Table 1-1 Nuclear Data for Precious Metals

Naturally Occurring Isotope	Isotopic Abundance (%)	Radionuclide formed by (n,γ) reaction				Radioactive daughter			Production Factor	
		Identity	σact. (barn)	$T_{1/2}$	Radiation (Mev)	Identity	$T_{1/2}$	Radiation	T_{ir} = 19 hr.	T_{ir} = 1 week
$^{96}\mathrm{Ru}$	5.7	$^{97}\mathrm{Ru}$	0.21	2.88 day	E.C.γ:.216	-	-	-	0.0019	0.0089
$^{102}\mathrm{Ru}$	31.3	$^{103}\mathrm{Ru}$	1.44	40 day	β^-:0.22,0.10,0.71 γ :(0.040),0.50,0.61	$^{103}\mathrm{Rh}$	57 min.	1.T:0.04	0.0060	0.050
$^{104}\mathrm{Ru}$	18.3	$^{105}\mathrm{Ru}$	0.7	4.5 hr.	β^-:1.15,1.08,1.87 γ:0.72,0.21 - 1.7	$^{105m}\mathrm{Rh}$ $^{105}\mathrm{Rh}$	45 sec. 37 hr.	1.T.:0.130 β^-:0.57,0.25,0.26 γ:0.32	0.084	0.088
$^{103}\mathrm{Rh}$	100	$^{104}\mathrm{Rh}$	11	4.4 min.	1.T.:0.077 γ: 0.051				10.69	10.69
		$^{104}\mathrm{Rh}$	144	42 sec.	β^-:2.44 γ: 0.56, 1.24				139.93	139.93
$^{102}\mathrm{Pd}$	0.96	$^{103}\mathrm{Pd}$	4.8	17 day	E.C. γ:(0.040),0.052-0.36				0.00145	0.0112
$^{108}\mathrm{Pd}$	26.71	$^{109m}\mathrm{Pd}$	0.2	4.8 min.	1.T. 0.18					
		$^{109}\mathrm{Pd}$	12	13.5 hr.	β^-:1.03 γ: 0.088				1.88	3.01
$^{110}\mathrm{Pd}$	11.81	$^{111m}\mathrm{Pd}$	0.04	5.5 hr.	1.T.:0.17,0.28 γ :1.69,0.5	$^{111m}\mathrm{Ag}$	74 sec.	1.T.:0.065		
		$^{111}\mathrm{Pd}$	0.2	22 min.	β^-:2.13 γ :0.065	$^{111}\mathrm{Ag}$	7.5 day	β^-:1.05,0.71 γ :0.34	.00189	.0123
$^{184}\mathrm{Os}$	0.018	$^{185}\mathrm{Os}$	200	93.6 day	E.C. γ's:0.646	-	-	-	0.00011	0.001
$^{189}\mathrm{Os}$	16.1	$^{190m}\mathrm{Os}$	.008	10 min.	γ's:.50,.62,.36	-	-	-	0.00068	0.00068
$^{190}\mathrm{Os}$	26.4	$^{191m}\mathrm{Os}$	8.6	14 hr.	1.T.:0.014	$^{191}\mathrm{Os}$	16 day	β^-:0.142	0.73	1.19
		$^{191}\mathrm{Os}$	3.9	15 days	β^-:0.142	$^{191m}\mathrm{Ir}$	6.9 sec	γ :0.042,0.129	0.019	0.15
$^{192}\mathrm{Os}$	41	$^{193}\mathrm{Os}$	1.6	32 hr.	β^-:0.677-1.136 γ's:.139,0.073,.107-0.56	-	-	-	0.12	0.34

Table 1-1 continued

^{191}Ir	37.3	^{192m}Ir	250	1.5 min	I.T.:0.058	^{192}Ir	74.4day	See further		
		^{192}Ir	750	74.4 day	E.C. β^-:0.100-0.673 γ:.136, .32, .47				1.43	12.68
^{193}Ir	62.7	^{194}Ir	110	19 hr.	β^-:2.24, 1.90 γ:.33, .29, .65	-	-	-	17.94	35.81
^{190}Pt	0.0127	^{191}Pt	150	30 day	E.C. γ:0.54,0.36,.41	^{191}Au	.2 hr.	E.C. γ:.091,.048,.16,.13	0.00167	0.00802
^{192}Pt	0.78	^{193m}Pt	2	4.4 day	I.T.:0.136 γ: 0.013	^{193}Pt	500 y	E.C.	0.00094	0.0053
		^{193}Pt	14	500 y	E.C.				-	-
^{194}Pt	32.9	^{195m}Pt	1.2	4.1 day	I.T. 0.030 γ: 0.099	^{195}Au	183 day	E.C. γ: 0.093,0.03,0.13	0.0019	0.011
^{196}Pt	25.3	^{197m}Pt	0.05	1.5 hr	I.T. 0.346, γ:0.05 β^-:0.73 γ:0.28, .13	^{197}Pt	20 hr	See further		
		^{197}Pt	0.9	20 hr	β^-:0.67, 0.48 γ: 0.077, 0.19,0.27	-	-	-	0.058	0.11
^{198}Pt	7.21	^{199m}Pt	.03	14 sec	I.T.:0.39 γ: 0.032	^{199}Pt	30 min	See further		
		^{199}Pt	4	30 min	β^-:1.7,0.7-1.6 γ: .54, 0.075-0.96	^{199}Au	3.15 d.	β^-:30, .25, .46 γ .158, .208, .050	0.022	0.031
^{197}Au	100	^{198}Au	98.8	64.8 hr.	β^-:0.96,0.29,1.37 γ: .412, .674	-	-	-	9.22	41.82

Table 1-2. Fission-produced nuclides of Ru and Pd

Nuclide of Interest	Fractional Fission Yield	Reaction	Production Factor	
			T_{ir} = 19 hr.	T_{ir} = 1 week
^{103}Ru	.03	$^{235}U(n,f)^{103}Ru \xrightarrow[40d.]{\beta^-} {}^{103m}Rh \xrightarrow[57min.]{\gamma} {}^{103}Rh$	0.00073	0.0061
^{105}Ru	.009	$^{235}U(n,f)^{105}Ru \xrightarrow[4.43hr.]{\beta^-} {}^{105}Rh \xrightarrow[36hr.]{\beta^-} {}^{105}Pd$	0.015	0.016
^{109}Pd	.0003	$^{235}U(n,f)^{109}Pd \xrightarrow[13.5hr.]{\beta^-} {}^{109m}Ag \xrightarrow[40sec.]{\gamma} {}^{109}Ag$	.00033	0.00053
^{111}Pd	.00019	$^{235}U(n,f)^{111}Pd \xrightarrow[22min.]{\beta^-} {}^{111}Ag \xrightarrow[7.5d.]{\beta^-} {}^{111}Cd$	0.000024	0.00016
^{112}Pd	.00017	$^{235}U(n,f)^{112}Pd \xrightarrow[21hr.]{\beta^-} {}^{112}Ag \xrightarrow[3.2hr.]{\beta^-} {}^{112}Cd$	0.00014	0.0003

Many of the radionuclides of Ru, Rh, Pd and Ag are produced by fission of ^{235}U. Production factors for n,f reactions of importance have been calculated and are tabulated in Table 2-1 along with the pertinent reactions and the fractional fission yields. The capture cross-section of ^{235}U is 580 barns, its abundance is 0.72%, and its physical atomic weight 235.0.

The production factors permit comparison of the relative yields of various radionuclides as a function of the concentration of the parent elements in the sample of interest. For example, in a sample with equal contents of U and Ru the ratio of n,γ to n,f activities is 0.0060/0.00069 = 8.7 and 0.084/0.0014 = 60 for ^{103}Ru and ^{105}Ru, respectively. These data indicate the degree of interference of ^{103}Ru and ^{105}Ru produced by thermal fission of ^{235}U.

The relative sensitivities of the precious metals by neutron activation analysis are as follows for a 19 hour irradiation: Rh $>$ Ir $>$ Au $>$ Pd $>$ Os $>$ Ru $>$ Pt. For a 1 week irradiation the relative order of sensitivities are Rh $>$ Au $>$ Ir $>$ Pd $>$ Os $>$ Pt $>$ Ru. The use of production factors does not take the time of decay of the radionuclides from the end of irradiation to the start of counting into account.

The applicability of neutron activation analysis to precious metal analyses of natural materials is discussed below.

Ruthenium

Any of ^{105}Ru, ^{103}Ru or ^{97}Ru may be used to determine Ru, although the latter two nuclides have very low production factors. Fission-produced ^{103}Ru and ^{105}Ru interfere with the determination of Ru in many geological materials. Ru has been successfully determined in chondritic meteorites by Bate and Huizenga (1963), and by Crocket, Keays and Hsieh (1967) without fission interference. Chondritic and iron meteorites have a Ru/U ratio of approximately 100 and the proportion of Ru activity produced from n,γ reactions to that from n,f reactions is therefore 100x0.0060/0.00069 = 870 for ^{103}Ru and 100x0.084/0.0014 = 6000 for ^{105}Ru.

In acidic and basic rocks, however, the Ru/U ratios are much different. Ru probably is at the same level of concentration in a given rock as Ir and Os, with which it has considerable geochemical coherence. If it is assumed that Ru does have comparable values to Os and Ir, then the concentrations of Ru in G-1 and W-1 are 0.06 and 0.25 respectively (see Table 7-5). Heier and Rogers (1963) give the average U content of acid and basic rocks as 8 and 0.6 p.p.m., respectively. Using the production factors, it may be seen that with such large (10^5 and 10^3) U/Ru ratios, the determination of Ru in silicates containing large amounts of U is unfeasible. Ultrabasic rocks, and certain minerals such as sulphides may have low enough U contents to minimize fission interference and thus permit use of the ^{103}Ru and ^{105}Ru activities.

^{97}Ru is free of fission interference, but its yield is low. However, it has been employed for determination of Ru in ordinary chondrites by Bate and Huizenga, and in carbonaceous chondrites by Crocket, Keays and Hsieh. Hsieh (1967) determined Ru in Sudbury sulphides by counting ^{97}Ru, but found the Ru content of G-1 and W-1 to be too low to permit measurement by this nuclide.

Rhodium

Schindewolf and Wahlgren (1960) have determined Rh in chondritic meteorites by neutron activation analysis. Despite the high yield of

^{104}Rh its short half-life (4.4 minutes) precludes inclusion of Rh in any analytical scheme involving the other precious metals as considered here. Determination of Rh would necessitate processing immediately after the end of irradiation, and would present an extremely serious radiation hazard if the irradiation had been of 8 to 19 hours duration.

Palladium

^{109}Pd with a half-life of 13.5 hours has been used by a number of researchers for determination of Pd. Brown and Goldberg (1949), Goldberg et al. (1951), and Smales, Mapper and Fouche (1967) have used ^{109}Pd for analysis of iron meteorites; Vincent and Smales (1956), and Crocket and Skippen (1966) for analysis of igneous rocks; and Morris, Hill and Smith (1963) for analysis of sulphides. ^{109}Pd has a good yield but is subject to interference produced by ^{235}U fission in acid rocks. Crocket and Skippen concluded that fission interference may cause results to be 10% high for determination in acid rocks.

^{111}Pd has a yield which is 10^3 lower than that of ^{109}Pd for a 19 hour irradiation but the much higher Pd content of chondritic and iron meteorites permits its use for Pd determinations in such materials. Reed (1963) used 7.5 day ^{111}Ag (produced by decay of ^{111}Pd) to determine the Pd content of the pallasite Pantar. Greenland (1967) has used 17 day ^{103}Pd to determine Pd in chondritic meteorites. Its yield is also low and so its applicability to the study of Pd in terrestrial rocks is limited. However, ^{103}Pd is not subject to interference from ^{235}U fission and so the nuclide could be of use in determination of Pd samples which contained too high a U/Pd ratio to permit use of ^{109}Pd or ^{111}Pd (or ^{111}Ag).

Osmium

Because of low Os abundance in most terrestrial materials, Os is one of the more difficult elements to determine in such materials. The increased level of Os in iron and chondrite meteorites permits determination of the metal by several different Os nuclides. Bate and Huizenga (1963) determined Os in cosmic and terrestrial samples by counting both 94 day ^{185}Os and 15 day ^{191}Os. For a week-long irradiation, the yield of the 15 day nuclide is 10^3 greater than that of the 94 day nuclide. To get a greater yield for ^{185}Os it is necessary to increase the length of irradiation considerably. ^{185}Os does not emit a beta particle so it is necessary to use a gamma counter for its detection. Morgan (1965), Morgan and Lovering (1964) and Lovering and Morgan (1964) have determined Os in terrestrial materials, iron and stony meteorites, and in tektites by counting the beta activities emitted by ^{191}Os and ^{193}Os. Both of these nuclides are γ - emitters as well as β^- - emitters and so can be determined by either γ or β^- counting. Because of the long half-lives of ^{185}Os and ^{191}Os, long irradiations (several weeks) are necessary to obtain good yields.

Iridium

Although Ir is highly depleted in terrestrial materials, its sensitivity is very high due to the large capture cross-sections of the stable isotopes. Rushbrook and Ehmann (1962), Baedecker and Ehmann (1965) and Baedecker (1967) have determined Ir in a large number of meteorites, tektites, and some terrestrial rocks by counting the 0.316 MeV and 0.47 MeV gamma-ray photopeaks of 74 day ^{192}Ir. Cobb (1967) has determined Ir in meteorites by counting the 0.29 and 0.316 MeV photopeaks of ^{194}Ir and ^{192}Ir respectively. His method was non-destructive; the irradiated meteorite was counted directly, with no chemical processing, with a lithium-drifted germanium detector. Either differential gamma spectrometry or gross beta counting may be used to determine ^{192}Ir and ^{194}Ir. A gain in yield by a factor of approximately 9 is obtained for ^{192}Ir when the length of irradiation is extended from 19 hours to a week.

Platinum

The determination of Pt in terrestrial materials by neutron activation analysis is extremely difficult because of the poor sensitivity for Pt and a lack of chemical reagents which are specific for Pt.

Morris, Hill and Smith (1963) determined the Pt content of Sudbury, Ontario sulphides by beta-counting 20 hour ^{197}Pt. They did not find sensitivity a problem as the Pt content of the sulphides was approximately 500 p.p.b., a concentration level which is 50 times that of Pt in G-1 and W-1, according to Das Sarma, et al. (1965) who found 8.2 p.p.b. and 9.2 p.p.b. in these materials, respectively. Baedecker and Ehmann (1965) determined Pt in meteorites and terrestrial rocks by counting the 0.158 MeV photopeak of ^{199}Au which results from the beta decay of ^{199}Pt. Although the yield of ^{199}Au is only one-third of that of ^{197}Pt, its use involves a chemical procedure that is highly specific for Au and therefore results in a radiochemically pure Au counting source. ^{199}Au can be either beta-counted or gamma-counted, but the presence of a high Au/Pt ratio in the sample precludes beta-counting. Considerable interference in gamma-counting also results when the ratio Au/Pt is high because of the ^{197}Au (n,γ)^{199}Au reaction.

Although not reported in the literature, it was found in the course of the present research that 4.4 day ^{193}Pt and 4.1 day ^{195}Pt could be used to measure Pt concentrations. These nuclides do not emit betas but do emit low energy gammas which are highly converted to monoenergic electrons which may be detected by a thin-window geiger or proportional counter. They have lower yields than either ^{197}Pt or ^{199}Pt, but their yields can be increased by longer irradiations.

Gold

In general, Au is more readily determined by neutron activation analysis in a wide range of terrestrial rocks and meteorites than any other precious metal. Goldberg et al. (1951), Vincent and Smales (1956), and Vincent and Crocket (1960) determined Au in a variety of igneous rocks and meteorites by measurement of the β^- activity emitted by 2.70 day ^{198}Au. One of the problems with beta-counting is that if the Pt/Au ratio is large, it is not possible to distinguish on the basis of the decay curves the contribution of 3.15 day ^{199}Au (produced from ^{198}Pt) which could be high. It can be shown, however, (see Appendix A) that for a 19 hour irradiation an interference of 1% from ^{199}Au would require a weight ratio of Pt/Au in the sample of 11/1. Shcherbakov and Perezhogin (1964), DeGrazia and Haskin (1964), Baedecker and Ehmann(1965), and Mantei and Brownlow (1967) have determined Au in hundreds of rocks and minerals of a large variety of types and in several dozen meteorites by gamma-counting the 0.412 MeV photopeak of ^{198}Au. Gamma counting avoids the problem of interference from ^{199}Au radiation. Cobb (1967) has measured the Au content of iron meteorites in a non-destructive method by counting the 0.412 MeV photopeak with a solid-state detector.

Of the precious metals considered, only Rh, because of the short half-life of ^{104}Rh, cannot be integrated into a comprehensive analytical scheme for the other precious metals. In certain materials where the precious metal content is high enough to avoid sensitivity problems (e.g. chondritic and iron meteorites, and sulphides in which each precious metal has a concentration of 10 p.p.b. to 10 p.p.m.), Ru, Pd, Os, Ir, Pt, and Au can be determined simultaneously in the same sample with an irradiation period of approximately 24 hours. If longer irradiations (such as one week) are used to increase the sensitivities of certain elements such as Ir and Os which might have low levels of concentration, the cooling period required before the sample can be safely processed is so long that most of the ^{109}Pd, ^{197}Pt and ^{105}Ru will have decayed. To circumvent this problem, the following procedure could be adapted: irradiate the sample for one week, or longer if advantageous, and allow it to cool to permit decay of activities of short to intermediate half-lives. Following this intermediate cooling period, the sample is re-irradiated for a short time, say about 6 or 8 hours, cooled for 3 or 4 hours, and then processed. If the longer lived isotopes of Pd, Pt, and Ru (that is 17 day ^{103}Pd, 4.4 day ^{193}Pt and 4.1 day ^{195}Pt, and 40 day ^{103}Ru) are counted, it may be possible to incorporate the analysis of 4.4 minute ^{104}Rh into a scheme with the other precious metals if such a procedure is adapted. For materials of very low precious metal content such as terrestrial rocks, sensitivity is the critical factor and longer irradiations are preferable, particularly for Ir and Os. Au, Pd and Ir can be determined by 1 day irradiations although Ir, at the concentration levels in G-1 and W-1 is quite difficult. Fission interference and low yields of ^{97}Ru make the determination of this element in common rocks and minerals impracticable by activation analysis.

CHAPTER II

SAMPLE PREPARATION

1. Whole Rock Analysis

Samples of the standard rock silicates G-1 and W-1 and of a sulphide standard supplied by Falconbridge Nickel Mines were obtained in a form suitable for direct analysis. 100 mg each of G-1 and W-1 and approximately 30 mg of the sulphide standard were weighed directly in quartz ampoules. The samples were sealed with polyethylene plugs.[1] Refer to Figure 2-1 for dimensions of the ampoules.

Some of the meteorite specimens required crushing which was performed under acetone in a small agate mortar known to be free of precious metals. Approximately 50 mg of each meteorite specimen was weighed into a quartz ampoule which was then capped with polyethylene.

To reduce the possibility of self-shielding by the sulphide during irradiation and to prevent losses upon opening the ampoule and transferring the sample from it, some of the sulphide standards were mixed inside the ampoule with approximately 100 mg of Analytical Reagent Grade Al_2O_3 which contained no detectable precious metals. The distribution of Al_2O_3 and sulphide is illustrated in Figure 2-1.

2. Individual Mineral Analysis

A flow sheet for preparation of individual mineral specimens is

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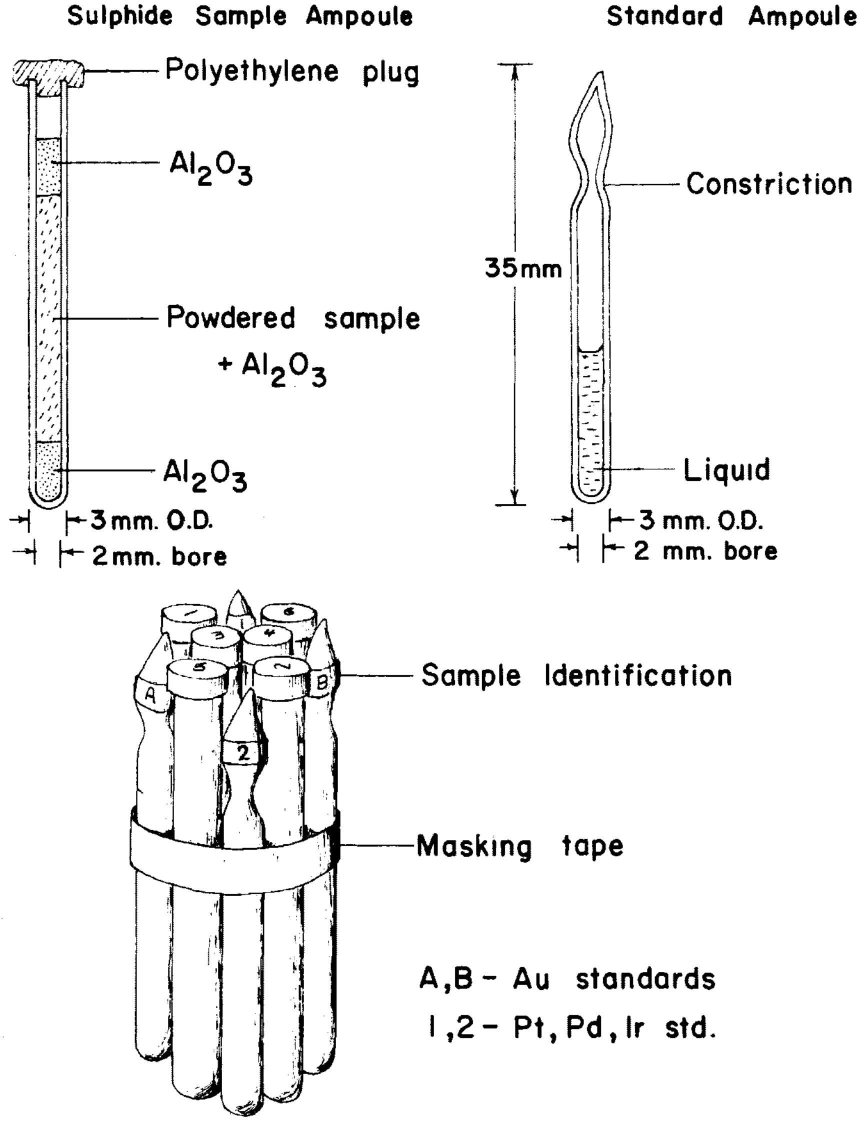
[1] To cap the ampoule, a small piece of polyethylene was melted and placed on the open end of the ampoule. The molten plastic was then partially pushed down to fill the space with a flat side of a pair of tweezers.



Samples and standards ready to be placed in Aluminum can for irradiation

Figure 2-1 Sample and Standard Irradiation Arrangement presented in Figure 2-2. Sample preparation consisted of disaggregating the rock and isolating the various mineral phases of interest. The majority of the specimens consisted of silicates plus pyrrhotite and chalcopyrite; in addition, some contained pentlandite, cubanite, and magnetite.

The sulphide samples were prepared by breaking apart a few grams of the specimen in a small steel percussion mortar which had previously been cleaned by crushing pure quartz in it. The crushed sample was sized in a small plastic sieve with silk bolting cloth to yield a fraction of 100-200 mesh size which was washed with distilled water and rinsed with acetone to remove the fines.

Two methods were used to obtain a rough concentrate of sulphide and oxides. In samples containing greater than 10% sulphide, it was usually possible to pre-concentrate the sulphide before screening by hand-picking sulphide grains. In specimens containing less than 10% sulphide, the sulphides were gravity concentrated after sizing by means of an elutriator (see Figure 2-3) which yielded a heavy mineral fraction consisting of 40-70% sulphides.

This rough concentrate was placed on a paper tray and magnetite and magnetic pyrrhotite were removed from it by the use of a hand magnet. This separated magnetic portion was concentrated by passing a hand magnet (wrapped in paper) through the concentrate and transferring the magnetics to a new paper tray, leaving behind the non-magnetics. This was repeated 15-25 times and resulted in a magnetic sulphide-oxide portion that was 99% pure. In general, the magnetite content was quite low so the concentrate consisted of essentially pure pyrrhotite. Samples of pure magnetite were obtained by hand-picking the coarsely-crushed specimen before screening.

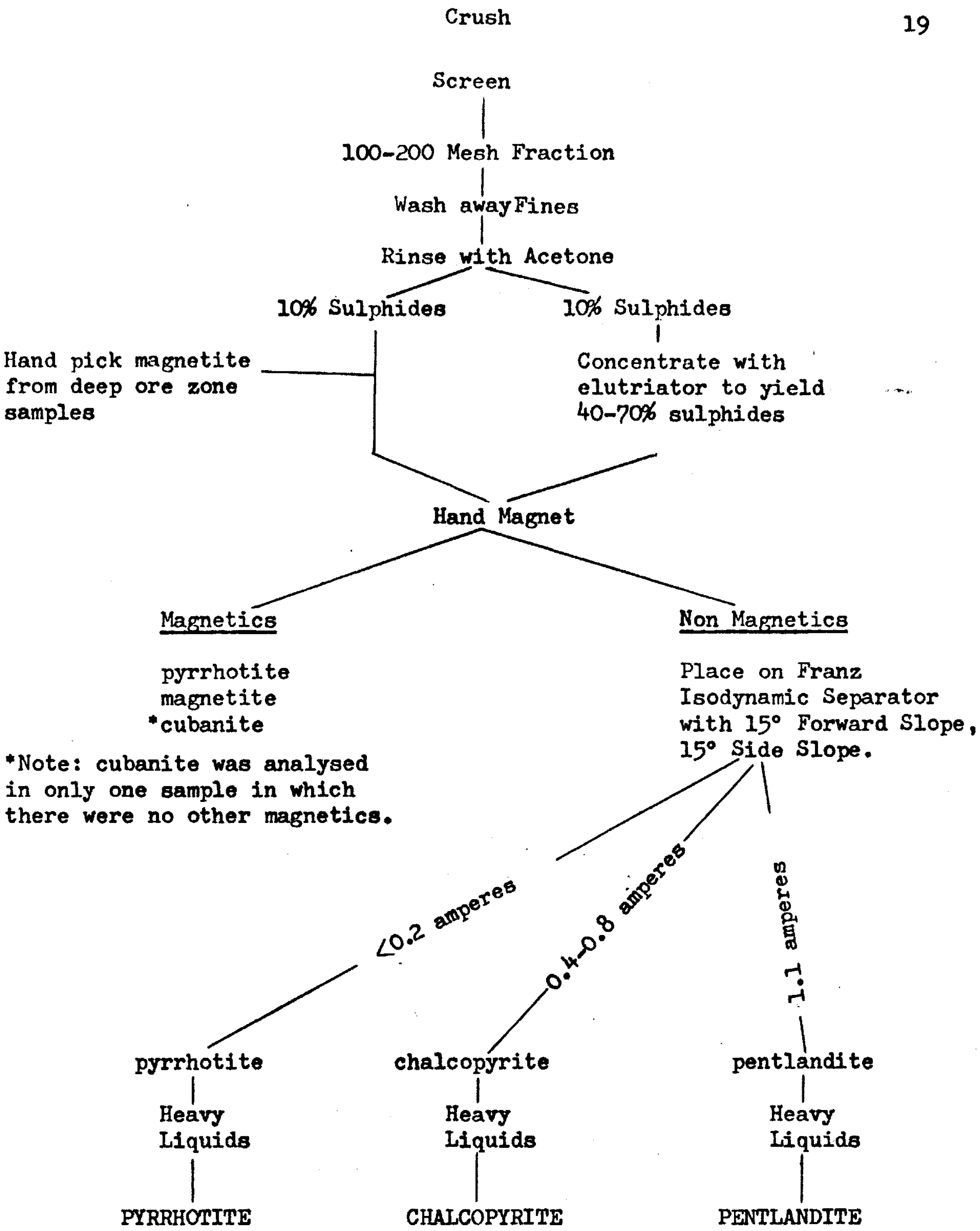


Figure 2-2 Flow sheet for separation of minerals of typical chalcopyrite-pyrrhotite-pentlandite assemblage.

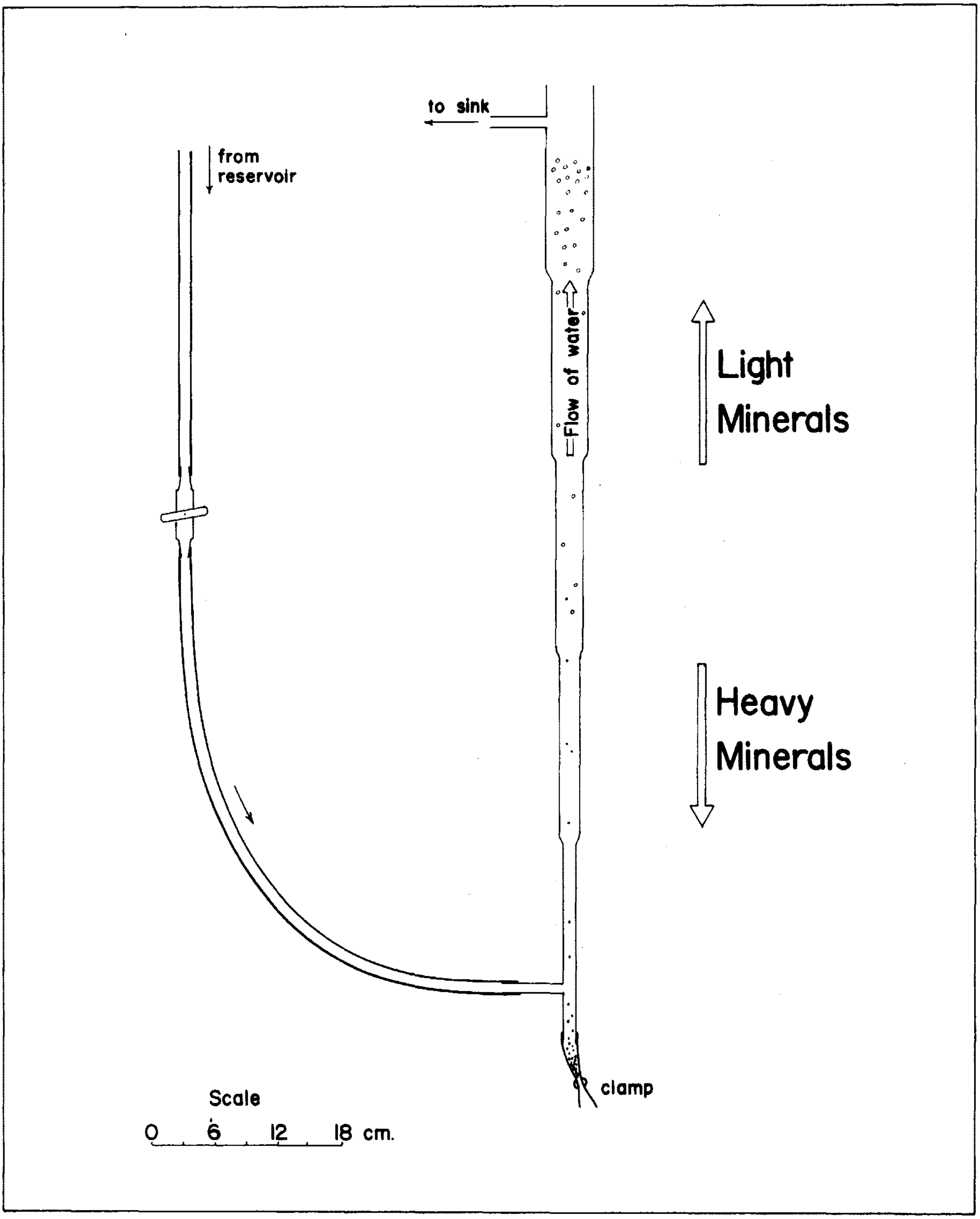


Figure 2-3. Illustration of elutriator used to concentrate heavy minerals.

In those specimens in which magnetite represented a significant proportion of the opaque phase, both hand-picked magnetite and magnetite plus pyrrhotite were analysed. The amount of precious metal in the pyrrhotite was then determined on the basis of a modal estimate of the pyrrhotite in the magnetite-pyrrhotite phase.

After removal of the magnetic fraction, the sample was placed on a Franz Isodynamic Separator which was set with a 15° side slope and a 15° forward slope. The current was adjusted first to remove as many of the non-sulphides as possible and later to concentrate each of the sulphide phases. Chalcopyrite was concentrated at a current setting of 0.4-0.8 amperes, pentlandite at a current setting of greater than 1.1 amperes, and "non-magnetic" pyrrhotite at a setting of 0.2 amperes or less.

In those samples in which silicates still persisted, heavy liquids (tetrabromethane and methylene iodide, specific gravities 2.96 and 3.33 respectively) were used to obtain a pure sulphide concentrate, the purity of which (determined by point counting) was at least 98%.

Millerite, bornite, and calcite specimens were hand-picked with the aid of a binocular microscope. Cubanite was concentrated with a hand magnet.

The pure mineral concentrate was pulverized under acetone in an agate mortar and 20-30 mg of the concentrate were weighed in quartz ampoules. The sulphide samples were mixed inside the ampoules with Al_2O_3.

3. Sample-Standard Positioning during Irradiation

After the sample ampoules were sealed they were arranged with the standard ampoules as shown in Figure 2-1. Standard ampoules containing the same precious metal(s) were positioned on opposite sides of the samples so that the average neutron flux seen by each pair of standards would be the average flux received by the samples.

CHAPTER III

FLUX MONITOR STANDARDS

1. General considerations

Selection of a standard to monitor the neutron flux involves consideration of several factors, including (1) variation in neutron flux, (2) flux attenuation, and (3) ease of chemical processing.

i) Variation in neutron flux. The standard should be as close as possible to the sample because of variation in the neutron flux. Bate *et al.* (1959) reported a 4 per cent flux gradient per inch along the axis of the irradiation can in the Argonne CP-5 reactor. Skippen (1963) reported a maximum variation of 5 per cent in the neutron flux in the McMaster Research Reactor across the sample container (an aluminum can 3/4" in diameter and 1 3/4" in length) on the basis of one experiment employing palladium as a target. The variation could be higher in another irradiation position.

ii) Flux attenuation. Differential self-shielding or flux attenuation between standard and sample whereby strong absorption of neutrons on the outside of material of high neutron absorption cross-section results in a decreasing flux gradient towards the interior of the sample could produce substantially different specific activities (counts per unit time per unit weight) between a sample and standard. Vincent and Crocket (1960) found that an evaporated acid solution containing a few milligrams of gold gave a specific activity some 37 per cent higher than a gold foil 0.002 inches in thickness. The neutron flux was 10^{11} neutrons cm^{-2} sec^{-1}.

The effect of differential self-shielding may be very serious if resonance effects are involved. Consider for example, the case of gold. ^{197}Au has a resonance energy level at 4.8 eV. For neutrons of this energy, the capture cross-section is 30,000 barns, 300 times greater than the cross-section of the metal when the neutron energy is 0.025 eV, the most probable energy of thermal neutrons. If thermal neutrons are involved, the neutron flux in a gold foil 0.002 inches thick will be 93.3% of the flux had the foil not been there (see Appendix B). However, if resonance energy neutrons were involved, only 5.6% of these neutrons would penetrate to the center of the foil. In general, the proportion of resonance energy neutrons to the total number of neutrons is small, but it is evident that the total flux will be depressed by an amount proportional to the percentage of resonance neutrons in this flux.

To avoid the possibility of differential self-shielding the standard should exhibit the same density of atoms as the sample and, ideally, be of the same weight as the sample.

iii) Standard Processing. Ease of processing and reproducibility of duplicates are prime requirements of a good standard. Such a standard might be one having the same matrix as the sample, and containing a known amount of the metal of interest. However, this type of standard would require the same extensive radiochemical processing as the sample. The best standard is one which requires a minimum of chemical processing.

One of the simplest forms of a standard would be a strip of the metal (e.g. Pd foil) wrapped around the sample ampoule. This type would minimize errors due to variations in neutron flux and would require little chemical processing. However, as Vincent and Crocket (1960) noted, metal foils introduce self-shielding problems. Skippen prepared standards by weighing a dilute acid solution of palladium into a vial and evaporating the liquid to dryness. Here again, there may be self-shielding by the standard: the metal would tend to remain in the liquid, and so the bulk of the metal would be concentrated in the last liquid to evaporate. The metal would then be irradiated as a mass rather than a thin film.

Two different types of standards were tested in this research. One type was prepared by weighing a drop of dilute acidic precious metal solution onto a mylar strip or an aluminum foil, evaporating to dryness with a heat lamp, and spraying with a commercial plastic fixative. This was the type of flux monitor used by Rushbrook and Ehmann (1962) for the determination of Ir, and by Bate and Huizenga (1963) for Os and Ru. In the gamma counting techniques used by the above it was possible to count the irradiated monitors directly, without chemical processing. This type of standard was discarded in the present research because beta counting methods were generally used and a separation of precious metal activities from the bulk activity of the mount was required. Also, the use of an aluminum mount did not permit the standard solution to be contained in an acid medium, which reacts with aluminum. As a liquid standard is prepared for use over periods of several months it should be stored in an acid medium to ensure stability of the standard.

The type of standard used in this research was a dilute acid precious metal solution. This solution was weighed into a quartz ampoule and placed next to the sample vial during irradiation. The advantages of a liquid standard are ease of processing, little or no flux attenuation, and good reproducibility. A disadvantage is the occassional generation of high gas pressure inside the ampoule after long (1 week) irradiations.[1] The high gas pressure can result in an explosion upon opening of the ampoule with consequent loss of the standard.

2. Preparation of Standard Solutions

The standards were prepared by weighing[2] solutions of known Pt, Ir, Pd and Au concentrations and densities into quartz ampoules the dimensions of which are given in Figure 2-1. It was necessary to make up two standards, one for Au and the other for Pd, Ir and Pt as ^{199}Au is produced from Pt by the reaction.

$$^{198}Pt\,(n,\gamma)\,^{199}Pt \xrightarrow{\beta^-} {}^{199}Au$$

i) Carrier Solutions. Solutions of each of the metals were prepared from "Specpure" palladium foil, gold foil, platinum sponge, and ammonium chloroiridate obtained from Johnson, Matthey and Company. The metallic Pd, Pt and Au were taken into solution with concentrated HCl and a minimum amount of concentrated HNO_3. Each of the solutions were then diluted to 100 ml with 3N HCl in a volumetric flask. The $(NH_4)_2IrCl_6$ was dissolved directly in 3N HCl and the solution diluted to 100 ml with the same reagent. The concentrations of the metals in each of these solutions were approximately 5 mg Pd/ml, 20 mg Au/ml, 20 mg Pt/ml, and 3 mg Ir/ml.

Aliquots of each of these solutions were taken to prepare the flux monitor standards. The remainder of the solutions were used as carrier solutions. Additional carrier solutions, prepared as required throughout

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[1] To keep the generation of gas to a minimum prepare the standard in a low acid medium (about 1-2N HCl) and use small standard ampoules.

[2] All weighing was performed on a 5-place "Mettler" balance.

the program, were made up from commercial grades of the metals and complexes in the same manner and concentrations as noted above.

ii) Standard Solutions. The carrier solutions were diluted to the desired concentration and appropriate aliquots taken and combined to give a standard solution containing 0.256 μg Pd/ml, 0.08711 μg Ir/ml, and 24.4 μg Pt/ml in 3N HCl solution. A standard solution containing 0.02017 μg Au/ml in 3N HCl was prepared by dilution from the Au carrier solution.

The densities of the standard solutions were determined with a calibrated 1 ml pipette by pipetting several 1 ml aliquots of the solutions into weighing bottles. The determination of the weights of these 1 ml aliquots permitted computation of the densities of the standard solutions.

3. Preparation of Standards

Approximately 25 mg of the standard solutions were inserted into weighed quartz ampoules by means of small polyethylene capillary pipettes. The inside walls of the ampoules above the liquids were carefully wiped out with paper tissue to ensure that no drops of solution adhered to the walls. (Weighed liquid stranded on the capillary walls could be lost on closure of the ampoule following weighing.). The capillary tubes plus liquid were then reweighed to give the weight of the liquid. After weighing, the tubes were sealed in a hydrogen flame.

CHAPTER IV

SEPARATION OF Pd, Ir, Pt and Au BY ANION EXCHANGE

1. Introduction of feed solution to resin bed.

The resin used in this research was chromatographic grade "Rexyn 201*(Cl)" which is a strongly basic organic exchange resin normally obtained in the chloride form. This resin is similar to "Dowex 2" except that it retains anionic species more strongly than "Dowex 2".

Table 4-1, reproduced from Hicks et al. (1953), delineates the behaviour of a large number of chemical species on "Dowex 2" resin. It can be seen from the table that if a complex sample is fed onto the resin beds in a solution of acid strength 1M in HCl or less, virtually all of the elements of the periodic table except the noble metals plus Sn, Hg, Bi, Sb, Ag, W and Po will pass through the resin. This results in a highly efficient separation of precious metals from the major constituents of many rocks and minerals.

The behaviour of Ir is more complicated than that of Pt, Pd or Au as its retention on the resin is dependant not only on the HCl molarity of the feed solution but also on the oxidation state of the metal. Figure 4-1, reproduced from Berman and McBryde (1958), illustrates the dependence of the distribution coefficients of platinum metal complexes on HCl molarity. Berman and McBryde measured the distribution coefficients of the metals in hydrochloric acid solutions relative to the anion exchanger Amberlite IRA-400 which has similar adsorption properties to Rexyn 201*.

Table 4-1 Elution of Elements from "Dowex 2" Anion Exchange Resin (After Hicks *et al.*, 1953)

Eluting Agent	Elements Eluted
12M HCl	Alkali Metals, Alkaline Earths, Rare Earths
	Sc, Y, Ti (III), V (II) (III) (IV), Ni, As (III) (V), Se (IV), Tl (I), Pb (II), Bi (III), Cu (II) slowly, Al, Cr (III), Fe (II), Mn (II).
6-9M HCl	Ti (IV), V (V), Ag*, Ta*, Pt (II), Zr, Hf.
3-6M HCl	Fe (III), Co, Ge, Nb*.
1-3M HCl	Zn, Ga, Mo (VI), In, Sn (IV), Te (IV), Te (VI), Pb (II).
Below 0.01M HCl	Sn (II), Hg (II), Bi (III), Sb (V) slowly.
3M $HClO_4$	Po, Cd, Sb (III), Sb (V) slowly.
1M NH_4OH	Pd, Ag, Sb (III), Sb (V).
1M NaOH	W.
Not eluted	Tc*, Ru, Rh, Re, Os, Ir, Pt (IV), Au (III), Tl (III).

* In trace concentrations only

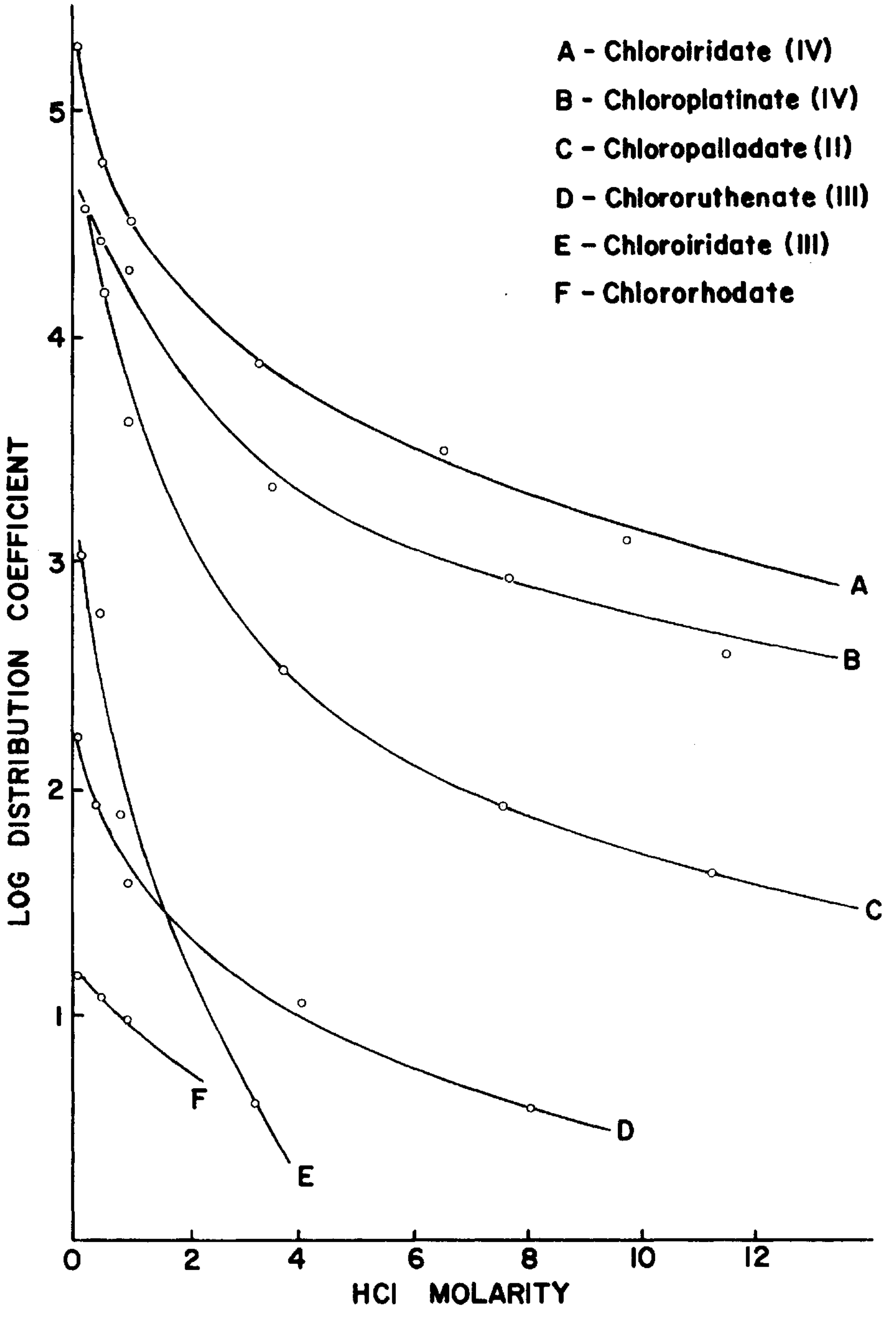

Figure 4-1 The distribution coefficients of rhodium, iridium, platinum, palladium, and ruthenium in hydrochloric acid solutions. (after Berman and McBryde)

As can be seen from Figure 4-1, the lower the chloride concentration, the more strongly the complexes adhere to the column. Hence, sample solutions should be fed onto the resin beds with the lowest HCl concentration feasible.

The distribution coefficient of Ir(III) is 1700 times less than that of Ir(IV) at a molarity of 0.5. Maximum adsorption of chloroiridate (IV) by the exchanger necessitates the presence of an oxidizing agent because the resin is a mild reducing agent and capable of reducing Ir(V) as demonstrated by Cluett et al. (1955). Berman and McBryde found that cerium(IV) is an effective oxidant although the use of Ce limits the acid concentration permissible to the range 0.5M to 1M. In acid solutions below this range the ceric salts start to hydrolyse while in solution possessing a greater molarity than 1M, chloride is oxidized to chlorine. For greatest adsorption of the complexes on the column, considering all the factors, an acid concentration of 0.5M HCl is recommended.

Rushbrook and Ehmann (1962) used a 0.7M HCl solution containing 0.002 moles of $(NH_4)_2Ce(NO_3)_6$ per ml to stabilize Ir(IV) when introduced to a "Dowex 1-x8" anion exchange column 12.5 cm in length and 8 mm in diameter. In the present research it was found that a carrier solution containing 0.002 moles of $(NH_4)_2Ce(NO_3)_6$ per ml resulted in low yields for Ir, but when the ceric ion concentration was doubled, satisfactory yields were obtained. Whether this difference in results between the two sets of conditions was due to the type of resin used or the dimensions of the columns involved (12.5 cm length compared to 1.5 cm length in this research) was not investigated.

The ceric complex decomposes rapidly, even when the solution is within the proper chloride molarity range. In order that the oxidant remain effective throughout the introduction of the feed solution to the column, it is necessary to have a high initial concentration of ceric ion and the solution must be as freshly prepared as possible.

2. Elution of the complexes from the column.

When the complexes are adsorbed by the anion exchange resin in the presence of ceric ion, the metals are present in their highest oxidation states. They may be recovered from the exchanger by several different eluting agents.

$Pd^{II}Cl_6^{-4}$ is the most easily eluted of the complexes. It can be removed with concentrated HCl solutions (greater than 9M HCl), dilute ammonical solutions (1M NH_4OH), dilute thiourea solutions (i.e. 0.1M thiourea in 0.1M HCl), and with dilute perchloric acid solutions (i.e. 0.5M $HClO_4$).

The elution of Ir(IV) is most conveniently accomplished by first reducing the ion to the tervalent state with a reducing agent such as a 1% solution of hydroxylamine hydrochloride. This reagent removes part of the Ir(III) while the remainder is readily eluted with 2M HCl or acids of greater strength, as can be observed from Figure 4-1. Berman and McBryde (1958) report recoveries of 88 to 96% employing this type of procedure. They also report that ammonical solutions and perchlorate solutions yield the same order of recoveries. In the present research, a solution consisting of 0.1M thiourea in 0.1M HCl, which was used to elute Pd, Pt and Au from the column, was found to reduce the Ir(IV) to the tervalent state but elute none of it. The thiourea solution was followed by 100 ml of 6M HCl which removed 95 to 100% of chloroiridate (III).

The most satisfactory eluting agent for Au(III) is a solution of 0.1M thiourea in 0.1M HCl. Baedecker (1964) used this elutant to remove Pt, Au and Hg from an anion exchanger. During the early stages of the present work, low chemical yields were obtained for gold. This was thought to be due to incomplete recovery of the gold from the exchange resin. It was believed that the thiourea removed part of the gold but the remainder of the metal was unavailable to the eluting agent. To correct for this, part of the Au(III) was removed with thiourea and aqua regia was then added to "release" the remainder of the Au(III) which was eluted with a further addition of thiourea. Introduction of the aqua regia step appeared to improve recoveries of Au considerably. However, a tracer experiment late in the research programme showed the aqua regia step to be unnecessary. Figure 4-2 presents the results of the experiment using ^{198}Au as a tracer and shows that approximately 150 ml of thiourea will elute all the Au while 90% of the Au is eluted by 100 ml of thiourea. The early loses of Au were due to incomplete recovery of the metal from the thiourea, after the elution step.

According to Berman and McBryde dilute or concentrated solutions of HCl, HNO_3, or H_2SO_4 do not quantitatively elute Pt(IV). They found quantitative recoveries of the chloroplatinate(IV) could be achieved with 2.4M solutions of either zinc chloride or cadmium chloride in 9M HCl if the column was surrounded by a hot-water jacket at 96°C. They also found that 60 ml of 2.4M $HClO_4$ would quantitatively remove the Pt(IV). In the present work, however, it was found 2.4M $HClO_4$ was an ineffective elutant for Pt(IV), removing only 50% of the complex in the first 50 ml of solution. A tracer experiment (see Figure 4-3) showed that a 0.1M solution of thiourea

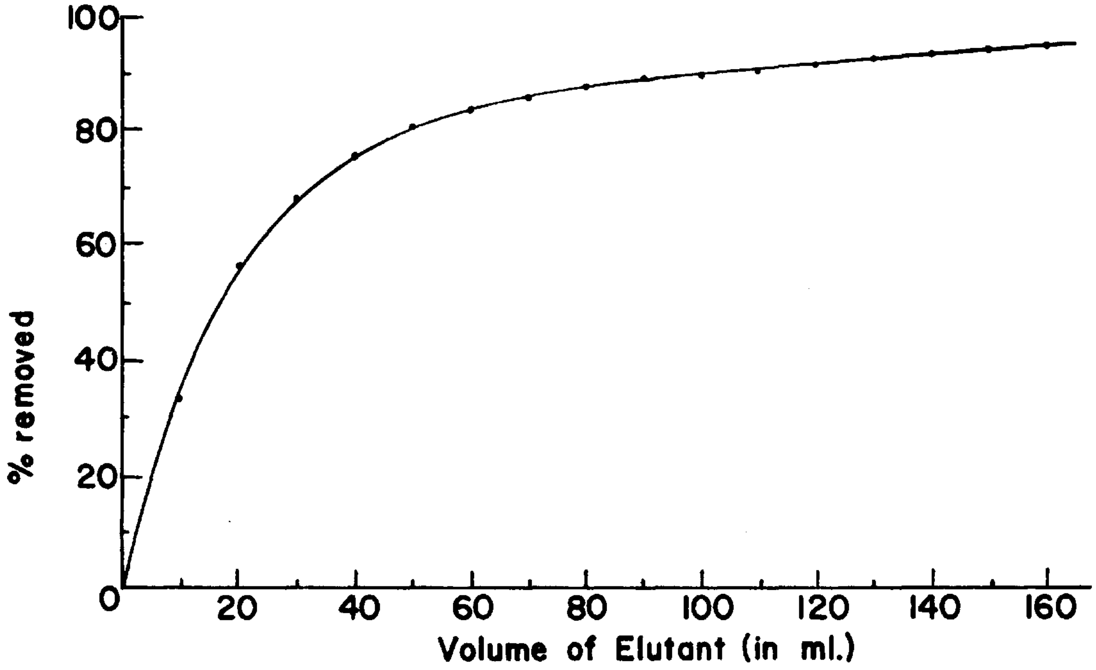

Figure 4-2 Elution of Au^{III} from Rexyn 201 resin with 0.1 M thiourea in 0.1 M HCl

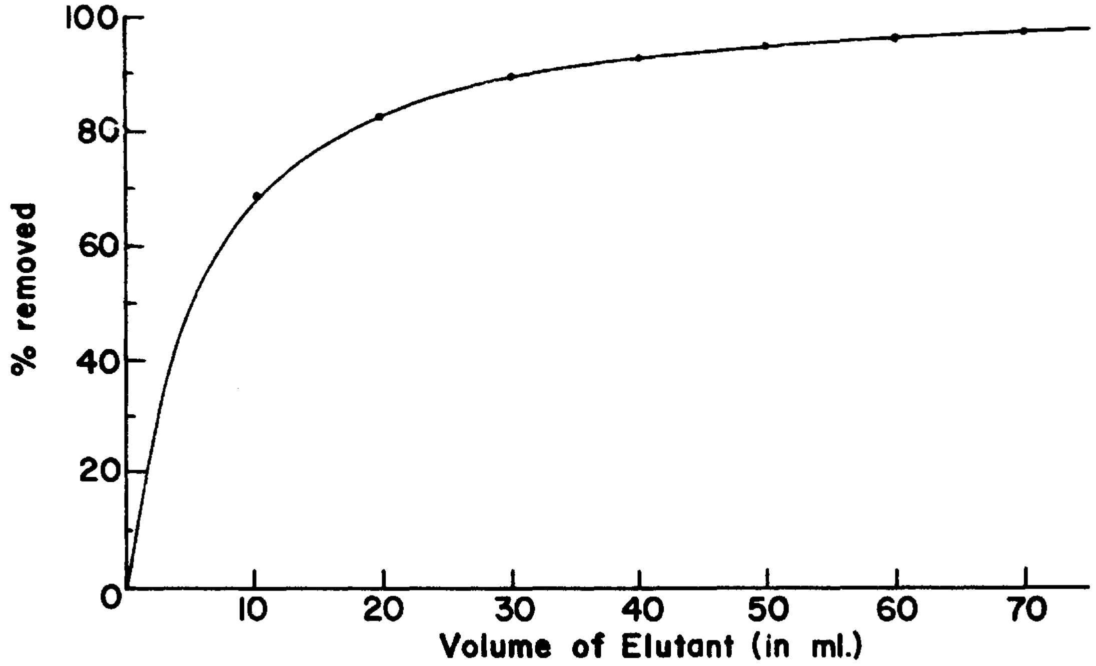

Figure 4-3 Elution of Pt^{IV} from Rexyn 201 resin with 0.1 M thiourea in 0.1 M HCl

in 0.1M HCl was an effective eluting agent, stripping 98% of the Pt(IV) in 70 ml of solution.

In the early stages of the research program, only the five platinum metals were analysed. As Os and Ru were removed by distillation of the tetroxides Pt, Pd, and Ir were fed onto the column. Preferential elution of the metals off the column was used to separate the metals. This was accomplished by reducing Ir^{+4} to Ir^{+3} with 1% hydroxylamine hydrochloride and eluting the Ir^{+3} with 2 N HCl. This was followed by elution of Pd with 9 M HCl and then elution of Pt with 2.4 M $HClO_4$. Later in the program, analysis of Au was incorporated into the program. As the most satisfactory eluting agent for Au(III) is a solution of 0.1M thiourea in 0.1M HCl which also elutes Pd and Pt and reduces Ir^{+4} to Ir^{+3}, this reagent was used to elute Au, Pd, and Pt and reduce Ir^{+4} to Ir^{+3} which was eluted with 6M HCl.

CHAPTER V

EXPERIMENTAL METHOD

Figure 5-1 is a flow sheet of the analytical method developed during the course of this research. Only the "non-volatile" elements, Pd, Pt, Ir and Au were determined by the writer while Os and Ru were determined on the same specimens by S. Hsieh. The method has been used in its entirety for analysis of meteorites and in one experiment for analysis of G-1 and W-1. Details of the method for Os and Ru are found in Hsieh (1967). The following procedure is used when all six elements are to be determined.

The irradiated sample and carriers are fused in an alkali flux, the fusion cake is leached with H_2O and transferred to the distillation flask of the apparatus shown in Figure 5-2. After addition of H_2SO_4 and H_2O_2, OsO_4 is distilled at 85 to 90°C and absorbed in NaOH. The OsO_4 is purified by a solvent extraction procedure involving extraction into CCl_4. Metallic Os is precipitated by a zinc reduction step and the metal is mounted on a vycor planchet for counting.

After distillation of OsO_4, the distillation flask is cooled to 40°C, $NaBrO_3$ is added, and the flask is heated to 105°C. The distilled RuO_4 is caught in cold NaOH and purified by a precipitation procedure involving precipitation of RuO_2 by addition of ethanol to the RuO_4-NaOH solution. The RuO_2 is dissolved and Ru° metal is precipitated with Zn.

The residual solution in the distillation flask is transferred to a 400 ml beaker and evaporated to a volume of 30 ml. It is then trans-

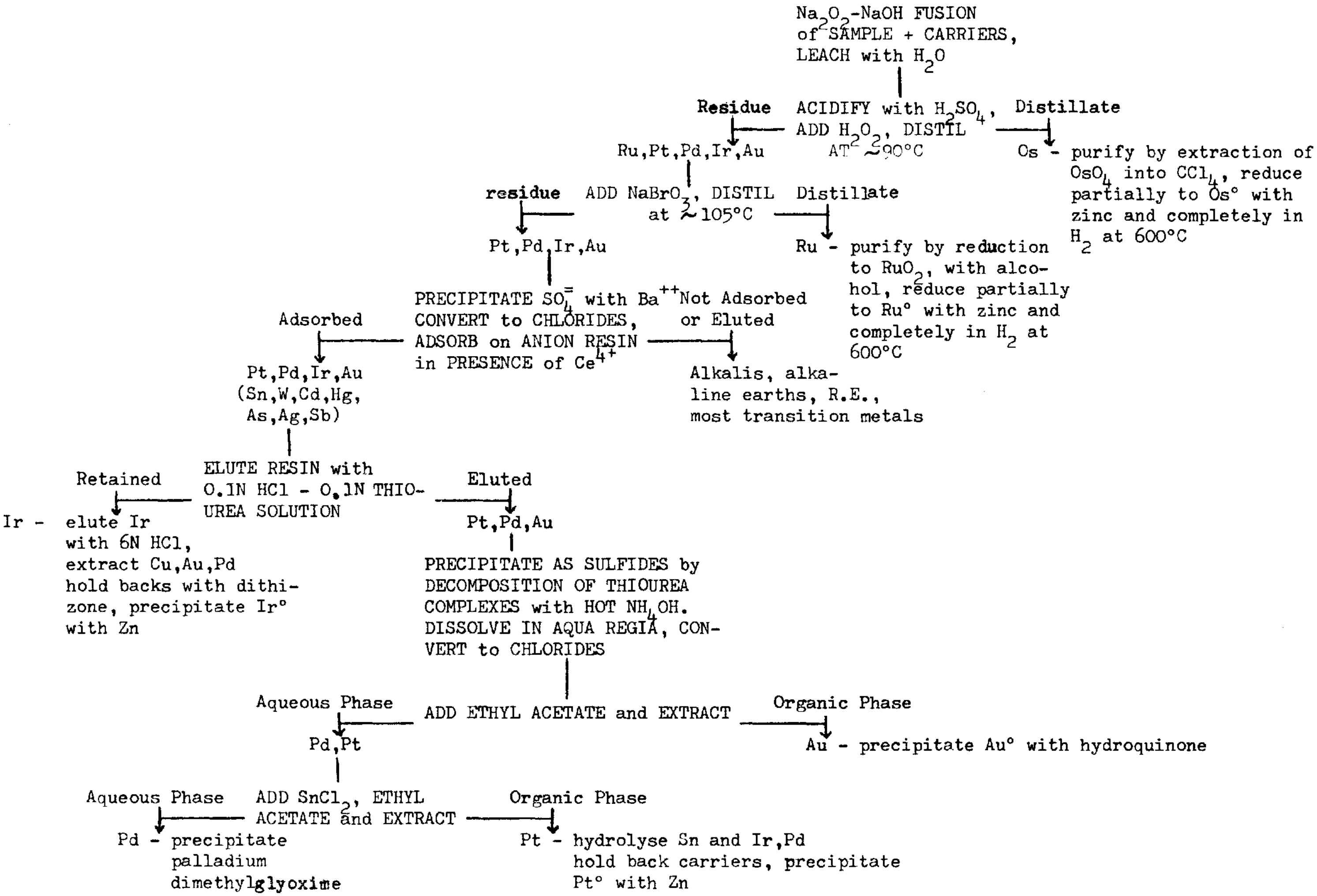

Figure 5-1. Generalized Flow Chart for Precious Metal Analysis Procedure

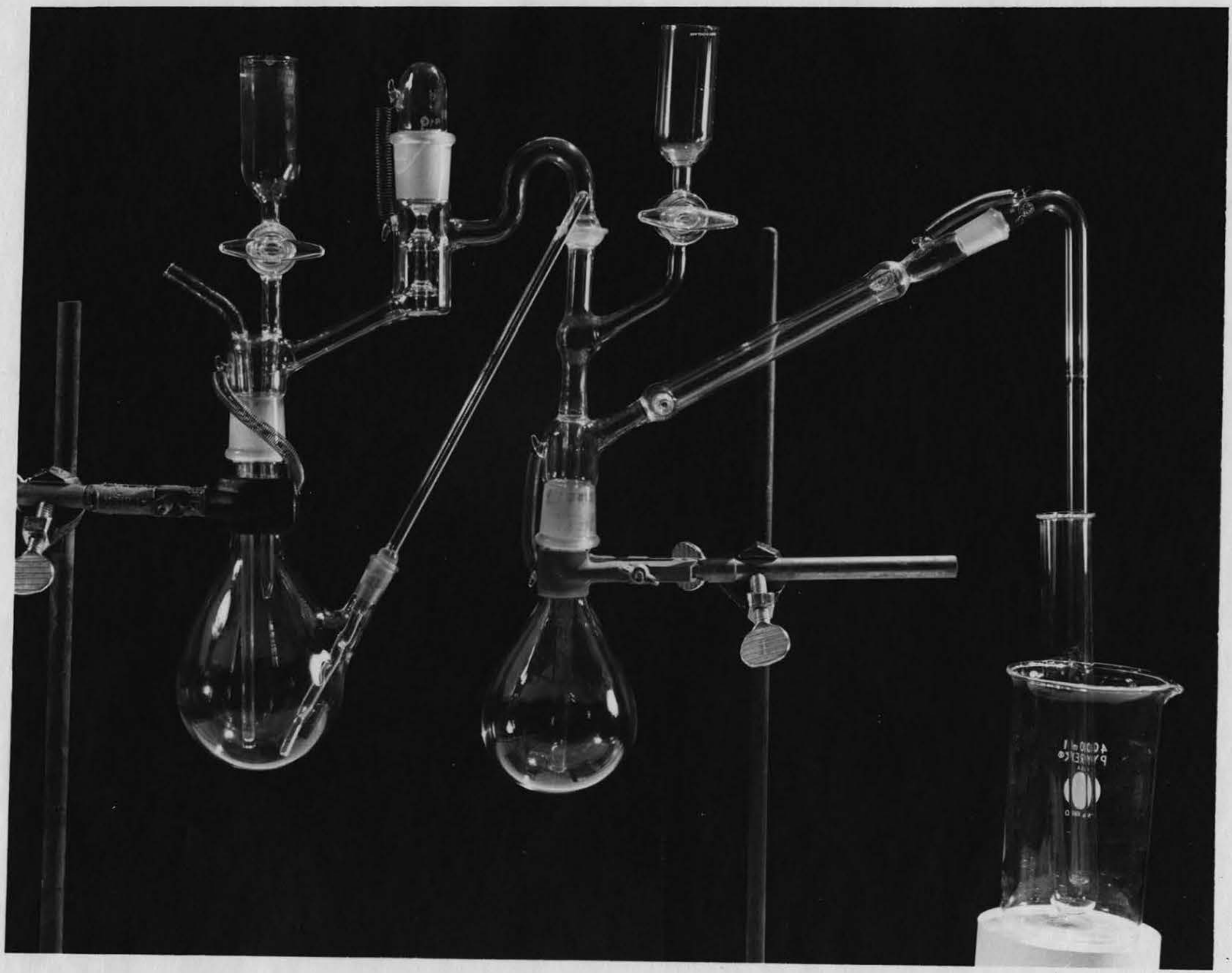

Figure 5-2. Distillation apparatus used for distillation of OsO_4 and RuO_4

ferred to a centrifuge tube and a sufficient quantity of a saturated $BaCl_2$ solution is added to precipitate all sulphate as $BaSo_4$. After removal of the sulphate, the solution is transferred to a 400 ml beaker and evaporated to dryness. The salts are digested in aqua regia and the procedure as outlined in detail below starting in Step iii, under Dissolution, is followed for determination of the non-volatile metals.

1. Analytical Procedure for Samples.

i) Carrier. Add 1 ml Pd (5 mg Pd/ml), 1 ml Au (20 mg/ml), 1 ml Pt (20 mg/ml), and 3 ml Ir (3 mg Ir/ml) carrier solutions to a 25 ml. zirconium crucible and carefully evaporate to dryness under an infra-red lamp. Adjust a stream of clean air to flow across the lips of the crucibles to facilitate evaporation. The salts of the metallic complexes will precipitate on the bottom of the crucible.[1]

ii) Fusion. Cover the evaporated salts in the crucibles with 1 gram of Analytical Reagent grade Na_2O_2 and transfer the irradiated samples from the quartz vial to the crucible.[2,3] Cover the sample with another gram of Na_2O_2 and add 2 grams of NaOH pellets. Cover the crucible and heat over a weak meeker burner flame for 2 or 3 minutes until the flux darkens to prevent splattering. Finally, increase the flame until the bottom of the crucible is a bright cherry red and continue heating for 5-10 minutes.

iii) Dissolution. Allow the crucible to cool and carefully add 10 ml of H_2O. Transfer the contents of the crucible 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. Carefully add concentrated HCl to the beaker until the solution is acidic and clear. (A few flecks of silica will be present following a silicate fusion.) Place the beaker on a hot plate and evaporate to incipient dryness with the aid of an infra-red lamp and an air stream. Cover with a watch glass, add 10 ml aqua regia (1 HNO_3;3HCl), and digest the salts in the acid for 10 minutes.[4] Take to dryness, add a second 10 ml portion of aqua regia, and again evaporate to dryness. Add 6 ml of concentrated HCl and evaporate to dryness. Add a further 6 ml of HCl and evaporate to incipient dryness. 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.[5] The double treatment with HCl is necessary to ensure complete removal of HNO_3. Dissolve the salts in 30-40 ml of 0.5M HCl which contains 0.004 moles of ceric ion per ml of solution (prepare by dissolving 1.096 grams of Ce^{+4} (NH_4)NO_3 in 10.0 ml of 0.5 M HCl and add 1 ml of this solution to every 49 ml of 0.5 M HCl).

iv) Ion Exchange. Filter the solution through a Whatman № 41 paper onto an anion exchange column (see Figure 5-3) pretreated immediately prior to the introduction of the sample solution with 50 ml of 0.5M HCl containing ceric ion. It is important to pretreat the column as rapidly as possible to keep the cerium in the quadrivalent oxidation state.[6] Rinse the beaker and filter paper with a few ml of 0.5M HCl. Allow the sample solution to pass through the resin bed at the rate of 1 ml/minute.

Elute Pd, Pt and Au with 130 ml of 0.1 M thiourea solution which is 0.1 M in HCl into a 400 ml beaker. Wash the column free of thiourea with 2 or 3 ml of H_2O and add to the main thiourea solution. Add 15 ml of concentrated NH_4OH to the thiourea solution, place on a hot plate,

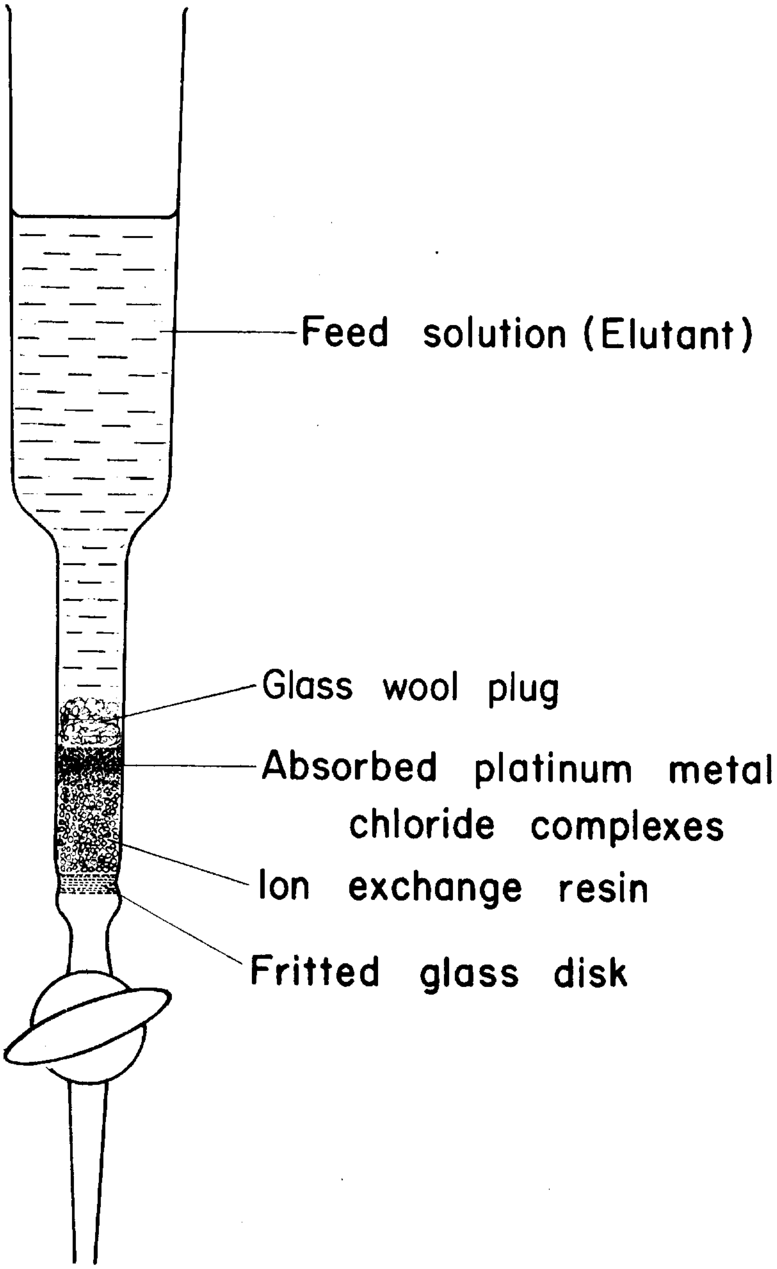

Figure 5-3 Illustration of Ion exchange column. Glass wool plug prevents disruption of resin upon addition of solutions to column.

and evaporate to about a 50 ml volume.[7]

Elute Ir with 100 ml of 6M HCl and collect the elutant in a 250 ml beaker. Add 10µgCu, 10µgAu, and 10µgPd as chlorides.[8] Place on a hot plate and evaporate to a few ml.

v) Gold, Palladium, Platinum

a) The addition of NH_4OH to the thiourea solution causes precipitation of the sulphides of Au, Pd and Pt. When the volume of the solution has been reduced to 50 ml, transfer with the aid of ethanol to a 60 ml centrifuge tube. Centrifuge and discard the supernatant. Wash the precipitate with hot H_2O and ethanol. Discard the washings. Slurry the sulphides with ethanol and transfer to a 50 ml beaker with a disposable pipette. Place on low heat and take to dryness. Add 5 ml of aqua regia, cover, and digest for 10 minutes.[9] Add holdback carriers containing 1 mg Ir and 10µgCu as the chlorides. Evaporate to dryness and remove HNO_3 with two treatments of conc. HCl. Take up in 15 ml of 6M HCl, transfer to a 125 ml separatory funnel, and extract the Au into 15 ml of ethyl acetate by shaking for 1 minute. Transfer the aqueous phase to a fresh separatory funnel and reserve for determination of Pt and Pd.

b) Gold Add 15 ml of 6M HCl to the separatory funnel containing the $AuCl_4^-$ and shake for 1 minute. Discard the HCl. Pour the organic phase into a 100 ml beaker and add 20 ml of 2M HCl. Place over a low heat source and evaporate the ethyl acetate. The $AuCl_4^-$ passes into the aqueous phase. When the organic layer is no longer visible, boil the solution strongly to drive off any ethyl acetate dissolved in the aqueous phase. Allow the temperature of the solution to drop to 50 to 60°C and add 0.5 grams of hydroquinone to precipitate Au°. Transfer to a centrifuge tube, centrifuge and discard the supernatant. Wash the precipitate twice with H_2O and ethanol, then with ethanol alone, and plate out on a pre-weighed Cu planchet.

c) Platinum Add 20 ml of ethyl acetate to the aqueous phase from step v(a) and shake for 1 minute. Discard the organic phase. Add 5 ml of 10% $SnCl_2$ solution to reduce $PtCl_6^=$ to $PtCl_4^=$.[10] Extract the $PtCl_4^=$, with two 15 ml portions of ethyl acetate. Transfer the aqueous phase, which contains $PdCl_4^=$, to a 100 ml beaker, and evaporate on a hot plate. Add 1-2 ml of 10% $SnCl_2$ and 25 ml of 6M HCl to the organic phase and shake for 1 minute. Discard the aqueous phase and repeat. Transfer the organic phase to a 100 ml beaker, add 1 mg Cu, 1 mg Fe, and 1 mg Au as chlorides and evaporate to dryness. Destroy the organic residue with a few ml of aqua regia and convert to chlorides by two treatments with concentrated HCl, heat to near boiling, and adjust the solution to pH of 1.5 by adding 6M NaOH to precipitate the hydrated oxide of tin.[11] Heat solution to boiling, add 10 ml of 10% sodium nitrite, and boil the solution for 2 to 3 minutes to convert $PtCl_6^=$ to $Na_2\left[Pt(NO_2)_6\right]$. Adjust the pH to 10 by the addition of 6M NaOH and $NaHCO_3$ to precipitate Au, Cu and Fe (Pt stays in solution).[12] Transfer to a centrifuge tube and centrifuge. Filter the supernatant through a Whatman N° 41 filter paper into a 100 ml beaker. Add concentrated HCl to destroy the platinum-nitro complex and any excess sodium nitrite. Evaporate to dryness, treat with aqua regia, then with two portions of HCl, and take up in 2M HCl. Warm the solution over a hot plate and reduce the $PtCl_3^=$ to Pt° with Zn°. Centrifuge and decant the washings.

Wash the precipitate twice with H_2O and ethanol, then once with ethanol. Slurry with ethanol, transfer to a copper planchet, and dry with infrared heat.

d) Palladium Reduce the volume of aqueous phase from step v(c) containing the $PdCl_6^=$ to 3-4 ml. Add H_2O until the total volume is 20 ml and transfer to a centrifuge tube. Add 5 ml of 1.5% dimethylglyoxime in ethanol to precipitate Pd-dimethylglyoximate and centrifuge. Decant the supernatant and wash the precipitate with enough ethanol to reduce the surface tension of the precipitate. Centrifuge and discard the washings. Destroy the precipitate by adding a few ml of aqua regia and carefully warming the centrifuge tube. Destroy the HNO_3 with two treatments of concentrated HCl. Take the $PdCl_4^=$ up in 10 ml of 2M HCl, add 10 ml of H_2O, and then 5 ml of 1.5% dimethylglyoxime in ethanol. Centrifuge the resulting precipitate, decant the supernatant, wash the precipitate twice with H_2O and ethanol, then once with ethanol, and plate out on a pre-weighed aluminum planchet.

vi) Iridium $IrCl_6^=$ is contained in the second elutant obtained from step (iv). Evaporate the solution to 1-3 ml and take up in H_2O such that the solution is 0.5M in HCl. Transfer to a separatory funnel and add 20 ml of 0.001% dithizone in chloroform.[13] Shake for 1 minute. The dithizonates of Cu, Ag, Au and other metals are extracted into the chloroform. Repeat the extraction until the aqueous phase causes no discolouration of the dithizone solution. Flush out all traces of dithizone with pure chloroform. Transfer into 100 ml beaker, place on a hot plate, and evaporate to dryness. Treat with aqua regia, destroy any HNO_3 with two treatments of HCl and take up in 2M HCl. Place on a hot plate and precipitate Ir° with Zn° powder.[14] Centrifuge, decant supernatant and treat the metal with aqua regia for a few minutes. Add H_2O and centrifuge. Decant the liquid. Wash the Ir° twice with H_2O and ethanol, then once with ethanol, and plate out on a copper planchet and dry with an infra-red lamp.

2. <u>Analytical Procedure for Standards</u>.

i) Immerse the vial containing the standard solution in hot 6M HCl. Remove and wipe the vial thoroughly with tissue to remove any absorbed radioactivity. Warm the top of the ampoule to drive any vapour down the ampoule into the solution. Cool the vial thoroughly, scratch and break at the constriction. Place the ampoule containing the Au standard in a 50 ml beaker containing 1 ml of Au carrier, and the ampoule with the Ir, Pd and Pt standard in a beaker containing 1 ml Pd, 1 ml Au, 1 ml Pt and 3 ml Ir carriers. Each beaker also contains 1 mg of NaCl to act as a holdback carrier for any active sodium and a total of 10 ml solution approximately 6M in HCl. Cover, place on a hot plate and heat gently so that air is driven out of the ampoule. Remove from the hot plate and cool. The carrier solution will enter the tube and interchange with the standard solution. Place on a hot plate and heat for 20 minutes. With the aid of a capillary disposable pipette transfer the solution to a new 50 ml beaker. Quantitatively flush all traces of the irradiated standard solution from the ampoule with the carrier solution. Wash the ampoule twice with hot 6M HCl and transfer the washings to the main solution. Discard the empty vial to active waste.

ii) <u>Gold</u> Transfer the Au solution to a 125 ml separatory funnel and increase the volume to 20 ml 6M in HCl. Add 20 ml of ethyl acetate and shake for 1 minute to extract the $AuCl_4^-$. Discard the aqueous phase and continue as for the samples in section v(b).

iii) Platinum, Palladium, Iridium and Gold Transfer the standard solution containing Pt, Pd, Ir and Au into a 125 ml separatory funnel, rinse the beaker with 6M HCl, and pour the rinsings into the separatory funnel. The volume in the funnel should be 20 ml. Add 20 ml of ethyl acetate and shake for 1 minute. Run the aqueous phase into a fresh separatory funnel and retain for the determination of Pt, Pd, and Ir. The organic phase contains ^{199}Au produced from the decay of ^{199}Pt. Treat this phase as for the sample Au in section v(b).

Add 20 ml of ethyl acetate to the separatory funnel containing the aqueous phase and shake for 1 minute. Discard the organic layer and run the aqueous layer into a 100 ml beaker. Place on a hot plate, evaporate to a small volume, and add 10 ml of H_2O. Add 5 ml of 10% $NaBrO_3$ and heat. Adjust the pH of the boiling solution to 6 or 7 first with NaOH and finally with $NaHCO_3$. Add a second 5 ml portion of 10% $NaBrO_3$ and boil to coagulate the hydrated oxides of Ir and Pd. Pt stays in solution. Transfer to a centrifuge tube and centrifuge.

iv) Platinum Filter the supernatant through a Whatman N° 41 paper into a 100 ml beaker. Place this on a hot plate, evaporate to incipient dryness, and digest the salts with aqua regia to destroy any $NaBrO_3$. Convert to chlorides with two portions of concentrated HCl and take up in 20 ml of 3M HCl. Transfer to a separatory funnel and treat as for the sample Pt in section v(c) with the following exceptions. Do not add Cu, Fe or Au holdback carriers or perform the subsequent hydrolysis of these metals in the presence of sodium nitrite. However, it is necessary to hydrolyze Sn at pH 1.5 and remove the precipitate. After the removal of the tin, acidify the solution with concentrated HCl and precipitate Pt° with Zn powder, as in the sample procedure.

v) Palladium Wash the hydrated oxides of Pd and Ir with hot H_2O, centrifuge, and discard the washings. Destroy the oxides with aqua regia and treat twice with concentrated HCl to destroy HNO_3. Take the chloride complexes up in 20 ml of 1M HCl. Add 5 ml of 1.5% dimethylglyoxime to precipitate the Pd and continue with the palladium as for the samples after the first precipitation with dimethyglyoxime in section v(d).

vi) Iridium Filter the supernatant through a Whatman N° 41 paper into a 100 ml beaker. Place on a hot plate, evaporate to dryness and destroy the excess dimethyloglyoxime with aqua regia. Treat the residue twice with concentrated HCl and take up in 2M HCl. Add Zn powder to precipitate Ir°. Transfer to a centrifuge tube, decant the aqueous phase, wash the Ir° twice with H_2O, and ethanol, once with ethanol, and plate out the Ir on a pre-weighed copper planchet.

3. Notes on the Analytical Method

1. The addition of the carrier prior to the fusion of the sample ensures complete interchange of active Pd in the sample and inactive Pd from the carrier. This interchange is absolutely necessary. The high temperature of the fusion (~700°C) promotes high mobility of all species in the molten fluxes.

With $PtCl_6^=$ in the carrier solution, it is necessary to dry out the salts immediately prior to fusion, because $PtCl_6^=$ is deliquescent and the presence of H_2O destroys the peroxide.

2. The use of Na_2O_2 as a flux has been discussed by Rafter (1950). The NaOH and Na_2O_2 produce a strongly oxidizing, alkaline environment in the crucible and ensure dissolution of Os, Ru and Ir which are practically insoluble by any other means. The alkali flux oxidizes Os and Ru to the VIII state which permits the distillation of their tetraoxides.
3. All chemicals used in the procedure are of Analytical Reagent Grade.
4. Digestion in aqua regia converts the precious metals to chloro-complexes in their highest oxidation states. The aqua regia treatment must be followed by a digestion with concentrated hydrochloric acid to remove all HNO_3, as nitrate would interfere with many of the subsequent analytical steps. In this procedure aqua regia digestions are always followed by evaporation of the solution to incipient dryness and subsequent removal of traces of nitrate by two digestions with concentrated HCl.
5. The last traces of HCl must be driven off in order to control the pH of the solution when placed on the ion exchange resin.
6. In steps involving Ce^{+4} it is necessary to complete the chemistry as rapidly as possible to minimize hydrolysis of the ceric complex.
7. Do not have hydrochloric acid fumes in the same fume hood as thiourea solutions undergoing evaporation. Also, do not evaporate the thiourea solutions to less than 1/3 of their original volume. Both HCl fumes and excessive evaporation of the thiourea result in dissolution of the sulphides.
8. In the presence of large quantities (that is, greater than 10 p.p.b.) of iridium such as are found in carbonaceous chondrites, virtually radio-

chemically pure Ir° may be precipitated directly from the 6M HCl eluant. In this case, do not add the holdback carriers or perform the subsequent dithizone extraction. In chalcopyrite specimens, ^{110}Ag is the chief radiochemical contaminant. The addition of two portions of $AgNO_3$ will scavenge all Ag activity and, again, it is not necessary to perform a dithizone extraction, especially if the Ir° is determined by gamma counting.

9. It is advisable to dissolve the sulphides in a small beaker rather than in the centrifuge tube as the short time of aqua regia treatment in a tube is insufficient to dissolve all of the Pd sulphide.
10. The stannous chloride solution should be prepared fresh for each experiment as $SnCl_2$ oxidizes to $SnCl_4$ on standing. If it is desired to avoid weekly preparations of reagent, keep the stannous chloride in a dark, cool location with a piece of metallic tin in the solution.
11. The hydrated oxide of tin becomes colloidal at alkalinitis greater than pH=7. It is therefore necessary to centrifuge the sample and dispose of the precipitate before addition of the sodium nitrite.
12. Gilchrist (1943) states that in boiling solutions containing sodium nitrite,gold is precipitated as the metal at pH=6 and copper and iron are precipitated as hydrated oxides at pH=10. The platinum nitro-complex is stable in boiling solutions up to pH 14.
13. $IrCl_6^=$, Fe^{+++}, and $PtCl_6^=$ all oxidize dithizone and hence prevent extraction. Various reagents may be used to convert $IrCl_6^=$ to $IrCl_4^=$, $PtCl_6^=$ to $PtCl_4^=$ and Fe^{+++} to Fe^{++} but the most effective means of performing these reductions without altering the forms of the extractable complexes is to shake the sample solution with a concentrated solution of dithizone.

The concentrated dithizone reduces the metals to their lower oxidation states, thus eliminating the interference effects of Fe^{+++}, etc.

14. To perform the Zn precipitation properly, warm the solution to 70°-80°C and slowly add an excess of Zn. Then, add concentrated HCl to dissolve the Zn excess. Follow with a further addition of Zn and then HCl. Some of the Ir will precipitate as $IrO_2.H_2O$ with a single treatment of Zn and will subsequently be lost when the precipitate is treated with hot 2M HCl. Repeated additions ensure that most of the Ir in the precipitate is present as metallic Ir.

CHAPTER VI

COUNTING EQUIPMENT AND TECHNIQUES

1. Beta Counting

i) Equipment For beta counting a low background Nuclear Chicago planchet counting system which included the following principal components was used: scaler-timer, automatic sample changer, gas flow Geiger-Mueller counting tube with coincidence shielding, and a paper tape printing lister which gave a record of sample number, time and count data. The system had an average background of 1.5 c.p.m.

Samples and flux monitor standards were mounted on either $1^{1}/4"$ diameter plain aluminum planchets or $1^{1}/4"$ diameter copper planchets with molded concentric rings.

ii) Decay Curves Decay curves for both samples and standards were followed to establish radiochemical purity. For a 12 hour irradiation, counting of the Pd, Ir and Pt samples began approximately 30 hours after the end of the irradiation while counting of the Au samples started 40 hours later. During the time lapse between the end of irradiation and the commencement of counting, all of the short-lived activity (e.g. 22 minute ^{111}Pd) had decayed. Each sample was counted at least twice per half-life until a good decay curve over at least three half-lives was established. In cases in which some long-lived contaminant appeared in the decay curve, counting was continued until the curve could be resolved and the counting rate due solely to the isotope of interest obtained. Figure 6-1 illustrates a typical decay curve of the radioactivity produced from platinum

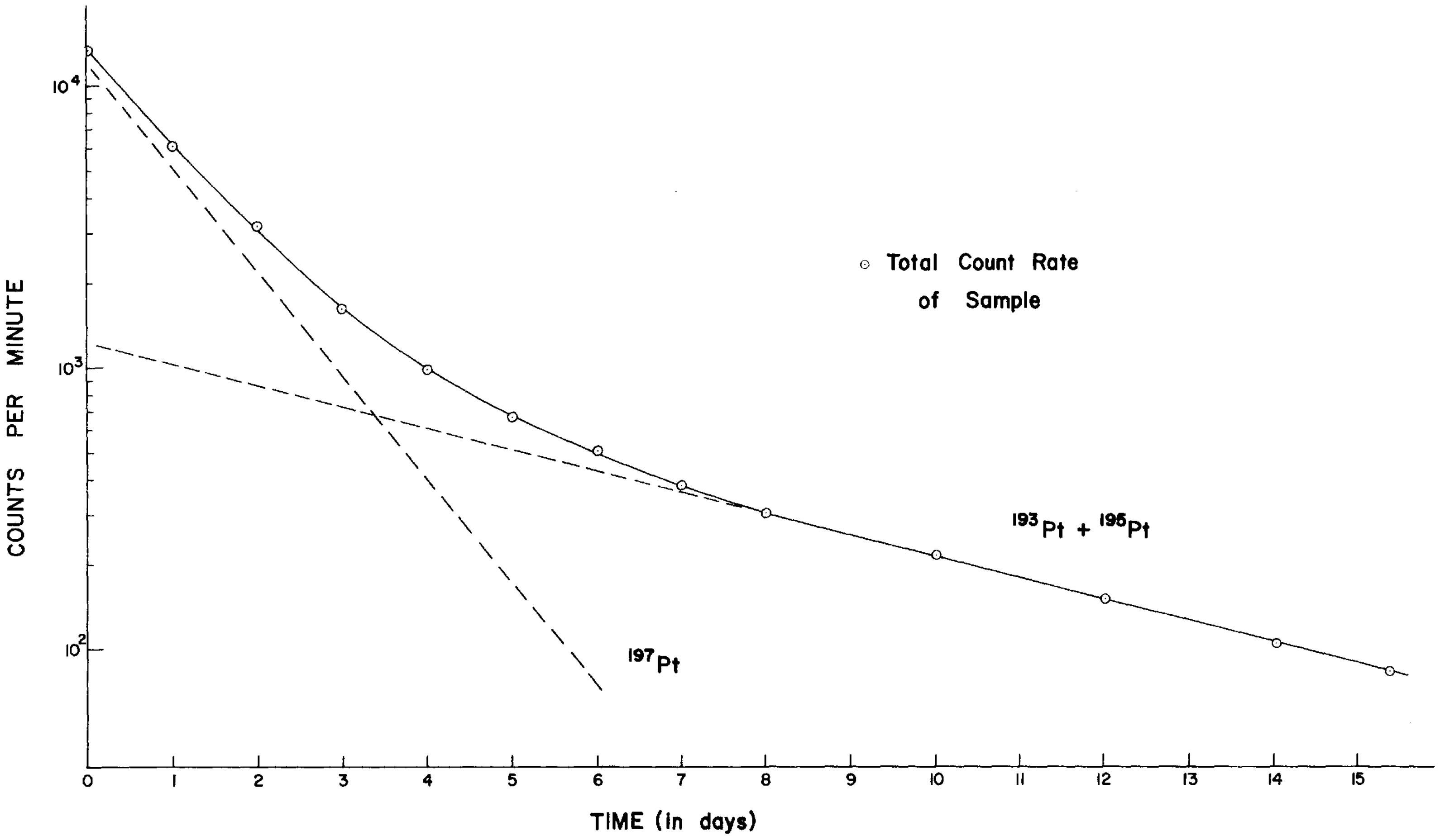

Figure 6-1 Decay curve of platinum sample illustrating 96-hour ^{193}Pt + ^{195}Pt component

in samples containing that metal. Subtraction of 4.1 day ^{195}Pt and 4.4 day ^{193}Pt from the total curve leaves the curve representing the contribution of 20 hour ^{197}Pt to the total activity. In the case of iridium, with 19 hour ^{194}Ir and 74 day ^{192}Ir, samples were counted twice per half-life for the first ten days, then once a week for 6 weeks, and finally once a month for periods up to a year. Calculations based on both the 74 day activity and on the resolved 19 hour activity were made to determine Ir content of many samples, especially of the silicate rock standards, with good agreement between results derived from activities of the two isotopes.

The flux monitor standards were counted over the same period as the samples. Calculations were based on comparisons of the counting rates of standards and samples at equivalent times after the end of irradiation.

Machine drift was monitored by three uranyl acetate standards of approximately 5000 c.p.m. The uranyl acetate was fixed on copper planchets by spraying with a heavy coat of Krylon, a transparent commercial varnish. Over one 7 month period, one of the uranyl standards averaged 3534c.p.m. for several hundred measurements. According to Friedlander and Kennedy (p.258), the expected standard deviation of a reasonably large number M of counts is given by $\sqrt{M}$. Thus, the actual number of counts given off by the standard may range from 3534+60 = 3594 to 3534-60 = 3474 counts. It was found that the actual number of counts ranged from 3571 to 3491 which variation was within the counting statistical error. It may be concluded that the counting system was quite stable and any errors in the measurements were due to counting statistics and not machine drift.

iii) Source Geometry To minimize errors due to source geometry it is imperative that the distribution of radioactive materials on both the sample and standard planchets be uniform. Otherwise, different orientations of the material may produce differences in counting rates of up to 20% due to varying sensitivity of the detector (personal communication Dr. K. Fritz). Pd presents no difficulty with regard to source geometry as the palladium dimethylglyoximate precipitate dries as an even thin film on the aluminum planchets. In the case of Pt, Ir and Au the samples are counted as the metals which tend to be lumpy. Mounting on a flat surface may result in an uneven distribution of the metal on the planchet. Use of copper planchets with molded concentric rings enables one to mount sample and standard with uniform geometrics.

iv) Self-absorption Self-absorption of beta particles also presents a serious problem particularly for beta counting of ^{198}Au(β^-max. = 0.96MeV). The Au metal precipitate produced by hydroquinone reduction of $AuCl_4^-$ tends to produce particles of an extremely variable size range. Self-absorption is proportioned to the thickness of the source and consequently the larger particles may be expected to have apparent lower specific activities due to this effect. The geometry of the particles vary from roughly spherical to quite angular. In a tracer experiment, spherical particles with the same specific activity but varying weights were counted to determine the effect of self-absorption. As the particles had been precipitated from a homogeneous solution of ^{198}Au and ^{199}Au chlorides, the activity of each particle should be proportional to its weight. The apparent specific activity (c.p.m. per unit weight) for each particle has been plotted against the particle's weight in Figure 6-2. Data for the larger particles is not as accurate as that for the smaller particles because it was more difficult to obtain large spherical particles. A decrease in specific activity with increasing source weight is apparent from the data. Pt and Ir precipitates are generally comprised of metallic particles of

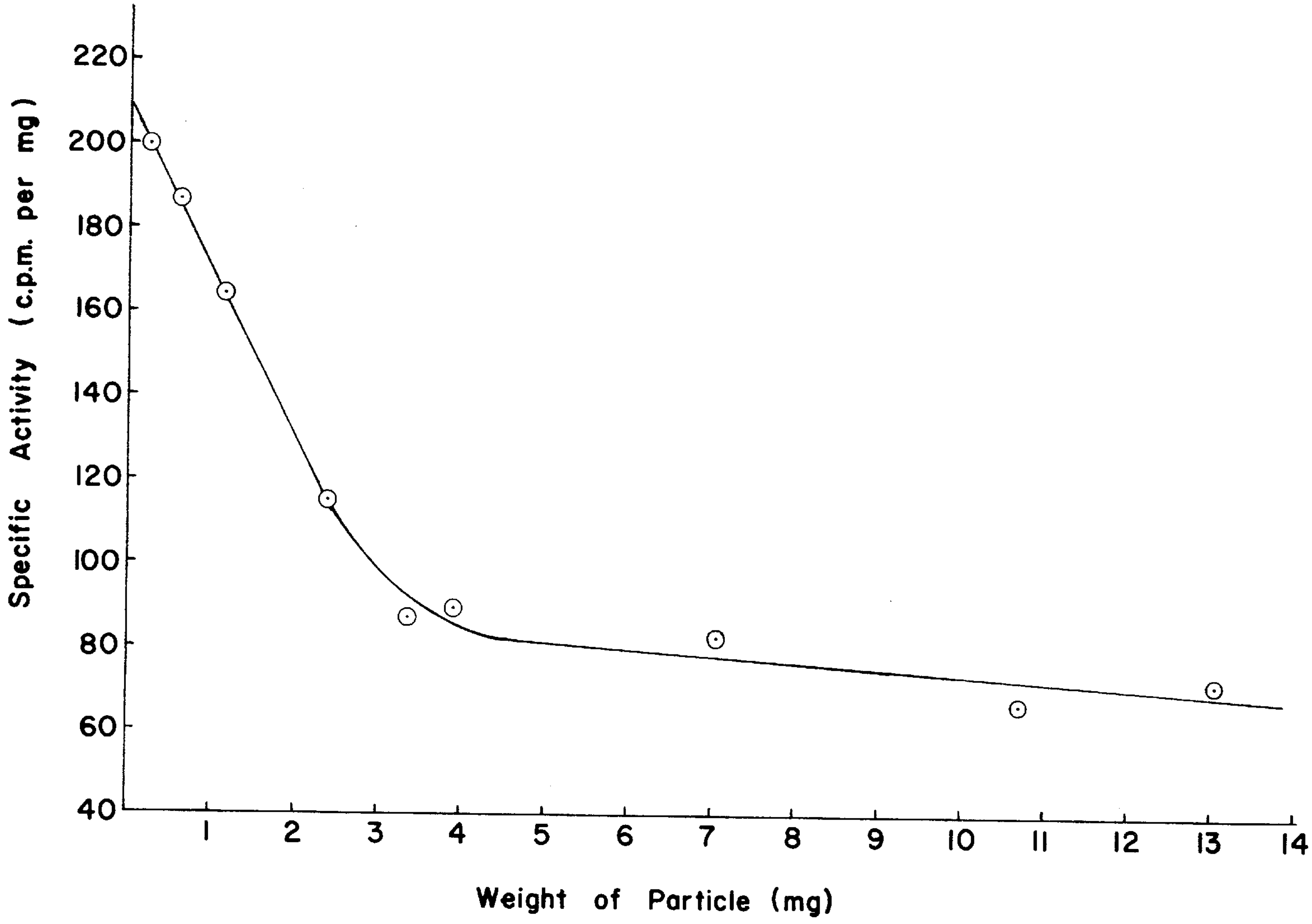

Figure 6-2 Diagram showing decrease in specific activity with increasing particle size

roughly equal sizes varying somewhat with the chemical yield of the sample. During sample mounting, it is necessary to mechanically disaggregate the precipitate so that the metallic particles of sample and standard are of the same size. This can be accomplished with the disposable pipette used to transfer the metal to the counting planchet.

In general, the particle size of the standard is greater than that of the sample as the chemical yield of the former is often the higher. This results in a lowering of the specific aotivity of the standard relative to the sample, or, an apparent greater concentration of the metal in the specimen analysed. An estimate of the error due to differential self-absorption between gold samples and standards can be made with reference to Figure 6-2. The specific activity of a particle infinitely small is 210. If the average weight of particles is 1 mg, each particle will have a specific counting rate of 170 which corresponds to a 20 per cent reduction in the counting rate. In the first few analyses for gold the seriousness of the self-absorption effect was not realized. These analyses included determinations of Au in the Falconbridge sulphide matte standard. The average figure for Au by the present method was 12% higher than by previous methods and may have been higher due to self-absorption in the standard. The chemical yields of the standards were higher than the samples in these experiments, but unfortunately no record was kept of the relative particle sizes of standards and samples for these initial determinations.

In all of the later determinations of gold the particles were broken apart with the disposable pipette used to mount the samples. The maximum size of the particles was 0.4 mg resulting in a maximum specific activity depression of 8%. Thus, in the most extreme cases of a sample consisting of very fine particles and a standard comprised of coarse particles up to 0.4 mg in weight the error due to self-absorption would be 8%.

v) Sample Mounting Procedure During automatic sample changing of Pt, Ir and Au specimens, some movement or even loss of the sample from the planchets may occur. To prevent this, both samples and standards are sprayed with "Krylon", a transparent varnish, after weighing and determination of chemical yield. A thin uniform film of "Krylon", can be obtained by arranging samples and standards side by side and spraying for 5-6 seconds from a height of approximately 10 inches. The spray must be allowed to dry thoroughly before counting because even small amounts of hydrocarbons evaporating from the slightly wet plastic will eventually seal the gas outlet pores in the detector tube with subsequent malfunctioning of the counter.

To test the effect of non-uniform application of the spray on the differential absorption of beta particles, various thickness of "Krylon" were applied to a sample of ^{192}Ir (β^-max. = 0.67 MeV). The initial counting rate of the sample was 423 c.p.m. After spraying the sample heavily for 10 seconds with the fixative, the counting rate was 375 c.p.m., corresponding to a reduction of 11%. It was possible to spray samples and standards so that the difference in film thickness covering them was equivalent to,or less than, two seconds of spray application, which corresponds to a maximum error of less than 2%. This error was considerably less than errors which would have resulted from either differences in sample geometry due to movement of the metallic particles on the planchets or loss of sample from the planchet if the sample had not been sprayed.

2. Gamma Counting

i) Equipment Initially, samples were counted with a single-channel scintillation spectrometer (Baird-Atomic Model N°) while later on in the research programme gamma-counting was performed with a Nuclear Data 256 channel analyser. The Baird-Atomic system consisted of the following components: (1) high-voltage supply unit; (2) a 2" x 2" well-type thallium activated NaI crystal (well dimensions were 21/32" diameter x 1 35/64" deep) coupled to an RCA photomultiplier tube; (3) pre-amplifier; (4) amplifier; (5) single channel integral-differential analyser; (6) cold cathode ray tube scaler; and (7) an electric timer. The multi-channel system consisted of: (1) a high voltage supply unit; (2) a solid 3" x 3" NaI(Tl) crystal detector with photomultiplier tube; (3) pre-amplifier; (4) amplifier; and (5) 256 channel Nuclear Data analyser and storage unit with a special readout to either an oscilloscope or IBM typewriter. For the present study, only half of the available channels were utilized.

ii) Identification of Radiochemical Contaminants The scintillation detector is much more versatile than a beta counting system as it can discriminate between various gamma energies as well as provide data for decay curves. Differential gamma spectrometry was used advantageously in the study to determine contaminants present in some of the G-1 and W-1 analyses, particularly for Ir determinations. The energy spectra were calibrated against ^{137}Cs (photopeak at 0.66 MeV) and compared with the spectra given by Heath (1964). With the single-channel analyser, corrections for instrumental drift (necessary when following decay curves) as determined from the ^{137}Cs spectrum, were made by adjustment of the analyser gain.

iii) Calculations of metal content Gamma counting was also employed to supply counting statistics for the calculation of Au, Pt and Ir in the meteorite specimens and in some of the sulphides. Unfortunately Pd does not have a gamma photopeak amenable to determination of the metal by scintillation detection. Figures 6-3 and 6-4 illustrate typical gamma spectra of sample and flux monitor for Ir, Pt, and Au. Determinations for Au were made by integrating the areas under the 0.412 MeV photopeak for sample and standard. For Ir, the areas under both the 0.32 MeV and 0.47 MeV were integrated and calculations based thereon. In the case of Pt, it was necessary to base calculations on the counting rate of ^{199}Au which is produced by the reaction $^{198}\mathrm{Pt}(n,\gamma)^{199}\mathrm{Pt} \xrightarrow{30\ \mathrm{min}} {}^{199}\mathrm{Au}$. Figure 6-4 gives the gamma ray spectrum of gold separated from an irradiated meteorite specimen and the corresponding spectra for the gold and platinum flux monitors. Unfortunately, ^{199}Au is also produced by double neutron capture of ^{197}Au. The ^{199}Au gold produced from stable gold is evident in the gold flux monitor spectrum. To calculate platinum content on the basis of the ^{199}Au produced from that metal, it is necessary to subtract from the total ^{199}Au activity that activity which is due to double neutron capture of ^{197}Au. This can be accomplished by matching the 0.208 MeV photopeaks of sample and gold flux monitor spectra, and subtracting the gold flux monitor spectrum from the sample spectrum. This leaves the portion of the 0.158 MeV photopeak produced by the platinum.

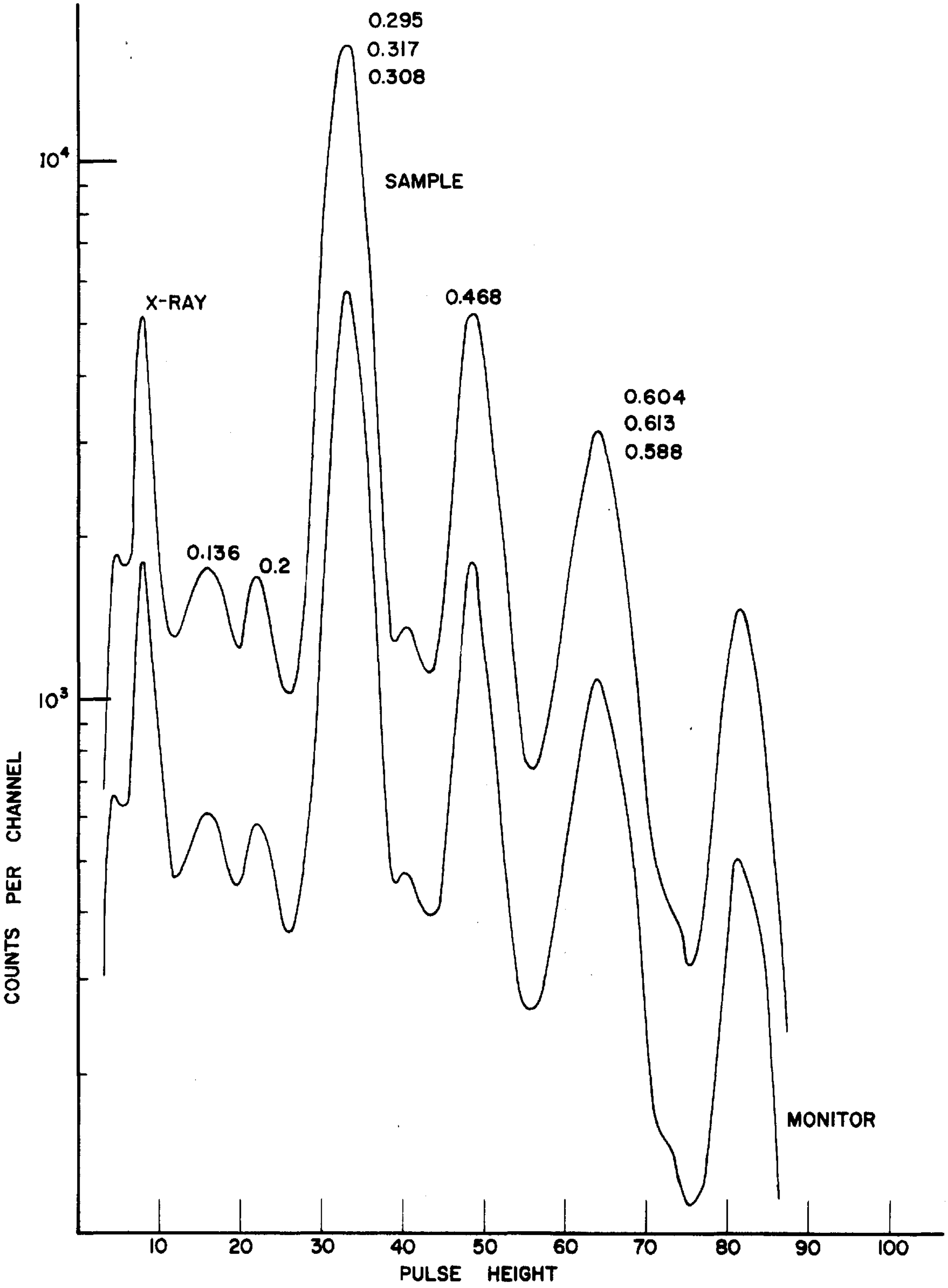

Figure 6-3. Typical gamma-ray spectrum for iridium extracted from an irradiated chondrite and the corresponding iridium flux monitor.

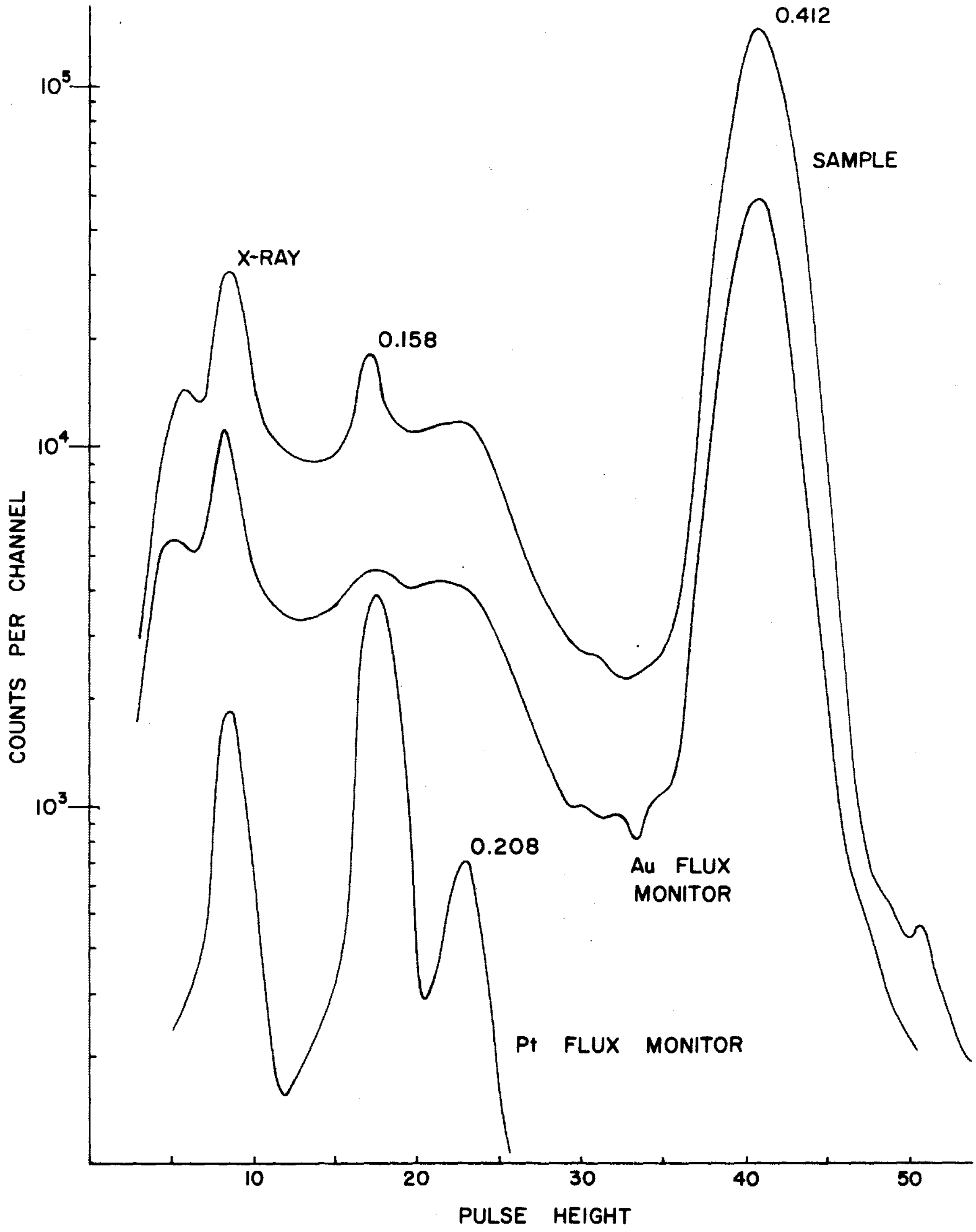

Figure 6-4. Gamma-ray spectrum for gold separated from an irradiated carbonaceous chondrite sample and the corresponding spectra for the gold and platinum flux monitors.

CHAPTER VII

ASSESSMENT OF ANALYTICAL METHOD

The value of the analytical data obtained by an experimental technique may be assessed by observing the accuracy, precision, and sensitivity of the method. An estimate of the accuracy of the method may be made by comparing the results produced by the method to those obtained by other workers on the same standard materials. Two silicate standards and one sulphide standard were chosen for comparison in this study as all had been independently analysed by other workers and also had matrices similar to that of the samples analysed in this study. The precision of the method may be obtained by noting the internal consistency of data for the same material, that is, agreement between individual analyses on the same material. Sensitivity limits vary with the analytical conditions and are determined primarily by the irradiation conditions and the size of the sample analysed. Problems with the analysis of platinum arose and are discussed in the last section of this chapter.

1. Irradiation Conditions

Samples and flux monitors were irradiated in the McMaster Research Reactor which is a light-water moderated research reactor with a thermal neutron flux of approximately $2x10^{13}$ neutrons/cm^2/sec operating at a power level of 1-2 megawatts. Fuel elements in the reactor are MTR type elements with a nominal loading of 196 gm ^{235}U at an enrichment of approximately 93%. The length of irradiation varied from 8 to 19 hours with a few irradiations extending to a week.

Table 7-1 Precious Metal Analyses of G-1 (in p.p.b.)

Metal	This Work	Nuclide and Radiation Counted	Previous	Reference
Pd	1.7			
	2.2		<10, <10	Vincent and Smales (1956)
	1.3	^{109}Pd, β^-		
	1.6		1.6(4)	Crocket and Skippen (1966)
	1.7			
	2.1		2.5±1(2)	Grimaldi and Schnepfe (1967)
	Average 1.8±0.3(16.7%)			
	Average corrected for fission contribution = 1.6[1]			
Ir	$\leq$0.038†	^{192}Ir, β^-	6(1)	Rushbrook & Ehmann (1962)
	$\leq$0.050			
	0.039		$\leq$0.07(1)	Baedecker & Ehmann (1965)
	0.044	^{192}Ir, γ (0.32 MeV)		
	$\leq$0.036†			
	$\leq$0.056			
	Average 0.044±0.008(18.2%)			
Au	4.4			
	5.1		4.6±0.8(5)	Shcherbakov & Perezhogin (1964)
	1.9	^{198}Au, β^-		
	4.0		4.6, 4.3	Vincent & Crocket (1960)
	3.8			
	2.8		2, 2.0	Baedecker & Ehmann (1965)
	3.1			
	2.7			
	2.6	^{198}Au, β^- (0.412 MeV)		
	2.9			
	Average 3.3±0.9(27.3%)			

[1] As discussed by Crocket and Skippen (1966), Pd isotopes produced by ^{235}U fission contribute significantly, probably about 13%, to the Pd activity of G-1. The experimental result has been decreased by this amount giving 1.6 p.p.b. Pd as the best estimate.

† Sample obtained from Dr. J. Maxwell; all other samples obtained from Dr. M. Fleischer.

Table 7-2 Precious Metal Analysis of W-1 (in **p.p.b.**)

Metal	This Work		Nuclide and Radiation Counted	Previous	Reference
	Sample A*	Sample B‡			
	11.8				
	12.1			20,17	Vincent & Smales (1956)
	11.8			15.8±1.4(10)	Crocket & Skippen (1966)
Pd	13.5				
		11.2	^{109}Pd, β^-		
	12.7	10.0		9.0(20)	Grimaldi **and Schnepfe (1967)**
	12.5	11.7			
		11.6			
	11.9	11.5			
	12.0	10.5			
		10.2			
	9.7	10.7			
Average	12.0±1.0 (8.3%)	10.9±0.7 (6.1%)			
Grand Average	11.5±1.1(9.6%)				
	0.31†		^{192}Ir γ		
	0.33		(av. for 0.32 and 0.47 MeV γ's)	≤0.01	Baedecker & Ehmann (1965)
	0.26†		^{192}Ir, β^-		
	0.30				
Ir	0.23*		^{192}Ir and ^{194}Ir β^-		
	0.25				
	0.19*		^{192}Ir, γ		
	0.22		(0.32 MeV)		
Average	0.26±0.05(19.2%)				
	6.4				
	4.9			5.0±0.6(8)	Shcherbakov & Perezhogin (1964)
	6.7				
	6.3		^{198}Au, β^-	8.5,8.4	Vincent & Crocket (1960)
	5.7				
Au	5.7			4,4.8,4.9	Baedecker & Ehmann (1965)
	6.6				
	4.6			4.9	Hamaguchi <u>et al</u>.(1961)
	5.5				
	6.2				
	6.2		^{198}Au, γ		
	4.8		(.412 MeV)		
Average	5.8±0.7(12.1%)				

* Sample obtained from Dr. M. Fleischer
‡ " " " Dr. F. Flanagan
† " " " Dr. J. Maxwell
All other samples obtained from Dr. M. Fleischer.

Table 7-3 Precious Metal Analyses of a Cu-Ni Sulfide Matte

Metal	This Work (ppm)	Nuclide and Radiation Counted	Falconbridge Nickel Laboratories	Mineral Sciences Division D.E.M.R. Ottawa
Pd	5.70	^{109}Pd,β^-	5.14	
	5.70	(all data)		
	5.60			
	5.20			6.00
	3.94			
	5.68			
average	5.30±0.70(13.2%)			
Ir	0.98	^{194}Ir,β^-	0.79	
	1.02	(all data)		
	0.76			0.86
	0.90			
	0.82			
	0.98			
average	0.91±0.10(11.0%)			
Pt	5.0	^{197}Pt,β^-		
	6.6		5.49	
	6.9	^{193}Pt,β^-		5.52
	5.0			
	6.9			
	6.5	^{197}Pt,β^-		
	6.6	^{193}Pt,β^-		
average	6.2±0.8(13.0%)			
Au	1.80			
	1.67	^{198}Au,β^-	1.99	1.85
	1.95			
	1.77			
average	1.80±0.12(6.7%)			

2. Source of Standards

The silicate standards analysed, G-1, a granite from Westerly, R.I. and W-1, a diabase from Centerville, Va., were prepared by the U.S. Geological Survey during an investigation of the precision and accuracy of analyses of silicate rocks between a large number of laboratories (Fairbairn *et al.*, 1951). One split each of these standards was originally obtained from Dr. M. Fleischer of the Survey. Later a second split of W-1 was obtained from Dr. F. Flanagan, also of the Survey, although the only determinations made on the second portion were for Pd. In the presentation of the Pd data (see Table 7-2), these two splits of W-1 have been referred to as Sample A and Sample B, respectively. 500 mg each of G-1 and W-1 were obtained from J.A. Maxwell, Geological Survey of Canada for analysis of Ir.

The sulphide standard, a copper-nickel matte concentrate, was supplied by Falconbridge Nickel Mines Ltd. It has previously been analysed by both the Falconbridge Nickel Company's Thornhill, Ontario Laboratory and by the Department of Energy, Mines and Resources, Ottawa. The composition of the matte was as follows: 50 per cent Ni; 20-25 per cent Cu; 20-25 per cent S; 1 per cent Fe; and 1 per cent Co.

3. Presentation of Data

The analytical results for the standards are tabulated in Tables 7-1 7-2 and 7-3 and compared therein with previously published results. These tables give the data for each analysis together with essential details of the counting procedures, the average value with standard deviation, and the coefficient of variation in parentheses. Duplicate samples were run in the same irradiation and the two values obtained from the same irradiation are grouped together.

The procedures used by the D.E.M.R. Laboratory have been described by Faye and co-workers (1961a, 1961b, 1964, 1965). It is to be noted that the copper-nickel matte used by these workers in the development of their analytical scheme was similar to, but not the same as, the material described in the present work. Their scheme involves a fire assay procedure in which the precious metals are collected in tin which is subsequently dissolved and the individual metals isolated by ion exchange, distillation, and solvent extraction processes. The Falconbridge Laboratory's procedure involves a coprecipitation of precious metals on metallic copper with spectrophotometric determination of individual elements. Dr. W. Ott of Falconbridge kindly supplied the analytical data for this standard.

The extensive analytical data on the well known granite and diabase rock standards (G-1 and W-1) have recently been summarized by Fleischer (1965, 1967). Previous determinations of the precious metals in the standards have been made by neutron activation analysis, with the exception of some colorimetric determinations of Pd by Grimaldi (1966).

4. Detection and Sensitivity Limits

Detection and sensitivity limits may be calculated from either a theoretical basis or from actual experimental conditions. Winchester (1960) has calculated theoretical sensitivity limits for most of the elements for 1 hour and 150 hour-long irradiations. Sensitivity limits for the analytical method described here have been calculated on the basis of actual activities detected by the counting system. A detection limit is defined here as the minimum concentration of an element in a 100 mg sample which will produce 3 c.p.m. above a 1.5 c.p.m. background, whereas the "identification" limit is the minimum concentration required to enable the decay curve to be followed over three half-lives. The detection limits presented here correspond to the "sensitivity limits" of other researchers such as Winchester.

The choice of a minimum counting rate of 3 c.p.m. was not arbitrary but was selected because the activity produced from a sample decaying at a rate proportional to 3 c.p.m. can be readily distinguished from the background activity. The background counting rate of the beta counting system measured over intervals of 1-2 hours during a period of two years was established to have an average of 1.5 c.p.m. and a variation within the standard deviation of the counting statistics. Now, it is practical to measure the counting rate over an interval of two hours, so that the total number of counts due to the background would be 180 for this length of time. If the counting rate of the sample is 3 c.p.m. then the total number of counts due to background and sample is 520. Using the formula given by Friedlander and Kennedy, p.261, the respective counting rate of background and of background plus sample and their standard deviations [1] are then given as:

$$R_b = \frac{180 \pm \sqrt{180}}{120} = 1.50 \pm 0.11 \text{ c.p.m.}$$

$$R_t = \frac{520 \pm \sqrt{520}}{120} = 4.50 \pm 0.19 \text{ c.p.m.}$$

The counting rate of the sample alone, that is, the net counting rate, is given by:

$$R_{\text{total}} = R_{\text{background}} = 4.5-1.5 = 3 \text{ c.p.m.}$$

and its standard deviation is:

$$\sqrt{(0.11)^2 \pm (0.19)^2} = 0.22$$

$$\text{Hence, } R_{\text{net}} = 3.0 \pm 0.2$$

which is statistically different from the counting rate and standard deviation of the background.

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[1] The standard deviation of $\underline{n}$ counts is given by $\sqrt{n}$.

It is desirable to establish a decay curve, especially in beta-counting, for there is always a definite possibility that some low level quantity of contamination may be present. Detection limits are thus minimum concentration values whereas identification limits, as defined here, are estimates of the minimum quantity of metal necessary to prove the identity of a radionuclide by beta decay curve analysis. The concept is not applicable to differential gamma spectral analysis. The two types of limits calculated on the basis of real counting rates encountered in this research are tabulated in Table 7-4.

Table 7-4 Sensitivity and Detection Limits

Isotope	Half-life	Detection Limit (in p.p.b.)		Sensitivity Limits (in p.p.b.	
		T_{ir}=19hrs	T_{ir}=1week	T_{ir}=19hr	T_{ir}=1week
^{109}Pd	13.5 hr	0.04	---	0.3	---
^{192}Ir	74 day	0.07	0.008	0.56	0.064
^{194}Ir	19 hour	0.008	----	0.064	---
^{198}Au	65 hour	0.004	0.0017	0.032	0.014
^{197}Pt	20 hour	1.5	---	12	---
^{195}Pt	4.1 day	30	5.7	240	49

Detection limits for gamma counting with the Nuclear Data multichannel system have been calculated on the basis of a 100 mg sample, 400 minute live counting time, and a total counting rate equal to twice the background. For a 19-hour irradiation, the detection limits are as follows:

Element	Isotope Counted	Detection Limit (p.p.b.)
Pt	^{199}Au	6
Ir	^{192}Ir	0.1
Au	^{198}Au	0.02

For an irradiation time of 1 week, the detection limit for Ir becomes 0.01 p.p.b.

The detection limit for Pt is given for gamma counting of the ^{199}Au photopeak with an energy of 0.158 MeV (see Figure 6-4). Unfortunately, a peak at this same energy is present in the spectrum of ^{198}Au produced by irradiation of stable ^{197}Au. For equal amounts of Au and Pt in the sample, the number of disintegrations at the 0.158 MeV energy level due to ^{198}Au activity is 12 times that due to ^{199}Au activity. Thus, for recognition of ^{199}Au, there must be at least 24 times as much Pt as Au in the sample.

5. Precision

If it is assumed that the distribution of the metals within each standard is uniform then the standard deviation calculated from the total analyses of each metal in each standard is an estimate of the precision of the analytical method for analyses of that metal. However, the dispersion of analytical data may include a component due to sample inhomogeneity as well as analytical error. There are no physical means of assessing the randomness of the precious metal distribution within each sample but it was demonstrated that it is not entirely uniform. Nine analyses of one split of W-1 (Sample A in Table 7-2) gave an average concentration of 12.0±1.0 p.p.b. Pd whereas eight analyses of another split of W-1 gave an average concentration of 10.9±0.7 p.p.b. According to the Students "t" test, there is greater than 98% probability that the means are significantly different. The fact that different splits may have different precious metal contents indicates that distribution throughout each split may not be uniform and hence a part of the standard deviation for each metal may be due to sample inhomogeneity.

The standard deviation of a number of observations on the same population is defined as (Dixon and Massay, p.19):

$$S = \sqrt{\frac{\sum_{i=1}^{N}(X_i-\bar{X})^2}{N-1}}$$

where S = standard deviation

X_i = result in p.p.b. for the ith replicate

$\bar{X}$ = mean result

N = number of replicates

In order to compare variability between metals one may calculate the coefficient of variation,

$$C = \frac{100\ S}{\bar{X}}$$

Analyses of gold should have the greatest precision as gold has high sensitivity and is the easiest of the metals to obtain with high radiochemical purity. However, the reverse is the case, as can be seen by examining the coefficients of variation. The large standard deviation of gold may be due in part to differential self-absorption effects (see page 54) but not all of it, for results by gamma counting, where there is no self-absorption, show the same low precision as results by beta counting.

One of the disadvantages of a neutron activation analysis scheme which incorporates the determination of a short-lived isotope is the small sample size that can be irradiated. The problem is most acute when one is attempting to establish the average metal content of a large population. Such a sample must be processed and counted within a limited time of irradiation to determine the short-lived isotope. Following irradiation, samples must be "cooled" before processing in order to permit decay of the bulk of the huge quantities of short-lived radioactivity and hence reduce the health hazard of handling this radioactivity. A 100-200 mg sample is the largest sample size that can be safely processed during the determination of 13.6 hour ^{109}Pd. A sample as small as 100 mg may not be representative of the whole population and analyses of a group of such samples may reflect the variation of the metal of interest from sample to sample.

It may be concluded that the coefficients of variation presented in Tables 7-1, 7-2 and 7-3 are not true estimates of the precision of the analytical method but include variations due to the small sample sizes analysed.

6. Accuracy

The accuracy of the method may be evaluated by comparing the results of this work to previous determinations on the same materials.

i) Palladium Two previous sets of determinations for Pd by activation analysis and one by colorimetry have been done on G-1. The results of this work agree very well with that of Crocket and Skippen (1966) but are more than a factor of 6 lower than that of Vincent and Smales (1956) who reported maximum values only, and are a factor of 1.5 higher than that of Grimaldi (1967) who determined Pd by a colorimetric method. However, Grimaldi performed only two analyses on G-1 and his average value has a large standard deviation. The results of Vincent and Smales (1956) were based on extremely low counting rates - only 2 counts per minute above background - whereas the present results were based on counting rates of the order of 30-80 c.p.m. above a background of only 1.5 c.p.m. These high initial counting rates permitted the construction of decay curves with 16 hour half-lives produced by the decay of 13.6 hour ^{109}Pd and 21 hour ^{112}Pd. The ^{112}Pd is produced from uranium fission and contributes approximately 13% of the total activity for a decay of 20 hours following a 16 hour irradiation (Crocket and Skippen). Because of the similar half-lives of the two isotopes it is not possible to resolve the decay curve graphically. However, it can be shown that a radioactive sample of Pd containing 13% ^{112}Pd and the balance ^{109}Pd decays with a half-life of 16 hours by adding curves of 21 hour half-life and 13.6 hour half-life in the appropriate proportions. ^{112}Pd decays to ^{112}Ag which has a half-life of 3.2 hours. Thus, at the time the samples are beta-counted, ^{112}Ag will be in transient equilibrium with the parent ^{112}Pd and the main radiation seen by the detector will be the 4.05 MeV β^- from ^{112}Ag.

As noted by Crocket and Skippen, neutron activation analysis of Pd in acidic rocks is probably subject to errors of at least 10% from ^{235}U fission products alone unless the U-content is known. Two procedures might be adapted, however, to minimize this error. Firstly, it may be possible to assess the contribution of ^{112}Ag (β^-max. = 4.05 MeV) to the total beta activity by using an absorber to absorb the ^{109}Pd (β^-max. = 1.03 MeV) beta. This would permit a correction for U-fission interference to be made. Secondly, it is possible to write computer programmes which can readily resolve decay curves which would be impossible to resolve graphically. Computerized resolution of such decay curves would not only allow determination of Pd in acidic rocks but could also permit determination of the U-content of the rock.

As mentioned in the discussion of precision of Pd analysis in W-1 there appear to be distinctly different Pd concentrations in the various splits of W-1. The pooled average of Pd analyses of the splits of W-1, 11.5 p.p.b. Pd, is 31% lower than the value of 15.8 p.p.b. Pd reported by Crocket and Skippen but is 24% higher than the value (9.0 p.p.b.) obtained by Grimaldi (1967).

The counting system employed in the present study was superior to that used in the work of Crocket and Skippen. The background of the present system was 1.5 c.p.m. compared to 15 c.p.m. for the system used by the latter. Further, the sensitivity of the detector in the Nuclear Chicago system was much higher as it had a thin mylar window whereas the other detector had a relatively thick gold window. The liquid flux monitor standards used in this research were less prone to effects of differential flux attenuation than the dry standards employed by Crocket and Skippen. Grimaldi, using a colorimetric method, found the Pd content of 20 samples of W-1 to average 9.0 p.p.b. All of the colorimetric determinations were made on 10 gram samples - larger by a factor of 100 than the sample size used in the present study. However, the good precision (± 1.1 p.p.b. for 17 samples) of the present study would appear to preclude any large error due to the small sample size analysed. On the other hand, there is the possibility of losses during chemical processing in any colorimetric method.

When one examines the accuracy of the method at even higher Pd concentrations, it is difficult to see how the results by the present method can be high by a factor of 0.24. Analysis of the Cu-Ni matte indicated the Pd content to be 5.3 p.p.m., which is within 2% of the average of previous determinations, 5.4 p.p.m.

The same Pd flux monitor standard was used throughout the work, both for the standards and for sulphide samples. The Pd content of the solution was checked against other liquid standards, once half-way through the analytical programme and again at its conclusion. The standard was first checked against one prepared by J. H. Crocket and later against one prepared by R. Martindale. In both cases, the Pd content of the solution compared favourably with that of the new standard solutions.

To summarize, it would appear that the method is highly accurate for Pd determinations in sulphides and many silicate specimens but may be subject to errors of at least 10 per cent in specimens containing large amounts of uranium.

ii) Iridium Only one analysis apiece has been reported for the Ir content of G-1 and W-1, both values being determined by Baedecker and Ehmann (1966)[1], and both being maximum concentration levels. Early analyses for Ir in these standard rocks in this work gave values much higher than those reported by Baedecker and Ehmann, typical values being as follows:

Ir Content (p.p.b.)

Experiment	W-1	G-1
M-15	0.61,0.43	Values high and erratic (0.5-6 p.p.b.)
M-16	0.61,0.44	

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[1] A figure of 6 p.p.b. Ir in G-1 was reported by Rushbrook and Ehmann (1962) but has been replaced by the more recent determination.

As these early analyses were thought to be high by factors of 10 to 100 compared to the concentration levels reported in print it was assumed that the samples of G-1 and W-1 used in this laboratory had been contaminated with Ir. 500 mg each of G-1 and W-1 were obtained from J. Maxwell, Geological Survey of Canada and these were analysed for Ir in two experiments, the results being as follows:

Experiment	W-1	G-1
M-31	0.26,0.30	0.038,0.050
M-34	0.31,0.33	0.036,0.056

The decay curves in these experiments were followed for over a year, with the subsequent establishment of the 74 day ^{192}Ir component. In the earlier experiments, decay curves had been followed for a relatively short time without the establishment of the half-life of the long-lived component. Calculations were based on figures obtained by subtracting an assumed 74 day activity from the curve, leaving the 19 hour component. Graphical resolution of decay curves is a subjective art and hence although 19 hour components were obtained these could not have been entirely due to ^{194}Ir. As later decay curves of G-1 showed, there is a great deal of Ru contamination. Similarly, the W-1 samples may have contained a short-lived contaminant - undoubtedly some, though in greatly reduced quantities, Ru contamination was present. Further analyses of the original splits of G-1 and W-1 showed that they contained the same order of concentration of Ir as those obtained from J. Maxwell.

The concentration of Ir found in G-1 is approaching the sensitivity limit of the method and so should be regarded as a maximum value only. The value of 0.26 p.p.b. Ir determined for W-1 is 5 times higher than the value reported by Baedecker and Ehmann but is believed to be an accurate estimate of the concentration of Ir in W-1 for the following reason.[1] Ir and Os show strong geochemical coherence (Goldschmidt, 1954) due to their almost identical atomic radii (1.35 and 1.34 A°, respectively). In economic deposits they are always found together. They occur as asmoiridate in placer deposits, and in magmatic deposits such as those of the Merensky Reef they are present in equal proportions. Further, this research has shown that they exhibit strong coherence in the Sudbury sulphide deposits. From Table 7-5, which tabulates the Os contents reported for G-1 and W-1, it is seen that W-1 contains approximately 5 times the amount of Os contained in G-1.

Table 7-5 Os content of G-1 and W-1

G-1	W-1	Reference
0.076	0.27	S. Hsieh (1967
0.072	0.24	
0.065±0.039	0.226±0.055	J. W. Morgan (1965)
0.048	0.285±0.043	
0.020	0.46	Bate _et_ _al_. (1963)
0.056	0.30	Average

Because of the strong geochemical coherence of Ir and Os one would expect the same concentration levels of Ir in G-1 and W-1 as have been found for Os. The present study indicates that this is the case. Also, one expects the concentration of Ir and Os to be higher in basic rocks than in

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[1] Baedecker and Ehmann used an acid dissolution in their procedure which may not completely dissolve all of the Ir and/or may not leave the active and carrier Ir in the same oxidation state. See Appendix D for further discussion of this.

acidic rocks because the highest concentrations of the platinum metals have been found in the most "basic" rocks, that is, ultramafic rocks. It should again be mentioned that the Ir determinations were made on two different lots of the standard rocks. For these reasons, a value of 0.26 p.p.b. Ir is believed to represent an accurate estimate of Ir content of W-1.

The amount of Ir determined by the present study in the sulphide standard, 0.91 p.p.m. Ir, is 14% higher than the average of previous determinations, but only 5.7% higher than the value determined by the Mines Branch laboratory. Also, the D.E.M.R. value is well within the standard deviation of the present figure.

iii) Gold The accuracy of the method for the analysis of gold may be estimated by examination of the data presented in Tables 7-1, 7-2 and 7-3. The standard deviations of the values determined for G-1 and W-1 by the present study and that determined by Shcherbakov and Perezhogin (1964) are within the quoted standard deviations. The value presented here equals the average of previous determinations for G-1. For W-1, the present value is somewhat larger than the average of previously determined figures, but is in good agreement with the average value of 5.0 p.p.b. Au determined by Shcherbakov and Perezhogin for 8 samples. The sulphide matte value is 6.8% lower than the average of previous determinations.

As mentioned elsewhere, one of the difficulties of determination of Au by beta counting is self-absorption, which usually tends to give apparently higher metal concentration in the sample. Thus, one may ask if the reason why the Au content of W-1 as determined by the present method is higher than by other methods is not simply due to self-absorption effects. However, some of the samples were counted by a gamma-counting system in which self-absorption effects are negligible and the results by both counting methods agreed.

In beta counting of samples, not only is ^{198}Au counted but ^{199}Au, produced from Pt, is also counted. If the level of Pt in a sample is high relative to the Au content, the ^{199}Au content would be serious. On the basis of experimental data, it can be shown that the contribution of ^{199}Au to the total Au activity is 0.26% in G-1, 0.16% in W-1 and 0.30% in the sulphide matte standards (See Appendix A). It is concluded that ^{199}Au produced from Pt is a minor contributor to error in the determination of Au in these standards when beta counting techniques are employed. In the analyses of Sudbury sulphides, it is estimated that the maximum contribution of ^{199}Au is 2.7%.

iv) Platinum For irradiation of a 100 mg sample for 19 hours, the detection limit of Pt is approximately 1.5 p.p.b. but the identification limit (with the requirement that the longer-lived component of the decay curve be followed for three half-lives) is 12 p.p.b.-which is slightly above the Pt metal contents of 8.2 p.p.b. in G-1 and 9.2 p.p.b. in W-1 reported by Das Sarma *et al.* (1965). These sensitivity limits are based on the assumption that the Pt sample may be recovered absolutely radiochemically pure, a state which is most difficult to attain. Calculations based on total activity present in the sample without construction of a decay curve would be maximum estimates which could be highly inaccurate. Because of the close proximity of the Pt metal content of G-1 and W-1 to the sensitivity limit for that metal, it was not considered advisable to report concentration levels for Pt in the silicate standards.

Several attempts were made to determine Pt in the silicate standards by analysing 1000 mg samples irradiated for a week. However, large amounts of gas were generated during irradiation, forcing the silicates out of the silica vials containing them. The samples, when analysed, were highly contaminated. The nature of the evolved gas was not determined, but may have been hydrogen gas produced from water adsorbed on the rock material.

The concentration of Pt in the sulphide matte is much higher and analytical data are reported in Table 7-3. The average value is 17.5% higher than that reported by the Department of Energy, Mines and Resources, but the standard deviations of the two averages overlap. There is no obvious reason why the present work should yield higher results. It may be that the standard was made up incorrectly - there was no check made on its concentration of Pt. Difficulty was experienced in obtaining a pure Pt metal source because small quantities of tin were co-precipitated with some of the samples rendering high chemical yields. Some workers (e.g. Morris, Hill and Smith (1963) have determined chemical yields for Pt after counting by colorimetric methods. It was not thought expedient to introduce this method of determination here as it appeared throughout much of the research that it was impossible to obtain radiochemically-pure platinum by the present analytical scheme. For the same reasons few determinations for Pt were made on the sulphide samples as it appeared that the samples were highly contaminated. However, it was shown that the long-lived component present in the decay curves was characterized by a consistent 4.0-4.1 day half-life and that the sample and standard decay curves were identical. There is strong evidence that this component results from the decay of the isomeric states of two platinum nuclides (see Appendix C).

7. Radiocontaminants in Iridium Samples

During determination of Ir in G-1 and in some of the chalcopyrite samples, long-lived radionuclide contaminants were found in the Ir samples. The problem was especially acute in the analysis of G-1 because of the very low Ir content of that material (0.044 p.p.b.).

In the case of Ir determinations in G-1, a ruthenium contaminant was strongly indicated by the presence of a prominent energy peak at approximately 0.47 MeV in the Ir spectra (^{103}Ru has a photopeak at 0.50 MeV). The decay of this peak was followed with the single channel analyser and it was shown to have a half-life of 40 days, the half-life of ^{103}Ru. There are probably equal quantities of Ir and Ru in G-1 and as the chemistry is designed for Ir, not Ru, it is somewhat surprising that Ru should appear as a contaminant. During early attempts to analyse Ru in G-1, results of approximately 200 p.p.b. Ru were obtained. Virtually all of the Ru activity was produced from fission of ^{235}U, for the Ru content of G-1 is very probably less than 1 p.p.b. (Ru, Ir and Os possess considerable geochemical coherence; and as the latter two have concentrations of 0.044 p.p.b. and 0.074 p.p.b. in G-1 respectively, then the Ru content should not be greater than 1 p.p.b.). During chemical processing, some of this fission-produced Ru must accompany the Ir. Ru behaves the same as Ir on the anion exchange column and in any dithizone extraction etc. In the absence of the distillation step normally used during analysis of Ru, removal of Ru may be accomplished by the following procedure. Following fusion, the sample could be taken up in H_2O and a hold back carrier containing RuO_4 added. Addition of a small quantity of ethanol would cause the precipitation of RuO_2 which could be removed by centrifuging or filtering. To ensure complete removal of the Ru contaminant, the procedure should be repeated.

Some of the Ir samples derived from chalcopyrite were contaminated with a long-lived isotope. Beta counting proved that the isotope had a half-life of approximately 250 days, but it was not until the samples were gamma counted that the isotope was identified as 250 day ^{110}Ag with photopeaks at 0.66 and 0.88 MeV. Hawley (1962) reports that the average content of Sudbury chalcopyrites is 183 p.p.m. which is 10^4 to 10^6 greater than the concentration of Ir in most chalcopyrites. Although AgCl is insoluble in dilute HCl, it is soluble in concentrated HCl solutions. Ag reacts the same as the other precious metals on the anion exchange column (see Table 4-1) and would tend to follow Ir. Radioactive Ag may be removed at any of several different stages during the chemical treatment of Ir. However, as some radiochemical Ag may also be a minor contaminant in some of the other precious metal samples, especially Pd, it is best to remove it as early as possible. Prior to addition of the sample solution to the exchange column, the Ir is in 0.5 M HCl. Addition of a small amount of $AgNO_3$ solution to this would cause the precipitation of AgCl which can be removed by centrifuging or filtering. The precipitation should be repeated.

The fact that both Ru and Ag appear as contaminants suggests the possibility that analysis of these could be incorporated into the analytical scheme without too much difficulty (and the distillation of Ru avoided). This would be especially feasible if the samples were gamma-counted,for the photopeaks of Ru, Ir and Ag are distinctly different.

CHAPTER VIII

GEOCHEMISTRY

The precious metals are both siderophilic and chalcophilic occurring predominantly as pure metals and alloys and to a much lesser extent combined with sulphur, tellurium, bismuth and arsenic. For the most part the platinum metals are concentrated in the early stages of differentiation of basic magmas and are consequently most abundant in magmatic mafic and ultramafic bodies and associated ore deposits, especially of the chalcopyrite-pyrrhotite-pentlandite type. Gold, on the other hand is commonly enriched in the residual solutions of magmas (especially granitic magmas) whereas it is generally of low concentration in pyrrhotite-pentlandite ore magmas associated with gabbroid magmas. Under certain conditions, the platinum metals are carried through the differentiation process because of their lack of affinity for the silicate minerals, in which case they are concentrated in the products of late hydrothermal solutions. Primary economic deposits of the platinum metals are restricted to areas of mafic and ultramafic massifs whereas gold deposits are generally associated with hydrothermal veins related to granitic magmas. Much of the world's supply of the metals has come from placer deposits. Previous reviews of the geochemistry of the precious metals may be found in Goldschmidt (1954), Rankama and Sahama (1950), Zvyagintsev (1941, 1946, 1950), Gmelin (1938), Quiring (1962) and Wright and Fleischer (1965).

In the following sections, the physiochemical parameters of the metals will be described in order to discuss the basic reasons for distribution of the precious metals.

1. Valence

The precious metals are situated at the hiatus in the increasing valence states of the transition metals and as a result the valencies within the group are quite different. The oxidation states of the transition metals are listed in Table 8-1.

Table 8-1 Oxidation States of the Transition Metals

$\mathrm{Ti}^{\mathrm{IV}}$ (+4)	V^{IV} (+5)	$\mathrm{Cr}^{\mathrm{III}}$ (+6)	$\mathrm{Mn}^{\mathrm{II}}$ (+7)	$\mathrm{Fe}^{\mathrm{II,III}}$ (+6)	$\mathrm{Co}^{\mathrm{II,III}}$ (+4)	$\mathrm{Ni}^{\mathrm{II}}$ (+6)	$\mathrm{Cu}^{\mathrm{I,II}}$ (+3)
$\mathrm{Zr}^{\mathrm{IV}}$ (+4)	Nb^{V} (+5)	$\mathrm{Mo}^{\mathrm{VI}}$ (+6)	$\mathrm{Tc}^{\mathrm{IV,VII}}$ (+7)	$\mathrm{Ru}^{\mathrm{III,VI}}$ (+8)	$\mathrm{Rh}^{\mathrm{I,III}}$ (+6)	$\mathrm{Pd}^{\mathrm{II,IV}}$ (+4)	Ag^{I} (+3)
$\mathrm{Hf}^{\mathrm{IV}}$ (+4)	Ta^{V} (+5)	W^{VI} (+6)	$\mathrm{Re}^{\mathrm{IV,VII}}$ (+7)	$\mathrm{Os}^{\mathrm{IV,VI}}$ (+8)	$\mathrm{Ir}^{\mathrm{III,IV}}$ (+6)	$\mathrm{Pt}^{\mathrm{II,IV}}$ (+6)	$\mathrm{Au}^{\mathrm{I,III}}$ (+3)

IV = most common oxidation state

+4 = highest oxidation state

From left to right in a row, the highest oxidation states increase regularly to a maximum valency of +8 for Ru and Os and +7 for Mn. Past this hiatus, oxidation states decrease in value. Hence, the oxidation states of Os and Ru are distinctly different from those of the remainder of the precious metals. Os for example, has a stable tetroxide (OsO_4) with Os in the VIII state, whereas Ir's highest common oxidation state is IV. Similarily, high oxidation states are progressively more stable towards the bottom of any group.

Valence plays a major role in the geochemistry of an element. As low oxidation states are generally more common than higher oxidation states, elements which have stable low oxidation states should be more reactive than elements which have stable high oxidation states. One would predict that Ru, Ir and Os, because of their high oxidation states, would tend to be more inert than the other precious metals.

2. Radius

Due to the Lanthanide contraction, corresponding atoms and ions of the second and third row of the transition series have similar radii. There is more similarity in size (and in chemical behaviour) between elements of the second and third rows than between elements of the first and second rows. Thus, Rh and Ir are similar but distinctly dissimilar to Co.

Precious metals exist, probably not as simple cations in a magma but as complexes that would have to be broken down at the site of a growing crystal in order to release the cation. Hence, discussion of ionic radii with respect to the geochemistry of the precious metals is irrelevant. Of much greater significance than the ionic radii are the metallic and covalent radii. The atomic radii of the transition metals and some of the semi-metallic elements are shown in Figure 8-1 along with their crystal structure type. The atomic radii given are for 12-fold coordination of the metals, with the following exception. The coordination of the B subgroup metals is so irregular that the concept of a precise radius ceases to have any very definite meaning (Evans, 1964). For these metals, the atomic radius shown is that of half the distance of closest approach.

The usual requirements of similar valence type and equivalent radii apply for substitution by the precious metals of major elements in sulphides and alloys. A further requirement for complete solid solution to occur between two metals is that they should have the same crystal structure. The platinum metals combine with all of the elements in Figure 8-1 with radii within 15% of that of Os to form alloys or compounds which are bound together by bonds of metallic to covalent character. The mode of combination of the precious metals with some of the metals has been compiled in Table 8-2.

Table 8-2 Mode of Combination of Precious Metals with Various Elements

	Au	Pd	Pt	Ir	Os	Ru	Fe	Co	Ni	Cu	Rh	Ag	Te	As	Bi
Au	A	A	B	D	D	D	B	B	A	A	B	A	C	B	E
Pd	A	A	A	A	E	B	A	A	A	A	A	A	C	C	C
Pt	B	A	A	A	B	B	A	A	A	A	A	C	C	C	C
Ir	D	A	A	A	A	B	A	A	E	B	A	D	C	C	C
Os	D	E	B	A	A	A	B	A	B	D	E	E	C	E	D
Ru	D	B	B	B	A	A	B	A	B	D	B	B	C	C	D

A-continuous solid solution series
B-limited solubility of each metal in the other
C-combine to form compounds
D-very little solubility of one phase in the other
E-no data available

It will be noted that they combine, at least to some extent, with most of the elements listed in the table. Continuous solid solution series exist between elements which have the same crystal structure, such as Pd and Cu, whereas there is little solid solution of elements such as Os and Ru

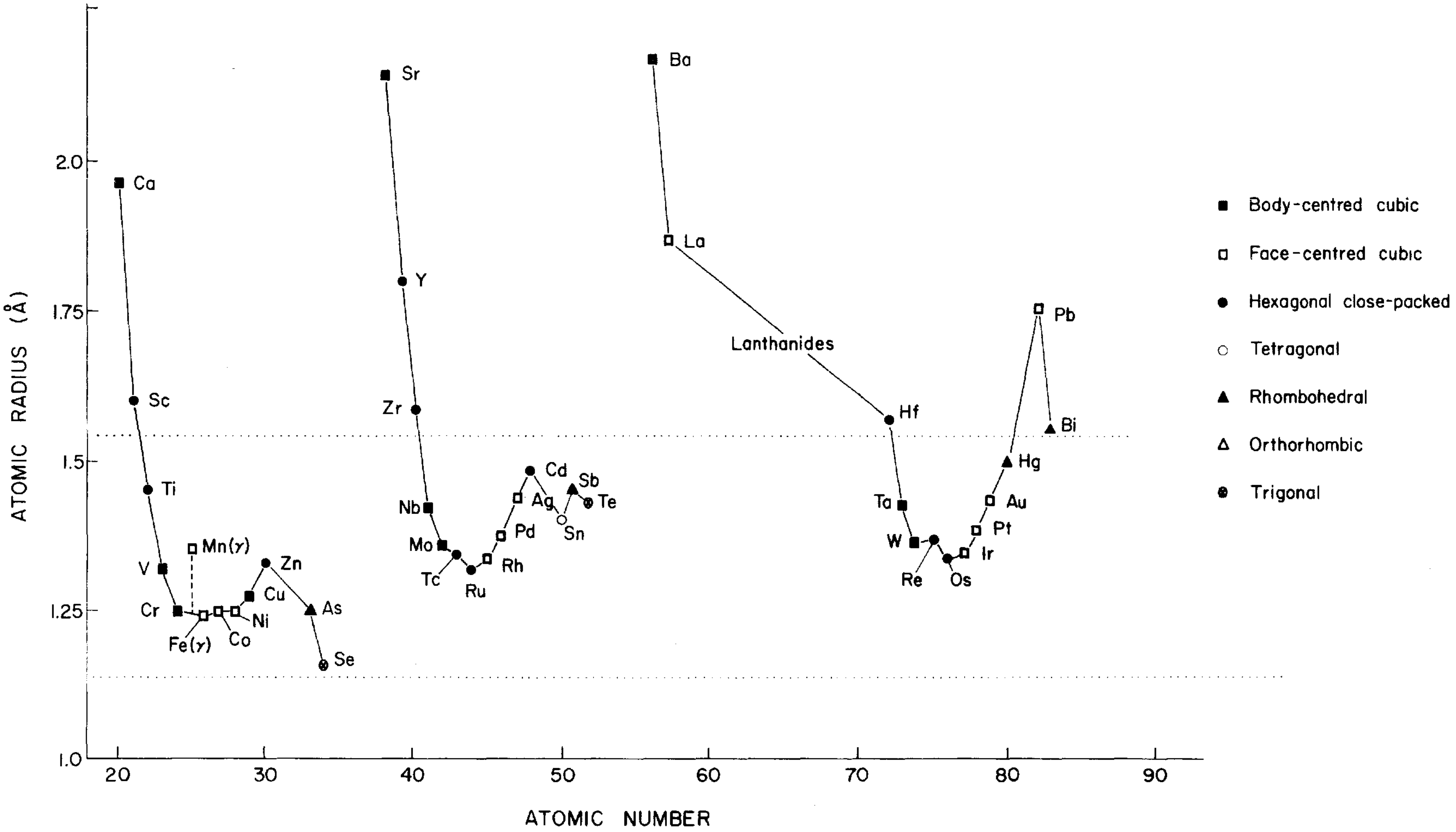

Figure 8-1 The atomic radii of the transition metals and some B sub-group metals. Dotted lines cut off radii within 15 % of atomic radius of Os. Radii are for 12-fold co-ordination except for radii of B sub-group metals, for which radii are half the distances of closest approach.

(hexagonal close-packed structure) with Cu (face-centered cubic structure).

Table 8-3 gives the ranges in chemical composition of the naturally occurring compounds of the platinum metals. The limits of composition of the natural alloys are poorly known, partly because of the great difficulty in analysis of the platinum metals, but largely because of the inhomogeneity of the material analysed. Borovskii et al. (1959), Genkin (1959), Genkin et al. (1962, 1963), Stumpfl (1961) and Kingston (1966) illustrated that alloys of the platinum metals commonly occur as complex intergrowths of minute grains; they have employed the electron-probe microanalyser to study the naturally occurring platinum metal alloys and in the process have discovered many new minerals.

Although sulphides of the precious metals (braggite, cooperite, vysolskite, and laurite) are major natural compounds of the metals, many other minerals exist which are comprised solely of metals, and, as such must be regarded as alloys. All elements which combine with the precious metals also occur as native metals, and all, except Pb and S, have metallic radii within 15% of the radii of the precious metals. Except for As, Te, Sb, Sn, Pb and Bi all have the same crystal type as the precious metals. The fact that each precious metal forms naturally occurring minerals with at least some of these metals is a result of similar concentration processes which tend to bring the metals together in sufficient concentration to cause crystallization of intermetallic phases.

In theory, on the basis of valence and radius considerations alone, the precious metals may substitute in ionic structures (for example, silicates) substituting for such major elements as Ni, Fe, Cu and Ti. However, as will be shown below, substitution of the precious metals in ionic structures is unlikely because of energy reasons. They do form an extensive

Table 8-3 Chemical composition of compounds of the platinum metals (after Wright and Fleischer, 1965 and Fleischer, 1967)

Mineral Formula	Braggite $(Pt,Pd,Ni)S$	Cooperite $(Pt,Pd)S$	Geversite $PtSb_2$	Hollingworthite $(Rh,Pd,Pt,Ir)AsS$	Merenskyite $(Pd,Pt)(Te,Bi)_2$	Irarsite $(Ir,Ru,Rh,Pt)AsS$	Kotulskite $Pd(Te,Bi)_{1.2}$	Laurite $(Ru,Os)S_2$	Michenerite $(Pd,Pt)(Bi,Te)$	Moncheite $(Pt,Pd)(Bi,Te)_2$	Niggliite $PtSn$	Sperrylite $PtAs_2$
Element												
Pt	59	80.2-82.5	45	10.3-18.4	0-1.8	12.6	0-1.1	---	8.4-9.3	18.6-42.0	58.5-63.3	23.8-63
Ir	Present	Present		1.4-3.1	---	23.0	---	11.4	---	---	---	17.8
Os	---	---		---	---	---	---	0-20.9	---	---	---	---
Pd	18-20.9	0-4.3		8.7	23.1-33.2	---	31.1-45.9	---	11.7-16.9	0-9.3	---	2.1
Rh	Present	---		24.6-30.8	---	7.2	---	---	---	---	---	11.6
Ru	Present	---		12.8	---	9.4	---	33.67	---	---	---	---
Au	---	---		---	---	---	---	---	---	---	---	---
Fe	---	---		---	---	---	---	---	---	---	---	0-0.7
Cu	---	---		---	---	---	---	---	---	0-8.0	---	0-0.7
Ni	2.8-4.7	0-0.1		---	---	---	---	---	---	---	---	---
Pb	---	---		---	---	---	---	---	---	---	---	---
S	16.8-19.0	14.3-17.5		13.0-13.9	---	11.6	---	21.4-33	---	---	---	10.8
Te	---	---		---	50.8-56.3	---	36.1-44.0	---	28.8-37.6	33.5-55.4	---	---
As	---	---		32.6-34.0	---	34.5	---	---	---	---	---	30.7-41.9
Sb	---	---	51.5	---	---	---	---	---	---	---	---	0-0.5
Bi	---	---		---	14.2-15.1	---	17.2-24.9	---	42.3-45.0	7.5-31.7	---	---
Sn	---	---		---	---	---	---	---	---	---	38.0-42	0-4
Hg	---	---		---	---	---	---	---	---	---	---	---

Mineral Formula	Stibiopalladinite Pd_3Sb	Stannopalladinite $(Pd,Pt)_3Sn_2$	Vysotskite $(Pd,Ni,Pt)S$	Zvyagintsevite $(Pd,Pt)_3(Pb,Sn)$	Unnamed mineral (based on one analysis each)													
					B	C	D	E	F	G	I	J	K	L	M	N	O	P
Element																		
Pt	---	15-20	4.1-5.5	7.5	47.0	22.0	36	50.5	50.5	---	---	6.0	51.7	50	---	---	---	---
Ir	---	---	---	---	5.0	Major	---	---	---	---	---	---	---	2.5	---	---	---	11.4
Os	---	---	---	---	---	Major	---	---	---	---	---	---	---		---	---	---	20.9
Pd	70.4-73	40-45	57.1-61.9	55.0-55.6	---	---	---	---	---	43.6	53.5	62.0	---	28	33.1	27.8	15	---
Rh	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Ru	---	---	---	---	---	---	3	---	---	---	---	---	---	---	---	---	---	33.0
Au	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Fe	---	0.3-2.3	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Cu	---	5-12	---	---	---	---	---	---	---	---	16.0	5.0	16.8	---	---	---	---	---
Ni	---	0.1-0.7	14.2-16.6	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Pb	---	---	---	25.0-38.0	---	---	---	---	---	---	---	---	---	---	29.0	---	---	---
S	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	21.4
Te	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	38.5	---	---
As	---	---	---	---	46.8	32.5	28	---	---	---	---	---	---	---	---	---	---	---
Sb	25-28	---	---	---	---	---	---	34.7	26.4	25.2	31.3	30.0	---	---	---	---	---	---
Bi	---	---	---	---	---	---	---	---	15.3	32.2	---	---	22.0	30	36.4	1.6	86	---
Sn	---	28-33	---	12.0	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Hg	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	12.0	---	---

series of alloys and compounds with a number of metals and semi-metals and commonly occur in nature combined with elements of the same atomic radius and crystal type.

3. Energy Factors

The factors which control the reactivity of an element are its ionization potentials, electron affinities, lattice energies and oxidation states. Those factors dependent on the above are electrode potentials, electronegativities, and the heats of vaporization and dissociation. Electronegativities control to a large measure the type of bonding between two elements; elements having large differences in electronegativities form ionic bonds while elements whose electronegativities are similar form covalent bonds. Ionization potentials may similarily be used to indicate which type of bond a cation will form (Ahrens 1953, 1964) and its geochemical tendencies. Generally, it is not one, but a combination of factors, which determine an element's behaviour.

i) Ionization Potentials Cations with low ionization potentials tend to form ionic structures with anions while those which have high ionization potentials tend to polarize the anions with which they combine. This polarization deforms the bond and induces covalent character. The net result is that the bond is weak. If the ionization potential is very high, deformation will be so large (and the bond so weak) that the cation will remain native.

Table 8-4 lists the ionization potentials of the precious metals and a few elements representative of some of the other groups for comparison. It is immediately obvious why noble gases are inert as they have extremely high first ionization potentials. Metals of Group Ib and VIII have siderophillic tendencies, as their high ionization potentials indicate they should

Table 8-4 Ionization Potentials of some of the Elements in Electron Volts (after Ahrens, 1964).

Alkalis	I	II	III	IV	V
Li	5.390	75.619	122.420	-	-
Na	5.138	47.290	71.628	98.880	138.367
Noble Gases					
He	24.581	54.403	-	-	-
Ne	21.559	40.955	(63.450)	97.024	126.260
Alkaline Earths					
Be	9.320	18.206	153.850	217.657	-
Mg	7.644	15.031	80.117	109.294	141.231
Halogens					
F	17.418	35.012	62.689	87.139	114.214
Cl	13.014	23.798	39.649	53.450	67.801
Groups VIII & Ib					
Fe	7.868	16.178	30.643	(56)	(79)
Co	7.875	17.052	33.491	(53)	(82)
Ni	7.633	18.147	35.165	(56)	(79)
Cu	7.724	20.286	37.079	(59)	(83)
Ru	7.364	16.758	28.459	(47)	(63)
Rh	7.461	18.072	31.049	(46)	(67)
Pd	8.334	19.423	32.921	(49)	(66)
Ag	7.574	21.481	34.818	(52)	(70)
Os	8.732	(17)	-	-	-
Ir	9.1	-	-	-	-
Pt	8.962	18.558	(29)	(41)	(55)
Au	9.223	20.045	(30)	(44)	(58)
Groups VIa, and VIIa					
Cr	6.764	16.493	30.950	(49)	(73)
Mo	7.097	16.151	27.133	(46)	(61)
W	7.982	(17.7)	(24)	(35)	(48)
Mn	7.432	15.636	33.690	(53)	(76)
Tc	7.276	15.258	29.537	(43)	(59)
Re	7.875	(16.6)	-	-	-

but it is not obvious from the ionization potentials alone why the precious metals should be more inert than Fe, Co, Ni and Cu. One of the reasons why the precious metals are noble is their oxidation states. For example, the highest stable oxidation state of Fe is III while that of Os is VI. The ionization potential of Fe^{III} is 30.6 eV while that of Os^{VI} is greater than 60 eV. Hence, although equivalent oxidation states of Os and Fe have similar ionization potentials, a much higher potential is required to oxidize Os to its highest stable state than that necessary to oxidize Fe to its highest stable state.

ii) Electronegativity The concept of electronegativity (which is defined as the power of an atom in a molecule to attract electrons to itself) has also been used to predict bond types. Unfortunately, there is considerable doubt about the electronegativities of the noble metals. Two sets of values (see Table 8-5) have been calculated. The earlier set, that of Pauling, assigned very high electronegativities to the noble metals. Skippen (1963) Baedecker (1967) and Shcherbakov and Perezhogin (1964) using Pauling's values, attributed the absence of the noble metals in silicates to the high electronegativities of the metals. Ringwood (1955) stated that cations with high electronegativities form bonds with intermediate covalent-ionic character which weakens the resultant bond. A metal with a high electronegativity attracts electrons to itself and has a tendency to polarize the anion, which results in the production of a bond with considerable covalent character. However, the bonding of the silica tetrahedra to cations in silicate structures is largely ionic and hence the noble metals would tend not to enter such structures. A more recent set of electronegativities, which Cotton and Wilkinson (1962) claim to be more accurate, assigns the noble metals intermediate values and indicates that they are

H 2.1 2.1																
Li .97 1.0	Be 1.47 1.5											B 2.01 2.0	C 2.50 2.5	N 3.07 3.0	O 3.50 3.5	F 4.1 4.0
Na 1.01 0.9	Mg 1.23 1.2											Al 1.47 1.5	Si 1.74 1.8	P 2.06 2.1	S 2.44 2.5	Cl 2.83 3.0
K 0.91 0.8	Ca 1.04 1.0	Sc 1.20 1.3	Ti 1.32 1.6	V^{V} 1.45 1.5	Cr^{III} 1.56 1.6	Mn^{III} 1.60 1.5	Fe^{II} 1.64 1.65	Co 1.70 1.7	Ni 1.75 1.7	Cu^{II} 1.75 2.0	Zn 1.66 1.5	Ga 1.82 1.6	Ge 2.02 1.7	As 2.20 2.0	Se 2.48 2.3	Br 2.74 2.8
Rb 0.89 0.8	Sr 0.99 1.0	Y 1.11 1.2	Zr 1.22 1.4	Nb 1.23 1.6	Mo^{IV} 1.30 1.6	Tc 1.36 -	Ru 1.42 2.05	Rh 1.45 2.1	Pd 1.35 2.0	Ag 1.42 1.8	Cd 1.46 1.5	In 1.49 1.6	Sn^{II} 1.72 1.65	Sb^{III} 1.82 1.8	Te 2.01 2.1	I 2.21 2.6
Cs 0.86 0.7	Ba 0.97 0.85	La 1.08 0.85	Hf 1.23 1.3	Ta 1.33 1.4	W^{VI} 1.40 2.1	Re 1.46 -	Os 1.52 2.1	Ir 1.55 2.1	Pt 1.44 2.1	Au 1.42 2.3	Hg 1.44 1.8	Tl 1.44 1.5	Pb 1.55 1.7	Bi 1.67 1.8	Po 1.76 2.0	At 1.90 2.4

Table 8-5 Electronegativities of the Elements. Lower figure of each pair is that of Pauling and others as listed by Fyfe (1951). Upper figure is that of Little and Jones (1960). Valence states of elements (where indicated) apply to lower figure only.

slightly less electronegative than Fe, Ni and Cu. The two conflicting sets of electronegativities render the application of the concept somewhat ineffective.

iii) <u>Lattice Energies</u> Lattice energy is the decrease in energy accompanying the process of bringing the ions or atoms, when separated from each other by infinite distance, to the positions they occupy in a stable lattice. Before a metal can react with another element it must first be dissociated into individual atoms which are then ionized. If a metal has a high lattice energy, it will tend not to dissociate but to remain inert. Although it is difficult to measure lattice energies directly, good qualitative estimates can be obtained from melting point data and heats of vaporization and dissociation. The binding energies (which are equivalent to the heats of sublimation) of the transition elements are plotted in Figure 8-2.

An example of the role of lattice energy in determining an element's reactivity may be shown by comparing the reactions of metallic sodium and silver with water to produce the ions in aqueous medium. The half-reactions may be written as follows:

	ΔH^o		ΔH^o
1) $Na(s) = Na(g)$	26	$Ag(s) = Ag(g)$	67
2) $Na(g) = Na^+(g) + e^-(g)$	118	$Ag(g) = Ag^+(g) + e^-(g)$	174
3) $\underline{Na^+(g) = Na^+(aq)}$	$\underline{-95}$	$\underline{Ag^+(g) = Ag^+(aq)}$	$\underline{-111}$
$Na(s) = Na^+(aq) + e^-(g)$	49 Kcal.	$Ag(s) = Ag^+(aq) + e^-(g)$	130 Kcal.

These half-reactions as written contain the electrons as a gas, but that is unimportant for the comparisons. Since ΔH is positive, the larger positive value for silver means a smaller tendency for the reaction to go. Silver is a noble metal while sodium is a base not only because silver has a higher

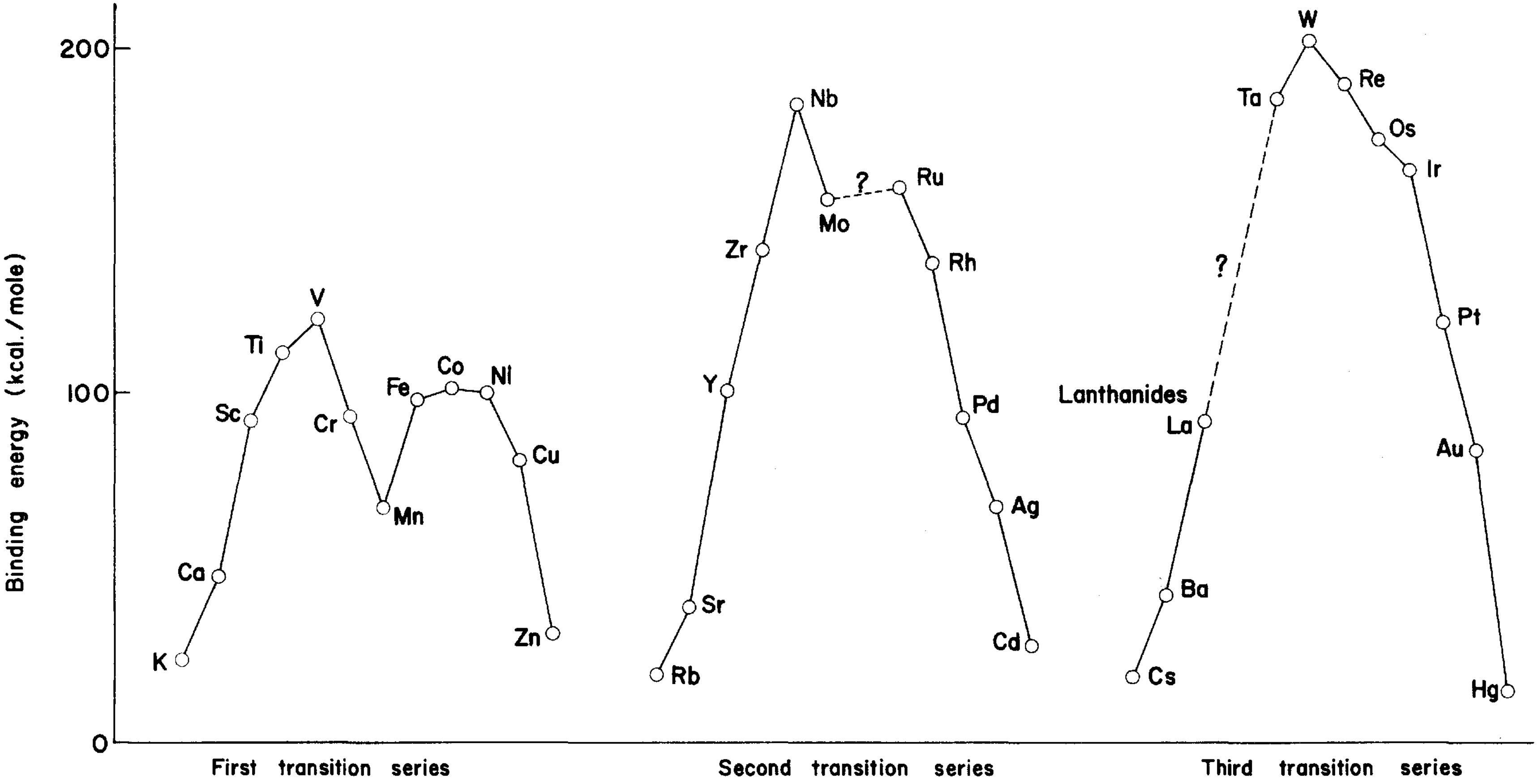

Figure 8-2 The binding energies of the transition metals

ionization potential (2) but also because its sublimation energy (1) is almost three times that of sodium. Of the precious metals, Os, Ru and Ir are the most inert, remaining unattacked by any acids up to the boiling point. They can be dissolved by an alkaline oxidizing fusion. Massive Rh does not dissolve in aqua regia, but dissolves when finely divided. Pt and Au readily dissolve in aqua regia, and Pd (and Ag) dissolves in nitric acid. The relative order of inertness of the precious metals is amply illustrated by Figure 8-2. The most inert members of the group (Ru, Os and Ir) have the highest binding energies; Rh, with intermediate inertness, has an intermediate value for the binding energy; and Pt, Pd and Au, which are the least inert of the metals, have the lowest binding energies. Also, the more inert members of the group have binding energies much larger than those of Fe, Ni and Cu.

iv) Oxidation Potentials Oxidation potentials also indicate a metal's reactivity. Metals with large positive potentials are reactive, while those with large negative oxidation potentials tend to be inert. Latimer (1952) has given electrode potentials for the couples listed in Table 8-6.

The electrode potentials indicate why Zn is reactive while the precious metals are noble. According to the electrode potentials, Au should be the most unreactive, while Rh should be the most reactive of the noble metals. The electrode potentials do not correspond precisely to the order of reactivity of the elements with common laboratory reactives; for example, Au and Pt readily react with aqua regia, but Rh, Os and Ir do not.

Table 8-6 Electrode Potentials of the Precious Metals

	E°(in volts)
$Zn \longrightarrow Zn^{++} + 2e^-$	0.763
$Fe \longrightarrow Fe^{++} + 2e^-$	0.440
$Fe \longrightarrow Fe^{+++} + 3e^-$	0.036
$Ni \longrightarrow Ni^{++} + 2e^-$	0.023
$Cu \longrightarrow Cu^{++} + 2e^-$	-0.337
$Cu \longrightarrow Cu^{+} + 1e^-$	-0.521
$Rh \longrightarrow Rh^{+++} + 3e^-$	-0.8
$Os \longrightarrow Os^{++} + 2e^-$	-0.85
$Pd \longrightarrow Pd^{++} + 2e^-$	-0.987
$Ir \longrightarrow Ir^{++} + 2e^-$	-1.1
$Ir \longrightarrow Ir^{+++} + 3e^-$	-1.15
$Pt \longrightarrow Pt^{++} + 2e^-$	Ca.-1.2
$Au \longrightarrow Au^{+++} + 3e^-$	-1.50
$Au \longrightarrow Au^{+} + 1e$	Ca.-1.68

v) Thermodynamic data Goldschmidt proposed an empirical, geochemical classification of the elements based on their affinity for metallic iron, sulphide and oxide plus silicate using the terms siderophile, chalcophile and lithophile, respectively to describe these tendencies.

Thermodynamic data for the oxides and sulphides of the precious metals and of pertinent base metals are in Table 8-7. Mason (1958) noted that if the heat of formation of an oxide is greater than that of FeO, the element is lithophile. If the oxide has a lower heat formation than FeO, the element is chalcophile or siderophile.

Equations of the type

$$Ir_2O_3 + 3Fe \longrightarrow 2Ir + 3FeO \qquad \Delta H=-122$$

may be written for each of the precious metal oxides. In each case, the reactions as written have large heats of reaction and free energies which indicate that the reactions should proceed to the right, i.e. the element tends to prefer the metallic state. This indicates that the elements are much more siderophilic than lithophilic. It may similarily be shown that the precious metals are more chalcophilic than lithophilic by reactions such as

$$PdO + FeS \longrightarrow PdS + FeO \quad \Delta H = -55.4$$

In all cases, the reaction proceeds to the right with large negative changes in enthalpy and free energy. This indicates that in the presence of an iron sulphide phase, the oxides of the precious metals will react to form their respective sulphides.

Thermodynamics may also be used to predict whether an element is more siderophilic than chalcophilic or vice versa. Free energies of reactions of the type $n.M + m.FeS \longrightarrow m.Fe + Mn\ Sm$ (where $\underline{n}$ and $\underline{m}$ are whole numbers) have been calculated and are tabulated in Table 8-7. Reactions which involve production of the monosulphides of the precious metals proceed with negative free energy changes for all of the metals except Ir and Pt. This indicates that the metals (except Ir and Pt) are more chalcophile than siderophile. However, in reactions of the element with FeS to produce disulphides or higher sulphides, such as

$$2Ir + 3FeS \longrightarrow 3Fe + Ir_2S_3 \quad \Delta F = +14.1$$

the free energies of the reactions are positive.

Although Pd and Pt commonly occur in nature as the monosulphide (e.g. braggite, (Pd, Pt, Ni)S) monosulphides of Ru, Os, Rh or Ir are unknown. The latter occur in such minerals as laurite, $(Ru,Os)S_2$ in which the metals have high oxidation states. If, disulphides are more common than the monosulphides, then the precious metals are more siderophilic than chalcophilic and will enter an iron-rich phase in preference to a sulphide phase. It must be emphasized that the above considerations are generalizations only. Certainly, in a magma, the sulphide phase is not pure FeS but FeS plus Ni, Cu, Co,.....According to Smith (1961) Na is partitioned equally as weight per cent Na_2S and Na_2O between iron sulphide liquid and iron silicate liquid and it is partitioned in the ratio 1/1.87 between iron sulphide liquid and a calcium iron alumino-silicate liquid. Not only would the presence of Na_2S increase the free energy of the sulphide liquid, but it would also decrease the liquid miscibility gap between sulphide liquid and silicate liquid. The addition of these components would tend to increase the free energy of the resultant solution, and thereby increase the siderophilic tendencies of the precious metals. Further, many of the sulphides of the precious metals decompose at high temperatures.

The relative chalcophilic tendencies of the elements have been illustrated in Table 8-7, where the sulphides have been listed in order of increasing negative free energies. It can be seen that RuS is the most stable of the sulphides whereas PtS is the least stable, these sulphides having free energies of 38.5 and 18.6 respectively. The order of decreasing siderophilic tendency should be

$$\mathrm{Pt} < \mathrm{Ir} < \mathrm{Os} < \mathrm{Pd} < \mathrm{Rh} < \mathrm{Ru}$$

In summary, the precious metals tend to enter the metallic phase, but where this is not present, they enter the sulphide phase in preference to the silicate plus oxide phase.

4. Bonding and Structure Types

Bond type is a factor governing the tendency of an element to enter a given phase. The types of structures (which are dependent on bonding) formed by many of the precious metal chalconides are listed in Table 8-8. Included in the table is a brief description of the type of coordination in each of the structures.

Table 8-7 Thermodynamic data for the sulphides and oxides of the precious metals, iron, nickel, copper and sodium (all data for 298°C.)

Sulphide	$-\Delta H_{f°}$	$-\Delta F_{f°}$	S°	$\Delta F^*_{React.}$	Oxide	$-\Delta H_{f°}$	$-\Delta F_{f°}$	S°
RuS	39.2 (1)	38.5 (1)	12 (1)	-15.2				
RuS_2	47.0 (1)	44.1 (1)	12.4 (1)	+ 1.5	RuO_2	52.5 (2)	39.7 (2)	-
RhS	37.2 (1)	36.2 (1)	12 (1)	-12.9	RhO	22.5 (2)	16.6 (2)	-
Rh_2S_3	81.6 (1)	79.8 (1)	32 (1)	- 9.9	Rh_2O_3	68.3 (2)	48.9 (2)	-
RhS_2	42.5 (1)	41.1 (1)	18 (1)	+ 5.5				
PdS	35.8 (1)	34.4 (1)	12 (1)	-10.1	PdO	20.4 (3)	14.4 (3)	-
PdS_2	39.0 (1)	37.1 (1)	18 (1)	+ 9.5				
OsS	26.4 (1)	25.4 (1)	12 (1)	- 2.1				
OsS_2	37.4 (1)	37.2 (1)	23.3 (1)	+ 9.4	OsO_2	62 (2)	49.5 (2)	-
OsS_3	42.6 (1)	40.3 (1)	23 (1)	+29.6				
OsS_4	48.0 (1)	44.3 (1)	26 (1)	+48.9	OsO_4	91.7 (3)	70.5 (3)	34.7 (3)
IrS	23.0 (1)	21.7 (1)	12 (1)	+ 1.6				
Ir_2S_3	56.2 (1)	55.8 (1)	30.2 (1)	+14.1	Ir_2O_3	68 (2)	49 (2)	-
IrS_2	31.0 (1)	31.5 (1)	25.6 (1)	+15.1	IrO_2	44 (2)	32 (2)	-
PtS	20.2 (1)	18.6 (1)	12.0 (1)	+ 4.7	PtO	17 (2)	11 (2)	-
PtS_2	26.6 (1)	24.3 (1)	17.3 (1)	+22.3	PtO_2	32 (2)	19 (2)	-
AuS	-	-	-		Au_2O	-	-	-
					Au_2O_3	-0.8 (2)	-18.8 (2)	-
FeS	22.72(4)	23.32(4)	16.1 (1)		FeO	63.7 (4)	58.4 (4)	12.9 (4)
FeS_2	42.52(4)	39.84(4)	12.7 (1)		Fe_2O_3	196.51(4)	177.1 (4)	21.5 (4)
NiS	17.5 (4)	-			NiO	58.4 (4)	51.7 (4)	57 (4)
CuS	11.6 (4)	11.7 (4)	15.9		CuO	37.1 (4)	30.4 (4)	10.4 (4)
Cu_2S	19.0 (4)	20.6 (4)	28.9		Cu_2O	39.84(4)	34.98(4)	24.1 (4)
$CuFeS_2$	-	45 (5)	-					
Cu_5FeS_4	-	89 (5)	-					
Na_2S	89.2 (4)				Na_2O	99.4 (4)	90.0 (4)	66.0 (4)

Enthalpy and free energy data in Kcal/mole. Numbers in parenthesis refer to the following references: (1) McDonald & Cobble (1962), (2) Glassner (1957), (3) Latimer (1952), (4) Rossini et al. (1952) and (5) Bartholome(1958)

* $\Delta F_{React.}$ = Free energy charge for reactions of the type

$$x.M + y.\ FeS \longrightarrow y.Fe + MxSy$$

Table 8-8 Structures of the Precious Metal Chalconides*

Nickel Arsenide	Pyrites	Square Planar	Cadmium Iodide
FeS	FeS_2	PdS	$Pd\ Te_2$
FeSe	Ir_3S_8	PtS	$Pt\ S_2$
FeTe	OsS_2	AuS(?)	$Pt\ Se_2$
NiAs	$OsSb_2$		$Pt\ Te_2$
NiS	$OsSe_2$		$Rh\ Te_2$
CoS	$OsTe_2$		
IrTe	$RhTe_2$		
PdSb	PdS_2		
PdTe	$PdSe_2$		
PtBi	$PtAs_2$		
PtSb	$PtBi_2$		
RhTe	RhS_2		
	RuS_2		
	$RuSe_2$		
	$RuTe_2$		

Description of structures:

(1) Nickel arsenide has a structure in which each metal atom is surrounded octahedrally by 6 As atoms and also has two near metal atoms which are coplanar with 4 of the As atoms. There is considerable metallic bonding between the "near" metal atoms.

(2) Pyrite may be visualized as a distorted NaCl structure in which Fe atoms occupy Na positions and S atoms occur as discrete S_2 units and are situated with their centres at the Cl positions but turned in such a way that they are not parallel to any of the cube axes. The S-S distance within the S_2 group is such that each Fe atom is surrounded by 6 S atoms at the corners of a nearly regular octahedron, while each S atom is bound to one other S atom and to 3 Fe atoms.

(3) In a square planar array, the metal atoms are coordinated to 4 S atoms and all atoms are coplanar.

(4) Cadmium Iodide has a structure in which each Cd atom is octahedrally co-ordinated to 6 I atoms. Each I atom is co-ordinated to 3 Cd neighbours.

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* Information taken from the following sources: Cotton and Wilkinson (1962), Evans (1964), Hansen and Anderko (1958) and Wyckoff (1960).

Pt^{II}, Pd^{II}, Cu^{II}, Ni^{II} and Au^{III} form 4 coordinated complexes with most common anions (Cotton and Wilkinson, 1962). Many structures of these ions are square planar as a result of hybridization of the d,s, and p orbitals to form the square planar dsp^2 hybrid. Hence, PtS, PdS and (Pt, Pd, Ni)S have tetragonal structures in which the bonding configuration is square planar (Evans, 1964). However, in chalcopyrite the Cu atom forms the sp^3 hybrid orbital which results in a tetrahedral arrangement of the orbitals. Ni^{II} and Fe^{II} do not form a square planar bond with S but form d^2sp^3 hybrids which have octahedral configurations and the NiAs structure. Pd^{II} and Pt^{II} have many similarities to Cu^{II} and Ni^{II} but their substitution for these elements may be inhibited by their strong tendency to form square planar bonds. Ni^{+2}, Fe^{+2},Ru^{+2}, Os^{+2}, Co^{+3}, Rh^{+3}, Pt^{+4} and Pd^{+4} form octahedral complexes with d^2sp^3 hybrid bonds (Cotton and Wilkinson). Thus each divalent ion should be able to substitute for Fe. Although the bonds formed by Ir^{+3}, Pt^{+4} etc., are similar to the bonds formed by Ni^{+2}, and Fe^{+2}, there is a large charge difference. According to Sidgwick (1950) RuS and OsS do not exist, a fact which is not surprising as the II valence state is unstable for Os and Ru. The structure of IrS was not found in the literature. Ir^{II} is 5-coordinated in its complexes and so would not enter in Fe-Cu-Ni compounds in which the coordination is either 4 or 6.

PdSb, PdTe, IrTe etc. have the NiAs structure and so substitution of the cations of these compounds for Fe and Ni could occur. Most of the chalconides of the precious metals have either the pyrite structure or the layered cadmium iodide structure.

Craig (1966) studied the appearance of phases during cooling of a sulphide of composition corresponding to that of the average Strathcona footwall massive ore. This sulphide had a composition of 1.5 per cent Cu, 4.5 per cent Ni, 55.47 per cent Fe, and 38.53 per cent S. From the freezing point (1105°C) of a liquid of this composition to 450°C at which temperature chalcopyrite commenced to exsolve, one homogeneous phase existed: Cu-Ni-rich pyrrhotite solid solution. These experiments indicate that considerable Cu and Ni may be accommodated in pyrrhotite solid solution and, supposedly, Cu enters cations positions in the NiAs structure at high temperatures. At lower temperatures, Cu cannot exist in the octahedral FeS structure and so exsolves. Although little is known about the structures of the precious metal chalconides at high temperatures, many of them probably enter the pyrrhotite solid solution at high temperature due to the greater degree of randomness of the structure. They may later be exsolved as the solid solution cools, as are chalcopyrite and pentlandite. Whether they were incorporated into the structures of these two minerals would depend on the type of bonding involved. In general, on the basis of structure types the precious metals do not readily enter into common sulphide phases (pyrrhotite, chalcopyrite or pentlandite) and so they should exsolve from the pyrrhotite solid solution to form individual platinum minerals.

The initial sulphide solid should be a pyrrhotite solid solution possessing the NiAs structure. Thus, the important consideration is not whether an element will crystallize into the chalcopyrite (or pentlandite) structure but rather whether it will be accepted into the pyrrhotite solid solution. Few of the precious metal chalconides have the NiAs structure. However, other compounds (e.g. chalcopyrite and pyrite) are dissolved in the pyrrhotite solid solution and later are exsolved (pyrite is really a reaction product between pyrrhotite and coexisting liquid) and so many of the precious metals probably could substitute into the high temperature sulphide. If this occurs, then the element is removed from the residual solution. An element's mode of occurrence in the liquid far outweighs its substitutional properties - if it were a metallic particle or tied up in a strongly-bound complex it might be unavailable for substitution, whereas if it were a simple cation or in a weakly bound complex it might be highly available. Another possible mode of occurrence of the precious metals in sulphides is in defect structures within the sulphides, either as native metals or as mineralloids of S, Te, Se. Because of the non-stoichiometry of sulphides, and the resultant variation in charge of a specific cation within the structure, a precious metal of high charge may substitute for a major cation. In a silicate, where the structure is more ordered, such a substitution would be less likely to occur. The extremely low concentrations of the precious metals enhance their probability of entering major sulphide structures through either effects of defect structures or non-stoichiometry.

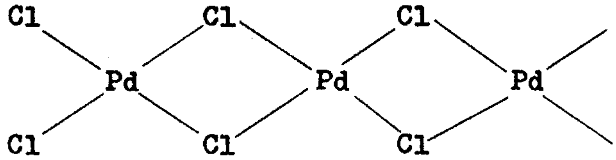
5. Complexes

None of the precious metals exist as simple cations in solution but combine with ligands to form a large number of complexes. The stabilities of most precious metal complexes at high temperature are unknown but their stabilities probably increase. Ogryslo (1935) and Zvyagintsev(1941) have demonstrated that Au is readily soluble in dilute solutions of hydrosulphide (NaHS) in which the Au is probably complexed as the polysulphide, AuS^-. Zvyagintsev showed that the solubility of Au in these solutions increases rapidly with increasing temperature. It is believed that the polysulphide becomes more complex with increasing temperature.

All of the precious metals form stable complexes with such ligands as the halides (e.g. $PtCl_6^=$) and thiocyanate (e.g. $Rh(CNS)_6^=$) but such complexes probably do not exist in a sulphide magma. (The introduction of H_2S into aqueous solutions of the precious metals generally causes precipitation of the sulphides.)

Pt, Pd and Au form many stable complexes with S, such as the polysulphides, $M^I_2\,Pd\,S_3$, $M^I_4\,Pt_3S_6$. Ru, Os and Ir form few complexes with S, and those that form are weak (pers. comm. Dr. A. Corsini). Ir^{III} forms the complex $(NH_4)_3\,Ir\,S_{15}$ in which the S forms three divalent S_5 groups, but it is unlikely such a complex would be stable in a sulphide liquid.

The cause for the large difference in the types of complexes formed may be connected to the types of bonding each cation prefers. Pt, Pd, Au and Cu form square planar hybrid orbitals and also sulphide complexes. The alkaline polysulphides of Cu can have any composition from Cu_2S_2 to Cu_2S_5. As the bonding in many of these complexes is square planar, stable chain complexes can be constructed. For example, the structure of $PdCl_2$ is that of a bridge complex:



Os, Ru, Ir and Fe form octahedral or tetrahedral complexes which are not so amenable to the construction of chains.

Many of the elements can be placed into two classes with regard to their bonding types. Ahrland (1966) described class (a), or hard acceptors, as those metals whose coordination is governed by the electrostatic interaction existing between charges of opposite signs. The bonding of (a) acceptors is essentially ionic. He described class (b) or soft acceptors, as those whose coordinating ability does not regularly increase with increasing charge or decreasing radius of the acceptor. Such acceptors do not prefer the small donor atoms F,O, and N but rather their heavy congeners. This indicates that the complexes formed contain bonds of a mainly covalent character. Ahrland states that the factors which produce (b)-class acceptors are as follows:

1) a large number of d-electrons in their outer shell. Acceptors with less than six d-electrons never exhibit very strong (b) properties, and less than five means (a)-properties in all but a very few cases,

2) a large polarizability,

3) ability to polarize the donor, i.e. large ionization potential,

4) for acceptors of a given net charge and outer electronic configuration, the polarizability will increase with the number of electron shells. Thus, acceptors of high periods have more (b)-class properties than acceptors of the same type but lower period, and

5) easily polarized donors (e.g. S, Te, Se).

A partial classification of (b)-acceptors is given below:

	Ions	Configuration
Most typical (b)-acceptors	Cu(I), Ag(I), Au(I)	d^{10}
	Pd(II), Pt(II), Au(III)	d^8
	Pd(IV), Pt(IV)	d^6
Moderately Strong(b)-acceptors	Ru(II), Rh(III), Os(II), Ir(III)	d^6
	Ru(III), Rh(III), Os(III), Ir(IV)	d^5

Pd, Pt and Au are stronger (b)-acceptors than Ru, Rh, Os and Ir; this implies that Pd, Pt and Au form stronger complexes with donors such as S, Se and Te. They do so because they have more d-electrons, larger atomic radii (and hence the ions are more easily polarized), lower stable oxidation states (hence more d-electrons), and high polarization properties. Comparison of the first ionization potentials of Ru (7.364), Rh (7.461) and Pd (8.334) indicates that Pd has considerably more polarizing power than Ru or Rh and so should be a stronger (b)-acceptor.

Hence, because sulphur is an easily polarized donor and forms covalent complexes, Pd, Pt and Au are better acceptors than Ru, Rh, Os or Ir. If metal complexes form in a solution containing sulphur species, the first three metals are more likely to occur as complexes than the latter four.

CHAPTER IX

REVIEW OF THE SUDBURY LITERATURE

1. General Geological Setting

The Sudbury Nickel Irruptive, which outcrops as an elliptical ring with the long axis running 37 miles east-northeast and the short axis 17 miles, consists of an outer ring of norite and an inner ring of granophyre. Figure 9-1 illustrates the general geology of the Sudbury area and the locations of most of the larger mines active at the present time. The Irruptive lies within the Southern Province of the Precambrian Shield five to ten miles north-west of the "Grenville Front".

The rocks bounding the Irruptive on its northern and eastern flanks consist of Archean granites and quartz-plagioclase-augite gneisses. The complex is bounded on the south by an apparently conformable series of metamorphosed Huronian volcanic and sedimentary rocks which strike east-northeast and dip at steep angles, mainly to the north. This succession faces south stratigraphically and ranges upwards from greenstones, through greywackes, to a conglomerate and an overlying quartzite. Some Killarnean intrusive granites lie between the Irruptive intrusion and the Huronian sediments on the southern border.

Within the complex is a stratified group of rocks known as the Whitewater Series whose constituent members outcrop in concentric rings, and dip towards the center of the complex. The Series is younger than the basement rocks to the south of the basin. The lowest unit in the

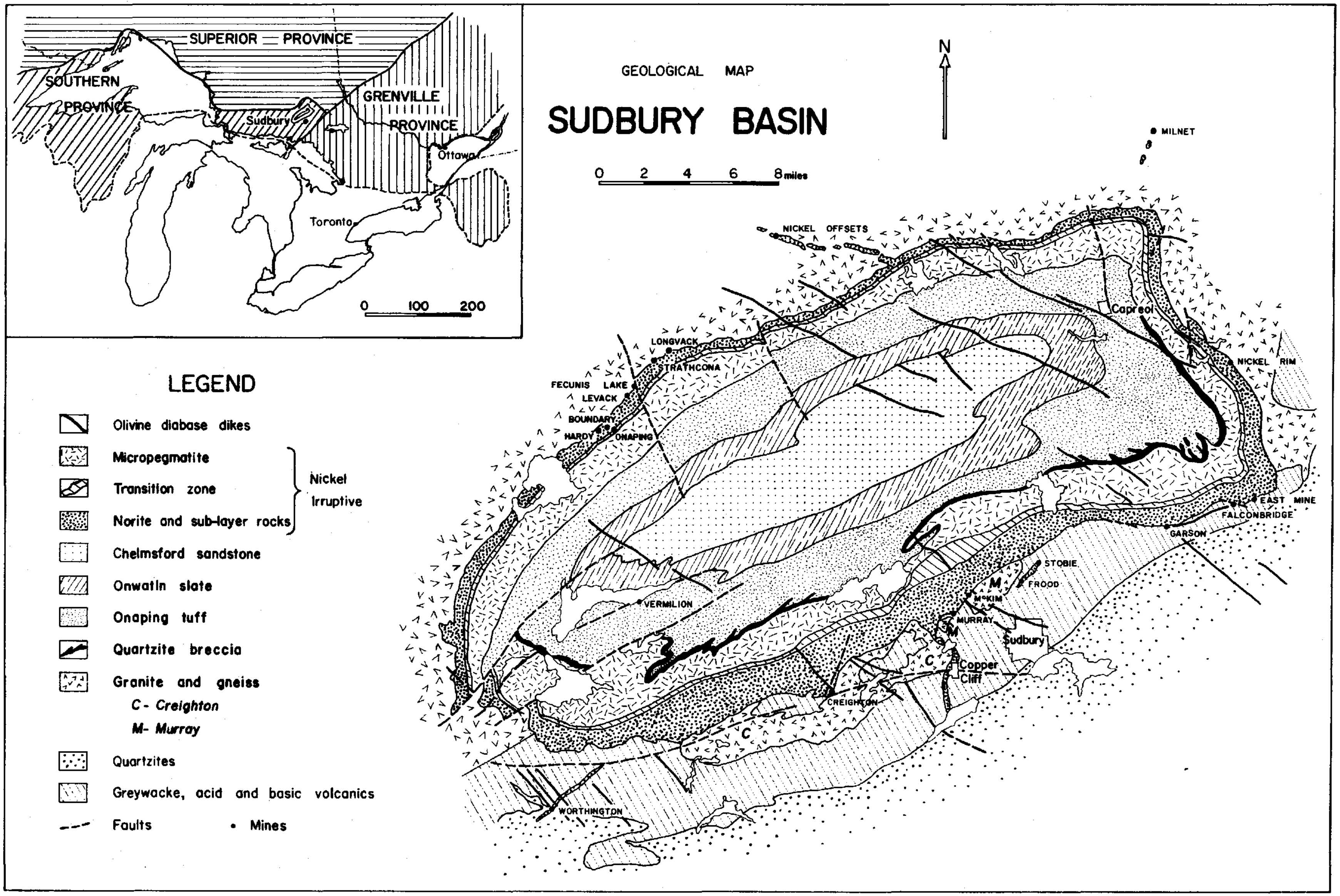


Figure 9-1. Index map of the Sudbury Irruptive and location of some of the more important mines. (Modified after Hawley, 1962.)

series rests on the Irruptive and is a volcanic formation variably described as tuff, agglomerate or ignimbrite and known as the Onaping tuff. The middle unit is termed the Onwatin slate and the upper, which consists of a massive greywacke, the Chelmsford Sandstone.

Problems in the rocks south of the norite have been ones of stratigraphy and correlation, the nature and origin of the Copper Cliff "rhyolite" and the ages of the intrusive granites at Creighton and Murray Mines. Detailed mapping by Phemister (1956) showed that the Copper Cliff "rhyolite" lies between older, dominantly volcanic rocks on the north and the McKim greywacke on the South. The unit has been interpreted as a hypabyssal intrusion and was dated by Fairbairn _et al_. (1965) at 2.35×10^9 years. The geological relationships of the intrusive Creighton and Murray granites with respect to the norite have led to considerable controversy. Sullivan (1957) contended that intrusion of the quartz diorite, found in the "offset" deposits and at the base of the norite near some of the sulphide bodies, was a distinct intrusive and later than that of the norite. He stated that the granite intruded the norite, and the quartz diorite intruded the granite. Rb-Sr age dating by Fairbairn _et al_. (1965) clarified the problem, yielding ages of 2.14 and 1.72 billion years for the Murray and Creighton granites and the micropegmatite-norite, respectively. To explain the apparent cross-cutting relationships of the norite by the granite, Collins (1936) suggested remobilization and injection of granitic material during the intrusion of the norite.

Another problem of both economic and geological interest is that of the origin of the Sudbury breccias, which are extensively developed around the periphery of the basin and for some miles beyond. The breccias were noted by early workers including Coleman (1913) and Collins and later described by Yates (1938), Fairbairn and Robson (1941), Cooke (1946), Thompson (1957), Zurbrigg et al. (1957), and Speers (1957). Many breccias host ore, the most outstanding example being the great Frood breccia zone which extends for many miles. Speers showed that most breccias are pre-norite but many were remobilized during intrusion of the Irruptive. The origin of the breccias has not been resolved. Absence of large scale fault movements is indicated by continuity of the stratigraphy and lack of shearing. Water or water vapour may have played a major role during the development of the breccias, but the later intrusion of the Irruptive may have imposed a high temperature metamorphism which destroyed hydrous silicates formed during the brecciation stage. Forces leading to the injection of the Nickel Irruptive may be related to the widespread formation of the breccias.

2. The Sudbury Nickel Irruptive

The contact of the Irruptive with the basement rocks dips inwards at 30° to 60° except in the southwest where the dip is nearly vertical and in the southeast where the contact dips as much as 65° away from the center of the complex. The inner contact against the Whitewater series apparently always dips towards the center. The outer part of the Irruptive consists of an augite norite (Johannsen, 1937) which grades inwards through a transition zone into an inner ring of granophyric, alkali feldspar-rich rock known as micropegmatite. A phase of the norite, quartz diorite, is found in the five "offsets" which are dyke-like protrusions of igneous rocks that project away from the outer perimeter of the Irruptive into the surrounding country rock (see Figure 9-1). It is also a basal unit of the norite in the main part of the complex and is intimately associated with the ores. The complex has been interpreted as the surface expression of each of the following: (1) a folded-differentiated sill; (2) a ring-dyke complex; (3) a differentiated funnel shaped intrusion; (4)a meteorite crater; and (5) a lava flow.

Walker (1897) was the first to propose the differentiated sill hypothesis, which later received support from Coleman (1905, 1913), who was the first to map the whole of the Irruptive. Coleman concluded that the norite and micropegamtite had differentiated by crystallization <u>in situ</u> from a single flat-lying sheet of magma intruded along the unconformity between the Whitewater series and the underlying Archean and Huronian rocks. Collins (1934) suggested that the original magma of the Nickel Irruptive separated while in the liquid state into norite and micropegmatite magmas which subsequently crystallized to form the two layers. Proponents of the differentiated sill hypothesis argue that intrusion of the magma resulted in subsidence of the central area to form the present trough-shaped body.

The ring-dyke hypothesis was first made by Knight (1917) who suggested that two separate intrusions of magma, the first noritic and the second micropegmatitic, had been forced up around a block of younger rocks that had been down-faulted several thousand feet with respect to the rocks outside the basin. Phemister (1925), who subscribed to the multiple-intrusion theory, explained the transition zone as a hybrid zone formed by the mixing of the two intruded magmas. Williams (1956) and Thomson (1956) correlated the Onaping tuff with the more deformed volcanic rocks outside the basin. Thomson believed that the composite irruptive was intruded around the edges of a "ring-graben" following subsidence of the central basin, initiated by and subsequent to the Onaping volcanic activity.

The nature of the basal part of the Onaping tuff, which was called the "Trout Lake Conglomerate" by Coleman and later described by Burrows and

Rickaby (1929) as a rhyolite breccia, plays a key role in the composite irruptive theory. Thomson and Williams regarded the Onaping tuff as a combination of glowing avalanche deposits and andesite lava flows and the "Trout Lake Conglomerate" as rhyolitic material derived from Pelean domes and feeder dykes. The same volcanic activity that deposited the Onaping tuff gave rise to submarine lava flows, glowing avalanche deposits, and sediments outside the basin to form the Stobie formation. Stevenson (1960, 1961), however, considered the "Trout Lake Conglomerate" as a discontinuous stratigraphic horizon of quartzite and quartzite breccia that was intruded from below by the micropegmatite.

Stevenson mapped a zone immediately above the micropegmatite which consists of quartzite breccia and a fine-grained phase of the micropegmatite. He observed quartz pseudomorphic after tridymite and spherulitic intergrowths in this upper zone of the micropegmatite. Stevenson stated that these features indicate that the micropegmatite intruded the quartzite at a high temperature (800° to 900°C) and cooled rapidly after intrusion. Stevenson's observations throw doubt on the correlation of rocks inside and outside the ring and indicate that the complex may have exploited an unconformity rather than a system of fissures and faults. Further, Fairbairn et al. (1966) showed that the maximum age of the Onaping tuff is 1.7 billion years, whereas the basic volcanics of the Stobie group immediately southwest of the basin were dated at 2.01 billion years by Knight (1966).

Wilson (1956) noting that the Sudbury Irruptive has a broad, although poorly-defined, magnetite-rich layer equivalent to the massive magnetite layers of the Bushveld complex, suggested that the Irruptive was funnel shaped and it might have ultramafic layers at depth. According to

Hawley, H.F. Zurbrigg reported that crystal layering has been observed in the norite. Naldrett and Kullerud reported that Souch et al. (1967) confirmed that the dip of the primary foliation in the feldspars and pyroxenes is flatter than the dip of the outer contact of the Irruptive.

Naldrett and Kullerud (1965 and 1967), Cowan and Lee (1967) and Souch et al. (1967) reported that the norite has an inclusion-bearing sub-layer at its base that is rich in xenoliths ranging from norite to peridotite. On the basis of cross-cutting relationships, inclusions of one phase in another, and distribution coefficients for Fe and Mg between pyroxenes, Naldrett and Kullerud concluded that the sub-layer norite is a younger intrusive than the bulk of the norite. They indicated that the only source of the peridotite xenoliths would have been from some ultramafic layer of the Irruptive that had already solidified at depth, before intrusion of the younger noritic sub-layer magma.

One of the problems with the differentiated sill hypothesis is that the proportion of micropegmatite to norite (3:1 on the north range) is much higher than would have been produced if the original magma had had the composition of mafic magmas commonly responsible for sills, especially if the quartz diorite in the "offset" deposits represents the composition of the initial magma as suggested by Hawley.

A funnel shape for the intrusion eliminates the problem of the relative proportions of the major units as well as the main argument for two intrusive series. The observation of crystal layering and ultramafic xenoliths in the norite supports Wilson's concept of a funnel shaped intrusion with ultramafic layers at depth.

Dietz (1964) suggested that the basin is the result of the impact of a meteorite which provided the metals for the sulphide ore bodies. He based his theory on the presence of shatter cones in the country rocks around the basin. French (1967) interpreted the Onaping tuff as a breccia resulting from the fall-back of material into a crater originally blasted out by the impact of a large meteorite. Naldrett (1967) concluded that "the hypothesis of a meteoritic impact triggering a sequence of events which led to the formation of the Sudbury ores is not inconsistent with known geological relations". He stated that derivation of the ore from a meteorite is inconsistent with the available geological data. One cannot accept the hypothesis as proven unless it can be established that the type of shatter cones and shock textures reported by Dietz and French are produced solely in nature by meteoritic impact and not by other natural phenomena such as volcanic explosions.

Other differentiated lopoliths (e.g. Bushveld, Stillwater, Skaergaard) have extensive ultramafic layers. Such layers are not exposed at Sudbury, nor have they been intersected by deep diamond drill holes. Further, gravitational studies by Miller and Innes (1955) indicate there is no considerable amount of ultramafic rocks at depth. Hamilton (1960) interpreted the Sudbury basin as an overflow part of the north flank of a huge lopolith, the bulk of which has been removed by erosion and which contained the missing mafic and ultramafic differentiates. The lopolith was essentially extrusive in origin and the Onaping tuff represents the true cap-rock of the complex. Hamilton pointed out the chemical similarities-high Na_2O, K_2O, Fe, low Al_2O_3 and CaO-of the tuffs and micropegmatite, indicating they are co-genetic. It is highly questionable that lava flows the size of which is postulated here are ever formed in nature. In proposing the model, Hamilton assumed that there were no ultramafic layers at depth. However, since his paper was published several workers (Naldrett, Cowan, Souch) have recognized ultramafic xenoliths in the norite which could only have been derived from depth, under the basin. Further Naldrett reported Wilson as stating in November, 1966 that a gravity high occurs within the basin. This could be due to an accumulation of dense ultramafic material at the base of the Nickel Irruptive.

The weight of the evidence available in the literature supports an hypothesis of a funnel-shaped, multiple injection of magma along the unconformable contact between overlying quartzite (the "Trout Lake Conglomerate") and older granites and meta-sediments. The first injection of magma, a granophyre, intruded, brecciated, and assimilated much of the overlying quartzites. It erupted through this thin roof-rock, spewing out the Onaping tuff in the form of glowing avalanches and andesitic lava flows. This was followed shortly by intrusion of the bulk of the noritic magma, the upper part of which mixed with the basal portion of the granophyric magma to produce the transition zone. As the magmas cooled, crystallization and settling of olivine and pyroxene crystals occurred with the formation of ultramafic layers at depth. A third injection of magma brecciated some of these layers and dragged the fragments along with it as it pushed up along the basal contact of the Irruptive. When movement of this sub-layer magma ceased, the xenoliths settled towards the base of the Irruptive where they now form breccia zones.

3. Sulphide Ores

The copper-nickel ores at Sudbury consist mainly of pyrrhotite, pentlandite and chalcopyrite with accessory cubanite, pyrite and magnetite. The ore bodies can be divided into two broad classes: (1) those that occur at or very close to the contact of the Irruptive and the underlying basement rocks (marginal deposits); and (2) those that are associated with the "offsets" ("offset" deposits). Figure 9-1 illustrates the disposition of the important ore deposits.

There are two principal schools of thought regarding the origin of the ores. One school contends that the sulphides are magmatic, formed by segregation and crystallization of a relatively dry sulphide melt which was introduced in solution in the initial magma. The other school states that the ores were introduced in a hydrothermal solution which concentrated the sulphides from the Irruptive magma and transported them to their present sites. A recent proposal by Kullerud (1963) suggests that sulphur derived from an external source has reacted with the silicates of the Nickel Irruptive and released copper and nickel to form the sulphides.

Early magmatists, such as Bell (1891) and Coleman (1905, 1913), noting the restriction of the ores to the base of the Irruptive and the absence of the extensive hydrothermal alteration products, proposed that an immiscible sulphide liquid separated from the Irruptive magma as it cooled and crystallized. This heavy liquid settled to the base of the Irruptive, collecting in pools which are now the ore bodies. With the development of more mines, it became obvious that some of the sulphides were introduced after consolidation of the noritic rocks. An example of this is at the Falconbridge mine where much of the ore occupies a steeply dipping fault zone at the Irruptive-footwall contact. To explain the late-stage emplacement of ore, one school of magmatists (Howe, 1914; Bateman, 1917) proposed that the ores were intruded with a younger igneous mass. Another camp (Coleman, Moore and Walker, 1929; Hawley, 1962) suggested that after segregation of an immiscible sulphide liquid and its collection in pools along the base of the Irruptive, some of the sulphide liquid was remobilized and injected into dilation zones along the contact of the consolidated norite and the footwall.

The hydrothermalists (Dickson, 1904; Knight, 1917; Wandke and Hoffman, 1924; Phemister, 1925) rest their case on the post-Irruptive age of the ore emplacement, textural evidence such as sulphides cross-cutting and replacing silicate grains, and the presence of some hydrothermal alteration. Biotite and a blue-green, sodium-rich amphibole are developed at silicate-sulphide contacts in some deposits and silicification has affected the wall rocks in the Falconbridge and East mines. However, Hawley stressed that biotite and amphibole alteration is not extensive and interpreted it as reaction between the silicates and sulphide magma which contained only small amounts of water. He attributed the silicification at Falconbridge and East mines to aqueous solutions which passed along the faults before the introduction of the sulphides.

The ores are associated with the quartz diorite. Yates, (1948) suggested that quartz diorite had acted as a favourable host rock for replacement by hydrothermal solutions. Because of the close association of ore and quartz diorite, an understanding of the origin of the latter is vital to the explanation of the ores. One interpretation of the unit is that it represents the original magma which subsequently differentiated into norite and micropegmatite. However, Collins considered it too basic, being closer in composition to the norite layer than to an average of norite and micropegmatite. Another possibility is that it represents noritic magma rendered siliceous by assimilation of acidic rock fragments. There is no evidence of any such assimilation and, in fact, reaction rims around basic fragments in the quartz diorite suggest the magma producing them was clearly a quartz diorite at the time the fragments were engulfed. Collins (1934, 1937) and Hawley (1965) suggested that acquisitions from the ore fluids, although largely composed of volatiles, such as water and soda, converted the basic magma of the lower part of the Irruptive to one from which amphiboles, biotite, quartz and other minerals of the quartz diorite were precipitated.

The exact relationship of the quartz diorite and the norite is not known, but the general consensus of opinion (Hawley, 1962; 1965; Yates, 1948; Naldrett and Kullerud, 1967) is that the quartz diorite is a closely related intrusive phase of the norite which slightly postdated the main body of the Irruptive.

Quartz diorite, as it occurs in the "offsets", is absent along the north range between the Hardy and Longvack mines (see Figure 9-1). Instead, a series of noritic intrusions with associated ultramafic xenoliths occur along the outer margin. These noritic rocks resemble the quartz diorite in the "offsets" and hence have been called quartz diorite in the field. However, they contain no K-feldspar and very little quartz (47% SiO_2 versus 60% SiO_2 in the quartz diorite of the "offsets") and hence are not true quartz diorites. The relationship between the two types of younger intrusions is not known, but they may be contemporaneous.

Kullerud (1963) questioned Hawley's model of introduction of the Irruptive and sulphide ores as a single miscible sulphide-silicate liquid which separated into two immiscible liquids upon intrusion of the magma. He stated that it was improbable that a liquid which was miscible in a magma chamber would become immiscible following intrusion if only the PT conditions changed. If sulphide-silicate immiscibility existed in the chamber, gravity settling of the sulphide liquid, with consequent depletion of the irruptive material in sulphides, would occur during generation of the magma. On the basis of experimental work performed by Kullerud and

Yoder (1963) demonstrating that sulphur gas reacts at high temperatures with silicates such as the olivines and pyroxenes to produce materials such as sulphides, magnetite, and quartz, Kullerud proposed an alternate model for the sulphide-silicate immiscibility scheme. He suggested that sulphur derived from an external source and introduced at a high temperature reacted with the consolidated silicates of the Nickel Irruptive, releasing iron, copper and nickel contained in the silicates to produce the sulphides of these metals and affecting the present composition of the quartz diorite. The introduction of sulphur at sufficiently high temperatures might lead to the formation of immiscible silicate-sulphide liquids at temperatures well below those of melting of the pure sulphides or silicates.

This "sulphurization" theory was discussed by Hawley (1965) in a paper in which he described upside-down zoning at the Frood mine. Hawley questioned the fact that if the sulphur was a free, mobile component, why did it not penetrate in some places well into the Irruptive. He presented textural and geochemical evidence which is difficult to explain with the new theory. At the surface, the ore at the Frood consists of disseminated sulphide globules in quartz diorite (see Figure 11-2). This grades downwards into a zone of rounded to club-shaped blebs of quartz diorite in massive sulphide. These silicate blebs are rimmed with black iron oxides and were considered by Hawley to have formed from immiscible silicate globules in sulphide liquid. This disseminated silicate-in-sulphide zone grades downwards into a massive sulphide zone below which is an ore zone consisting of stringer ore in siliceous and basic wall rocks with Cu-Ni-Pb-Zn-Sn-Bi-As-Te and precious metal mineralization. The ore body is zoned mineralogically, with high temperature minerals at the top of the deposit, low temperature and hydrothermal minerals at the lower extremities.

The Frood is also zoned with respect to individual metal concentrations. The ratio $\frac{Cu}{Cu + Ni}$ gradually increases from 0.43 at the surface to 0.87 at the 3000' level. As well, the ratio Ni/Co increases from 25.3 in the disseminated zone to 33.0 in the massive zone.

The reason for the zoning is two-fold. Firstly, there must have been a temperature gradient, with the heat source being the hot Irruptive above the "offset". Secondly, to explain the metal zoning, there must have been segregation of sulphide liquids. The chalcophilic nature of the metals decreases in the following series: Cu $>$ Ni $>$ Co $>$ Fe. When the ore body was forming, the first sulphide liquid to form would be Cu-rich. This would settle down through the less dense silicates to form the cubanite-chalcopyrite zone at the bottom of the deposit. Later sulphides would be less Cu-rich but more Ni-rich.

The weight of the available evidence indicates that the ores are essentially magmatic in origin and co-genetic with the norite. The sulphides are definitely associated with a younger noritic phase, be this quartz diorite or inclusion-bearing norite. Some of the sulphides probably separated as an immiscible liquid from the magma during its generation and lagged behind the magma as it was injected. Part of the sulphides may not have separated from the norite until crystallization of the olivines and pyroxenes of the ultramafic layers. During intrusion of the noritic sub-layer magma, these sulphide liquids were dragged up, suspended in the silicate magma, to be injected into the "offsets" and along the base of the Irruptive. In its new position, the sulphide liquid settled towards the floor of the Irruptive. Some of it was caught in structural traps and formed in situ deposits, such as the Frood-Stobie ores. Some of it collected in pockets along the floor of the Irruptive and was later, after consolidation of the norite, injected into dilation zones. The Falconbridge deposit is an example of sulphide liquid remobilized and intruded into a fault zone. In response to the thermal gradient created by the presence of the cooling norite, mineralogical and metallic zoning took place in some of the deposits. As the sulphides crystallized an aqueous phase was produced which caused some hydrothermal alteration and assisted in the re-distribution of the metals.

CHAPTER X

GEOLOGY OF THE STRATHCONA MINE

Cowan (1967) presented an excellent detailed description of the geology of the Strathcona ore body. Naldrett and Kullerud (1965, 1966, 1967) interpreted the results of petrological and experimental studies to postulate hypotheses on the origins of both the Strathcona ores and the Sudbury Irruptive. The terminology adopted by Naldrett and Kullerud, will be used in the discussion that follows.

The Strathcona ore deposit is one of a series of known ore bodies that occurs along a 6-mile, intensely mineralized stretch of the basal contact of the Irruptive in the northwest corner of the Sudbury basin (see Figure 9-1). The deposits are associated with embayments at the Irruptive's footwall contact, which varies in dip from 30° to 45° south, although locally the dip is much steeper or flatter, even horizontal. The Strathcona ore body has a strike length of one-half mile and dips that vary from 20° to 60° south in response to inflections in the footwall-Irruptive contact.

The geology and nature of the ore bodies of the Strathcona Mine are illustrated in Figures 10-1 and 11-1. The former is a vertical cross-section (21,200E) through the mine perpendicular to the average strike of the Footwall-Irruptive contact. Four horizontal mine level plans (2000, 2250, 2625 and 2750 foot levels) are given in Figure 11-1. The coordinates on the section and plans are in feet and refer to a grid laid out

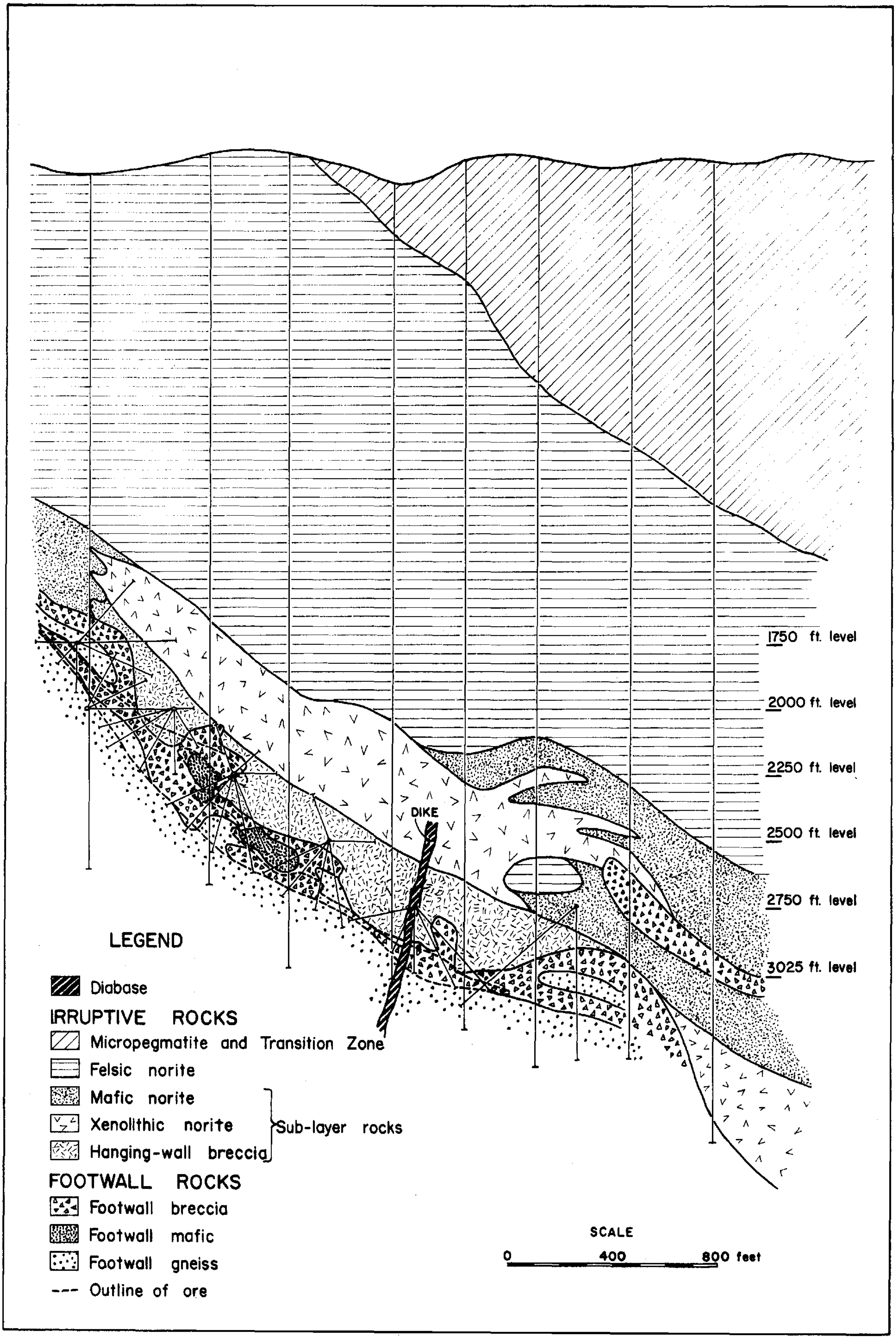


Figure 10-1. Vertical section (21,200E) through the Strathcona mine, illustrating the geology of the mine. (After Naldrett and Kullerud, 1967.)

by the mine engineers. Table 10-1 lists the rock units on the section and mine plans.

Table 10-1 Rock units in the vicinity of the Strathcona Mine

Diabase dikes	
Footwall breccia	
Nickel Irruptive	
Marginal intrusions	
Hanging-wall breccia	contemporaneous
Xenolithic norite	
Mafic norite	
Main body of Nickel Irruptive	
Micropegmatite	relative ages are uncertain
Transition zone	
Felsic norite	
Footwall gneiss	

N.B. Rock units are listed in chronological order (unless stated otherwise) with the youngest units at the top of the table.

1. Rock Units of the Footwall

The oldest rock in the mine, the footwall gneiss, is a fine-grained, quartz-plagioclase-augite gneiss with a xenoblastic granular fabric. Plagioclase occurs as a mosaic of small anhedral equant grains with well developed Carlsbad and Albite twinning. Quartz occurs as (1) small anhedral grains dotted among plagioclase grains; (2) lens-like segregations of anhedral interlocking grains; and (3) as an interstitial filling. Augite occurs in clusters of small anhedral grains. The gneiss contains numerous fine-grained, dark mafic inclusions consisting of augite, hypersthene, and brown hornblende ranging in size from several inches to 100 feet in length. Where these mafic inclusions exceed 50 per cent of the rock, the footwall complex has been classified and mapped as footwall mafic gneiss.

Between the granitic footwall complex and the base of the Irruptive is the footwall breccia, known locally as the "late granite breccia". This unit has a metamorphic texture which is like that of the footwall gneiss. Plagioclase occurs as a mosaic of rounded grains, while pyroxene is highly altered to amphibole, talc and rarely chlorite. Quartz occurs both as anhedral interlocking grains and interstitially, surrounding plagioclase grains. The footwall breccia and gneiss are similar, except that (1) the breccia is much richer in apatite and K-feldspar; (2) pyroxenes of the breccia are more highly altered; and (3) minor orthopyroxene occurs only in the breccia.

The contact between the granitic gneiss and the footwall breccia varies from sharp to gradational. Near the contact, the breccia is composed of gneissic fragments ranging in size from 10 feet down to the limit of vision dispersed in a darker grey matrix. In places, tongues of breccia penetrate into unbrecciated footwall gneiss, in others the contact is gradational. Near the contact with the footwall gneiss, the brecciated fragments consist solely of blocks of granite gneiss, whereas near the footwall breccia-Irruptive boundary fragments of norite, pyroxenite and peridotite predominate.

Speers (1957) suggested that the breccia originated from fracturing and pulverizing of the granite gneiss with subsequent recrystallization of the powdered rock in the presence of small quantities of material from an external source.

2. Rock Units of the Irruptive

Rocks representative of the transition zone or micropegmatite are not exposed in the mine workings, but have been intersected by diamond drill holes. The transition zone rock is a coarse-grained, hypidiomorphic granular rock consisting of about 60 per cent leucocratic silicates, 30-35 per cent mafic silicates, and 5-10 per cent titaniferous magnetite. The former consist of 10-15 per cent of a granophyric intergrowth of quartz and K-feldspar, 5-10 per cent quartz, and 3-8 per cent K-feldspar besides that in the granophyric intergrowths, and 40 per cent plagioclase. The mafic silicates are hypersthene and augite that have been altered to uralitic amphibole and 2-5 per cent biotite.

The lower part of the Irruptive, as exposed at Strathcona, can be separated into three mappable units which have been termed felsic norite, dark norite and hanging-wall breccia by mine geologists. The dark norite can be subdivided into two types on the basis of texture and mineralogy, mafic norite and xenolithic norite (the latter is termed basic norite by the mine geologists). Naldrett and Kullerud subdivided the dark norite represented in Figure 1-9 into its two components.

The oldest norite phase, felsic norite, is a coarse-grained hypidiomorphic granular rock. It is composed of 50 per cent subhedral zoned plagioclase laths, 30 per cent highly altered clinopyroxene crystals (in the ratio 1:2), and 10 per cent interstitial quartz and K-feldspar that exhibit some granophyric intergrowth. The pyroxene alteration products include uralitic amphibole, chlorite and biotite. The felsic norite contain both ilmenite and magnetite, with the former being the more predominant oxide. It contains less granophyric intergrowth and less-altered pyroxene, than the micropegmatite and transition zone rocks.

Under the felsic norite are the sub-layer rocks composed of mafic norite, xenolithic norite, and hanging-wall breccia. Felsic norite occurs as xenoliths in mafic norite and, because of this and other field relations, is thought to be older than the mafic norite. The presence of fragments of mafic norite in both the xenolithic norite and the hanging-wall breccia, and xenolithic norite chilled against mafic norite indicates that xenolithic norite is younger than mafic norite.

Mafic norite is a dark grey, medium-grained rock composed of 40 per cent large zoned euhedra of labradorite, 30 per cent hypersthene, and 10 per cent clinopyroxene. The texture of the rock varies between hypidiomorphic and poikilitic. It contains up to 10 per cent of a granophyric intergrowth of quartz and K-feldspar. Mafic norite is texturally and mineralogically very similar to felsic norite except that is has a higher proportion of mafic minerals, has less uralitized pyroxene, tends to have poikilitic texture, and has an oxide assemblage in which magnetite predominates over ilmenite.

Xenolithic norite is fine to medium-grained and has a distinctive intergranular texture. It consists of 40 per cent euhedral hypersthene plates with 20 per cent augite in a matrix of small interlocking laths of subhedral plagioclase. Very little quartz or K-feldspar is present, and no granophyric intergrowths have been observed. Some uralitization of pyroxene can be observed but much less than is present in felsic norite rocks. Magnetite again predominates over ilmenite.

Mafic norite contains up to 10 per cent anorthositic inclusions which appear to be identical to those in the felsic norite but contain no ultramafic inclusions. Inclusions in the xenolithic norite, on the other hand, are predominantly ultramafic, ranging from norite to peridotite. The size of the inclusions vary from pea-size to tens of feet across.

Where inclusions exceed 30 per cent of the xenolithic norite by volume, the rock has been mapped as the hanging-wall breccia. This latter rock is essentially xenolithic norite rich in inclusions,and contacts between it and the xenolithic norite are completely gradational. Reaction rims on olivine-rich fragments consist of 80 per cent hypersthene and 3 per cent interstitial plagioclase and are considered to have formed by high temperature recrystallization. The ultramafic inclusions in the hanging-wall breccia are believed to have been dragged up by, and emplaced with, the xenolithic norite. Due to gravitational settling they were concentrated in their present positions, in embayments along the base of the Irruptive.

Because zones of footwall breccia protrude back into xenolithic norite and fragments of xenolithic norite are found in the footwall breccia, it is obvious that the footwall breccia is the youngest unit in the mine. In some places the contact between the hanging-wall and footwall breccias are gradational in which case the rock in the zone of mergence is referred to as "contact-breccia". These contact-breccias are frequently found between xenolithic norite and footwall breccia and are believed to be zones of xenolithic norite or hanging-wall breccia caught up in the same brecciation that caused the formation of the footwall breccia.

3. Ore Zones

A noritic embayment appears to be the primary structural control for the Strathcona ores, as can be observed from the vertical section and the horizontal plans (Figures 10-1 and 11-1). Hanging-wall breccia is extensive within the pronounced embayment (600 feet thick on the 2250 level)in contrast to those places along the base of the Irruptive where the contact is regular and steeply dipping and the breccia is thin or absent. Footwall breccia occurs around the embayment and extends away from the Irruptive rock as much as 600 feet horizontally. The section shows that hanging-wall breccia is thickest and most heavily mineralized in areas within this embayment. In addition, local thickenings in the ore are related to projections of norite into the footwall complex. This is well illustrated on the 2250 level where a pronounced, heavily mineralized nose occurs in the axial plane of the embayment.

The Strathcona ore body is a series of lenticular subparallel ore lenses which parallel the curvature of the norite embayment. The ore body can be subdivided into three major ore zones which are called the hanging-wall zone, main zone and deep ore zone.

i) Hanging-wall Zone The hanging-wall ores, which represent 10 per cent of the ore reserve, are within the matrix of the dark norite and hanging-wall breccia. Although some massive sulphides are present, the ore generally consists of disseminated composite grains of sulphides which occupy linked interstices between silicate grains. A definite concentration of sulphide blebs occurs near the basal contact of the hanging-wall breccia, especially where the basal contact of the Irruptive flattens. In places towards the base of the hanging-wall breccia large, unmineralized ultramafic and mafic bodies stand out in a matrix composed of up to 60% sulphide and 40% silicate. The textural relationships between sulphides and silicates indicate an approach to equilibrium conditions. Alteration of silicate grains in contact with sulphides is restricted to thin reaction rims and may have been produced by minor amounts of water associated with the sulphide phase.

It is believed that the hanging-wall ore formed by gravitational settling of an immiscible sulphide liquid which was contained in the sub-layer rocks and in this sense represents an in situ ore. The sulphide liquid settled into structural sites along the base of the sub-layer rocks, along with ultramafic xenoliths suspended in the mafic norite. Some of this liquid may later have been remobilized during formation of the footwall breccia.

ii) Main Zone Most of the main-zone ore, which constitutes 70 per cent of the mine's ore reserve, occurs in a series of lenticular lenses within the footwall breccia either as disseminations, patches and stringers, or massive bands. The disseminated sulphides appear to be restricted to a variety of the footwall breccia that has a somewhat higher proportion of mafic fragments than average. The most common type of ore, breccia ore, consists of patches and stringers of sulphides. Bands of massive sulphides are most common adjacent to the footwall of the main zone and occur at the base of the footwall breccia and in the adjacent gneiss complex. Sulphides within these bands have flow structures around the larger rock fragments.

The main zone ore generally has the same mineralogy as the hanging-wall zone, being composed of blocky pyrrhotite grains with both interstitial and exsolved flames of pentlandite. Chalcopyrite, which is much more abundant than in the hanging-wall ore, occurs as discrete grains which mantle all other sulphides in the massive and stringer ore, and as veinlets and stringers. Chalcopyrite is distributed erratically but is concentrated along the footwall of the main zone.

There is widespread evidence of replacement of silicates by sulphides. Epidote, chlorite, and poikiloblastic green and brown biotite are commonly associated with the sulphides, and silicates adjacent to the sulphides have reaction rims of hydrous minerals. These alteration products indicate the presence of some water at the time of sulphide introduction.

It is thought that the main zone ores were emplaced in the porous granite breccia and in fractures in the adjacent gneiss complex by the injection of a sulphide magma containing moderate amounts of water. This magma may have been co-genetic with the Irruptive rocks or it may have been derived from a magma chamber at depth.

iii) Deep Zone The deep zone ores are enclosed within the granitic gneiss complex and consist of arcuate, flat-lying, en echelon bands of massive sulphides separated from each other by barren granite gneiss. This type of ore comprises 20 per cent of the mine's reserve. Parts of the deep zone ores occur as much as 300 feet below the base of the Irruptive.

The chief differences between the ores of the main zone and the deep zone are the increase in grain size and the increase in the quantities of magnetite and chalcopyrite in the latter. Pyrrhotite grains often exceed 5 mm in diameter and contain a large amount of exsolved pentlandite. Veinlets of chalcopyrite are common at the footwall of the deep zone. The ore contains 10 per cent magnetite often present as perfectly octahedral grains averaging 0.5 mm in diameter. Magnetite is often locally concentrated into irregular bands, composed of a compact aggregate of magnetite grains, up to 8 inches across.

Contacts of sulphides and granite gneiss are sharp and there is no evidence of alteration or melting of the silicates by the sulphides. It appears that the stringers were emplaced in dilation fractures which may have developed in the granite gneiss subsequent to the cooling of the Irruptive and formation of the granite breccia. It is not known whether the deep zone sulphides were injected at the same time as the main zone sulphides or not.

4. Millerite-bearing Stringers

The late stage of mineralization is represented by several minor sulphide minerals. The most important of these is millerite which occurs in massive chalcopyrite stringers along with pentlandite and minor amounts of bornite, pyrite, violarite, magnetite and ilmenite. The millerite-bearing stringers occur as much as 1500' below the base of the norite and deep into the granite complex. The stringers fill fractures in the complex which has been altered to quartz-epidote with scattered coarse brown garnet and amphibole. They are believed to have been formed by late-stage sulphide-bearing fluids related to the formation of the main ore zones.

Of even greater significance to the present study is the fact that microprobe studies show that minute grains of unidentified minerals which are associated with these stringers contain significant proportions of platinum and palladium as well as bismuth, tellurium and selenium (Cowan).

5. Distribution of Metals in the Ore

Cowan (1967) has contoured the variation of nickel content of the ore body on the basis of some 3000 samples that were analysed for Ni, Cu and S. Contour plans illustrating the distribution of nickel in iron-nickel sulphides from three different levels are shown in Figure 10-2.

The nickel content of sulphides in the hanging-wall zone is low and uniform, varying between 2.5 and 3 per cent. In contrast, the main ore zone is strongly zoned with contours closely spaced and nickel values increasing from 3 per cent adjacent to the Irruptive contact to a maximum of 5.0 per cent at the footwall contact. As can be observed from Figure 10-2,the nickel contours closely parallel the basal contact of the Irruptive, and they cut across individual ore stringers where these diverge from an attitude parallel to the contact. Contours parallel the contact even where it forms embayments or projects back into the hanging-wall breccia, as for example in the western part of the mine on the 2,250 foot level.

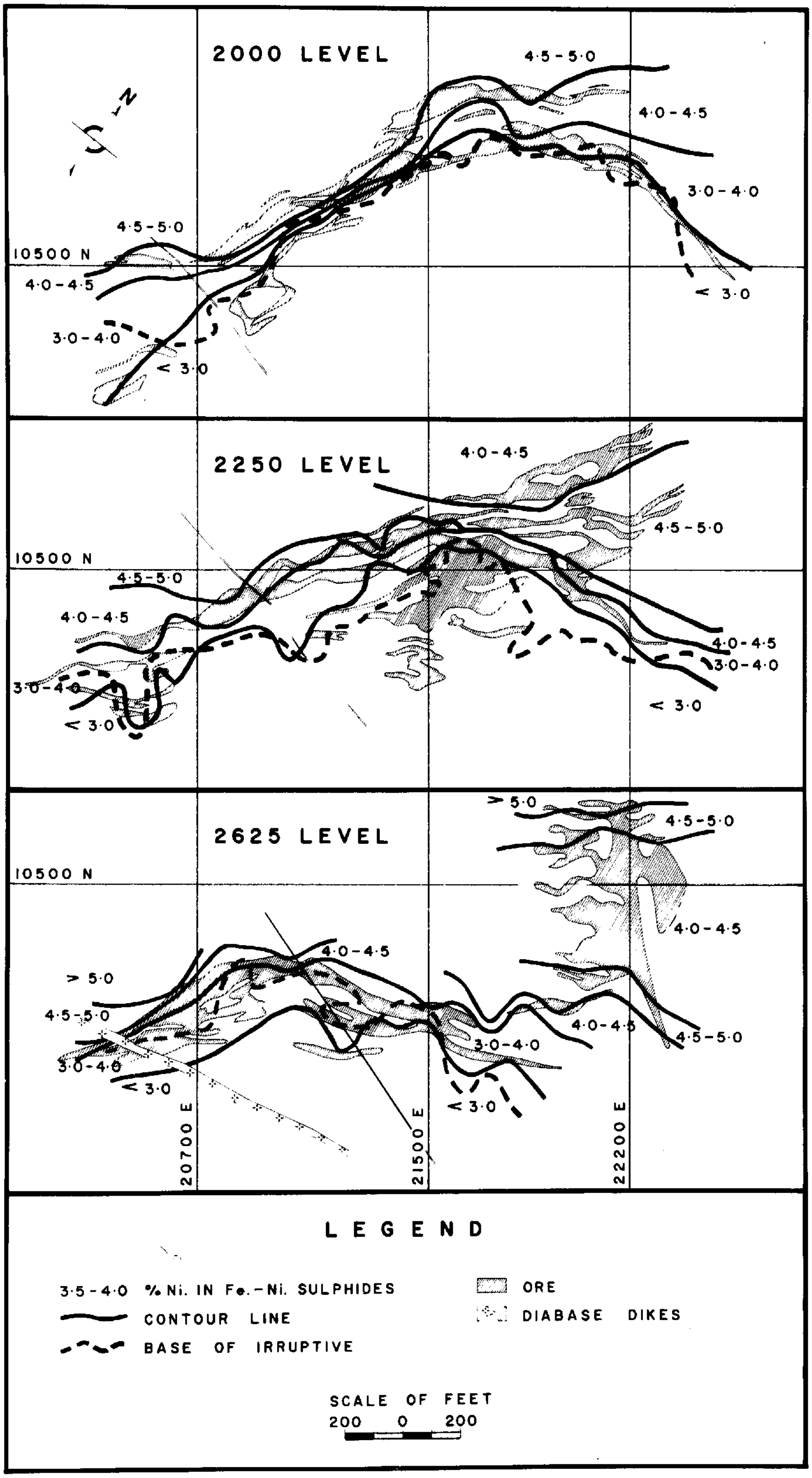


Figure 10-2 Contour plans showing the percentage and distribution of nickel in iron-nickel sulphides (after Cowan, 1967).

Variation in the deep zone ore is not as great as in the main zone, with nickel values ranging from 4.0 to 5.0 per cent. Some of the sulphides that form the upper part of the deep zone have slightly higher nickel contents than sulphides in the center of the zone. This may indicate that these upper stringers of the deep-zone should be regarded as part of the main zone.

The distribution of copper within each zone is less uniform than that of nickel, but a similar trend of enrichment away from the base of the Irruptive exists. Hanging-wall sulphides contain less than 1 per cent copper while those of the main zone and deep zone contain from 1 to 3 per cent copper, with local enrichments of greater than 4 per cent copper along the bases of both the footwall ore zones. The Cu/Ni ratio increases steadily from hanging-wall to footwall in the main zone.

Another metal which varies in its per cent content in sulphide is cobalt. The average Ni/Co ratio of sulphides in the hanging-wall zone is 15.7; in the main zone it is 21.6 while in the deep zone it is 43.5. Microprobe studies on 20 samples show that there is 1.10 per cent cobalt in the pentlandites of both the main and deep zones but 2.00 per cent cobalt in those of the hanging-wall.

Explanations regarding the cause of the metal zoning must take into account the lack of zoning in the hanging-wall zone compared to the very pronounced zoning in the main-zone ore. It has already been noted that there were greater amounts of water in the footwall granite breccia than in the sublayer rocks. The metal zoning may have been produced by diffusion of metals, in response to a thermal gradient induced by the cooling but still hot Nickel Irruptive, through an aqueous phase which was associated with the sulphide magma and brecciated host rocks.

CHAPTER XI

DISTRIBUTION OF Au, Ir, Pd IN SUDBURY SAMPLES

Specimens were collected from a number of mines in the Sudbury area with the assistance of members of the geological staffs of both Falconbridge Nickel Mines (specimens from Falconbridge and Strathcona mines) and the International Nickel Mines (Frood, Creighton, Garson and Levack mines).

Due to necessary time expended on the development of the analytical procedure the number of samples analysed for the precious metals had to be limited to 57. The majority of the samples analysed were pyrrhotites (25) and chalcopyrites (20). Other minerals analysed include pentlandite (3), magnetite (3) and one each of millerite, bornite, cubanite and calcite. Several analyses on gersdorffite-chalcopyrite from stringer ore and one whole rock analysis on an ultramafic xenolith complete the analytical work on Sudbury samples. The bulk of the specimens analysed were from the Strathcona mine, which was selected because it contained a number of interesting ore types, was still in the development stage and because other pertinent geological studies on the mine were in progress. Samples from the Frood-Stobie, Creighton and Falconbridge mines were also analysed. Information for each specimen regarding sample type, location, host rock and precious metal data is in Tables 11-1 and 11-2.

Analysed pyrrhotites consisted of a minimum of 99% pyrrhotite plus magnetite. Impurities were mostly composite grains which included silicates but little or no chalcopyrite. The pyrrhotite phases contain small

Table 11-1 Specimen location, host rock and analytical results from Strathcona specimens* (in p.p.b.)

Sample	Mine Co-ordinates			Host Rock and Ore Type		Mineral	Au	Pd	Ir
	Level	Northing	Easting						
20-16	2000	10695N	21000E	F.W.B.	M.O.Z.	po cpy	3.5 44	55 2120	2.5 1.5
20-17	2000	11060N	21500E	F.G.	D.O.Z.	po	2.3	380	28.4
20-18	2000	10950N	21800E	F.W.B.	M.O.Z.	po	1.2	300	1.2
20-21	2000	10785N	22200E	H.W.B.	D.S.	po	1.0 2.3	7.2 9.5	9.7 9.7
20-22	2000	10770N	22200E	H.W.B.	D.S.	po	1.7 1.4	19	59 36
20-24	2000	10770N	22000E	H.W.B.	D.S.	po	1.7	123	34
20-25	2000	10770N	21900E	H.W.B.	D.S.	po	3.2	11.5	150
20-27	2000	10735N	21700E	H.W.B.	D.S.	po	3.7	23	26
20-28	2000	10700N	21600E	H.W.B.	D.S.	po	2.4	22	17
20-29	2000	10665N	21500E	Ultramafic xenolith		mte	0.7	11.4	1.2
20-29	2000			in H.W.B.		whole rock	4.8	57.3	2.8
20-30	2000	10660N	21400E	H.W.B.	D.S.	po	1.1	361	104
20-31	2000	10760N	21300E	F.W.B.	M.O.Z.	po	54	2.2	26 15
22-20	2250	10770N	21700E	F.G.	D.O.Z.	po cpy	25 580	8.2 550	48.7 34.2

cont.

Table 11-1 (cont'd.)

Sample	Mine Co-ordinates			Host Rock and Ore Type		Mineral	Au	Pd	Ir
	Level	Northing	Easting						
22-26	2250	10575N	21465E	F.W.B.	M.O.Z.	po	6.2	25	1.5
							8.6	47	1.4
						cpy	32	241	0.8
22-27	2600	10750N	22000E	F.G.	D.O.Z.	cpy	44	1300	0.4
22-28	2610	10610N	22300E	F.G.	D.O.Z.	cpy	48	532	1.7
22-29	2425	10610N	22400E	F.G.	D.O.Z.	cpy	-	1130	2.8
242-1	2200	10390N	21290E	F.G.	M.O.Z.	mte	4.3	12.2	0.14
242-2	2280	10390N	21290E	F.G.	M.O.Z.	mte	0.19	1.9	0.03
							0.28	0.8	0.4
						po	35	104	1.3
							11	123	0.9
						cpy	34	464	1
						pn	140	101	1
242-3	2345	10390N	21290E	F.G.	M.O.Z.	cpy	13	1680	0.3
						pn	9.0	3010	2.9
25-11	2500	10360N	21445E	F.W.B.	M.O.Z.	po	26	495	.3
							35	270	.4
						cpy	135	886	0.8
25-14	2615	10580N	22100E	F.G.	D.O.Z.	cpy	18.0	800	1.0
25-15	2715	10545N	22200E	F.G.	D.O.Z.	cpy	13.2	29	0.8
							18.8	800	

cont.

Table 11-1 (cont'd.)

Sample	Mine Co-ordinates			Host Rock and Ore Type		Mineral	Au	Pd	Ir
	Level	Northing	Easting						
27-1	2750	8975N	21215E	Felsic Norite	D.S.	po	23.7	87	6.1
3	2750	9055N	21275E	Mafic Norite	D.S.	po	15.4	36	11
							13.1	48	13
4	2750	9130N	21340E	Mafic Norite	D.S.	po	28	89	10.7
								143	10.7
7	2750	9370N	21525E	H.W.B.	D.S.	po	2.9	31	64
							2.9	22	88
9	2750	9480N	21615E	H.W.B.	D.S.	po	6.7	67	38
							4.9	60	80
11	2750	9600N	21690E	H.W.B.	D.S.	po	6.0	22	44
							8.2	23	44
13	2750	9750N	21690E	F.G.	M.O.Z.	po	9.3	316	4.2
						cpy	9.1	630	0.3
						millerite	44	11,350	.4
		Millerite vein deep in Footwall gneiss				cpy	19	330	.03
						cpy	4	6	.4
						bornite	13	36	.01

*Symbols used in table:
cpy = chalcopyrite
cub = cubanite
ger = gersdorffite
mte = magnetite
pn = pentlandite
po = pyrrhotite

F.W.B. = Footwall Breccia
F.G. = Footwall Granite Gneiss
H.W.B. = Hangingwall Breccia
D.O.Z. = Deep Ore Zone
D.S. = Disseminated Sulphides

Table 11-2 Specimen location, host rock and analytical results for specimens from the Falconbridge, Frood and Creighton mines (in p.p.b.)

Sample Identification	Mine	Level	Host Rock & Ore Type	Mineral	Precious Metal Content			
					Au	Pd	Ir	Pt
F-26-33	Falconbridge	2602	Massive Breccia Ore	cpy	15.5	17	30 2.1	-
F-29-6#1	"	2902	Gersdorffite-Chalcopyrite Stringer	ger+cpy	2500 1700	14000 14000	222 157 322	-
F-43-42#2(b)	"	4350	Chalcopyrite Stringer	calcite	0.23	0.7	0.1	-
				cpy	27	89	180	-
F-2	Frood	1000	D.S. in quartz diorite	po	3.7 6.9	15 66	175 296	-
				cpy	25.2 20.3	201 164	50 59 272	-
F-A	"	1000	D.S. in Quartz Diorite	Total Sulphide	2.7 1.7	122 308	27 18	-
F-C	"	1000	Massive sulphides with Quartz Diorite Inclusions	pn	1.7 1.6	15.9 11.6	52 49	-
F-18	"	3100	Massive Sulphides	cub	562	11000	1.0	
F-20	"	2950	Massive Sulphides	po	32 48	100 68	0.28 0.45	-
				cpy	90	78	1.4	-
F-22	"	3400	Siliceous Ore	cpy	234	940	0.96	-
F-29	"	3300	Massive Sulphides	cpy+po	223	2730	10 136	12600 10800
C-B-1	Creighton	?	Chalcopyrite Stringer	po cpy	19 68	140 547	1.6 0.5	- -

*Symbols used in table:

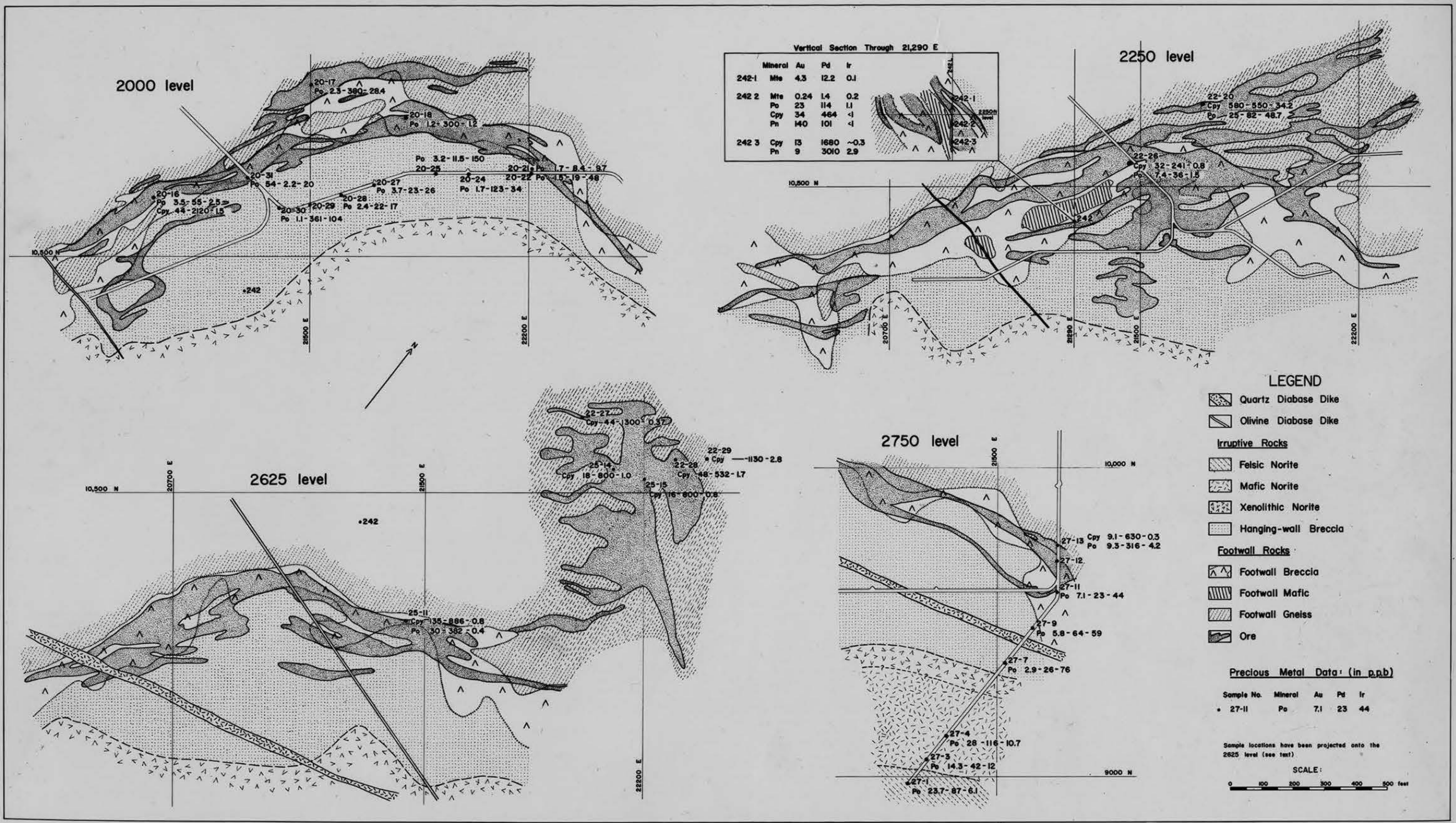
cpy = chalcopyrite
cub = cubanite
ger = gersdorffite
pn = pentlandite
po = pyrrhotite
D.S. = Disseminated Sulphides

amounts of chalcopyrite and pentlandite as exsolution lamellae. Hawley (1962) stated that the purest pyrrhotite which can be concentrated contains 0.5% Ni, all of which is present in finely exsolved pentlandite. The magnetite content of the concentrates was 2 to 3% but as shown by analyses of samples 241-1 and 242-2 contributes very little to the total precious metal content of the samples.

Hawley stated that the Ni content of Sudbury chalcopyrites ranges from 0.008% to 3.70% and averages 0.25% Ni. Most of the Ni in chalcopyrite is present in fine grained inclusions of pentlandite. The chalcopyrite samples, besides this included pentlandite, contained a maximum of 1% impurities all of which were silicates. The other analysed samples were hand-picked and did not include any visible impurities.

The distribution of Pd, Ir and Au at Strathcona with the exception of the samples from the millerite vein, have been plotted in Figure 11-1. All of the samples have been located exactly with regard to the mine level plans except for the samples plotted on the 2625 level. Sample 25-11, the only sample from the 2500 level, has been plotted on the 2625 level with regard to its rock and ore type environ on the 2500 level. Samples 25-14, 25-15, 22-27, 22-28 and 22-29,all from diamond drill holes, are located in the deep ore zone in footwall gneiss. The locations for these samples have been projected vertically onto the 2625 level. Thus all of the samples shown on this level are in their proper rock type, ore type and Ni/S zone and have only been displaced vertically to facilitate the pictorial view of the precious metal distribution. The millerite bearing veins are situated deep into the footwall gneiss complex, up to 1500 feet below the basal contact of the Irruptive, and, consequently, it is not practical to illustrate their position.

Figure 11-1. Distribution of Au, Pd, and Ir in the Strathcona Mine



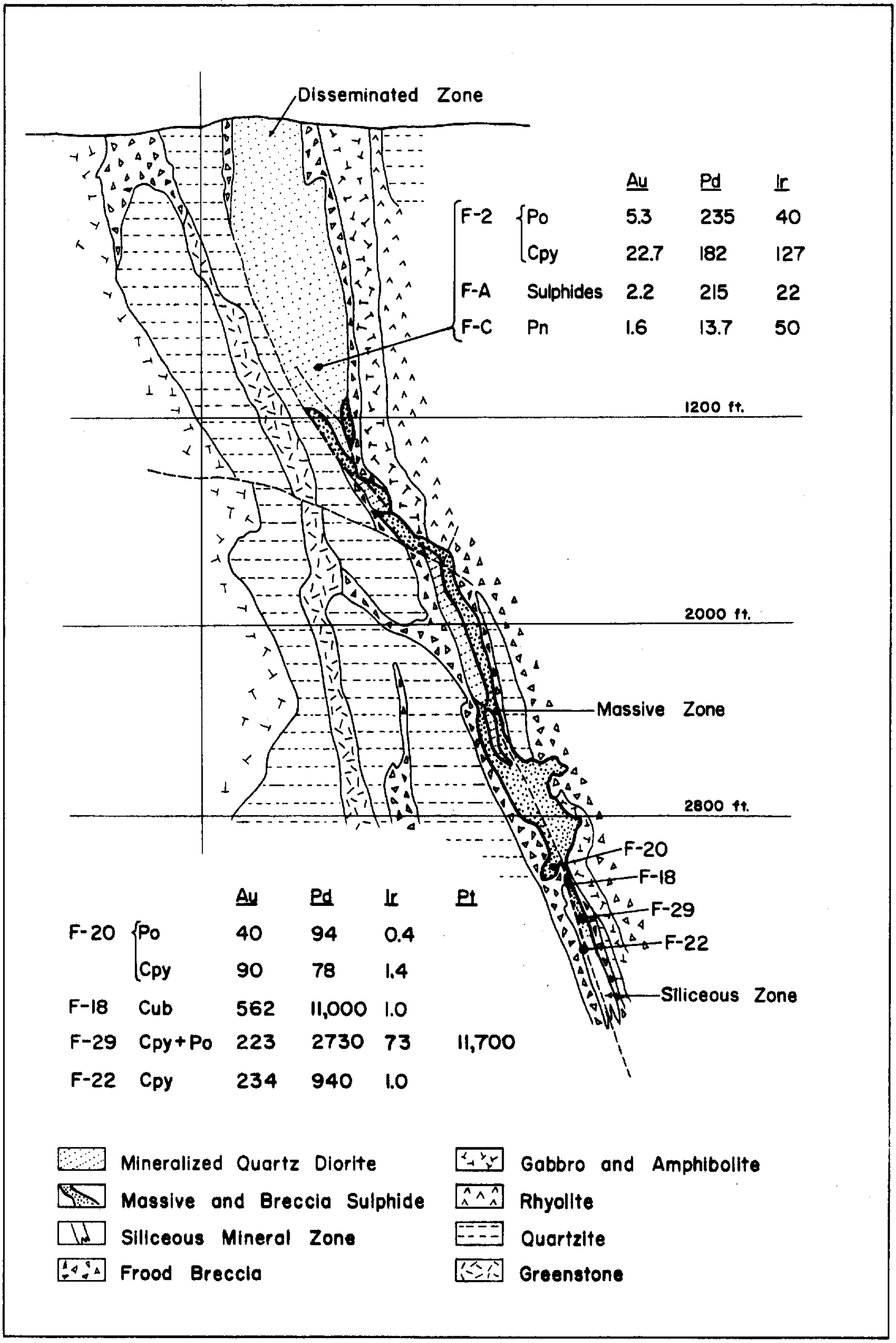
Distribution of Au, Pd, and Ir in the Strathcona Mine

Specimens from the Frood-Stobie Mine have been projected onto a vertical cross-section through the Frood mine to illustrate sample location with respect to the zone from which the sample was taken (see Figure 11-2). Precious metal data accompany sample location in the figure.

Insufficient samples from the Falconbridge and Creighton mines were analysed to warrant a diagrammatic presentation of the data. All but one of the specimens were taken from chalcopyrite stringers, the distribution of which are quite erratic, as discussed earlier. Data for these specimens are presented in Table 11-2.

As can be seen from Tables 11-1 and 11-2, agreement between duplicate analyses varies from good to non-existent. Because of the good reproducibility obtained with the method when analysing standards (G-1, W-1 and the sulphide matte) and carbonaceous chondrites for which there is very little evidence of sample inhomogeneity, it is believed that large differences between duplicates are not due to analytical errors but are real. It is thought that the distribution of the metals in the sulphides is erratic, especially where the precious metal content is high. As there is limited solid solution of the metals in sulphides (which would result in a homogeneous distribution), the tendency appears to be to form mineralloids which have an erratic distribution when high precious metal concentration levels are involved.

Individual analyses cannot be regarded as absolute values, but taken together (e.g. all hanging-wall pyrrhotites) they do give average values which probably represent significant averages. Data for Os and Ru (collected by S. Hsieh), presented along with the precious metal determinations made in this study in Tables 11-3 and 11-4 illustrate that the few apparently erratic Ir values are not due to analytical errors,



		Au	Pd	Ir
F-2	Po	5.3	235	40
	Cpy	22.7	182	127
F-A	Sulphides	2.2	215	22
F-C	Pn	1.6	13.7	50

		Au	Pd	Ir	Pt
F-20	Po	40	94	0.4	
	Cpy	90	78	1.4	
F-18	Cub	562	11,000	1.0	
F-29	Cpy+Po	223	2730	73	11,700
F-22	Cpy	234	940	1.0	

Figure 11-2 Vertical cross-section at Frood showing major zones in ore body and precious metal contents of samples analysed. (After Zurbrigg *et al.*, 1957.)

Table 11-3 Precious Metal Content of Strathcona Pyrrhotites (in p.p.b.)

	Au	Pd	Ir	Os	Ru	% Ni/S†
Hanging-wall Mafic Norite						
	23.7	116	6.1	2.2	7.2	2.5
	14.3	42	12	13	27.1	2.5
	28	87	10.7	10.7	22.7	2.5
Average	22	81.7	9.6	8.6	19.0	
Hanging-wall Breccia						
	2.9	26	76	67.8	214	2.5
	5.8	64	59	17.9	44	2.5-3.0
	7.1	23	44	18.8	46	3.5-4.0
	1.1	361+	104	8.0	20.3	2.5-3.0
	2.4	22	17	4.6	9.7	2.5-3.0
	3.7	23	26	-	-	2.5-3.0
	3.2	11.5	150	52.1	172	2.5-3.0
	1.7	123+	34	-	-	2.5-3.0
	1.7	8.4	9.7	8.2	24.4	2.5-3.0
	1.5	19.0	48	-	-	2.5-3.0
	54*	2.2	20	3.4	5.1	3.0-4.0
	3.1	62.1 (24.9)+	53.4	22.6	53.6	
Average, all Hanging-wall Pyrrhotites	7.5	66.3	44.0	20.5	44.1	
Footwall Granite Gneiss and Breccia						
	3.5	55	2.5	2.9	4.0	4.5-5.0
	1.2	300	1.2	1.9	3.0	3.0-4.0
	7.4	36	1.5	6.9	2.0	3.0-4.0
	30	382	0.4	6.4	4.2	4.0-4.5
	23	114	1.1	1.3	7.5	4.0-4.5
	9.3	316	4.2	0.7	4.3	3.5-4.0
	2.3	380	28.4*	18.9*	30.0*	4.5-5.0
	25	82	48.7*	35.7*	72.8*	4.0-4.5
Average	13.3	212	1.8	3.4	4.2	

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* Data omitted in calculating averages. See text for explanation.

\+ Average when the two high Pd values indicated are omitted.

† Percent Ni in Fe-Ni sulphides. Refer to Naldrett and Kullerud (1967) for the method used to calculate this value. Data supplied by J.C. Cowan, Falconbridge Nickel Mines Limited.

Table 11-4 Precious Metal Content of Strathcona Minerals other than Pyrrhotite (in p.p.b.)

Mineral	Position	Au	Pd	Ir	Os	Ru	%Ni/S
Cpy	Footwall Zone	44	2120	1.5	2.8	25.9	4.5-5.0
"	" "	32	241	0.8	3.7	10.2	3.0-4.0
"	" "	135	886	.8	5.3	9.1	4.0-4.5
"	" "	34	464	<1	0.8	1.2	4.0-4.5
"	" "	9.1	630	.3	1.2	3.5	3.5-4.0
"	Deep Ore Zone	44	1300	.4	-	-	4.0-4.5
"	" "	48	532	1.7	2.7	22.8	4.0-4.5
"	" "	580*	550	34.2*	18.0*	31.1*	4.0-4.5
"	" "	-	1130	2.8	4.7	16.4	4.0-4.5
"	" "	18	800	1.0	-	-	4.0-4.5
"	" "	16	800	.8	-	-	
"	" "	13	1680	.3	3.7	19.7	4.0-4.5
	Average	35.7	962	1.1	3.1	13.6	
Pn	Footwall Zone	140	101	<1	1.6	5.2	4.0-4.5
"	Deep Ore Zone	9	3010	2.9	3.1	38.8	4.0-4.5
Mte	" " "	4.3	12	.14	-	-	3.5-4.0
"	" " "	.24	1.4	<.03	-	-	4.0-4.5
Millerite	Millerite Vein	44	11350	<.4	-	-	High Pt
Cpy	" " "	19	330	<.03	-	-	
Bornite	" " "	4	6	<.4			
Cpy	" " "	13	36	<.01	-	-	
	Average	20					

* Value omitted in calculating averages. Sample (22-20) is at base of deep ore zone.

but due to real variations in Ir concentration. For example, in the footwall pyrrhotites, two Ir figures are approximately 20 times larger than the average Ir concentration of the footwall sulphides; however, the corresponding values for Os and Ru are likewise high.

To facilitate interpretation, the analytical data has been broken down with respect to the zone in which the sample occurs (Tables 11-3 and 11-4). Sample 27-1, although situated in felsic norite, has a sulphide assemblage atypical of that rock type but typical of the mafic norite, and has been grouped with the mafic norite sulphides. Samples 20-17 and 22-20 which have high Ir, Os and Ru contents for footwall sulphides, are from the deep ore zone (see Figure 11-1). The data for the three metals in these samples have not been used in calculating averages in the tables because the analyses are so much higher than the values for the remainder of the specimens analysed from the footwall zones. The Ir, Os and Ru in these sulphides was probably a late stage deposit; in particular, sample 22-20 is from a sulphide stringer at the base of the deep ore zone, which indicates it was deposited after crystallization of the bulk of the deep ore zone. The Au value for sample 20-31 (54 p.p.b. Au) has also been omitted in calculating the average Au content of hanging-wall pyrrhotites because it is more than 10 times larger than the average of 10 other hanging-wall breccia pyrrhotites. The sample was taken adjacent to the Irruptive-granite gneiss contact and has a higher % Ni in Fe sulphide value than other hanging-wall pyrrhotites. Data from the Strathcona deposit show that the hanging-wall zone pyrrhotites have high Ir, Os and Ru contents, and low Au and Pd compared to footwall pyrrhotites and chalcopyrites.

From the geological evidence it appears that the disseminated sulphides of the hanging-wall zone represent in situ ore. It is believed that they are either early high temperature crystallates of a differentiating sulphide magma or they represent sulphides that were injected with the youngest silicate intrusive but before injection of the footwall sulphides and hence are again "early" sulphides. Minerals in the footwall zones are later, and those in the millerite-bearing veins are very likely the youngest sulphide minerals present. The average value for Ir in the hanging-wall pyrrhotites is 44.0 p.p.b. whereas the average value in the footwall pyrrhotites and chalcopyrites combined is 1.4 p.p.b. - a factor of 31 less. The average value of Ir in the millerite vein is about 0.1 - a factor of over 400 less than the concentration of Ir in early, high-temperature pyrrhotites. On the other hand, Pd values in the hanging-wall zone, averaging 66.3 p.p.b. are a factor of 3 less concentrated than pyrrhotites of the footwall and 15 less concentrated than chalcopyrites. Another interesting feature can be observed if the hanging-wall pyrrhotites are sub-divided into those from the mafic norite and those from the hanging-wall breccia (see Table 11-3). The mafic norite pyrrhotites have higher Au and Pd but lower Ir, Os and Ru contents than the hanging-wall breccia pyrrhotites. However, they have lower Au and Pd, and higher Ir, Os and Ru contents than footwall chalcopyrites and pyrrhotites (except for Au in the pyrrhotite). These results are consistent with a model which propounds a single introduction of sulphides (in the xenolitic norite) which accumulated at the base of the Irruptive, differentiated, and was introduced into the footwall subsequent to the primary differentiation. In this model, the sulphides of the mafic norite represent undifferentiated sulphides, whereas the sulphides of the hanging-wall breccia represent early, high-temperature crystalline products of a differentiating magma. Sulphides of the footwall represent the residual material of this differentiating magma. It can be seen that the high temperature, differentiated, sulphides are enriched in Ir, Os and Ru but they are depleted in Au and Pd. Obviously, more analyses, especially of mafic norite sulphides need to be made to support this interpretation.

Four samples from a millerite-bearing vein, supposedly produced by the latest stages of the differentiated magma, were found to have extremely low Ir concentrations (near the detection limit of the element) and erratic Pd contents. The Pd content of the millerite specimen was the highest of any analysed mineral from the Strathcona mine, but the Pd contents of two chalcopyrite specimens analysed from the vein were lower than the averages of the chalcopyrites or pyrrhotites from any zone in the mine. Cowan (1967) reports that unidentified minerals associated with the millerite stringers contain significant proportions of Pt and Pd along with Bi, Te, and Se. It would appear that the precious metals form discrete mineralloids in these veins and their formation results in a large depletion in the precious metal content of co-existing sulphides. The depletion of Ir in these veins is extreme - up to 5000 times less than the average concentration in hanging-wall breccia pyrrhotites. The average Au content (20 p.p.b.) of minerals analysed from the millerite vein is greater than that of the hanging-wall pyrrhotites but it is less than that of footwall chalcopyrites.

The hanging-wall sulphides are composed predominantly of pyrrhotite but do contain chalcopyrite and pentlandite as well. The pyrrhotites of the hanging-wall analysed were not from ore zones (i.e. did not contain sufficient Cu and Ni to constitute ore). It may be argued that most of the Pd and Au of the hanging-wall sulphides is in the co-existing chalcopyrite phase, which was not analysed. However, there is no reason to suspect that in the co-existing chalcopyrite-pyrrhotite pairs, the chalcopyrite member in the hanging-wall should be more enriched in Pd and Au than the chalcopyrite member in the footwall. It is seen that in co-existing pairs in the footwall, the pyrrhotite is enriched in Pd and Au, along with the chalcopyrite. Thus, the hanging-wall sulphides are depleted in Pd and Au, relative to the footwall sulphides.

Zoning of the platinum metals may also be seen in the Frood mine. Specimens from the disseminated zone of sulphides have low Au and Pd but high Ir contents relative to sulphides from the massive and siliceous zones. One sample in the massive zone has an Ir content of 73 p.p.b. which is much higher than the average value of Ir from this location in the mine. However, the sample having the high Ir content also has a very high Pt content (12 p.p.b.) - in fact, of the Sudbury material analysed, this was the only sample which had sufficient Pt to enable analyses for that metal. It is not surprising therefore, to find that the sample is also enriched in Ir (this will be discussed in detail later).

Sulphides analysed from stringer ore in the Falconbridge and Creighton mines have high Au and Pd contents and, in two out of three cases, high Ir contents. One of the stringers, a chalcopyrite-gersdorffite stringer, contains the highest concentration of all three metals of any sample analysed. Only one of the samples analysed from these two deposits was from non-stringer ore, this being a chalcopyrite specimen from massive ore situated near the centre of the deposit. This sample had low Au, Pd and Ir contents.

Precious metal contents of co-existing pyrrhotites and chalcopyrites from Sudbury are listed in Table 11-5. It is seen that the

Table 11-5 Precious Metal Content of Co-existing Sulphides and Oxides From Sudbury (in p.p.b.)*

D.D.H. 242L, 2475'

Metal	Au	Pd	Ir	Os	Ru	Ni/S
Mte	0.24	1.4	.2	-	-	4.0-4.5
Po	23	114	1.3	1.3	7.5	
Cpy	34	464	0.8	0.8	1.2	
Pn	140	101	<1	1.6	5.2	

D.D.H. 242L, 2540'

Metal	Au	Pd	Ir	Os	Ru	Ni/S
Cpy	13	1680	3.7	3.7	19.7	4.0-4.5
Pn	9	3010	3.1	3.1	38.8	

Au		Pd		Ir		Os		Ru	
Po	Cpy	Po	Cpy	Po	Cpy	Po	Cpy	Po	Cpy
3.5	44	55	2120	2.5	1.5	2.9	2.8	4.0	25.9
7.4	32	36	241	1.5	0.8	6.9	3.7	2.0	10.2
25	580	82	550	48.7	34.2	35.7	18.0	72.8	31.1
35	135	382	886	0.4	.8	6.4	5.3	4.2	9.1
23	34	114	464	1.1	<1	1.3	0.8	7.5	1.2
9.3	9.1	316	630	4.2	.3	0.7	1.2	4.3	3.5
5.3	22.7	235	182	40	127				
40	90	94	78	0.4	1.4				
19	68	140	547	1.6	0.5				

* Au, Pd, and Ir data summarized from Tables 11-1 and 11-2. Os and Ru data taken from Hsieh (1967).

latter always contains more Au and more Pd (except for two cases in which the Pd contents are nearly equal) than do the former. Ir and Os, on the other hand, are generally enriched in pyrrhotite in preference to chalcopyrite. Ru shows no definite preference for either mineral, but as it is highly correlated with Ir and Os it probably is more highly concentrated in pyrrhotite on the average than in chalcopyrite.

Only two co-existing pairs of chalcopyrite and pentlandite were analysed (see Table 11-5). The two pairs showed reversals of precious metal content and hence the precious metals appear to be equally concentrated in both phases. Again, too few samples have been analysed to state that either pentlandite or chalcopyrite is definitely more enriched in some of the precious metals.

Two magnetite samples and one calcite specimen which co-exist with sulphides having a high precious metal content were found to have quite low contents of all the precious metals. Sulphides co-existing with one of the magnetite specimens (242-1) were not analysed, but the magnetite was extracted from a sample rich in chalcopyrite and pyrrhotite in a part of the main ore zone having a % Ni/S ratio of 3.5-4.0. This would mean that the sulphides co-existing with the magnetite would have precious metal contents close to the averages of the footwall pyrrhotites and chalcopyrites. The other magnetite specimen had Au and Pd contents lower by a factor of 100 than the co-existing sulphides. Calcite from a chalcopyrite stringer had much lower Au and Pd contents, while the Ir content of the calcite was lower by a factor of 1800, than the chalcopyrite.

Correlation matrixes between the metals were calculated using a computer program supplied by P. J. Lee. For all of the elements

(Au, Pd, Ir, Os, Ru) and % Ni/S in all the Strathcona specimens, the correlation coefficients tabulated in Table 11-6 were calculated.

Table 11-6 Correlation coefficients for Au, Pd, Ir, Os, Ru and % Ni/S in Strathcona samples

	Pd	Ir	Au	% Ni/S	Os	Ru
Pd	1.000					
Ir	-0.270	1.000				
Au	0.051	-0.030	1.000			
% Ni/S	0.460	-0.436	0.219	1.000		
Os	-0.262	0.761	0.003	-0.319	1.000	
Ru	-0.041	0.406	-0.034	-0.247	0.801	1.000

The strongest correlations are between the pairs Os and Ru, and Os and Ir. The next strongest correlations are between Pd and Ni, and Ir and Ru. A slight correlation exists between Au and Ni. Strong negative correlations between Ir and Ni, and Os and Ni can be observed. Weak negative correlation between Pd and Os, Pd and Ir, and Ni and Ru exist. There appear to be no relationships between the pairs Pd-Au, Ru-Pd, Ir-Au, Au-Os or Au-Ru.

Computation of correlation matrices indicates a weak negative correlation between Pd and Ir. However, if the Pd and Ir contents of all Sudbury pyrrhotites are plotted (see Figure 11-3) it becomes more evident that increasing Pd content results in decreasing Ir content. Also plotted on the diagram are the average Ir contents of pyrrhotites of the three geological zones at Strathcona. The trends of these averages further emphasize the correlation of Pd and Ir.

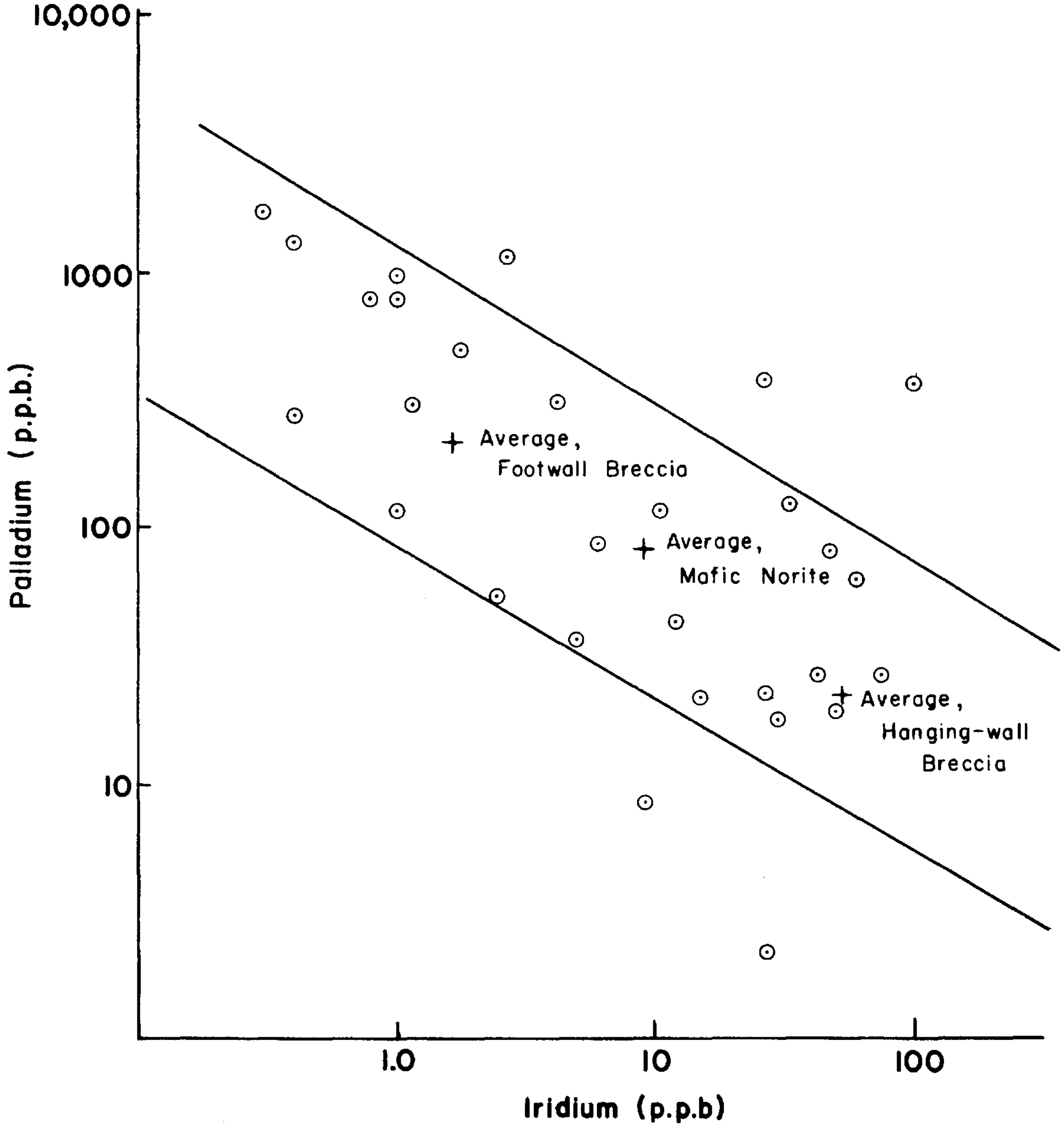

Figure II-3 Variation of Iridium-Palladium in Pyrrhotite

Some specimens were analysed for arsenic by a colorimetric procedure described in detail by Sandell (1959). The arsenic data are presented in Table 11-7 along with the corresponding Pd values. Pd and As show a strong positive correlation (Figure 11-4). As is also correlated with the other precious metals, but to a much lesser degree than with Pd. Much Pt occurs as sperrylite ($PtAs_2$) so a strong correlation between Pt and As should be expected. The highest precious metal data obtained in this study were for specimens taken from a chalcopyrite-gersdorffite stringer in the Falconbridge Mine.

Only one whole rock specimen, sample 20-29, a hanging-wall ultramafic xenolith was analysed in this study. Its composition is as follows: 60% orthopyroxene, 24% olivine, 13% plagioclase and 3% oxides. The specimen contained a small amount of sulphide but the material analysed was devoid of sulphides. The whole rock contained 0.7 p.p.b. Au, 10 p.p.b. Pd and 1 p.p.b. Ir. The value obtained for Au is lower than that obtained by Shcherbakov and Perezhogen (1964) for the average gabbroid (8.7 p.p.b.) or ultramafic rock (9.4 p.p.b.) and is also lower than the Au content (4.6 p.p.b.) of the chilled margin of the Skaergaard as reported by Vincent and Crocket (1960). The Pd content is close to that of the average continental basalt (8.5 p.p.b.) reported by Crocket and Skippen (1966). The latter also found the Pd content of a norite (containing less than 1% sulphide) from the Creighton mine to be 10.4 p.p.b. The Ir value for the xenolith (1 p.p.b.) is higher than the Ir content of W-1 (0.26 p.p.b.), but this would be expected because Ir is generally concentrated in ultramafic rocks. Magnetite extracted from the whole

Table 11-7 Arsenic content of some Sudbury sulphides

No.	Sample Identification	As(p.p.m.)	Pd(p.p.b.)
1	20-18(po)	46	300
2	20-22 po	4.8	19
3	20-25 po	5.7	11.5
4	20-30 po	40	361
5	22-20 cpy	3.6	550
6	22-28 cpy	23	532
7	22-29 cpy	530	1,130
8	25-11 cpy	45	886
9	25-11 po	2.3	270
10	242-3 cpy	35	1,680
11	Millerite	224	11,350
12	Cpy from millerite	3.2	330
13	Bornite	N.D.*	6.1
14	F-A (sulphide)	7.8	200
15	F-2 (cpy)	N.D.	36
16	F-18 cub	184	11,000
17	F-22 cpy	40	940
18	F-29 po cpy	46	2,730
19	F-26-33 cpy	3.2	17
20	F-29-6 #1 (gers + cpy)	350	14,000

* N.D. = Not detected

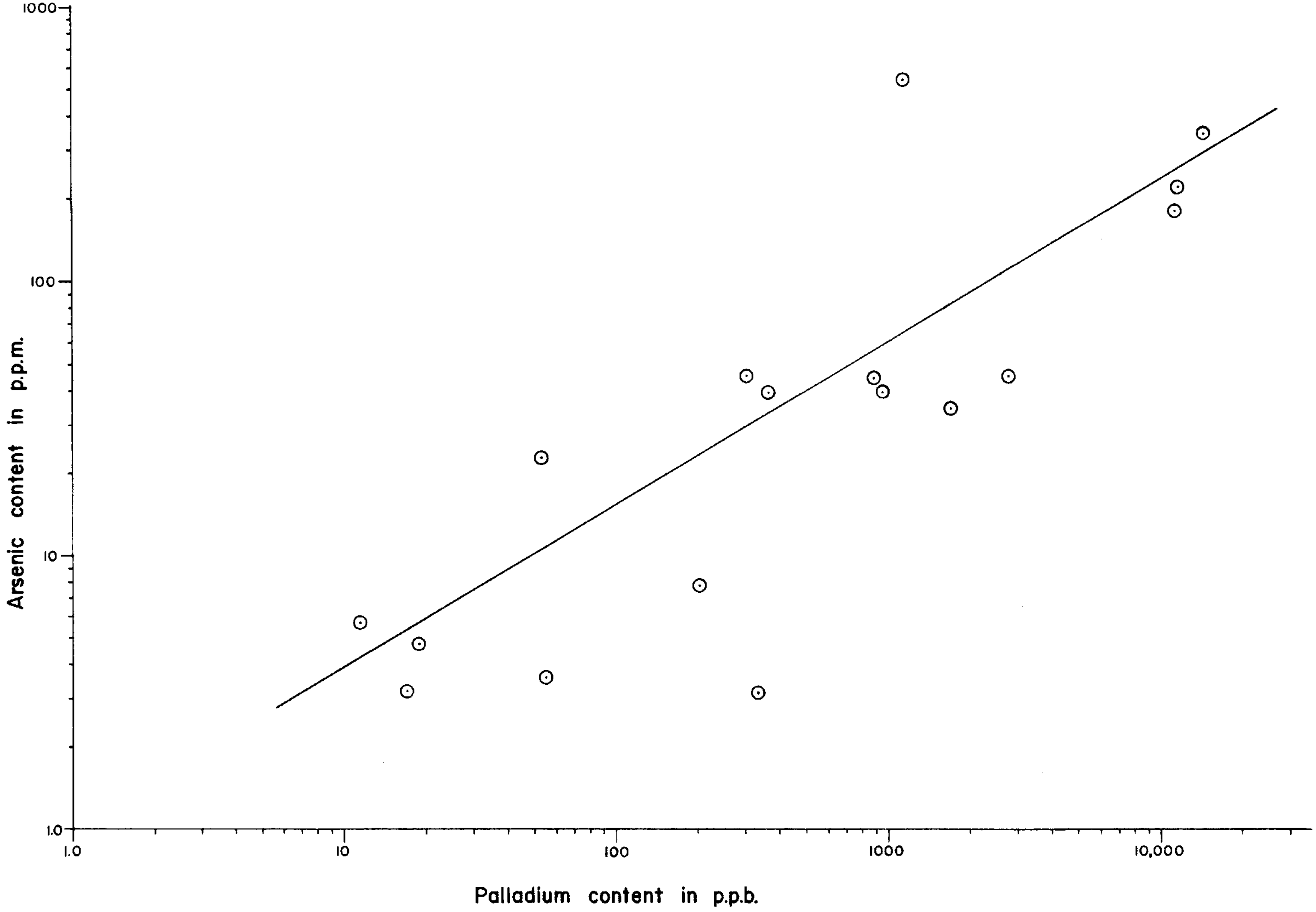

Figure II-4 Variation of Palladium content with Arsenic concentration rock contained higher Au (4.8 p.p.b.), Pd (57.3 p.p.b.), and Ir (2.8 p.p.b.) than the material from which it was extracted. Magnetite constitutes approximately 3% of the rock. The Pd value for magnetite appears to be high but further analyses from hanging-wall rock need to be made to establish accurate precious metal data for magnetite.

Summary

Ir, Os and Ru are highly concentrated in disseminated sulphides in xenolithic norite or quartz diorite, but strongly depleted in later minerals. Occasionally, they are present in very high concentrations in late stage mineralization such as the Frood siliceous zone. Pd and Au (and Pt) are highly enriched in later-stage mineralization, especially in late chalcopyrite specimens. The distribution of Au is much more erratic than that of Pd. None of the metals is enriched in oxides or calcite. In co-existing chalcopyrite-pyrrhotite pairs chalcopyrite is always enriched in Au and Pd. Ir and Os tend to be enriched in the pyrrhotite phase and the distribution of Ru is quite erratic. In co-existing chalcopyrite-pentlandite pairs, no systematic enrichment of one metal in a particular phase is apparent, although data are few. There is a strong correlation between arsenic and palladium.

CHAPTER XII

DISCUSSION

1. Mode of Emplacement of Strathcona Ore

Two hypotheses have been presented regarding the origin of the Strathcona ore. Cowan (1967) stated that there were two or perhaps multiple injections of sulphides. The hanging-wall sulphides, which appear to be in situ, were introduced with the xenolithic norite, but the footwall sulphides were introduced during a separate, later injection, into the porous zone of the footwall breccia. Naldrett and Kullerud (1967) state that the bulk of the sulphides were introduced with the xenolithic norite. Some of these sulphides remained in the xenolithic norite to form the hanging-wall ore zones but the remainder settled into fractures in the underlying gneiss. Brecciation along the contact between the footwall gneiss and the Irruptive then formed the footwall gneiss and remobilized the sulphides within the main ore zone. Both authors attribute zoning of Cu and Ni in the footwall sulphides to aqueous fluids which existed in the porous breccia and assisted in the redistribution of the metals in response to a thermal gradient. The aqueous fluids also caused sodium metasomatism within the footwall breccia.

It is the purpose of the following discussion to establish which hypothesis is more probable (and alter it where necessary), and to consider the role of the sulphide melt during brecciation of the footwall.

In addition to the sulphides in the xenolithic norite, small interstitial sulphide blebs also occur in the mafic norite, which is believed to pre-date the xenolithic norite. These sulphides are also *in situ* and hence are thought to have been injected with the mafic norite (Naldrett and Kullerud). The mafic norite sulphides analysed for precious metals were situated 150 feet above the floor of the Irruptive and 450 feet from the nearest ore zone (see Figure 10-1). The sulphides are thus older and spatially quite removed from the sulphides that accumulated along the base of the Irruptive.

The zoning of the base metals Ni, Cu and Co in the Strathcona mine is similar in many respects to the zoning of the same metals in the Frood mine as described by Zurbrigg (1957) and Hawley (1965). In the Strathcona mine, the percent Ni in Fe-Ni sulphides is uniform (2.5-3.0%) in the hanging-wall sulphides but increases in the footwall-sulphides systematically to reach a maximum of 5.0% at the base of the deep ore zone (refer to Figure 10-2). The distribution of Cu is much more erratic than that of Ni but generally increases towards the base of each ore lens in the footwall. Cowan gave the Ni/Co ratios in the hanging-wall, main, and deep ore zones as 15.7, 21.6 and 43.5, respectively. At Frood (refer to Figure 11-2) the zoning of each of the base metals is more extreme. According to data given by Hawley, the ratios $\frac{\text{Pn}}{\text{Pn+Po}}$ and $\frac{\text{cpy}}{\text{cpy+Po}}$ increase from 0.16 and 0.18 in the lower part of the disseminated zone to 0.36 and 0.84 in the cubanite zone (just above the siliceous zone) respectively.[1] The Ni/Co ratios in Frood pyrrhotites increase from 25.3 in the disseminated zone to 33.0 in the massive zone.

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[1] Pn = pentlandite po = pyrrhotite cpy = chalcopyrite.

It was assumed by Hawley et al. that the precious metals would also exhibit variations in zoned deposits, but the extent of these variations were unknown. The precious metals are highly concentrated in some late stage arsenide-chalcopyrite stringers and also in the siliceous zone at Frood. The present study has shown that the precious metals are highly zoned in the major ore types at Strathcona. Whereas the Ni and Cu contents of the ore increases by factors of 2 and 4, respectively, from the lower disseminated zone of the Frood to the cubanite zone, Pd and Au each increase by a factor of 20 while Ir decreases by a factor of 60.

Hawley (1962, 1965) firmly established that the injection of the Frood quartz diorite and its associated sulphides was a single stage event. He attributed the Ni-Cu zoning of the ore body largely to the result of fractionation of a sulphide magma, with the residual liquid becoming increasingly enriched in Ni and Cu and moving downward, away from the overlying hot Irruptive. This type of fractionation will be referred to here as crystallization down a thermal gradient.

With respect to the Strathcona mine Naldrett and Kullerud contend that although Hawley's hypothesis may account for the higher overall Ni and Cu contents of the footwall ore with respect to the hanging-wall ore, it cannot explain the highly regular zoning of the main zone ore. They contend that the xenolithic norite had solidified prior to brecciation and was therefore at a lower temperature than the minimum melting temperature of the sulphide ore at and after the time of brecciation. Hence, they state, the temperature at the time of introduction of a sulphide magma would have decreased towards the hanging-wall as well as toward the footwall.

Several points may be raised to counter Naldrett and Kullerud's objection to the differentiation of a sulphide magma giving rise to the zoning of the main zone ore as discussed in a later section.

Cowan noted that the footwall breccia is most abundant around the nose of the embayment in the Irruptive floor. Hawley quoted Michener (1940) as stating that the chalcopyrite and arsenide stringers bearing precious metals extend further into siliceous wall rocks compared with basic rocks such as gabbro, where values end abruptly. Neither author attempted to explain these observations but they may both be related to the intrusion of the sulphides. According to Clark (1966) the thermal conductivity of FeS_2 is more than a factor of 10 greater than that of norite or granite at 20°C. No information is available on the conductivity of pyrrhotite, but it would be expected that its conductivity would be somewhat greater than that of pyrite, not only because of its higher metal content but also because there is more metallic bonding in pyrrhotite. Skinner (1966) tabulated the per cent thermal expansion of various silicates. Some of his values are summarized below.

Mineral		Thermal expansion in volume percent from 20°C to 600°C
Microcline		1.029
Plagioclase	(An_{44})	.95
Plagioclase	(An_{95})	.78
Augite		1.37
Enstatite		1.74
Quartz		4.52

Norite is composed of silicates which have approximately equal values for thermal expansion. The thermal expansion of plagioclase is less than that of augite and enstatite (which is given as a close approximation to hypersthene). The footwall gneiss on the other hand contains 20-50% quartz whose thermal expansion is more than four times that of microcline or plagioclase. The net result of the differences in thermal expansion of the constituent minerals of granite gneiss and norite is that the former fractures due to heat much more readily than the latter. Hence, a hot sulphide liquid would be able to advance further into a granite than into a basic rock because the siliceous rock would fracture as the hot sulphide moved into it.

The fact that granite is readily fractured due to thermal expansion and that a sulphide melt is a much better heat conductor than silicates, may be applied to development of the granite breccia around the nose of the Irruptive protrusion at Strathcona. When the main mass of the Irruptive was introduced, only a small zone of the footwall gneiss would be heated up by the hot Irruptive due to the poor conductivity of the silicates. Some fracturing of the granite might occur, with the development of some contact breccia, but liquid norite would not migrate into these fractures because the zone of norite adjacent the contact would be chilled and solid. According to Naldrett and Kullerud, the contact temperature immediately after intrusion of the norite would have been 717°C assuming the norite was injected at 1200°C and the country rock was at 100°C at the time of intrusion. This contact temperature is much less than the minimum melting temperatures of either granite or norite. A different situation arises in the case where sulphides suspended in the xenolithic norite accumulate along the floor of the Irruptive.[1]

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[1] Naldrett and Kullerud have calculated that the average settling rate of sulphide droplets in the xenolithic norite magma would have been 0.93 feet per day. The average vertical distance from the top of the xenolithic norite to the Irruptive floor is 600 feet. Hence, the bulk of the sulphides would have settled to the Irruptive floor in less than 2 years.

The sulphide melt would have a high heat conductivity and would transfer heat efficiently from the hot Irruptive to the cold footwall gneiss. Due to the high temperature at the granite gneiss - sulphide melt contact, the granite would fracture as along the norite - granite contact. However, in this case the sulphide, which would still be liquid, would migrate into the fractures. The sulphide would remain liquid at the contact whereas the norite would solidify because (1) it would have a lower melting point than the norite and (2) the sulphide liquid, being a good thermal conductor, would conduct heat rapidly from the hot Irruptive to the cold footwall, thereby maintaining the high temperature of the sulphide adjacent the contact. Again, because it was an efficient thermal conductor, the sulphide melt would continue to fracture the granite gneiss ahead of it as it moved into the footwall, and could migrate to considerable distances in this manner.

This mode of introduction of the sulphide into the footwall implies that at least a part of the development of the Strathcona breccia was an auto-brecciation affected by the presence of a hot melt. A later, more extensive brecciation may have been superimposed and this initial zone may have acted as the focus of the later brecciation. Sodium metasomatism of the footwall breccia has occurred. It is suggested that the aqueous fluids which gave rise to this metasomatism evolved from the sulphide melt as it differentiated and assisted in the later brecciation of the gneiss around the nose of the norite protrusion. They may have also aided in the development of unmineralized breccia.

Cowan stated that the footwall gneiss breccia matrix was metasomatised and recrystallized but there is no evidence that it was melted. Near the footwall gneiss complex, the matrix is light-coloured and consists of material derived from the granitic gneiss. In other areas especially near intense sulphide mineralization, the matrix is darker and contains abundant small mafic patches and crystals that Cowan believed were derived from the Irruptive. This field evidence supports an interpretation suggesting that the sulphide melt moved into the granitic gneiss complex by a mechanism involving thermal fracturing of the gneiss and subsequent migration of sulphide liquid into the fractures. It would be expected that some norite adjacent to the sulphide melt would remain liquid and would migrate with the sulphide into the fractures, there to be assimilated by the granite gneiss breccia matrix. The norite magma adjacent to the granite gneiss would have solidified immediately upon intrusion of the magma. The footwall granite gneiss breccia adjacent to the Irruptive consists of fragments of granite gneiss, mafic norite, modified xenolithic norite and ultramafic xenoliths. Hence, development of the footwall breccia occurred after consolidation of the hanging-wall norite. If the sulphide melt had fractured its way into the granite gneiss, the major portion of the brecciation would not have occurred until a considerable portion of the sulphide melt had entered the footwall. During this time lag, the norite adjacent to the footwall would have solidified and hence could have been caught up in the brecciation.

Naldrett and Kullerud interpret the sulphide melt as having entered the footwall in one single, rapid intrusion. If this were the case, then the sulphide melt would indeed be at a higher temperature than both the granite gneiss complex and the overlying norite. Operation of Hawley's hypothesis, that of crystallization down a thermal gradient, would produce a zoning pattern in which minimum Cu and Ni concentrations occurred in the center of the main zone while maximum metal concentrations occurred at the base of the deep zone and at the top of the main zone, (that is, adjacent the Irruptive). As this is not the zoning pattern found, Naldrett and Kullerud correctly observe that the zoning cannot be primary in this situation. However, it is suggested here that the sulphide liquid did not enter the footwall in one quick intrusion but rather migrated into the gneiss more slowly, cooling gradually and undergoing fractional crystallizing as it did so. Because the sulphides were good heat conductors, a thermal gradient would exist in the migrating body with the "hot end" at or above 1000°C. This slow crystallization could produce the metal zoning observed, as will be explained in the following section.

2. Fractionation of a Sulphide Melt

Craig (1966) found that the melting interval of a pyrrhotite solid solution consisting of 82.5% pyrrhotite, 13.2% pentlandite and 4.3% chalcopyrite (which is the approximate composition of the sulphide of the main zone ore at Strathcona) was 1105° to 1149°C. When 15% Fe_3O_4 (which is the average magnetite content of the main zone ore) was added, the minimum melting temperature was reduced to 1019°C. Naldrett and Kullerud (1967) report that the presence of H_2O does not lower the melting point of the mixture appreciably and conclude that H_2O was not present in a sulphide melt such as that of Strathcona. Craig studied the appearance of phases during cooling of the sulphide melt of the composition indicated above and found that only one phase existed between 1105°C and 450°C, this phase being pyrrhotite solid solution. At about 450°C chalcopyrite exsolved from the solid solution. Craig found that the presence of magnetite had no effect upon the exsolution of chalcopyrite. Hence, if the Strathcona ores had cooled in the absence of a thermal gradient or had cooled quickly, they would have crystallized as a homogeneous solid solution.

Hawley (1965) suggested that the cooling sulphide melt which gave rise to the Frood ores differentiated as it cooled, with the residual liquids becoming progressively enriched in Cu and Ni and moving downward, away from the heat source. He stated this differentiation largely accounts for the metal zoning of the Frood and the enrichment of the siliceous zone in the volatile elements and many of the precious metals.[1] In the Fe - Ni - S system, the first sulphide phase to crystallize as the melt cools is FeS monosulphide (Kullerud, 1963), which appears at approximately 1150°C. With further cooling, Ni enters the pyrrhotite solid solution. Brett and Kullerud (1964) found that a liquid field appears in the Fe - Pb - S system at 717°C at a composition of 60% Pb, 14% Fe, and 26% S. This liquid field co-exists with pyrrhotite solid solution and increases rapidly in size with increasing temperature. When Cu is added to the system, a liquid field appears as low as 508°C (Craig and Kullerud, 1966). The addition of other volatile elements (for example Sn, Ag) would probably lower the minimum melting temperature even further. As a general rule, the more low temperature components that are put into a system, the lower is its minimum melting point.

In the case of the Strathcona ores, the parent sulphide magma tended to accumulate along the floor of the Irruptive. Due to the cooling influence of the footwall, the sulphide started to solidify. The first crystals to separate would be predominantly FeS with low Ni and Cu contents, these metals plus the more volatile elements entering the residual liquid. As the footwall fractured due to thermal expansion induced by the hot

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[1] The term volatile is applied to those elements which have low melting points as metals or as compounds.

Irruptive and its associated sulphide melt, the latter migrated into it, crystallizing as it proceeded, with the residual liquid becoming increasingly enriched in the more volatile components such as Ni and Cu. The amount of Ni (or Cu) which a phase contained would be a function solely of the temperature of solidification. Hence, all hanging-wall sulphides, because they solidified at the same high temperature (externally controlled by the Irruptive) would possess the same metal contents. Because a thermal gradient existed across the footwall, the sulphides contained therein would be zoned with respect to Ni and Cu, the sulphides adjacent the Irruptive having the lowest Ni and Cu content whereas those most removed from the Irruptive would have the highest Ni and Cu contents.

3. Evidence for Volatile Components in the Sulphide Melt

Naldrett and Kullerud (1967) statedthat water has little influence on melting temperatures of pyrrhotite-magnetite assemblages and that it cannot be appealed to as a flux to explain the occurrence of natural, low-temperature (that is, $< 900°C$) sulphide-oxide magmas. They conclude that if low temperature ore magmas exist (which they indicate to be unlikely), some other flux, must be responsible for lowering the melting point.

The bulk of the sulphides of the Frood mine may be considered to have been deposited from a dry magmatic melt. However, the siliceous zone at the base of the Frood consisting of such low temperature elements as As, Pb, Sn, Bi, Te, Se, Zn and Ag and the precious metals was deposited from what would normally be regarded as a hydrothermal solution.[1] Hawley

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[1] These elements have low melting points relative to that of Fe and Ni. The melting points of the metallic and semi-metallic metals, exclusive of the precious metals, found in the siliceous zone are as follows, in degrees Centigrade: Co-1495, Cu-1084, Fe-1536, Ni-1454; Ag-961, As-817, Bi-272, Pb-328, Se-227, Sn-232, Te-450, Zn-420.

(p. 536, 1965) stated that "the original ore fluids (at Frood), although composed largely of sulphides must have also carried other volatiles including water and probably soda". Yates (1948) stated that very little ore sulphides, either massive or disseminated, occur in norite, but that all of the ores are associated with a siliceous phase of the norite, quartz diorite. (This does not apply to the North Range deposits, which are associated with an inclusion-bearing sub-layer.) Hawley believed that the ore fluids which gave rise to the sulphide deposits converted the magma from which pyroxenes and other minerals of the norite were about to form to one from which amphiboles, biotite, quartz and other minerals of the quartz diorite were precipitated. The volatile components associated with the sulphides would assist in these conversions.

Further evidence that the sulphides contained volatile components may be cited. Wandke and Hoffman (1924) reported that a blue-green amphibole associated with and replaced by sulphides is developed most abundantly adjacent to them. Hawley quoted Michener (1940) as stating that the blue-green amphibole dies out rapidly away from sulphides and is a variety of hastingsite, a soda-rich amphibole. Presumably the soda was originally associated with the sulphide liquid. Water, which assisted in the conversion of pyroxene to amphibole, might also have been contained in the sulphide liquid.

Approximately 15% magnetite was contained in the original Strathcona ore magma. Thus, the magma contained a considerable amount of oxygen. According to Nagamori and Kameda (1965) the partial pressure of oxygen above a magma having the composition of the Strathcona ore at 1200°C is 2.5×10^{-11} atmospheres. Presumably, the oxygen would not be present as O_2 as the partial pressure of S_2 at 1200°C is approximately 1 atmosphere.

The oxygen may be present as SO_2 or SO_3 gas dissolved in FeS-rich liquid, or, more likely, may be present in the associated vapour phase. Oxygen may not be the only species dissolved in the Cu-Ni-Fe-S melt. Skappell (1927) has stated that Na is equally partitioned, as weight per cent Na_2S and Na_2O between iron sulphide liquid and a calcium iron alumino-silicate liquid. Hydrogen would also probably be present in the melt (or vapour phase), as H_2S, HS^-, or some other species. The fact that a sulphide melt of the composition of the Strathcona mine can contain large amounts of oxygen indicates that it can also contain considerable quantities of such elements as Na and H. With fractionation of the melt, these elements (i.e. Na, H, O, etc.) would tend to accumulate in the residual fluid and would finally form a water-rich phase.

Several field observations at Strathcona suggest that a volatile-rich phase developed during differentiation of the sulphide melt. Naldrett and Kullerud reported moderate soda metasomatism of silicates of the main zone which they attributed to aqueous solutions that migrated through the breccia zone after consolidation of the ore. It is suggested here that the aqueous phase and its dissolved silica and soda were intimately associated with the main sulphide melt. Further, the millerite-bearing stringers which occur up to 1500 feet below the norite are situated in an alteration zone composed of quartz-epidote with scattered coarse brown garnet and amphibole, and are believed to have formed from a metasomatic fluid at a temperature somewhat higher than 380°C (Cowan). They are believed to be a late stage mineralization related to the formation of the main ore zones.

The question may arise whether ore sulphides can be transported by aqueous solutions. Barnard and Christopher (1966) have shown that chalcopyrite can be dissolved readily, transported down a temperature gradient, and re-precipitated by a variety of aqueous solutions. Chloride solutions are the most effective aqueous media, but solutions of NaHS and $(NH_4)_2S$ also are effective agents for the transfer of chalcopyrite. $(NH_4)_2S$ may not occur in natural solutions, but NaHS is readily formed by the reaction of Na_2S and H_2O.

4. Differential Fractionation of the Precious Metals

In this discussion, the model of sulphide emplacement proposed in section 1 will be used as a working hypothesis. The actual mechanism of introduction of the sulphide into the footwall is unimportant provided it was at such a rate as to allow differentiation of the sulphide melt as it cooled. The mafic norite sulphides are accepted as representing undifferentiated sulphide liquid whereas the xenolithic norite sulphide are believed to represent the early crystal phases that separated from the sulphide melt which accumulated along the base of the Irruptive.

Table 12-1 Average precious metal data (in p.p.b.) for Strathcona pyrrhotites and chalcopyrites summarized from Tables 11-3 and 11-4

	Au	Pd	Ir	Os	Ru
Hanging-wall mafic norite pyrrhotites	22	82	9.6	8.6	19.0
Xenolithic norite breccia pyrrhotite	3.1	25	53.4	22.6	53.6
Footwall pyrrhotites	13.3	212	1.8	3.4	4.2
Footwall chalcopyrite	35.7	962	1.1	3.1	13.6

The data in Table 12-1 indicate that Ir, Os and Ru are insoluble in the sulphide melt and are concentrated with (or scavenged by) the first crystal phases which separate from the melt. Au and Pd tend to remain in the residual sulphide liquid and are consequently most enriched in the footwall chalcopyrites. Differences also exist within each of these "groups". The enrichment of Ir in the xenolithic norite pyrrhotite and its depletion in the footwall chalcopyrites, all relative to its concentration level in mafic norite, indicate that Ir is the most insoluble of the precious metals. That is, it is most highly enriched in the first crystals to separate from the cooling magma and consequently is the most depleted in the residual fluids.

To compare the relative mobilities of each of the metals it is of value to examine the metal ratios. This may be accomplished by comparing the content of each metal to the content of the most insoluble or the most mobile metal. As will be seen, Au is the most mobile of the precious metals, but it appears that Au has not remained within the system and consequently it cannot be employed as a reference metal. Thus, the best element to use for comparisons is Ir.

It is also useful to compare the precious metal ratios in each of the sulphide hosts to the ratios in the apparent primordial matter from which the Sudbury silicates and ores were derived. Many writers (for example Mason, 1960; Lovering, 1962; and Ringwood, 1961, 1962, 1966) have proposed that carbonaceous chondrites represent the composition of the primitive material from which the common chondrites and other meteorites have been formed. Ringwood (1966) stated further that the earth was formed from primitive dust similar in composition to the Type I carbonaceous chondrites. During the formation of the earth, accretion, melting and reduction occurred with the resultant formation of an Fe-Ni core which contains the bulk of the siderophilic metals originally contained in the primitive material. During this primary fractionation of material the precious metals acted as a homogeneous group if the data for meteorites may be used as a guide because precious metal ratios are the same in most meteorite classes. This statement may be verified by examination of the analytical data available for carbonaceous, olivine bronzite, olivine hypersthene and enstatite chondrites (refer to Appendix D). This is to be expected, for the meteorite parent bodies formed by reduction of primitive oxidized material (Ringwood, 1966) and during segregation of metal from silicates the precious metals would be in a reduced state and hence enter the metallic phase as alloys. Consequently, it may be seen that the earth's mantle, which formed during the primary differentiation of the earth, will contain the precious metals in their cosmic proportions.

It is not known if the Sudbury magma was derived directly from the mantle or not. However, until processes involving oxidation of the precious metals occurred, the metals would react as a homogeneous group.

In the sulphide ores, Ir was found to be the most insoluble precious metal and hence it has been selected as a normalization standard. The ratios of the concentrations of each of the other metals to the concentration of Ir in the various zones at Strathcona and Frood are in Table 12-1. The ratios for the precious metal contents of carbonaceous chondrites (taken from Appendix D) have been included for comparison.

Table 12-2 Ratio of each of Au, Pd, Os and Ru to Ir in carbonaceous chondrites and in Sudbury sulphides

Zone or Material	Au:	Pd:	Os:	Ru:	Ir
Carbonaceous Chondrites	.243	.96	1.03	1.28	1
Mafic norite pyrrhotite	2.27	8.34	0.90	1.98	1
Xenolithic norite pyrrhotite	0.058	0.47	0.42	1.01	1
Disseminated sulphides from Frood	1.33	2.70	-	-	1
Footwall pyrrhotite	7.14	118	1.88	2.32	1
Footwall chalcopyrite	32.2	908	2.78	12.33	1

If the mafic norite sulphides represent the most primitive sulphides at Strathcona, the precious metal ratios in them should most closely approximate the ratios of the metals in carbonaceous chondrites. Although the ratios of Os/Ir are similar, the ratios of each of the other metals to Ir in the mafic norite are larger than in carbonaceous chondrites. Hence, it must be concluded that the sulphides were not derived directly from the mantle but have undergone some form of differentiation since the mantle material was first melted.

From Table 12-2 it can be seen that each of the precious metals has a higher concentration relative to Ir in the mafic norite pyrrhotites than in carbonaceous chondrites.[1] Each of the metal ratios decrease from the mafic norite to the xenolithic norite pyrrhotites, with the Au and Pd ratios showing a greater decrease than those of Os and Ru. However, in progressing through the sequence disseminated Frood sulphides - Footwall pyrrhotites - Footwall chalcopyrite, the ratios of each of the metals

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[1] An exception to this is Os which appears to be less concentrated in the mafic norite pyrrhotites. Reference to Table 11-3 indicates that the average value for Os in the pyrrhotite may be low due to one low value out of three pieces of data available for this material.

increases rapidly, with the ratios of Au and Pd increasing to much larger values than those of Os and Ru. From the differences in net increase of each of the metal ratios it is possible to state the relative order of inertness of each member of the precious metal group.

In addition to the precious metal ratios given in Table 12-2, the proportion of each of Ir, Au, Pd and Os in carbonaceous chondrites, G-1, and W-1 may be used to determine the relative order of mobility. The ratios of the metals (relative to Ir) in these materials have been calculated from Tables 7-1, 7-2 and 7-5 and are tabulated in Table 12-3. In going through the sequence carbonaceous chondrites - W-1 - G-1, the concentration of each of the metals increases relative to Ir. This is the same trend as found in the Strathcona sulphides, with the most fractionated material (that is, the material which is the most fractionated product of the original mantle material) possessing the largest metal/Ir ratios.

Table 12-3 Ratios of Au, Pd and Os to Ir in Carbonaceous Chondrites, W-1 and G-1

	Au	Pd	Os	Ir
Carbonaceous chondrites	.243	.96	1.03	1
W-1	2.23	4.43	1.00	1
G-1	75.2	36.4	1.68	1

From Table 12-3 it can be seen that the Au/Ir ratio in G-1 is 300 times that of the same ratio in carbonaceous material. The Pd/Ir and Os/Ir ratios in G-1 are 40 and 1.5 times larger, respectively, than the same ratios in carbonaceous chondrites. This suggests that Au is the most mobile of the precious metals. In the Strathcona sulphides, Au is the least highly concentrated in the xenolithic norite even though its concentration level is high in the mafic norite pyrrhotite. The Au/Ir ratio in xenolithic norite is 40 times that of the same ratio in mafic norite sulphides whereas the Pd/Ir ratio in xenolithic norite is only 18 times the Pd/Ir ratio in mafic norite pyrrhotites. These ratios indicate that Au remains in the residual liquid phase during crystallization of the high temperature sulphides to a greater extent than any of the precious metals and hence is the most mobile of the metals. In the footwall sulphides, the Pd/Ir ratios are much greater than the Au/Ir ratios which at first appears contrary to the statement made above. However, it is believed that much of the Au is not precipitated in the footwall zone at all but, being an highly mobile element, is carried away, out of the system, in the residual aqueous liquids. This problem will be referred to again (page 193). The element with the second highest mobility is Pd. In the footwall chalcopyrites, the Pd/Ir ratio is 908 compared to the original ratio in the ores of 8.3. The variation of Ir with Pd is shown diagrammatically in Figure 11-3. Although there are considerable variations in each point plotted in Figure 11-3, the average Pd/Ir ratios in each of the sulphide zones are linear. Next to Ir, Os is the least mobile of the precious metals. The ratio Ir/Os in the footwall chalcopyrites and in G-1 is only a factor of ~2 higher than the Ir/Os ratio in carbonaceous chondrites. Compared to Pd, Os in hence virtually as inert as Ir. Ru is somewhat more mobile than Os, for the Ru/Ir ratio in footwall chalcopyrites is approximately 6 times higher than the same ratio in the mafic norite pyrrhotites.

On the basis of the analytical data, the order of mobility of the precious metals in a differentiating sulphide or silicate magma is:

$$Au > Pd > Ru > Os > Ir$$

Although no distribution data for Rh and Pt in sulphides have been collected in the present study, the relative mobilities of these metals may be predicted on the basis of their abundances in meteorites and in the Cu-Ni-rich sulphide ores of the Merensky Reef. Cousins (1964) reported that the proportions of the various precious metals in the ore of the Merensky Reef are as follows:

60% Pt, 27% Pd, 5% Ru, 2.7% Rh, 0.7% Ir, 0.6% Os, and 4% Au.

According to Wood (1963) the atomic abundance of Rh in ordinary chondrites is 0.27 atoms per 10^6Si atoms. During the present study, the atomic abundance of Pt was found to be 1.4. The weight ratios for each of the metals relative to Ir for chondrites and for the ores of the Merensky Reef are as follows:

	Ir	Au	Pd	Os	Ru	Rh	Pt
Chondrites	1	.243	.96	1.03	1.28	.19	1.87
Merensky Reef	1	5.72	38.6	0.817	7.14	3.86	81.7

Again, the increase in the ratio Au/Ir is much less than that of the increase in the ratio Pd/Ir, in the sulphides of the Reef. However, the increases vary by a factor of 2, whereas the increases between carbonaceous chondrites and footwall chalcopyrite are different by a factor of 100. Examining the increase in the ratios of Metal/Ir the following sequence of mobilities is derived with Au the most mobile:

$$Au > Pd > Pt > Rh > Ru > Os \gg Ir.$$

The sequence corresponds to the data of Smolin (1964) who studied the relationships between types of ultrabasic rocks and the suites of elements associated with each type. Smolin stated that Os and Ir are concentrated in dunite - harzburgite, Pt in dunite blastoid formations, and Pd in basic (i.e. gabbro?) rocks. He attributed the associations to density differences between the various precious metals, the heavy Os and Ir being concentrated in the densest silicates. Although Smolin's interpretation is not ascribed to here, his data are useful to predict where each of the metals separate in the fractionation process. Os and Ir are the first metals to be depleted during fractional crystallization and hence, must be the most inert metals. Pd, on the other hand is concentrated in basic rocks which are the products of considerable fractionation of the original parental material. This indicates that Pd is the most mobile of the platinum metals.

The precious metal ratios for the Merensky Reef are intermediate between those of the Strathcona footwall chalcopyrite and pyrrhotite and those of the disseminated sulphides of the Frood mine (refer to Table 12-1). This may indicate that the sulphide liquid was not a strictly "early" sulphide liquid but was indeed somewhat later. That is, the liquid was part of a larger mass of sulphide liquid from which the small portion represented in the Merensky now separated or, the sulphide liquid forming the Merensky Reef did not separate until a considerable proportion of the original silicate magma had crystallized. It has been generally stated, (for example by Wager, Vincent and Smales, 1957) that the earliest sulphides are the most Ni-rich and the reason why sulphides of bodies such as the Skaergaard are low in Ni is because they separated after most of the Ni had been incorporated into silicates. If this is true, then a large proportion of the Bushveld magma could not have been solidified before separation of the Cu-Ni sulphides. The most logical explanation for the origin of the sulphides of the Merensky Reef is that they represent only a part of a larger mass of sulphides, the bulk of which had crystallized at the time of introduction of the silicate magma giving rise to the Merensky Reef. The residual phase of this sulphide mass had become enriched in Ni-Cu sulphides, the precious metals, magnetite (chromite) and some volaties.

5. Mode of Occurrence of the Precious Metals

The mode of occurrence of the precious metals, as sulphides or alloys in the pyrrhotite solid solution, can be predicted from the prevailing S_2 fugacity. The S_2 fugacity co-existing with pyrrhotite solid solution can be estimated on the basis of experimental work by Toulmin and Barton (1964) and by Naldrett (1966).

Two varieties of pyrrhotite exist in the Strathcona mine: hexagonal, with a composition of from 47.4 to 47.7 atomic per cent Fe; and monoclinic with a composition of 46.7 atomic weight per cent Fe, corresponding to the formula Fe_7S_8. According to Naldrett, the monoclinic variety constitutes by far the largest portion of the pyrrhotite in the ore. Cowan (1967) contoured the distribution of hexagonal pyrrhotite and found that the hanging-wall zone and the bulk of the deep ore zone pyrrhotites are composed, of greater than 40 per cent hexagonal pyrrhotite whereas the bulk of the main ore zone pyrrhotites contain less than 20 per cent hexagonal pyrrhotite.

The estimated range in composition of the hanging-wall and main zone ore bodies of the Strathcona (taken from Naldrett and Kullerud, 1967) was plotted in Figure 12-1, which shows the variation in sulphur fugacity with composition of pyrrhotite solid solution at 600°C. The sulphur fugacity over the ores varied from 10^{-2} to 10^{-5}

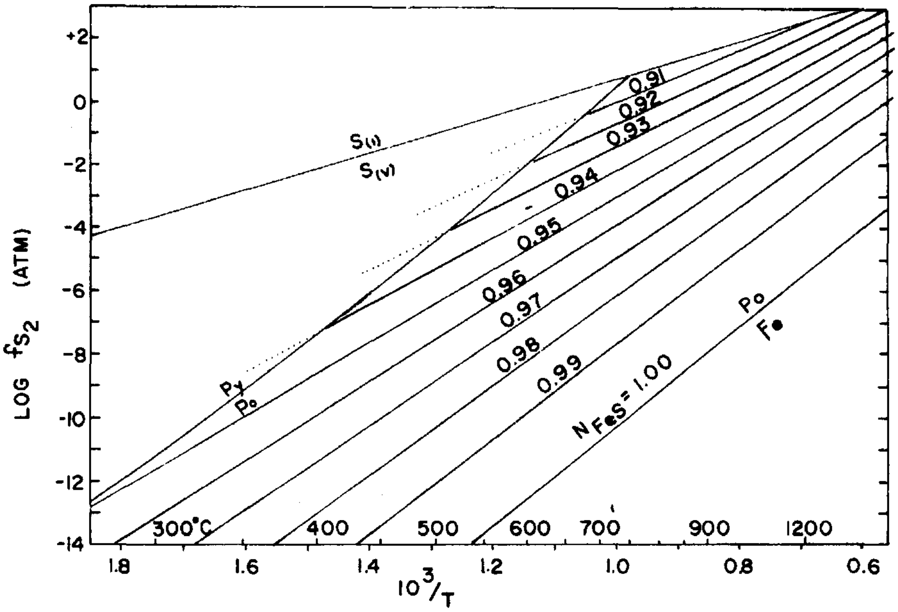

FIGURE 12-2 COMPOSITION OF PYRRHOTITE IN THE IRON-SULPHUR SYSTEM AS A FUNCTION OF TEMPERATURE AND FUGACITY OF S_2. N_{FeS} IS MOL FRACTION FeS IN THE SYSTEM FeS-S_2. (AFTER TOULMIN AND BARTON)

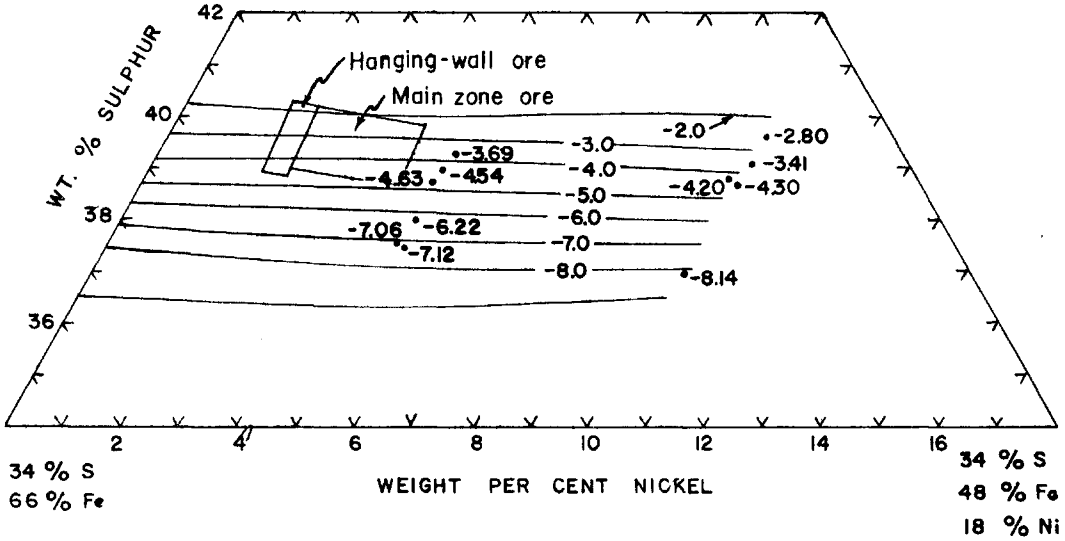

FIGURE 12-1 PORTION OF THE Fe-Ni-S SYSTEM SHOWING THE VARIATION IN SULPHUR FUGACITY, EXPRESSED AS $LOG_{10}(P_{S_2})$ WITH COMPOSITION OF PYRRHOTITE SOLID SOLUTION. POINTS AND THE ADJACENT FIGURES ARE EXPERIMENTAL DATA (AFTER A.J.NALDRETT, 1967.)

atmospheres at 600°C, with an average of $10^{-3.5}$ atmospheres. The addition of Cu to the system would increase the partial pressure of sulphur and so the average sulphur fugacity over the sulphides would have been close to 10^{-3} at 600°C. To estimate sulphur fugacities at lower temperatures, Toulmin's and Barton's diagram (reproduced in Figure 12-2) may be used. Figure 12-1 shows that compositions with up to 10% Ni have approximately the same sulphur fugacities as Fe-S compositions with no Ni. The average Strathcona pyrrhotite contains 39.5 weight per cent S or 46.7 atomic per cent Fe. This composition corresponds to a mole fraction of $N_{FeS} = 0.934$ in the system $FeS-S_2$. From Figure 12-2, it can be seen that a pyrrhotite with this mole fraction has a sulphur fugacity of $10^{-3.5}$ atmospheres associated with it at 600°C. Sulphur fugacities for nickeliferous pyrrhotites of known composition at lower temperatures can be determined directly from Figure 12-2.

For the reaction $\frac{4}{3}\ Ir + S_2 \longrightarrow \frac{2}{3}\ Ir_2S_3$ (1) Richardson and Jeffes (1952) have calculated that $\Delta F°_{1000-1600°K} = -64{,}500 + 44.66T$ (in calories). This relationship may be used to calculate free energy changes down to 298°K on the basis of ΔF's determined by McDonald and Cobble (1962). Free energy change is related to the partial pressure of sulphur by the relationship $\Delta F°_T = RT \ln f_{S_2}$ (in Kcal.). Using this expression, it may be shown that $f_{S_2} \geq 10^{-6}$ at 600°C for reaction (1) to proceed to the right. It has been shown that for the average Strathcona ore, $f_{S_2} = 10^{-3}$ atmospheres, which is 10^3 larger than the sulphur fugacity required to cause Ir metal to react with S_2 and produce Ir_2S_3 at 600°C. The minimum f_{S_2} over the ores would have been 10^{-5} which would have been sufficient for reaction (1) to proceed to the right.

For the reaction $2\ Pt + S_2 \longrightarrow 2\ Pt\ S$ (2) Richardson and Jeffes have found that $\Delta F°_{1000°-1700°K} = - 66{,}100 + 43.6T$ (in calories) and hence reaction (2) will proceed as indicated when $f_{S_2} = 10^{-7}$ or greater at 600°C.

McDonald and Cobble calculated ΔF_f's for the platinum metal sulphides at 298°K. As the free energy of formation for PtS is the highest of any platinum metal and as the ΔF's are generally proportional to one another at any temperature, it is evident that all of the platinum metals react with S_2 in a sulphide ore with composition similar to that of the Strathcona deposit. Hence, the elements exist as sulphides, not as native metals.

Although no thermodynamic data is available for Au_2S_3, it is possible to predict its mode of occurrence. All of the oxides in Table 8-7 (except those of Pd and Rh) have greater negative free energies of formation than the corresponding sulphides. If it is assumed that the oxide and sulphide of Au should behave in the same fashion, and as the free energy of formation of Au_2O_3 is a large <u>positive</u> value, then Au_2S_3 should have an even larger positive free energy of formation. As the free energies of formation of all oxides and sulphides become more positive with increasing temperature, it can be seen that the free energy of formation of Au_2S_3 will be positive at any temperature, and hence Au will remain as the metal.

Nagamori and Kameda (1965) have presented data relating the composition of liquids in the Fe-S-O system approximating the composition of sulphide-oxide ore magmas to the fugacities of oxygen and sulphur at 1200°C. According to their data, $P_{S_2} = 1$ for a liquid corresponding in composition to the Strathcona ore at 1200°C. Using the free energy expression obtained by Richardson and Jeffes (given above) for Pt and the equation relating free energy and partial pressure, it may be shown that $P_{S_2} = 1$ or more for the formation of PtS. In the case of Pt itself, it is thus not possible to state whether the element will be present as the metal or as the sulphide. However, for the other platinum metals, which have more negative free energies of formation than Pt, at least at 298°K, it is possible to state that they could not have been present as metals in the original sulphide-oxide melt at 1200°C.

It has been established that many of the precious metals do not exist uncombined in the sulphide melt. Ir and Os are among the first of the metals to separate from a crystallizing sulphide melt. FeS is the first major sulphide to precipitate. It is not possible to state whether a metal such as Ir will remain as a discrete sulphide (e.g. Ir_2S_3) or will be incorporated into the pyrrhotite solid solution. If the metal forms a discrete sulphide, it will probably be coprecipitated with the pyrrhotite solid solution. If Pt existed as the metal in the sulphide melt, it too would probably be coprecipitated with the pyrrhotites, by an absorption or electrostatic phenomenon. The fact that Pt (and, more particularly Au) is not concentrated in the early pyrrhotites is regarded as proof that Pt is not present as a neutral atom or compound. It may be argued that a low temperature element such as Cu will migrate down a temperature gradient, Pt, however, has a melting point higher than that of Fe, so a temperature gradient cannot be called upon to explain the concentration of Pt at the low temperature end of the gradient.

6. Distribution of Rh in the Sulphide Ores

Although Rh was not determined in this research, its geochemical behaviour may be predicted on the basis of previous work. Hawley (1962) stated that despite its large variation in the different minerals, Rh shows greater concentrations in pyrrhotite than in chalcopyrite. Hawley noted that determination of Rh by fire assay methods is prone to large errors due to losses occurring in slags and cupels. Ginzburg and Rogover (1961), in a study of the distribution of Cu, Ni, Co, Pt, Pd, Au and Rh in sulphides and silicates of the Noril'sk deposit, found 90% of the chalcopyrite samples analysed contained no Rh, while 90% of pyrrhotite samples contained Rh. They also found that chalcopyrite were much richer in Pd, Pt and Au than pyrrhotite samples.

Ginzburg and Rogover found a weak but positive correlation between Rh and Co and as Co is enriched in the high temperature pyrrhotites (that is, the disseminated sulphides in the quartz diorite or xenolithic norite) in both the Frood and the Strathcona mines (Hawley and Cowan), it may be expected that Rh is also enriched in these pyrrhotites.

On the basis of the data of these authors, it can be seen that Rh has a higher concentration level in pyrrhotite than in chalcopyrite and is also more highly enriched in the high temperature sulphides. In this respect it is similar to Ru, Os and Ir. On the basis of the precious metal proportions recovered from the Merensky Reef it has been shown in the previous section that Rh has a mobility intermediate between that of Pt and Ru.

7. Interpretation of Behaviour of the Precious Metals during Fractionation

The precious metals are commonly associated with a particular mineral or minerals. It is commonly assumed that they are incorporated in solid solution in the phase because of some mutual physio-chemical factor. In this section it is argued that although a precious metal may be concentrated with a particular mineral phase, the association is due to concentration of both the precious metal and the major element constituent of the pertinent phase in a late or residual phase. As an example of this, the association of Pd with chalcopyrite will be discussed.

Hawley _et al._ (1951) found Pt to be associated with pentlandite and Pd with chalcopyrite and mixed arsenides. Genkin (1963) stated that Rh and Pd are confined to pyrrhotite and that there is "a distinct dependence within the pairs Pd-Ni and Rh-Co". In a study of the sulphides of the Noril'sk deposit, Ginzburg and Rogover (1961) found Pd, Pt and Au to be concentrated in chalcopyrite while Co and Rh were concentrated in pyrrhotite. They state that Pd is correlated with Ni and that the relative Pd content for constant Ni content in chalcopyrite is 6 times greater than in pyrrhotite. They conclude that a Pd-carrier is present in chalcopyrite that is absent in pyrrhotite, but at the same time, that Pd is bound chiefly to Ni (that is, to pentlandite). In the present study, Pd was found to be strongly correlated with Ni and reached its highest concentration in chalcopyrite and pentlandite samples.

According to Hawley, the average Ni content of Sudbury pyrrhotites is 1.62% whereas in chalcopyrites the average Ni content is 0.25%. The bulk of the Ni in both chalcopyrite and pyrrhotite occurs in fine grained inclusions of pentlandite. As there is considerably more Ni in pyrrhotite than in chalcopyrite an enrichment of Pd in the former would be expected if Pd has a strong geochemical affinity for Ni. However, Pd is enriched in chalcopyrite, not pyrrhotite, and hence, although Pd is highly correlated with Ni, Ni cannot be regarded as the chief Pd - carrier. Chalcopyrite is a much better host than pyrrhotite for a number of metals as indicated in the following table which summarizes average trace element data in pyrrhotite and chalcopyrite given by Hawley (1962).

Table 12-4 Trace element content of Sudbury Pyrrhotite and Chalcopyrite

Elements	Pyrrhotite (%)	Chalcopyrite (%)
Cu	0.25	34.0
Ni	1.62	0.25
Co	0.064	0.001-0.019
Pb	0.000182	0.01 -0.019
Ag	0.000182	0.0183
Sn	N.D.*	<0.008%
Se	0.006	0.0097
Zn	N.D.	Present

*N.D. = Not Detected

Any or several of the metals listed in the above table may act as a carrier for a specific precious metal or the precious metals may be independently associated with the chalcopyrite. Trace elements which occur in greater abundance in chalcopyrite are also enriched in the siliceous zone at Frood. The siliceous zone minerals formed at a lower temperature and a later stage than did the massive and disseminated sulphides at Frood. Paragenetic studies at Frood show that the minerals of Bi, Te, Pb, Zn, Sn, Pd and native Au crystallized after crystallization of the major sulphides of Fe, Ni and Cu (Hawley, 1965). Genkin (1959) states that the platinum metals are invariably concentrated in the latest crystallizing chalcopyritic ores in the Noril'sk. In chalcopyrite veins richest in the platinum metals, platinum minerals are found as separate crystalline grains amidst chalcopyrite, cubanite and pentlandite. The platinum minerals are always the latest minerals to crystallize and tend to occur in the near-selvage zones of veins. Genkin found the platinum minerals to be accompanied by native Au, graphite and late sulphides such as galena, sphalerite and Pb-containing parkerite, $Ni_2(Bi, Pb)_2S_2$. The platinum metals in the Noril'sk deposit form a large number of compounds with elements such as Bi, Te, Cu, Sn, As and Pb (refer to Table 12-4) which summarizes the minerals that have been found in the Noril'sk and Merensky Reef deposits).

On the basis of mineral textures, Hawley has established the following order of paragenesis of the major Sudbury sulphides: nickeliferous pyrrhotite - exsolution pentlandite - chalcopyrite, with chalcopyrite being the youngest mineral. Experimental studies are in agreement with this order. It has previously been argued that the original sulphide liquids which gave rise to the ores at Strathcona and Frood have undergone considerable fractionation. During crystallization of the original liquid, Ni-Cu poor pyrrhotite solid solution was the first phase to crystallize, followed by nickeliferous pyrrhotite containing some Cu, which in turn was followed by pyrrhotite solid solutions containing increasingly greater amounts of Ni and Cu. Cu and the volatile metals accumulated in the residual phase. With decreasing temperature and increasing Cu content in the residual phase, chalcopyrite and cubanite crystallized. Because the residual phase had become enriched in most of the metals listed in Table 12-4 plus Bi, Te and the precious metals, minerals such as chalcopyrite and cubanite would be highly enriched in these elements compared to the early pyrrhotites. The last of the residual liquid to crystallize would do so at quite low temperature and would be highly enriched in the fluxing volatiles (for example, water), volatile metals (Pb, Zn, Ag etc.) and the precious metals.

It is concluded that chalcopyrite is enriched in the volatile metals and the precious metals because it was a late crystallizer, and not because these metals form dilute solid solution with chalcopyrite. Had there been a sufficient amount of an aqueous-rich residual phase which migrated away from the site of chalcopyrite deposition, chalcopyrite would not have accumulated such a large proportion of the precious metals. The original sulphide melt was initially quite dry (i.e. low in the fluxing volatiles) and although a considerable amount of the volatiles accumulated in the residual phase during fractionation, this was still small in proportion to the total amount of sulphides deposited.

It has been shown that many so-called "non-volatile" elements will diffuse quite rapidly down a thermal gradient. For example, solid diffusion of CuS at temperatures below 675°C down a thermal gradient have been found to proceed at a very appreciable rate (MacDougall _et_ _al_.,1961). It may be argued that such solid state diffusion of elements down thermal gradients accounts for metal zoning in deposits such as the Frood. This type of mechanism may account for zoning of metals such as Cu, Ni and many of the volatile metals (e.g. Ag, Pb, Zn) but it cannot explain the distribution of the precious metals. Pt and Pd have melting points which are higher than that of Fe, so they should not migrate to regions of lower temperature. Further, Ir and Os are concentrated in the early high temperature pyrrhotites (situated in the uppermost part of the mine), but are occasionally found highly enriched in the lowest most extremities of the Frood. This phenomenon cannot be explained by solid state diffusion down a thermal gradient.

The residual phase of a crystallizing sulphide magma becomes enriched in many volatile metals and in some metals with very high melting points. The enrichment of the residual phase in these metals may be governed by the same factor - the ability to form complex ions. In a sulphur-rich environment, the types of complexes formed would involve co-ordination with polysulphides or hydrosulphides.

As, Sb, Bi, Ag, Au, Pd and Pt are all known to form stable anionic polysulphide or hydrosulphide complexes such as the thioarsenite ion, AsS_3^{-3} or the aurous hydrosulphide AuS^-. The entry of any of these elements into the residual phase may encourage the entry of other complexing metals. Leddicotte (1961) states that PtS_2 will dissolve in polysulphide solutions and can be much more rapidly solubilized if As, Sn, Sb, or Au sulphides are present. The study of complex formation is normally carried out in an aqueous medium and the formation of poly-or hydro- sulphides usually requires the presence of an alkali sulphide. It has previously been argued that considerable amounts of Na may be present in a sulphide melt (and were at Frood and Strathcona). During the initial cooling of the sulphide melt, only small amounts of an aqueous phase would be present, and this would certainly not be present as molecular H_2O but combined in species such as HS^- and SO_2. However, all of the volatile components would enter the residual liquid phase. The possibility of the existence of sulphide complexes at magmatic temperatures and in a dry system is difficult to ascertain. The fact that the metals which form complexes in an aqueous medium at much lower temperatures enter the residual phase strongly implies that they do form sulphide complexes at high temperature.

Te and Se are also enriched in the siliceous zone but for a somewhat different reason than the metallic elements. Zainullin (1960) found a significant increase in the Se and a large increase in the Te contents in the series pyrrhotite-pentlandite-chalcopyrite in the ores of the Noril'sk. Zar'yan (1962) found Se and Te to increase regularly from disseminated ore to hydrothermal veins in the Kafan deposit. In the sulphide melt, Se and Te may exist as the anions Se^{-2}(1.93 Å) and Te^{-2}(2.11 Å) which may be excluded from early sulphides because of their large radii compared to that of S^{-2}(1.74 Å). Cotton and Wilkinson (1962) stated that it is unlikely that any of S, Te or Se exist as simple anions in solution and that they probably are present as polyanions such as Te_n^{-2}. Se, and even more so, Te, has a tendency to form anionic complexes. This may account for Te's comparatively greater enrichment in the late stage deposits of the Noril'sk.

The question arises why Pd, Pt, Au and Ag form strong complexes whereas Ir, Os, Ru and Rh do not. The former form stable polysulphide complexes because: (1) they are strong (b)-class acceptors, that is they form strong bonds with S, whereas Ir, Os, Ru and Rh are only moderately strong (b)-class acceptors; (2) the nature of the bonding of Pt, Pd, Au and Ag is conducive to complex formation as they form square planar bonds, whereas the more inert metals bond octahedrally; and (3) they have low stable oxidation states whereas Ir, Os, Ru and Rh have higher stable oxidation states.

The order of the mobilities of the precious metals, that is $Au > Pd > Pt > Rh > Ru > Os \gtrsim Ir$, established in Section 4 corresponds exactly to the order of decreasing lattice energies of the precious metals (refer to Figure 8-2). Au has the highest mobility of the precious metals and has the lowest lattice energy and melting point. Ir and Os are the most immobile of the metals and have the highest lattice energies and melting points. The lattice energy of an element plays a large role in its ability to form complexes. The fact that an element has a high lattice energy means that it binds its electrons closely to the nucleus which in turn means that the atom is difficult to polarize.

Elements which are difficult to polarize do not posses strong (b)-class character and hence do not form strong complexes with sulphur.

On the basis of Rh/Ir ratios in the Merensky Reef, Rh was placed between Ru and Pt in the order of mobility in Section 4. Physiochemical properties of Rh confirm this as the proper position for the metal in the sequence. Its melting point, lattice energy, and atomic radii are intermediate to those of the groups Ru-Os-Ir and Pt-Pd-Au. However, it is more similar to the former group in that it forms octahedral rather than square planar complexes, also Rh is not known to form complexes in polysulphide solutions (Sidgwick, 1950). According to Ginzburg and Rogover, Rh has a much higher concentration in pyrrhotite than in chalcopyrite and in this respect is again more similar to the group Ru-Os-Ir.

Au is normally concentrated in late stage hydrothermal deposits associated with granitic and quartz diorite plutons. This indicates that the gold complexes formed are the most stable of the precious metal complexes. Hawley and Rimsaite (1953) showed that Pd is the one Pt metal found in minute amounts in sulphides of hyrothermal gold ores, while Badalov and Terekhovich (1966) state that "unlike Pt, Pd is frequently associated with Ag, Au, Pb, Se and Te". These observations indicate Pd's ability to persist even in the more siliceous residual liquids of crystallizing magmas. The fact that Au is carried in hydrothermal solutions to quite low temperatures whereas only a small amount of Pd is found in hydrothermal veins, suggests that Au complexes are more stable than Pd complexes. Similarily the fact that Pd is the only metal found in hydrothermal veins strongly suggests that its complexes are more stable than any of the other Pt metals.

It has been established that most of the Os, Ru, Rh and Ir are concentrated in the early crystal phases of the sulphide melt, but occasionally they are enriched in the final residual phase. The metals appear to be virtually absent in the bulk of the sulphides which crystallize after the initial high temperature pyrrhotites separate. Os, Ru, Rh and Ir are moderately strong (b)-class acceptors but apparently at the high temperature and low volatile content of the sulphide melt when it first starts to crystallize, these metals do not form complexes to any great extent, but are either incorporated into or coprecipiated with the pyrrhotite solid solution. However, with lower temperature and greater volatile content in the residual phase, the complexes are stabilized and persist through the fractionation of the sulphide melt to be enriched in the residual products of crystallization.

The causes of precipitation of Pt, Pd, Au and any Os, Ru, Rh, or Ir that was carried in the residual aqueous phase would be decreasing temperature, the accumulation in residual liquids of sufficient concentrations of those elements that normally combine with the precious metals (for example, Sn, Te, Bi, As) to form intermetallic compounds, and reaction of the constituents of the residual liquids with the host rock.

It has already been noted (see page 177) that Au is not nearly as highly concentrated in the footwall chalcopyrite and pyrrhotite as the Au/Ir ratios in the mafic and xenolithic norite pyrrhotites indicate it should be. Very little Au enters the early xenolithic norite pyrrhotites although the original sulphide liquid contained a significant proportion of Au. Hence the bulk of the Au should be in the footwall chalcopyrites, but judging from the Pd/Ir ratios in the three zones, it is not. This strongly suggests that Au was taken into solution but was not deposited with the latest chalcopyrite as was the Pd, but remained in the water-rich solutions. At Strathcona the aqueous phase may have diffused away from the ore body through the footwall breccia. At Frood, the Au-bearing aqueous phase may have escaped through the Frood breccia or they may have migrated downwards, past the siliceous zone (see Figure 11-2) away from the heat source. Thus, there may be Au enrichment below the 3600 foot level at Frood.

The fact that Au is not more enriched in the siliceous zone at Frood than it is, may in part be due to the high stability of the Au complex (AuS^-) to low temperatures (Zvyagintsev, 1946) but also to the absence of Au reductants in the residual phase. Unlike the Pt metals which form a large number of intermetallic compounds with the elements that accumulate in the residual phase, Au combines only with Te to form tellurides and Ag to form electrum. AuS^- can be reduced by Te^- or AuTe but in the absence of these, will remain in solution until major changes occur in the carrying solutions (i.e. reduction in temperature, change in pH).

8. Chemical Form of Au during Fractionation of Silicate Magmas

Many workers (e.g. Vincent and Crocket, 1960, DeGrazia and Haskin, 1963, Mantei and Brownlow, 1967) have suggested that Au exists as neutral, uncharged atoms, perhaps in the form of finely dispersed particles, suspended in melts and in solutions. The neutral atoms precipitate at a more or less constant rate and are incorporated into the growing crystals by an inclusion phenomena, not by ionic substitution.

This interpretation arises from the fact that many analyses reveal no concentration changes throughout differentiation processes. The gold content of the highly differentiated Skaergaard rocks remained within 50%

of the original magma content of Au, while DeGrazia and Haskin found that a wide range of terrestrial materials had uniform Au contents.

The fact that Au was found to be highly fractionated during the crystallization of a sulphide melt prompted the question whether Au is present as a neutral atom in a silicate magma.

If Au exists as a neutral atom in silicate melts, then Ir, Ru and Os must likewise exist as uncharged atoms. Although the standard oxidation potential of Au is lower than any other metal, Au is more reactive than any of Ir, Ru and Os with regard to ease of dissolution. The partial pressure of sulphur in a silicate melt is much less than that necessary to stabilize the sulphides of Ir, Ru or Os. This implies that the latter must also exist as tiny uncharged particles suspended in solution and they should be engulfed by crystallizing-settling silicates at the same rate as the Au atoms. However, accumulations of Au and of Ir-Ru-Os occur at the opposite ends of the differentiation sequence. The former persists until the last hydrothermal solutions whereas the latter are precipitated with early harzburgite-dunites.

Further, reference to Table 12-3 indicates that there is a definite order to the mobility of Ir, Os, Pd and Au in silicate magmas with Ir being the most immobile and Au the most mobile. Thus, although it is possible that Au exists as a neutral, uncharged atom in a silicate melt, it is highly improbable.

Shcherbakov and Perezhogin (1964) found that the Au content of rocks decreases from basic to acid rocks and state that ferromagnesian silicates and mafic and ultramafic rocks are the most efficient precipitants of gold from hot solutions. They theorize that gold is isomorphously included in compounds that have a minimum amount of ionic character, examples of which are said to be olivine and pyroxene. Minerals with more ionic bonding (e.g. quartz and feldspars) do not contain chemically-bound gold. The authors employ the concept of electronegativity to explain the behaviour of Au, stating that Au, because it is highly electronegative, prefers covalent bonds. However, according to Little and Jones (1960) Au is less electronegative than many of the base metals, including iron, and so application of the concept is unwarranted (see Table 11-4).

On the basis of ionic radii, Au^{+1} (1.46 Å) can substitute for K^{+1} only (1.33 Å), while Au^{+3} (0.85 Å) should not be captured in place of Mg^{+2}(0.66) or Fe^{+3}(0.53 Å). Thus, if anything, Au should substitute in feldspars, not olivine or pyroxene. Using thermodynamic data, it has been shown earlier that Au much prefers the metallic state to substitution in any kind of ionic compound.

However, ultramafic rocks and mafic minerals do tend to be enriched in gold. Mantei and Brownlow (1967), who analysed a large number of co-existing minerals from the Marysville quartz diorite, found that the Au contents of the constituent minerals were as follows (in p.p.b.): 100-hornblende; 76-biotite; 65-quartz-feldspar; and 37-magnetite. Shcherbakov and Perezhogin found that magnetite contained 10 times more Au than amphibole and 4 times more Au than olivine or pyroxene. Mantei and Brownlow concluded that the concentration of Au in the various minerals was probably due to an inclusion or trapping phenomena of neutral Au atoms rather than to ionic substitution.

The reason for the enrichment of ultramafic rocks and certain ferromagnesian minerals in Au may be two-fold. Initially, in a magma, it is believed that Au may be present in the form of neutral atoms. These would tend to be precipitated with the early crystal differentiates. With crystallization, the volatile content of the magma (e.g. $S_2^=$, Cl^-, OH^-) would increase, the Au would be complexed, and would tend to remain in solution. Mafic minerals, especially amphiboles and micas might act as sites of decomposition of these complexes with the resultant precipitation of metallic Au which would be entrapped in the growing crystal. In general, however, the Au complexes would be stable and would persist throughout the history of the differentiating magma.

It is not known whether poly- or hydrosulphide complexes of Au may exist in a silicate magma. Perhaps the Au is complexed to some other volatile, such as Cl^-. However, Au does have a high affinity for S and it is known that up to 0.01% S can be dissolved in basaltic glass (Skinner and Peck, 1966). Cloke (1963) states that metals carried in polysulphide solutions may be deposited by any of 1) change in pH, 2) oxidation or reduction, or 3) reaction with iron minerals.

Decomposition of the polysulphide carrier solution may be accomplished by reaction with magnetite, for example,

$$2\ Fe_3O_4 + 9\ S^{-2} + 8\ H_2O \longrightarrow 3\ FeS + 3\ FeS_2 + 16\ OH^-$$

thereby causing precipitation of metallic Au at the magnetite site. Direct reaction of AuS^- may occur with a ferromagnesian silicate in a reaction such as

$$\underset{\text{Fe biotite}}{3\ KFe_3\ (AlSi_3O_{10})(OH)_2} + 9\ AuS^- \longrightarrow$$

$$\underset{\text{muscovite}}{KAl_2(AlSi_3O_{10})(OH)_2} + 9\ FeS + 9\ Au^\circ + 2K^+ + 4\ OH^-$$

The metallic Au would be incorporated into the growing magnetite, pyrrhotite or muscovite site.

It has been noted that a blue-green soda-rich amphibole occurs adjacent to sulphides in the Sudbury quartz-diorite. It has been suggested that soda and water associated with the sulphide caused the formation of the soda amphibole (which is not found removed from sulphides). An interesting problem would be the analysis of these amphiboles for precious metal content. If the foregoing argument holds, the soda amphiboles should be enriched in the precious metals relative to non soda-rich amphiboles.

9. Implication of Whole Rock and Magnetite Analyses

i) Whole Rock Analyses

One whole rock analysis was performed in the present study on a xenolith from the hanging-wall breccia. The whole rock was composed of 60% orthopyroxene, 23% olivine, 13% plagioclase and 4% magnetite, and hence the xenolith is classified as an ultramafic. No sulphides were present in the portion analysed, although a small amount ($\frac{1}{4}$%) was present in the specimen. Some of the oxide phase (again, no sulphides) was also analysed. Both whole rock and oxide samples were kindly analysed by Mr. L. Chyi. The data obtained are presented in Table 12-5 along with the contribution of the magnetite's content of each metal to the whole rock.

One other whole rock determination is available for comparison to the whole rock analysed here. This is a quartz diorite specimen containing about 1% pyrrhotite plus chalcopyrite from the Creighton mine. The specimen was found to have 11.5 p.p.b. Pd by Crocket and Skippen (1966) which figure is virtually identical to that obtained in this study.

Table 12-5 Au, Pd and Ir content of an ultramafic xenolith and of its oxide component

Element	Whole Rock (p.p.b.)	Magnetite (p.p.b.)	Contribution of Magnetite to Whole Rock(p.p.b)	Percent Contribution of Magnetite
Au	0.65	4.75	0.19	29.2
Pd	11.4	57.3	2.2	19.1
Ir	1.15	2.83	0.11	9.7

The quartz diorite analysed contained 1% sulphides, and much Pd is almost certainly contained in the chalcopyrite. However, even if this chalcopyrite contained 1000 p.p.b. Pd (the average of the footwall chalcopyrites at Strathcona) and if this chalcopyrite constituted ½% of the rock, the maximum contribution of the sulphide would be 5 p.p.b. This would mean that the contribution of the silicates and oxides is 6.5 p.p.b. which figure must be taken as a minimum value. It can be stated that the quartz diorite minus sulphides very probably contains a significantly less amount of Pd than does the ultramafic xenolith. Although only two figures are available, they do support a theory of differentiation of a silicate magma in which either Pd is being enriched in the early silicates or in a separating sulphide liquid phase.

The oxide phase extracted from the xenolith was highly enriched in all three metals compared to the whole rock. It must be emphasized that only two analysis were performed, so any conclusions based on these figures should be regarded with caution.

ii) Magnetite Analyses

Naldrett (1967) has shown that during the cooling of sulphide-oxide liquid of the composition of the ores of the Strathcona mine, pyrrhotite would be the first mineral to crystallize. According to his diagram of the Fe-S-O system (see Figure 12-3) approximately half of the pyrrhotite would have crystallized before the cotectic was reached and crystallization of magnetite would commence, provided the initial liquid contains 15% magnetite. Thus, the cooling sulphide-oxide liquid would become enriched in magnetite. This interpretation of a differentiating liquid appears to be substantiated at Strathcona where irregular bands of magnetite up to 8" in width are found in the deep ore zone (Cowan, 1967).

Several magnetites from the deep ore zone contained much lower precious metal contents than co-existing sulphides. According to Naldrett, the sulphides and oxides would have formed at the same time and hence would have been exposed to the same precious metal concentration in the melt. The fact that the sulphides have much higher precious metal content than the oxide phase complements the thermodynamic prediction that the metals are much more chalcophile than lithophile.

10. Economic Aspects

According to Hawley (1962), production from the Falconbridge Nickel Mines properties over a five year period yielded the following platinum metal percentages: Pt 36.6%, Pd 40%, Rh 8.8%, Ru 9.9%, and Ir 4.7%. Production from all of the Sudbury ores, averaged over a ten year period, were as follows: 46% Pt, 41% Pd, and 13% combined Rh, Ru and Ir. No Os is recovered from the Sudbury ores. Allen (1960) states that Os occurs in the ore to an amount something less than 1% of the Ru content and it is probably lost as the volatile tetroxide during smelting and fire

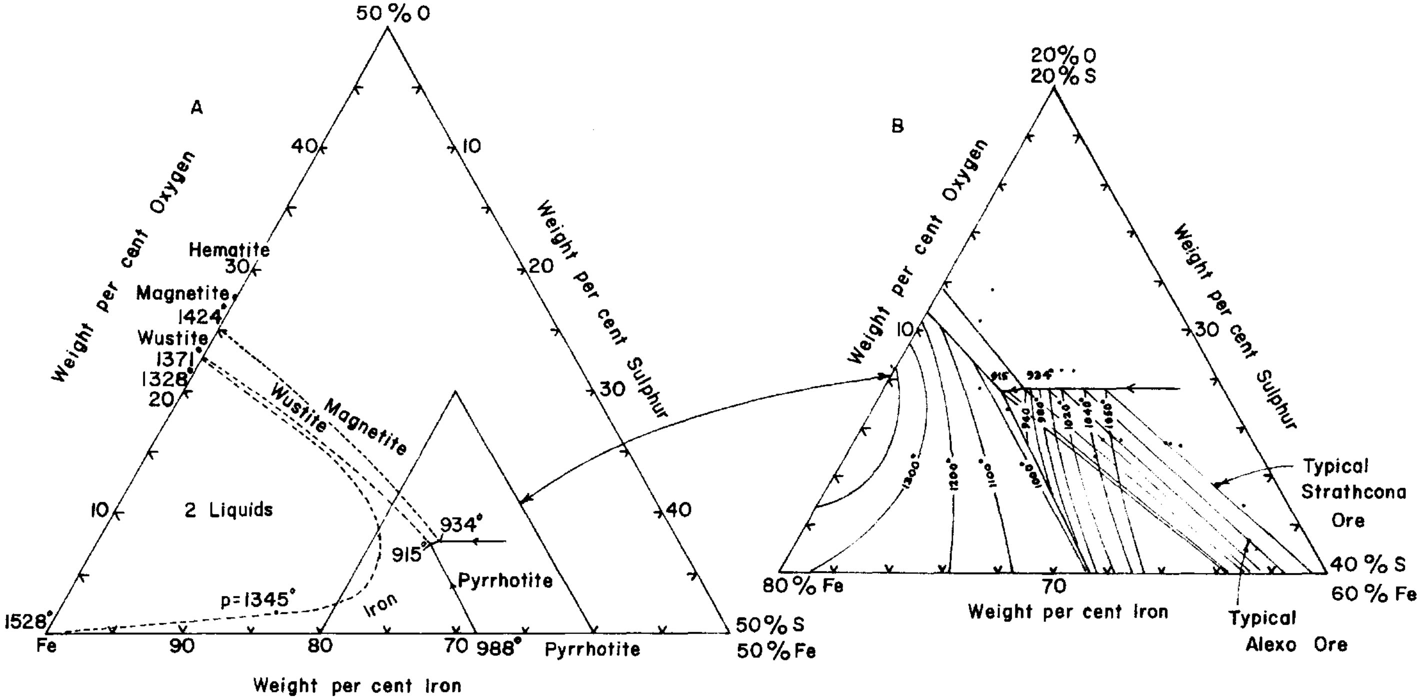

Figure 12-3 Liquidus relations in the iron-rich portion of the Fe-O-S system (after Naldrett, 1967)

assaying. However, according to the data obtained by Hsieh (1967) and the data of this study, the Os content of Sudbury sulphides averages 20 to 80% of the Ru content and is about the same as the Ir content; that is, 4.7% of the total platinum metals. In 1959, 319,570 ounces of total platinum metals were recovered from Sudbury (Allen). Hence, the amount of Os lost was somewhat more than 15,000 ounces.

According to Allen, ore at the Copper Cliff plant of the International Nickel Company is finely ground and then subjected to differential flotation which yields three products: copper-sulphide concentrate, nickel-sulphide concentrate, and iron sulphide concentrate. Precious metals are obtained from the first two flotation products but none are recovered from the iron-sulphide concentrate. Similarily, precious metals contained in the iron-sulphide concentrate from the Falconbridge properties are not recovered. It has been shown in this study that although much of the Pd, Pt and Au is concentrated in chalcopyrite and pentlandite, a substantial proportion of these metals also occur in the co-existing pyrrhotite. Further, the bulk of the Ir and Os, and to a lesser extent Ru and Rh, occur in high temperature pyrrhotites, some of which are not ore grade.

Data on the Strathcona footwall sulphides indicate that while chalcopyrite contained 982 p.p.b. Pd, co-existing pyrrhotite contained 212 p.p.b. . Hawley gives the ratios of the major ore minerals at Sudbury as follows: pyrrhotite: pentlandite: chalcopyrite = 70: 15: 15. The data suggest that pentlandite and chalcopyrite contain equal amounts of the precious metals. It can be shown that pyrrhotite contains 1/3 of the total amount of Pd present at Sudbury. If all of the Pd in chalcopyrite and pentlandite was recoverd in 1959, and as this amounted to 128,000 ounces, then the total amount of Pd present was actually 192,000 ounces. In other words, approximately 64,000 ounces of Pd were lost. An equivalent amount of Pt was not recovered.

An estimation of the relative proportions of the metals in the Strathcona ore may be obtained from the precious metal ratios in the mafic norite sulphides. These sulphides are believed to represent undifferentiated sulphide liquid and as such should be a guide to the precious metal ratios throughout the mine. The precious metal content of the Strathcona mafic norite pyrrhotites are as follows, in p.p.b.: 22 Au, 81.7 Pd, 9.6 Ir, 8.6 Os, 19.0 Ru. These values will be taken to represent the average tenor of the total mass of sulphides at Sudbury. It is believed that Ir/Pd and Os/Pd ratios in mines on the South Range of the basis may be higher than suggested here. One analysis from the main mass of the relatively undifferentiated Falconbridge mine ore contained equal amounts of Ir and Pd, while the Ir/Pd ratio of the disseminated sulphides of the Frood was 1/3.

The total amount of Pd present in the Sudbury ores was 192,000 ounces in 1959. The amount of Os present, but not recovered, was 8.3/81.7 x 192,000 = 19,500 ounces. In 1965 the price of Os was $280 per ounce, so the value of Os lost was considerable. Large amounts of the other precious metals (for example, 64,000 ounces of Pd in 1959) were not recovered.

Whether it is practical to recover the metals is difficult to say. It may be impossible to recover Pt, Pd, Ir, Rh and Au from the iron sulphide. Os and Ru, however, are probably lost as the volatile oxides and so it might prove economical to extract the metals from the smelter gases. Much Os and Ir, and smaller amounts of Rh and Ru occur in high temperature sulphides. A large part of these sulphides may not be regarded as ore on the basis of their Cu and Ni contents, but the fact that they contain large amounts of the same members of the precious metal group may render them ore.

To investigate the possibility of greater recovery of the more inert members of the precious metal group it is imperative to know their concentration in the ore as a whole. Falconbridge is a relatively undifferentiated body and so the precious metal content of that body could be established with as few as 10 composite samples. Due to the inhomogeneity of the metals in sulphides, it would be necessary to homogenize the samples. This could be accomplished by heating the sulphides in a hydrogen furnace at 600° to remove all of the sulphur as H_2S. The precious metals alloy with Cu-Fe-Ni metals and so would be dispersed evenly throughout the metallic phase if heated to a sufficiently high temperature. A small portion of this alloy would be taken for analysis of the precious metals. Reduction in a H_2 furnace prior to irradiation would also serve to reduce the weight of the sample by 36% and to avoid the production of 87 day ^{35}S which is generated in large quantities during irradiation of sulphides. This active sulphur is a β^- emitter and is released into the atmosphere in the form of SO_2 during the aqua regia treatment of the samples following irradiation. Reduction prior to irradiation would remove this health hazard.

11. Conclusions

The data support an hypothesis that the sulphides at Strathcona were injected with the sub-layer rocks, settled to the floor of the Irruptive, and migrated into the footwall, perhaps via thermal fractures caused by the presence of the hot, liquid sulphides. As the sulphide liquid migrated into the footwall, it underwent fractional crystallization with the liquid being enriched in metals such as Ni, Cu, Pt, Pd, Au, Bi, Te and Sb. This fractionation accounts for the zoning of the ore body, previously explained by solid-state diffusion or migration of the metals through an aqueous medium in response to a thermal gradient subsequent to solidification of the sulphides. The sulphides in the mafic norite and upper part of the xenolithic norite represent the original sulphide liquid while the sulphides which constitute the hanging-wall zone represent the first crystals to separate from the ore magma. The residual liquids became enriched in volatile components such as H_2O and Na_2O and the presence of thes (some of which would have been driven ahead of the sulphide liquid as it migrated into the footwall) may account for the soda-metasomatism observed in the footwall.

The fugacity of sulphur was sufficiently high that the precious metals existed either as sulphide compounds or complexes in the ore magma and as the former in crystallized phases. Metals which are enriched in the early pyrrhotites (e.g. Os and Ir) were insoluble in the sulphide liquid and formed either discrete sulphides which were coprecipitated with the first solids to separate, or were incorporated into the pyrrhotite solid solution. It is probable that if they entered the pyrrhotite solid solution they would have exsolved from it at lower temperatures.

The metals which were soluble in the sulphide liquid including mainly Pd, Pt and Au, but also small amounts of Ir, Os and Ru formed complexes and accumulated in the residual phases, where they finally crystallized by combining with S and elements such as Bi, Sb, Te and Pb, which had also accumulated in the residual volatile-rich liquids.

Although there are large differences in the behaviour of the groups Ir-Os-Ru (and -Rh) and Pd-Au-Pt, significant variations exist within each group and in fact there is a consistent variation throughout the whole of the precious metal group. The following order of mobility was established: Au $>$ Pd $>$ Pt $>$ Rh $>$ Ru $>$ Os $\geq$ Ir with Au the most mobile element. Ir is the most insoluble metal in sulphide (or silicate) magmas and is concentrated in the most primitive fraction of these magmas. Considerable Au may have migrated away from both the Strathcona and Frood ore bodies in the residual aqueous phase that developed.

Due to the fractionation of the precious metals during fractional crystallization of sulphide (or silicate) magmas, they may be used as indices to determine the degree of differentiation of material which has been derived from the mantle. For this purpose, the individual precious metal content should be compared to that of Ir which is the most insoluble of the metals and hence the most depleted in the later fractions of a magma. Primitive material should have precious metal ratios which are similar to those of carbonaceous chondrites. Os and Ir are enriched, relative to the other metals in the residual crystal phases, while the other metals are enriched relative to Ir and Os in the later fractions of differentiating magmas.

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APPENDIX A.

^{199}Au CONTRIBUTION TO TOTAL Au ACTIVITY

In beta counting of Au samples, ^{198}Au produced by the n,γ process on stable ^{197}Au, is the major radionuclide counted, but some ^{199}Au produced by the reaction $^{198}\mathrm{Pt}(n,\gamma)^{199}\mathrm{Pt} \xrightarrow{\beta^-} {}^{119}\mathrm{Au}$ is also counted. To estimate the contribution of ^{199}Au activity to the total activity, one can use either experimental data or theoretical calculations.

In several experiments, both ^{198}Au produced from the Au standard and ^{199}Au produced from the Pt-standard were counted. The experimental data from these experiments, along with the concentration of Pt and Au in each of the Cu-Ni matte, G-1 and W-1 are presented in the following table.

The Pt values for G-1 and W-1 are those obtained by Das Sarma et al. (1965), while the Au values are those obtained in this work. The Pt and Au values for the Cu-Ni matte are the average of this and previous work. The experimental data has been corrected for chemical yield and time of counting.

Gold Standard		
Weight of Au	6.84×10^{-4}	μgm
Counts obtained from ^{198}Au	772	c.p.m.
Platinum Standard		
Weight of Pt	9.4×10^{-1}	Ugm
Counts produced from ^{199}Au	1148	c.p.m.
Cu-Ni Matte		
Concentration of Pt	5.51	p.p.m.
Concentration of Au	1.92	p.p.m.
G-1		
Concentration of Pt	8.2	p.p.m.
Concentration of Au	3.3	p.p.b.
W-1		
Concentration of Pt	9.2	p.p.b.
Concentration of Au	5.8	p.p.b.

The ^{198}Au activity in any sample is given by

$$A({}^{198}\mathrm{Au}) = \frac{\text{c.p.m. }\left[\text{Std }{}^{198}\mathrm{Au}\right]}{\text{mg }\left[\text{Std }{}^{198}\mathrm{Au}\right]} \times \text{mg }\left[\text{Au in Sample}\right]$$

A similar expression can be written for $A({}^{199}\mathrm{Au})$.

The per cent contribution of ^{199}Au is given by

$$= \frac{A({}^{199}\mathrm{Au})}{A({}^{199}\mathrm{Au}) + A({}^{198}\mathrm{Au})} \times 100 \qquad \text{or}$$

$$= \frac{\dfrac{\text{c.p.m. }\left[\text{Std }{}^{199}\mathrm{Au}\right] \times \text{mg }\left[\text{Pt in sample}\right]}{\text{mg }\left[\text{Std }{}^{199}\mathrm{Au}\right]}}{\dfrac{\text{c.p.m. }\left[\text{Std }{}^{199}\mathrm{Au}\right]}{\text{mg }\left[\text{Std }{}^{199}\mathrm{Au}\right]} \times \text{mg }\left[\text{Pt in sample}\right] + \dfrac{\text{c.p.m. }\left[\text{Std }{}^{198}\mathrm{Au}\right]}{\text{mg }\left[\text{Std }{}^{198}\mathrm{Au}\right]} \times \text{mg Au in sample}} \times 100$$

Substituting the experimental values, this becomes

$$\frac{\text{mg }\left[\text{Pt in sample}\right]}{\text{mg }\left[\text{Pt in sample}\right] + 974 \times \text{mg }\left[\text{Au in sample}\right]} \times 100$$

When the Pt and Au concentration of G-1, W-1 and the Cu-Ni matte are substituted, in turn, the contributions of ^{199}Au are found to be 0.26% 0.16% and 0.30% respectively.

It has been theoretically demonstrated elsewhere (Crocket, Keays, and Hsieh) that the maximum contribution of ^{199}Au in these samples is 0.7% for G-1, 0.4% for W-1 and 0.9% for the Cu-Ni matte.

The above equation may be used to estimate the ratio of Pt/Au which may produce a given contribution from ^{199}Au. If this is 10% of the total activity, the ratio Pt/Au must be 107. In other words, for an error of 10% in the Au determinations, there must be more than 100 times as much Pt as Au in the sample.

To estimate the error in the Au analyses of the sulphide samples, it is assumed that an estimation of the Pt content of the samples analysed may be made on the basis of the Pd content of the samples. Hawley (1962) reported that the average ratio of Pt/Pd over a five year period from the Falconbridge Sudbury deposits was 1/1. If it is assumed that there is considerable geochemical coherence between Pd and Pt, then the Pt content of the samples analysed should be the same as the Pd content. At Strathcona, the largest ratio of Pd/Au is 27 in the footwall chalcopyrites. If it is assumed that the Pt/Au ratio is also 27, then the maximum ^{199}Au contribution will be 2.7%. If the samples are gamma-counted, this error may be avoided.

APPENDIX B

SELF-SHIELDING EFFECTS IN SAMPLES

Dr. R. H. Tomlinson, in a lecture series given at McMaster University during the 1966-67 academic session, presented a simplified method of a mathematical approach developed by Case, de Hoffman, and Placzek (1953), which can be used to calculate the depression in flux resulting from diffusion of neutrons through a sample with a finite cross-section. The method can be used for samples of a variety of geometrical shapes.

The procedure involves calculation of the mean free path of a neutron in the material of interest. This can be obtained from the relationship

$$\lambda = \frac{1}{N\sigma}$$

where N = number of atoms/cm^3

and σ = capture cross-section (in cm^2)

An expression a/λ or b/λ where $\underline{a}$ and $\underline{b}$ are geometrical dimensions of the bodies concerned ($\underline{a}$ = radius of a sphere, $\underline{b}$ = half-thickness of a slab of infinite length) is then obtained. Case, de Hoffman and Placzek have tabulated values of Pc (which is the collision probability of a neutron) for a large number of values of the ratio a/λ (or b/λ as the case may be). Pc values have been calculated for slabs, cylinders, spheres and hemispheres. A graphical display of the data is presented in Figure B-1. With a knowledge of Pc, Po (which is the escape probability of a neutron) can then be

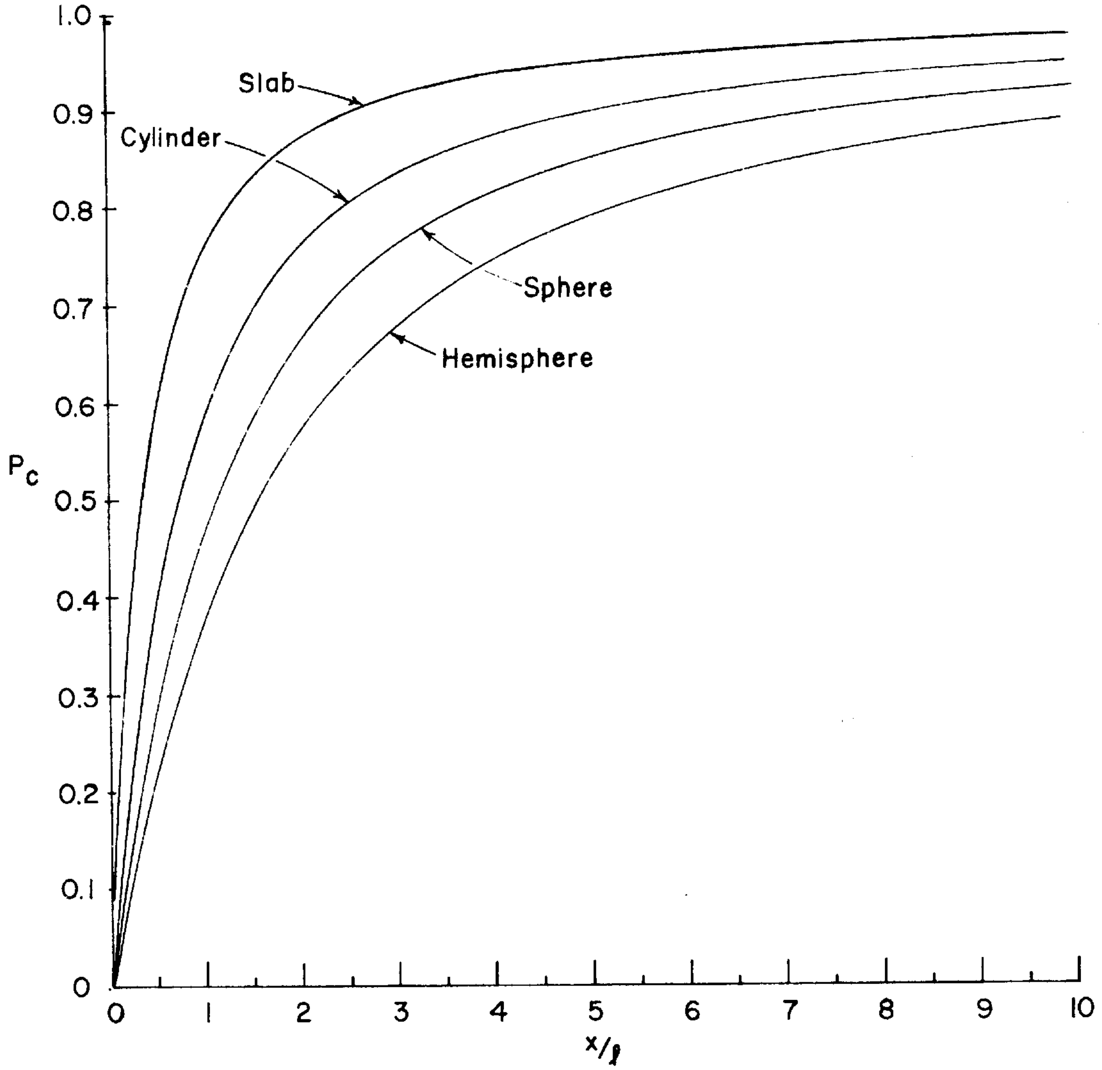

Figure B-1 Collision probabilities for uniform source density. For a cylinder a sphere, and a hemisphere, x is the radius; for a slab, x is the half-thickness. x is in units of mean free paths. (after Case, de Hoffman, and Placzek, 1953) calculated from the relation Po = 1 - Pc. Po is the ratio of the flux in the sample to that which would have been present had there been no neutron absorption. It may be expressed as $Po = \frac{Os}{O\infty}$

where Os = neutron flux in sample

O∞ = neutron flux with no sample

To illustrate the procedure, the flux depression in a gold foil 0.002" thick (or 0.00508 cm), the thickness of foil used by Vincent and Smales (1956), will be calculated both for thermal neutrons and neutrons of the resonance energy of gold.

$$\text{For gold,}\quad N = \frac{19.3}{197} \times 6.023 \times 10^{23}$$

$$= 5.88 \times 10^{22}\ \text{atoms/cm}^3$$

where 19.3 = density of Au

197 = molecular weight

6.023×10^{23} = Avogadro's number

The capture cross-section of thermal neutrons at 25°C is $100 \times 10^{-24}\,\text{cm}^2$. Hence, the mean free path is then

$$\ell = \frac{1}{N\sigma} = 0.170\ \text{cm}$$

For a slab of thickness 0.00508 cm, b = 0.00254 cm and $b/\ell = 0.015$. From Figure B-1, Pc = 0.067, and Po = 0.933. Hence, the neutron flux in the gold foil is only 93.3% of the flux had the foil not been there. For resonance neutrons with an energy of 4.8 eV, $\sigma = 30{,}000 \times 10^{-24}$ barns and $\ell = 5.67 \times 10^{-4}$ cm. For these parameters it can be calculated that $b/\ell = 4.48$ and (from Figure B-1) Pc = 0.944. Thus, the flux at the centre of the foil would only be 5.6% of the total flux had there been no self-shielding by the sample and if the total flux consisted of 4.8 eV neutrons. The McMaster Research Reactor has a total neutron/fast neutron ratio from 14/1 to 21/1 (personal communication from J. McDougall, Chief Reactor Superintendent). Only a small fraction of the fast neutrons will have an energy of 4.8 eV (refer to p.107 in Research Reactors) and so the depression in total flux due to absorption of neutrons at the resonance energy will be small.

For purposes of discussion, here, however, it is sufficient to have illustrated that use of a gold foil as a standard will result in a substantial decrease in specific activity of the standard due to flux attenuation.

In the present analytical scheme, up to 100 mg of material was taken for analysis. The maximum Au content of the samples analysed was 10 p.p.m. If it is assumed (under the most extreme case) that all of the Au contained in a sample is consolidated into a sphere within the sample, and not distributed homogeneously throughout the sample, then the weight of Au within this sphere would be 10^{-3} mg and the sphere's radius would be 0.00231 cm. For thermal neutrons, $\lambda = 0.170$ cm , $a/\lambda = 0.0136$, and $Pc = 0.0100$. Thus $Po = 0.99$ or there may be a 1% reduction in flux at the centre of the sphere.

If neutrons of the resonance energy of Au are involved, then λ becomes 5.67×10^{-4}, $a/\lambda = 4.07$ and $Pc = 0.821$. Hence, only 0.179 of the neutron flux seen at the surface of the sphere will be present at its centre if all of the neutrons have an energy of 4.8 eV. But, as noted earlier, only a maximum of 10% of the total neutron flux is composed of fast neutrons, and, further, the proportion of fast neutrons with a specific energy compared to the number of thermal neutrons is extremely small.

It may be concluded that the effect of concentration of all the gold in a sample into a single sphere would be to depress the specific activity of the gold by less than 1%. In general, there is much less than 10 p.p.m. in natural materials and it is highly unlikely that Au is concentrated in one single body within the sample. Consequently, the resultant analytical error due to flux attenuation effects will be negligible.

APPENDIX C.

ANALYSIS OF PLATINUM

The sensitivity for Pt is low because of the small capture cross-section of the metal. If the 20 hour ^{197}Pt isotope was the sole radioactive isotope present, then the decay curve would be a straight line having a slope equivalent to a half-life of 20 hours, and the sensitivity limit would be about 12 p.p.b. Morris, Hill and Smith (1963) analysed sulphide specimens from the Sudbury deposits and reported that the decay curves constructed from counting data gathered with a Geiger-Muller counter of the EHM 2/S type were straight lines possessing slopes equivalent to a half-life of 20± 1 hours. In the present study, all of the Pt samples and flux monitor standards had decay curves which, although parallel, were not straight lines. As well, the initial portions of the curves had half-lives of approximately 26 hours. Because there was such a large amount of the longer-lived activity, it was assumed that the samples were contaminated and although resolution of the decay-curves produced half-lives of 20 hours there was no certainty that the resolved curve represented Pt activity or some other (e.g. 19 hour ^{194}Ir) isotope. Some of the samples were followed for periods of several weeks and during this time decayed with half lives of 4.1 to 4.4 days. A typical decay curve for a sample is shown in Figure 6-1. It became apparent that this long-lived activity was produced by the decay of the isomers ^{193M}Pt and ^{195M}Pt which emit gammas with energies of 0.013 MeV and 0.099, respectively.

These gammas have a high degree of internal conversion to electrons which have energies corresponding to the γ-transition energy minus the binding energies of the K,L,M...shell in which conversion occurs. Wapstra, Nijgh, and Van Lieshout (1959) give the binding energies of electrons in the K and L shells of Pt as 78.4 and 13 KeV, respectively. The energies of the internally converted electrons are given below:

Isomer	Energy(KeV)	Binding Energy K Shell	Binding Energy L Shell	Energy (in KeV) Converted Electron K Shell	Energy (in KeV) Converted Electron L Shell
^{193M}Pt	30	78	13	---	17
	99	78	13	21	86
^{195M}Pt	136	78	13	58	123
	13	78	13	--	---

The internally converted electrons are mono-energetic and hence have a high counting efficiency.

The degree of internal conversion may be calculated from the internal conversion coefficients. For ^{195M}Pt, $\alpha_T = 7.2$ (Harriss et al 1965) and $\alpha_K = 90$ for ^{193M}Pt (Nuclear Data Sheet). The subscripts T and K represent total conversion coefficient and conversion coefficient of the K shell only, respectively. The per cent conversion is given by $\frac{\beta}{\beta+\gamma}\ 100$

where β = number of electrons given off

and γ = number of gammas emitted.

The internal conversion coefficient, $\alpha=\beta/\gamma$, and the per cent conversion is

$$\frac{\alpha \times 100}{\alpha + 1}$$

For ^{195M}Pt, this is 88 per cent and for ^{193M}Pt 99 per cent.

The reason other workers (e.g. Morris, Hill and Smith) did not detect the long-lived Pt component, although it was readily detected in this research, may be related to the relative sensitivities of the detectors employed. Geiger-Muller counters are generally equipped with mica windows which have a thickness equivalent to 1.5-4 gm/cm^2. The window of the detector in the present research had a thickness equivalent to 150 μg/cm^2. Because of its low density, this window is highly sensitive, allowing betas of low energy to pass through whereas a standard mica window absorbs low energy betas. The internally converted electron emitted from the K shell during decay of ^{195}Pt has an energy of 58 KeV compared to a maximum energy of 670 KeV for the beta emitted during decay of ^{197}Pt. For example, a 50 KeV beta has a range of 4 mg/cm^{-2} in aluminum (see Friedlander and Kennedy, (1955). If it is assumed that Al has a density equivalent to those of the micromil and mica windows, it can be seen that betas possessing an energy of 50 KeV will pass through a 1.5 μg/cm^2 window but not through a 1.5 gm/cm^2 window.

APPENDIX D.

PRECIOUS METAL ABUNDANCES IN SOME CARBONACEOUS AND ENSTATITE CHONDRITES

Trace element data have contributed significantly both to an understanding of processes involved in the formation of meteorites and to our knowledge of nucleosynthesis. While considerable data for the precious metals are available for the iron meteorites, much less has been accumulated for the ordinary chondrites and other classes of meteorites. In particular, the carbonaceous chondrites are represented by only a very few analyses for these metals. In view of the increasing reliance of cosmic abundance estimates on carbonaceous chondrite data it is essential to have accurate measurements of the elements in this class of meteorites.

The limited analytical data available on the carbonaceous chondrites indicated that their precious metal abundances were well within the sensitivity limits of the activation procedure developed in this work. Consequently, the writer, in conjunction with J. H. Crocket and S. Hsieh, used the procedure to analyse seven carbonaceous and two enstatite chondrites for Ru, Pd, Os, Ir, Pt and Au. All six metals were determined simultaneously. More details of the work may be found in Crocket, Keays and Hsieh (1967).

The specimens analysed were kindly supplied by: Dr. E. Anders, University of Chicago (Mighei, Orgueil, Ivuna and Cold Bokkeveld); Dr. G. Reed, University of Chicago (Lancé); and Dr. J. Douglas, Geological Suvey of Canada and the Meteorite Subcommittee, National Reseach Council of Canada (Alais, Nogoy, Abee, Indarch). Descriptions of each of these meteorites and a review of the carbonaceous chondrites may be found in papers by Mason (1962, 1966).

Results

The data collected in this work are tabulated in Table D-1 in which the data are expressed in parts per million (p.p.m.) and in atomic abundances (atoms metal/10^6 silicon atoms). The data are compared with previously published determinations in Table D-2. Agreement is fairly good except for Ir in Abee, and Os in Cold Bokkeveld. Aside from the usual analytical errors involved in activation analysis, sample inhomogeneity may be significant here as small samples (50 to 100 mg) were irradiated and because of the strong fractionation of precious metals between silicates and metallic nickel-iron (Nichiporuk and Brown, 1965; Baedecker and Ehmann, 1965). Fractions of specimens containing even slightly different amounts of the metallic phase would have large differences in precious metal content. The effects of fractionation would be especially strong in the enstatite chondrites (Indarch and Abee) which contain over 20 per cent metallic phase.

It is doubtful whether the effects of sample inhomogeneity could account for the large differences in Ir content of the enstatite Abee found in this work (0.32 p.p.m.) and in the only other published determination (0.083 p.p.m., obtained by Baedecker and Ehmann, 1965). As moderately good agreement was obtained for Au and Pt in Abee with previous work, it seems that the Ir disagreement is more likely due to chemical analytical problems than sample inhomogeneity. Many possible factors such as pre-irradiation contamination, post-irradiation contamination with 74 day ^{192}Ir

Table D-1

PRECIOUS METAL ABUNDANCES IN CARBONACEOUS AND ENSTATITE CHONDRITES

SPECIMEN	RUTHENIUM				PALLADIUM			OSMIUM			IRIDIUM			PLATINUM				GOLD		
	RU-96 PPM	RU-102 PPM	Mean PPM	Atoms per 10^6Si	PPM	Mean PPM	Atoms per 10^6Si	PPM	Mean PPM	Atoms per 10^6Si	PPM	Mean PPM	Atoms per 10^6Si	Pt-197, β^- PPM	Au-199, γ** PPM	Mean PPM	Atoms per 10^6Si	PPM	Mean PPM	Atoms per 10^6Si
Type I Carbonaceous Chondrites																				
ORGUEIL	0.76	0.74	0.75	1.97	0.52 0.62 0.62	0.59	1.48	0.56		0.79	0.30 0.47 0.49	0.42	0.58		1.0		1.4	0.13		0.18
IVUNA	0.78 0.74	0.69 0.74	0.74	1.92	0.61 0.54	0.58	1.45	0.62 0.60	0.61	0.86	0.42 0.40	0.41	0.57	1.7	0.9 1.1	1.2	1.6	0.12 0.16	0.14	0.19
ALAIS	0.58			1.65	0.33		0.90	0.34		0.52	0.38		0.57		0.6		0.9	0.10		0.15
AVERAGE-TYPE I			0.69	1.85		0.50	1.28		0.50	0.72		0.40	0.57			0.9	1.3		0.12	0.17
Type II Carbonaceous Chondrites																				
MIGHEI		0.85		1.81	0.62		1.26	0.73		0.83	0.69 0.62 0.61	0.64	0.72		1.3		1.4	0.13		0.14
COLD BOKKEVELD	0.84	0.82	0.83	1.80	0.57		1.18	0.77		0.89	1.25		1.43		1.4		1.6	0.12		0.14
NOGOYA	0.83	0.88	0.86	1.88	0.75		1.56	0.75		0.87	0.63		0.73		1.0		1.1	0.23		0.26
AVERAGE-TYPE II			0.85	1.83		0.65	1.33		0.75	0.86		0.84	0.96			1.2	1.4		0.16	0.18
Type III Carbonaceous Chondrites																				
LANCÉ	1.04 1.00	1.04 1.05	1.03	1.83	0.74 0.88	0.81	1.38	0.84		0.80	0.73		0.69	2.0	1.5 1.7	1.7	1.6	0.17 0.26	0.22	0.20
Type I Enstatite Chondrites																				
ABEE	1.01	0.92	0.97	1.52	0.79		1.18	0.78		0.65	0.32		0.27	1.3	1.3	1.3	1.1	0.22		0.18
INDARCH	1.09	0.92	1.01	1.68	0.80		1.27	0.74		0.66	0.25		0.22	1.4	1.1	1.25	1.1	0.22		0.19
AVERAGE-ENSTATITE CHONDRITE			0.99	1.60		0.80	1.23		0.76	0.66		0.29	0.25			1.3	1.1		0.22	0.19

*atomic abundance in atoms of precious metal per 10^6 silicon atoms

** platinum determination based on the reaction $^{198}\mathrm{Pt}\ (n,\gamma)\ ^{199}\mathrm{Pt} \xrightarrow[30\ \mathrm{min}]{\beta^-} {}^{199}\mathrm{Au}\ (T_{\frac{1}{2}} = 3.15\ \mathrm{days})$

Table D-2 Comparison with previous metal determinations

Specimen	Metal	This study (ppm)	Previous determinations	
			ppm	Reference
Orgueil	Os	0.56	0.44, 0.47	1
Mighei	Au	0.13	0.14	2
Cold Bokkeveld	Ru	0.83	0.70	3
	Os	0.89	0.58	3
	Os		0.57	1
Abee	Ir	0.32	0.083	4
	Au	0.22	0.37	4
	Pt	1.3	1.3	4

References:

1. Morgan and Lovering (1964)
2. Shcherbakov and Perezhogin (1964)
3. Bate and Huizenga (1963)
4. Baedecker and Ehmann (1965)

or failure to bring carrier and irradiated sample to the same valence state or to quantitatively dissolve sample iridium in the initial dissolution step may be involved. There is no basis at the present time for evaluating these possibilities. It may be pointed out, however, that Baedecker and Ehmann (1965) also found the Ir content of W-1 a factor of 5 lower than the Ir content of that material found in this research. It has previously been argued that the value for the Ir content of W-1 found in this work is probably more accurate than the published value (see page 75). Baedecker and Ehmann used an acid dissolution of the sample which may not be an effective means of dissolving the sample or, equally important, may not leave sample and carrier Ir in the same valence state. Baedecker (1967) has noted that Ir presented serious problems and has indicated that active and carrier Ir may have been in different oxidation states when introduced to the ion exchange resin following the normal chemical dissolution procedure. Baedecker performed a number of analyses of the same specimens both with an acid dissolution step and a sodium peroxide fusion. His Au and Ir data for those samples which he dissolved by different methods are shown in Table D-3. The method of dissolution has no apparent effect on the Au data, but for the Ir the method of dissolution seems critical. For a number of analyses for Ir, there is no difference but for several, the results by peroxide fusion are factors of 10 to 100 higher than by acid dissolution. Baedecker does not indicate which values he believes are the more accurate. However, fusions are known to be effective means of exchanging chemical species not only because of the high temperature of the fusion but also because the melt is highly oxidizing, with every chemical species being elevated to its highest oxidation state.

The average atomic abundances of the precious metals in carbonaceous chondrites as determined in this work are compared with the most recent compilation of Cameron (1967) (see Table D-4). Except for Ir, the carbonaceous chondrites data are approximately 10% higher than that of Cameron. Because Cameron's figures depend strongly on carbonaceous chondrite data, this comparison does not constitute an independent check on the abundance data as determined here.

Table D-3 Gold and Iridium in some U.S. Geological Survey Standard Rocks, taken from Baedecker (1967).

Specimen	Au (p.p.m.)		Ir (p.p.m.)	
	Acid Dissolution	Peroxide Fusion	Acid Dissolution	Peroxide Fusion
PCC-1 Std. Peridotite (Split 44, position 23)	0.9,0.4	0.8	0.4,0.6	6.6
DTS-1 Std. Dunite (Split 10, position 14)	1.3,0.6	0.4	0.3,0.4	0.5
BCR-1 Std. Basalt (Split 1, position 8)	1.3,0.5	1.0	0.7,0.2	1.1
AGV-1 Std. Andesite (Split 110, position 21)	0.9,0.5	0.5	0.5,0.3	0.7
GSP-1 Std. Granodiorite (Split 64, position 10)	2.1,1.2	0.7	0.7,0.4	1.1
G-2 Std. Granite (Split 100, position 6)	0.9,1.3	1.1	0.1,0.2	17.7

Table D-4 Average atomic abundances of precious metals in carbonaceous chondrites*

	Ruthenium	Palladium	Osmium	Iridium	Platinum	Gold
Average, this study	1.84	1.32	0.79	0.76	1.4	0.18
Cameron (1967)	1.6	1.5	0.71	0.43	1.13	0.20
Average, Type I	1.85	1.28	0.72	0.57	1.3	0.17
Average, Type II	1.83	1.33	0.86	0.96	1.4	0.18

* All values in atoms of metal per 10^6 silicon atoms

Table D-5 Comparison of atomic abundances in olivine-bronzite, olivine-hypersthene and carbonaceous chondrites*

Metal	Olivine-bronzite chondrites	Olivine-hypersthene chondrites	Reference	Carbonaceous chondrites (this study)
Ru	1.81 ± 0.23 (8)	1.13 ± 0.09 (7)	1,2	1.84 ± 0.09$_6$
Pd	Average, ordinary chondrites-1.00 (6)		3,4	1.32 ± 0.21^6
Os	0.89 ± 0.11 (5)	0.64 ± 0.19 (5)	2,5	0.79 ± 0.12
Ir	0.44 ± 0.05 (5)	0.29 ± 0.13 (8)	6	0.76 ± 0.28
Pt	1.36 ± 0.20 (4)	0.71 ± 0.02 (2)	6	1.4 ± 0.25
Au	0.19 ± 0.02 (6)	0.12 ± 0.02 (5)	6,7,8	0.18 ± 0.040

* All data are expressed in atomic abundances (atoms metal/10^6 silicon atoms).

References:

1. Hara and Sandell (1960)
2. Bate and Huizenga (1963)
3. Hamaguchi *et al*. (1961)
4. Sen Gupta (1967)
5. Morgan (1965)
6. Baedecker and Ehmann (1965)
7. Vincent and Crocket (1960)
8. Shcherbakov and Perezhogin (1964)

Discussion

The average atomic abundance for each of the three classes of carbonaceous chondrites and for the two enstatite chondrites have been plotted together with average precious metal atomic abundances compiled from the literature in Figure D-1. The bronzite and hypersthene data are tabulated in Table D-5 and compared with the average precious metal atomic abundance for all carbonaceous chondrites analysed in this study. Although the data in Figure D-1 represent a small sample, some generalization concerning the distribution of precious metals in chondrites are suggested: 1) Relative to silicon, the carbonaceous chondrites are generally enriched in precious metals compared to both the hypersthene and enstatite chondrites. Au is an exception as the enstatite chondrites are slightly higher in Au content than Type I and Type II carbonaceous chondrites. The bronzite and carbonaceous chondrites are of similar precious metal content except for Ir which is depleted in the bronzite chondrites. The depletion in the hypersthene chondrites is most striking. Using the average atomic abundances tabulated in Table D-5, the average depletion of precious metals in the hypersthene relative to the carbonaceous chondrites is approximately 40%. Ir, which is 62% lower in the hypersthene chondrites, is most strongly depleted but analytical error, as noted above, may be significant for Ir. 2) The three types of carbonaceous chondrites show little systematic variation in precious metal content. The only apparent trend is a small enrichment in Type II and Type III classes relative to Type I for all metals except Ru. However, the dispersion of Type I data is too large, due to the low precious metal content of Alais, to regard this trend as real. In general, the precious metals show remarkably little variation in the carbonaceous chondrites.

3) From Table D-1 it is apparent that Alais is at least as low or lower

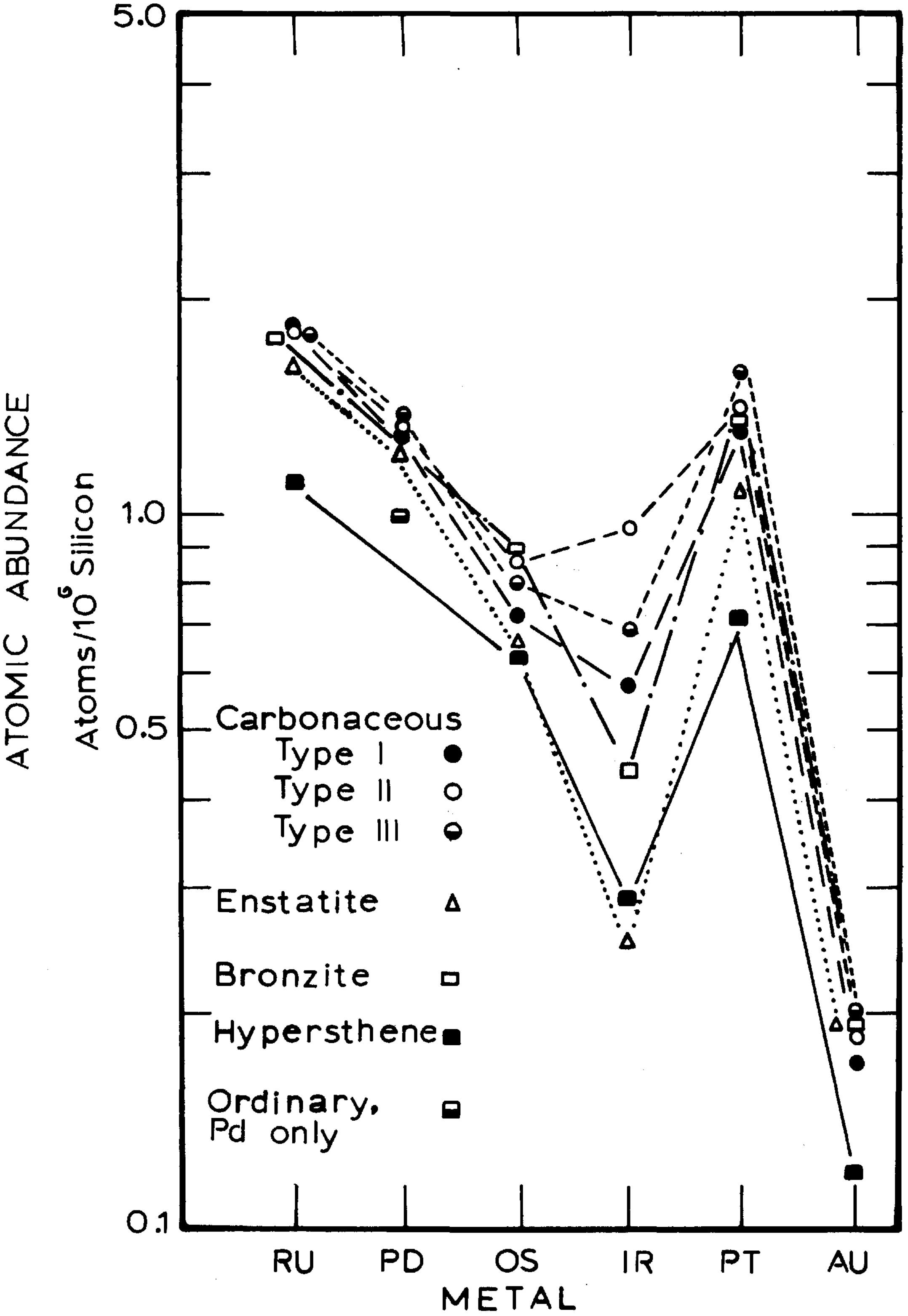

Figure D-1 Precious metal abundances in carbonaceous, enstatite, bronzite, and hypersthene chondrites.

than all other carbonaceous chondrites in precious metal contents. It is particularly low in Ru, Pd, Os and Pt. Determination of all precious metals in a single carbonaceous chondrite is clearly of considerable importance.

Many investigators including Ringwood (1961), Mason (1960) and Fish et al. (1960) consider that the chemical composition of carbonaceous chondrites closely approximates that of primitive solar material. Although important differences of opinion exist as to the relative importance of trace element fractionation processes occurring during or after accretion of meteoritic matter, it seems likely that the precious metal content of the parental or protolith material would be higher than in other chondritic derivative products. This is the observed relationship between the carbonaceous and hypersthene chondrites, the most abundant of all the chondritic meteorites, and suggests that a primitive compositional character for the carbonaceous chondrites is compatible with their precious metal abundances.

The generally accepted view that carbonaceous chondrites represent relatively undifferentiated material indicates that chemical fractionations occurring during the accretion of meteoritic matter are of importance in any consideration of trace element abundance patterns in these meteorites. Wood (1963) and more recently, Larimer and Anders (1967) have stressed the significance of the condensation history of meteorites. The latter authors have presented considerable evidence which argues that in the case of chondrites the abundance patterns of some thirty volatile elements were established during the condensation process.

For the precious metals, fractionation during accretion was probably minimal. The two main types of fractionation processes that might have affected them would be separation of volatile from non-volatile elements and metal-silicate fractionations. In the environment of a cooling solar nebula, the precious metals would be characterized by extremely low volatility. Larimer (1967) has presented a detailed analysis of the condensation temperatures of meteoritic matter. Using his method and assuming condensation as metals, the condensation temperatures of the precious metals were computed and tabulated in Table D-6.

For pure metals, condensation occurs at the temperature at which the partial pressure of the metal in the nebula equals the vapour pressure of the pure metal. If P(E) is the partial pressure of a gaseous species E, N(E) is the atomic fraction, and P_T is the total pressure, then

$$P(E) = N(E)\ P_T$$

If elements heavier than hydrogen are considered monatomic in the vapour state, then

$$N(E) = n(E) \sum_{i=H_2}^{i=K} n_i$$

where n(E) is the number of atoms of element E. In a gas of cosmic composition $n(H_2) = \frac{1}{2} A(H)$, $n(Pt) = A(Pt)_2$, and so on where A is the atomic abundance. As hydrogen would be by far the most abundant species,

$$N(E) \simeq 2\ A(E)/A\ (H)$$

$$\text{and} \qquad P(E) = \left[2A(E)/A\ (H)\right]\ P_T$$

Using this expression for partial pressure, the most recent compilation of A.G.W. Cameron (written communcation via Dr. J. Larimer) for hydrogen and iron atomic abundances, the average carbonaceous chondrite values (Table D-4)for precious metal abundances, and the vapour pressure curves of Honig (1962), condensation temperatures were computed for P_T = 1 atmosphere. The condensation temperatures change slightly if computed for

Table D-6 Precious metal condensation temperatures

Metal	Atomic abundance (per 10^6 silicon atoms)	Partial pressure	Condensation temperature (°K, 1 atm)
Ru	1.84	1.42	1875
Pd	1.32	1.02	1175
Os	0.79	0.61	2250
Ir	0.76	0.58	1925
Pt	1.4	1.08	1650
Au	0.18	0.14	1075
Fe	8.9×10^5	6.85×10^5	1850

lower total pressures but the temperature sequence of precious metal condensation remains the same.

If these temperatures are compared with those of Larimer (1967) for other metals, it is apparent that Ru, Os, Ir and Pt are among the first metallic condensates of a cooling solar nebula. Ru, Os and Ir will condense prior to metallic iron and Pt, Pd and Au after metallic iron. At these high temperature solid state diffusion of traces of precious metals into metallic nickel-iron alloy must have been extensive and it is suggested that metallic iron acted as a collector for these elements. If the precious metals were efficiently partitioned into metallic iron, their fractionation would be governed mainly by any metal-silicate separation that may have occurred. A very slight increase in iron to silicon ratio occurs from Type III to Type I carbonaceous chondrites. Indeed, a striking feature of their chemical composition is the uniform content of non-volatile elements (Mason, Table 4, 1962). In the absence of any significant iron-silicate fractionation, the relatively uniform precious metal content of the carbonaceous chondrites is no surprise. Further, the precious metal atomic abundances in these meteorites should provide good estimates of their cosmic abundance.