RHENIUM AND OSMIUM IN SOME CANADIAN ORES BY NEUTRON ACTIVATION ANALYSIS

By

J.N. SCHINDLER, B.Sc., M.Sc.

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RHENIUM AND OSMIUM IN SOME
CANADIAN ORES

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ABSTRACT
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TITLE: Rhenium and Osmium in Some Canadian Ores by Neutron Activation Analysis

AUTHOR: John Norman Schindler, B.Sc. (McGill University)
M.Sc. (University of London, England)

SUPERVISORS: Professors H.P. Schwarcz and J.H. Crocket

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SCOPE AND CONTENTS:

Neutron activation analysis procedures have been developed for the determination of rhenium and osmium in common metallic minerals from a wide variety of ore deposits. The Os method is based on double distillation, solvent extraction and precipitation of the metal. The Re method uses double anion exchange, solvent extraction and precipitation. The accuracy of the methods were checked against molybdenite and Cu-Ni matte standards. A literature survey of the rhenium and osmium is presented and the geology of the deposits is presented. The analytical results are discussed in terms of the current feasibility of dating ores by the Re-Os method, and their geological significance.

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ABSTRACT

Rhenium and common osmium have been determined by neutron activation analysis in these Canadian ore deposits: Heath Steele, New Brunswick; Kidd Creek, Strathcona and Adams Mine, Ontario; Craigmont, Granisle Copper and the Highland Valley Camp, British Columbia. Rhenium was determined at B.C. Molybdenum, Endako, Boss Mountain, Brenda Mines, Preissac-LaCorne Batholith, Gaspé Copper. The aim of the study was to evaluate the feasibility of dating a variety of ore deposits by the rhenium-osmium isochron method, and to obtain information on the distribution of rhenium and osmium in ores.

Osmium was purified by H_2SO_4-H_2O_2 distillation followed by $NaBiO_3$-HNO_3 and H_2SO_4 distillations. Rhenium was purified using H_2SO_4-H_2PO_4-HBr distillation and De-Acidite FF anion exchange resin, or with De-Acidite FF and Dowez 1-X8 anion exchange resins. The results for rhenium and osmium standards compare favourably with those of previous workers, except for Matte No. 7517.

Rhenium-enriched deposits are: (i) molybdenite deposits, particularly porphyry copper molybdenites, with rhenium abundances

at the 0,1% level, (ii) Strathcona, where rhenium ranging from 25 to 255 ppb. is three times more abundant than common osmium, (iii) the principal metallic minerals at Craigmont contain from 2 to 37 ppb. rhenium. Osmium is enriched at Strathcona and less so at the Adams Mine, where 3.20 ppb. Os occurs in banded magnetite iron formation.

Molybdenites excepted, half the rhenium abundances range from 0.1 to 0.9 ppb, one order of magnitude less than previously determined for ore minerals by neutron activation. Common osmium abundances are generally lower by two orders of magnitude than previously determined by neutron activation, and range from 0.01 to 0.09 ppb.

Calculated ^{187}Os* (radiogenic) in the principal minerals of ores 10^9 years old, is generally 10^{-12} to 10^{-14} gm/gm. This precludes application of the Re-Os isochron method to volcanogenic massive sulphide, banded iron formation, contact metasomatic and molybdenum-deficient porphyry copper ores of the types examined here.

Nickel-copper ores similar to the Strathcona deposits are amenable to Re-Os dating. The Strathcona ores could be used to refine the half-life of ^{187}Re. The Fiskenaesset area, Greenland, and uranium-copper-vanadium deposits of the Colorado Plateau warrant consideration in any such attempts. Investigation of selenium-rich minor minerals in volcanogenic massive sulphides are recommended for Re-Os studies.

The bulk rhenium content of porphyry Cu-Mo deposits appears to be significantly greater than that of porphyry Mo deposits.

CHAPTER I

INTRODUCTION

GENERAL STATEMENT

Rhenium, atomic number 75, and osmium, atomic number 76, are among the least abundant elements in the crust. In addition, rhenium is also widely dispersed. For example, its average abundance in some common igneous rocks is about 0.5 ppb and it is concentrated in relatively few minerals (Morris and Short, 1969). These factors combined to delay the discovery of rhenium until 1925, although Mendeleev had predicted the occurrence of element 75, which he named dvi-manganese, as early as 1869. The discovery of rhenium is generally credited, although by no means unequivocably so, to Noddack, Tacke and Berge (1925).

RHENIUM

Noddack and Noddack (1931), using a spectrographic method, performed a systematic search for rhenium in a wide variety of minerals, and were also the first to detect its presence in meteorites. A period of about twenty years ensued in which the main interest in the geochemistry of rhenium was restricted, albeit by the limitations of the technology of the times, to its distribution in ores of relatively high rhenium content (Hiskey and Meloche, 1940; Fleischer, 1959; Peterson et al. 1959, and Myers et al., 1960). It was not until neutron activation analysis was adapted to the analysis of rhenium (Brown and Goldberg, 1949) that reliable results for low abundance levels became attainable. The extent to which neutron activation analysis has since been used for the determination of rhenium is indicated in Table 1-1.

A considerable amount of work has been conducted by Russian researchers on the geochemistry of rhenium. These investigations have been based mainly on colorimetric methods of determining rhenium (Badalov et al., 1962; Morachevskii and Nechaeva, 1960; Razenkova and Poplavko, 1963, and Zhirov and Ivanova, 1959). A summary of the Russian literature on the geochemistry of rhenium forms the basis of a paper by Ivanov et al. (1972). Recent investigations by most other workers have been concerned mainly with the distribution of rhenium in meteoric and lunar materials.

OSMIUM

Osmium, a member of group eight and the third transition series, has the highest measured density of any element in the Periodic Table (Hammond, 1973). It is one of the least abundant elements of the platinum group and data on its geochemistry, even in platinum ores,

Table 1-1

Bibliography of Rhenium Abundances Determined by Neutron Activation Analysis

Material Analyzed	Reference
Iron meteorites:	Brown and Goldberg (1949); Goldberg and Brown (1950); Herr et al. (1960), (1961); Fouché and Smales (1966); additional references in Crocket (1971).
Chondrites:	Herr et al. (1961); Morgan and Lovering (1964); Morgan (1965); Perezhogin et al. (1965); Fouché and Smales (1967); Case et al. (1973); Keays et al. (1974).
Achondrites:	Perezehogin et al. (1965) quoted in Morris and Short (1969); Morgan (1965) b, quoted in Lovering and Butterfield (1970).
Lunar samples:	Lovering and Butterfield (1970); Herr et al. (1971); Lovering and Hughes (1971); Michel et al. (1972); Morgan et al. (1973); Keays et al. (1974); Ganapathy et al. (1973).
Tektites:	Lovering and Morgan (1964).
Igneous rocks:	Morris and Fifield (1961)a, b; Morgan (1965); Morgan and Lovering (1967); Lovering and Hughes (1971); Krahenbuhl et al. (1973); Morgan et al. (1973); Keays et al. (1974).
Sedimentary rocks:	Lovering and Morgan (1964).
Metamorphic rocks:	Morgan and Lovering (1967).

Table 1-I (continued)

Material Analyzed	Reference
Metallic minerals:	
(a) Molybdenites	Herr and Merz (1955); Hirt et al. (1963); Allegré et al. (1964); Morgan (1965); Ford (1965); Ishida et al. (1966); Herr et al. (1967); Morgan et al. (1968); Terada et al. (1970).
(b) Other sulphides	Morgan et al. (1968).
(c) Miscellaneous	
manganese oxides	Ishida et al. (1966);
columbite	Meshri et al. (1963).
Marine:	
(a) Waters	Scadden (1969); Matthews and Riley (1970); Olafsson and Riley (1972).
(b) Organisms	Fukai and Meinke (1962).
(c) Plants	Scadden (1969).
(d) Sediments	Olafsson and Riley (1972).

are limited. Platinum-bearing ores of igneous affiliations are associated with both Ni-Cu sulphides and with chromite in ultramafic and mafic rocks. In these ores, osmium is sufficiently concentrated to occur as the native metal, and to form native platinum group alloys such as iridosmine (Os: 32-80 wt. %), osmiridium (Os: <32 wt. %) and ruthen-osmiridium, as well as minerals in which it is alloyed in minor quantities with platinum and palladium. It also occurs as the sulphide minerals erlichmanite and laurite and the sulpharsenides osarsite and irarsite (Cabri, 1972).

Prior to the application of neutron activation analysis pre-analytical concentration was generally required for analysis of osmium in natural meterials. The results and sensitivity limits of these methods, which still represent the largest pool of osmium data, have been dealt with by Crocket (1969). Recently, Chung and Beamish (1968), using radioactive tracer techniques, investigated the quantitative distillation of trace quantities (50 to 70 μgm) of osmium in a method which has potential application to the carrier-free direct determination of osmium in ores.

Osmium abundances in the more common sulphide minerals in the Ni-Cu ores of Sudbury range from 0.68 to 68 ppb (Hsieh, 1967). Cumulate chromites from the Bushveld contain 52 to 114 ppb osmium (Gijbels et al., 1974), and massive segregations of chromite associated with an alpine peridotite contain 96 ppb whereas primary disseminated chromite contains 3.4 ppb (Crocket and Chyi, 1972). A single sample of galena concentrate from Australia yielded 3 ppb osmium (Morgan et al., 1968).

In common rocks osmium abundances are conspicuously low. From the limited data available it appears that in igneous rocks there is a tendency for osmium to be concentrated in ultramafic and mafic rocks with respect to felsic rocks as is shown in Table 1-2.

Table 1-2

Osmium Abundances in Some U.S.G.S. Rock Standards by Neutron Activation Analysis

Standard Number	Rock Type	Number of Analyses	Osmium 10^{-10} gm/gm	References
PCC-1	Peridotite	8	73	b, d, e, f, g
DTS-1	Dunite	3	10.8	a, d
W-1	Diabase	4	2.6	a, c
G-1	Granite	4	0.7	a, c

References: a=Morris and Fifield (1961)a; b=Morgan and Lovering (1967); c=Crocket et al. (1968); d=Gijbels et al. (1971); e=Lovering and Hughes (1971); f=Millard and Bartel (1971); g=Nadkarni and Morrison (1974).

Data on osmium in meteorites have been summarised by Crocket (1968). Average osmium abundances vary from 4.70 ppm for iron meteorites to 657 ppb for chondrites (see Table 5-14). Achondrites have an average osmium abundance of 2.87 ppb which is comparable with the osmium content of ultrabasic rocks (see Table 5-10).

A bibliography of osmium determinations by neutron activation analysis of materials relevant to this work is given in Table 1-3.

DATING BY THE RHENIUM OSMIUM METHOD

1. Decay and Half-Life of ^{187}Re

Rhenium is composed of two naturally occurring isotopes, ^{185}Re and ^{187}Re. ^{187}Re is radioactive and decays by a very low energy β^- (E_{max} 0.002 MeV) to ^{187}Os. Therefore, direct counting experiments have led to results varying by several orders of magnitude for both the half-life and for the decay energy. These results have been summarised by Hirt et al. (1963) and are given in Table 1-4.

The currently accepted value for the half-life of ^{187}Re, 4.3×10^{10} years, was obtained by use of the geological method (Hirt et al., 1963). In this approach, pioneered by W. Herr and his co-workers, very old molybdenites of "known" absolute age and with high rhenium contents were analyzed. The rhenium content was determined by neutron activation analysis and the radiogenic ^{187}Os determined by

Table 1-3

Bibliography of Osmium Abundances Determined by Neutron Activation Analysis

Material Analyzed	Reference
Iron meteorites:	Herr et al. (1960), (1961); Crocket (1972).
Chondrites:	Herr et al. (1961); Morgan and Lovering (1964); Morgan (1965); Vinogradov et al. (1972).
Achondrites:	Morgan (1965)b, cited in Lovering and Butterfield (1970).
Lunar:	Lovering and Hughes (1971).
Tektites:	Lovering and Morgan (1964).
Igneous rocks:	Bates and Huizenga (1963); Morgan (1965); Morgan and Lovering (1967); Crocket et al. (1968); Millard and Bartel (1971); Gijbels et al. (1971), (1974); Lovering and Hughes (1971); Crocket and Chyi (1972); Nadkarni and Morrison (1974).
Sedimentary rocks:	Lovering and Morgan (1964).
Metamorphic rocks:	Morgan and Lovering (1967).
Metallic minerals:	Morgan et al. (1968); Keays and Crocket (1970); Gijbels et al. (1971), (1974); Crocket and Chyi (1972).
Silicate minerals:	Gijbels et al. (1971), (1974).
Marine sediments:	Barker and Anders (1968).

Table 1-4

Half-life and Decay Energy for ^{187}Re obtained by Direct Counting

Half-life(years)	Maximum β energy (keV)	Reference
$(4\pm1) \times 10^{12}$	43	Naldrett and Libby (1948)
$(4-7) \times 10^{12}$	-	Sugarman and Richter (1948)
-	400	Curran (1952)
-	34	Gauthé and Blum (1953)
$>10^{15}$	<1	Dixon and McNair (1954); Dixon <u>et</u> <u>al</u>. (1955).
$<10^{11}$	<8	Suttle and Libby (1954)
$(2.1\pm0.5) \times 10^{11}$	2.4 ± 0.5	Walton (1957)
$(3.2\pm0.7) \times 10^{11}$	20	Naldrett (1958)
7.9×10^{10}	-	Kocol (1961)
$(1.2\pm0.4) \times 10^{11}$	3	Wolf and Johnston (1962)
$\sim 3\times10^{10}$	-	Watt and Glover (1962)

mass spectrometer using the technique of isotope dilution. No determination of common osmium is necessary with this method because the extremely low ratio of common osmium to radiogenic osmium ensures that the osmium in these molybdenites is essentially pure mono-isotopic radiogenic ^{187}Os (Hintenberger, 1954). Half-life values for ^{187}Re determined by the geological method are summarised in Table 1-5.

Table 1-5

Determination of the Half-life of ^{187}Re by the Geological Method

Half-life (years)	Reference
$5.10^{9} - 2.5\times10^{11}$	Herr <u>et al</u>. (1954)
8×10^{10}	Herr and Merz (1955)
$(6.2\pm0.7)\times10^{10}$	Herr and Merz (1958)
$(4.3\pm0.5)\times10^{10}$	Hirt <u>et al</u>. (1963)

The differences between the half-life values obtained by the direct counting experiments and by the geologic method are thought to reflect a fundamental property of the decay process of ^{187}Re. Gilbert (1958) and Wolfe and Johnston (1962) suggest that the decay of ^{187}Re is composed of a β^- component and an electron-creation component. At the present time the exact nature of this decay process is not completely known but in this work the disintegration of ^{187}Re will be referred to as a β^- decay.

2. Current Status of Chronology by the Rhenium-Osmium Method

(a) Meteorites

The work of Herr (1961) and Hirt et al. (1962) indicates that iron meteorites and the iron phases of stoney meteorites contain both sufficient quantities of rhenium and osmium and sufficiently large rhenium-osmium ratios to enable them to be dated by this method with currently available techniques. For example, the average abundance in twenty-six iron meteorites and in the iron phases of two stoney meteorites is essentially in the range of 1 to 50 ppm osmium, and 0.1 to 1.5 ppm rhenium. A value of 0.83 for the initial $\frac{^{187}Os}{^{186}Os}$ ratio in iron meteorites has been obtained by Herr et al. (1962).

(b) Terrestrial

Up to the present time the application of age dating by the rhenium-osmium method to terrestrial meterials has been centred mainly around molybdenites because of their ability to concentrate rhenium in large quantities. The initial work in this field was by Herr and Merz (1955) and Hirt et al. (1963), and these investigations still constitute the most detailed and comprehensive contributions concerned with the terrestrial applications of rhenium-osmium dating.

The essential methods used by these workers include determination of rhenium by neutron activation analysis, and determination of osmium isotopic ratios by mass spectrometry using the technique of isotope dilution. The procedures used for the determination of rhenium are described byHerr and Merz (1955). Osmium was analysed as the tetroxide using a 60° Nier-type mass spectrometer equipped with a multiplier detector (Herr _et al._, 1961). The limit of detection for radiogenic ^{187}Os is given as 2x10^{-7} gms with an accuracy of 10% (Hirt _et al._, 1963).

Radiometric ages for molybdenites by the rhenium-osmium method given by Herr and Merz (1955) are based on a value for the half-life of rhenium, 8x10^{10} years, which is now outdated. Seventeen age determinations for molybdenites by the rhenium-osmium method are given by Herr _et al._ (1967). Comparative ages for seven of these samples are presented by Herr _et al._ (1967) and are given in Table 1-6.

Riley (1967), using the technique of stable isotope dilution, made a study of the rhenium abundances of forty-two Australian molybdenites to evaluate their suitability to Re-Os geochronology. He calculated the radiogenic ^{187}Os content of the samples, and made the assumption that 1 ppm radiogenic ^{187}Os could be adequately determined by current techniques. He concluded that only seven of the forty-two molybdenites contained sufficient radiogenic ^{187}Os to be datable by the rhenium-osmium method.

Allegré et al. (1964) used the rhenium-osmium method to determine the apparent ages of molybdenites from Madagascar, Mexico and Morocco. The rhenium content was determined by neutron activation analysis, and the total ^{187}Os abundance (which varied from 0.25 to 2.20 ppm) was determined spectrophotometrically. Values for the apparent ages in the molybdenites varied from 197 to 320 m.y. However, no osmium isotopic ratios were determined and no dates obtained by other radiometric methods were provided for comparison. Esenov et al. (1970) conducted an investigation into USSR molybdenites, copper ores and polymetallic copper ores with high rhenium (230 to 1100 ppm) and high osmium (0.19 to 3.7 ppm) contents. Using a spectrophotometric method they claim to have measured ^{187}Os* (radiogenic) in these ores. However, no sensitivity limits for osmium are given and the description of the method employed raises doubts as to the validity of some of the results.

Table 1-6

Comparative Ages of Molybdenites

(After Herr et al. (1967) - Modified)

Sample Locality	Re/Os Age 10^6 years	Comparative Ages 10^6 years	Method	Reference and/or Remarks
Fiskenaesset, Greenland	3080±70	3040±50	Rb/Sr	Pankhurst et al. (1973)
Ivigtut, Greenland	1750±50	>1000		Geol. Survey Greenland, Rept. No. 11 (1966)
Tuftan, Iveland, Norway	1120±30	1040	Uraninite Age	Communication by Professor W. Herr with Dr. H. Neuman, Geological Museum, Oslo
Spikkestad, Norway	300±30	259	K/Ar	Faul et al. (1959)
		308	K/Ar	Mayne et al. (1959)
Shap Granite, England	430±20	475-510	K/Ar	Mayne et al. (1959)
		391±7	K/Ar)	Kulp et al. (1960)
		385±11	Rb/Sr)	
		380±19	Rb/Sr)	
Xamchab, South Africa	1130±30	∼1000	Uraninite Age	Communication by Professor W. Herr with Dr. Truter, Geol. Surv. S.A., Pretoria
Natasmine Southwest Africa	830±70			
Phoenix Prince Mine, Rhodesia	2070±140	∼2700	Not stated	Communication by Professor W. Herr with Dr. H. Neuman, Oslo

SCOPE AND PURPOSE OF THE PRESENT STUDY

Previous work on the application of Re-Os geochronology to ores have been concerned almost exclusively with minerals or ore deposits characterised by high rhenium and high osmium contents, including molybdenite-bearing ores and ores of the Dzhezkazgan class, e.g. Herr and Merz (1955), Hirt et al. (1963), Allegre (1964), Riley (1967) and Esenov (1970). These studies indicate a lack of universality in the applicability of the method. Obviously, if geochronology by the Re-Os method is to assume a more significant rôle the method must be applicable to a wider range of ore deposits. Further, there is a general paucity of information concerning the occurrence of rhenium and osmium in the metallic minerals found in common ore deposits. Morgan et al. (19~~6~~8) conducted an investigation of rhenium and common osmium abundances in molybdenites and some common sulphides, but unfortunately, the method used for the determination of osmium was relatively insensitive (1 to 5 ppb).

The purpose of this work is, in the first instance therefore, to assess the feasibility of dating base metal deposits directly by application of the Re-Os geochronology method using current techniques. Secondly, to provide data on the occurrence of rhenium and osmium in the metallic minerals which commonly comprise base metal deposits. In consideration of the primary objective samples within each deposit were chosen with the intent of maximizing the differences between Re-Os ratios. This was done with the intention of maximizing the potential for producing model Re-Os isochrons within any one particular ore deposit.

The ore deposits analyzed span large intervals in the geologic time scale and are representative of several classes of ore deposits which are world wide in distribution. They include Precambrian iron formation, cogmagmatic Cu-Ni ore, Archean and Paleozoic stratabound volcanogenic base metal deposits, a contact metasomatic deposit, and porphyry copper and porphyry molybdenum deposits. A variety of molybdenum deposits were also sampled. The materials analysed include both metallic mineral separates and massive sulphides.

All rhenium and common osmium abundances determined in this work were obtained by neutron activation analysis. This method is insensitive to the radiogenic $^{187}Os^*$, and because no mass spectrometry was undertaken, osmium isotopic ratios were not determined.

NEUTRON ACTIVATION ANALYSIS OF RHENIUM AND OSMIUM

1. General Considerations

Neutron activation analysis is a method of elemental abundance determination which is ideally suited to trace analysis. Detailed accounts of the general method are given by Moorbath (1960), Mapper (1960) and by Gijbels and Hoste (1971) with special reference to the noble metals. The method is based on measuring the induced radioactivity produced in an element by a (n,γ) reaction. The induced activity is directly proportional to the amount of the element present, hence by comparison of this activity with the activity induced in a standard irradiated under identical conditions the abundance of the element can be determined. For thermal neutrons the induced activity is given by:

$$A = N\sigma\phi(1-e^{-\lambda t})$$

where A = induced activity in disintegrations/second

N = number of target atoms

ϕ = thermal neutron flux in neutrons/cm^2/sec

σ = effective thermal neutron cross section in barns

(1 barn = 10^{-24} cm^2)

λ = decay constant of daughter nuclide in sec^{-1}

t = irradiation time (in the same time units as the decay).

In neutron activation analysis the most widely used source of neutrons is the atomic reactor. In this work samples were irradiated in the McMaster University Research Reactor which has a thermal neutron flux of about 1×10^{13} to 4×10^{13} neutrons/cm^2/sec.

Table 1-7

Nuclear Properties and Production Factors for Rhenium and Osmium

Element	Natural Isotopes	Isotopic Abundance atom %	σ (barns)	Radionuclide product for n, γ	Half-life	Decay and Energy in MeV	Production Factors	
							12 hr.	3 weeks
Rhenium	^{185}Re	62.93	110	^{186}Re	90.5 hours	β^-:1.07 0.93 γ :0.137D 0.123, 0.76, 0.63 E.C. γ 1.07	3.26	36.4
	^{187}Re	37.07	69	^{188}Re	17.0 hours	β^-:2.12 γ :0.155D .44-1.96	5.3	13.7
Osmium	^{184}Os	0.018	200	^{185}Os	93.6 days	E.C. γ 0.65 0.88, 0.072-0.75	1 week 0.00096	4 weeks 0.0035
	^{189}Os	16.1	0.008	^{190m}Os	10 mins.	I.T. 0.04 γ 0.50, 0.62 0.36, 0.19	0.00067	0.00067
	^{190}Os	26.4	12.5	^{191}Os	15.5 days	β^-:0.142	0.47	1.24
	^{192}Os	41.0	1.6	^{193}Os	32 hours	β^-:1.13 γ 0.139 0.073 0.107-0.56	0.34	0.34

Osmium data after Crocket et al. (1961)

2. Nuclear Data, Nuclear Reactions and Decay Schemes

The nuclear data for rhenium and osmium are given in Table 1-3. The production factor (P. F.) is given by

$$\text{P. F.} = \frac{\sigma a}{w}\left(1 - e^{-\lambda_1 t_{ir}}\right) \tag{1}$$

and for the first daughter product of species 1

$$\text{P. F.} = \frac{\sigma a}{w}\left(1 + \frac{\lambda_2}{\lambda_1 - \lambda_2} e^{-\lambda_1 t_{ir}} - \frac{\lambda_1}{\lambda_1 - \lambda_2} e^{-\lambda_2 t_{ir}}\right)$$

where σ = effective neutron cross section

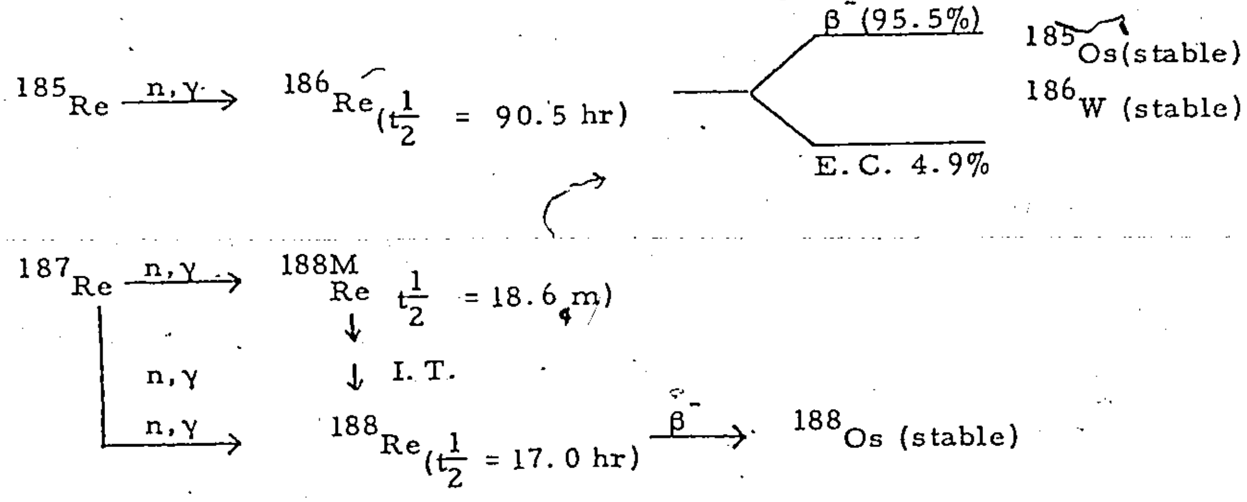
a = fraction abundance of the target nuclide

λ_1 = 0.693/half-life of the induced radionuclide

λ_2 = 0.693/half-life of the first daughter of species

t_{ir} = irradiation time

The following nuclear reactions occur when rhenium is irradiated with thermal neutrons



^{186}Re and ^{188}Re can also be produced during the neutron irradiation according to the following competing reactions:

$$^{184}W(n,\gamma)^{185}W \xrightarrow[t_{\frac{1}{2}} = 74 \text{ days}]{\beta^-} {}^{185}Re(n,\gamma)^{186}Re \quad \ldots\ldots \quad (1)$$

$$^{186}Os(n,p)^{186}Re \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

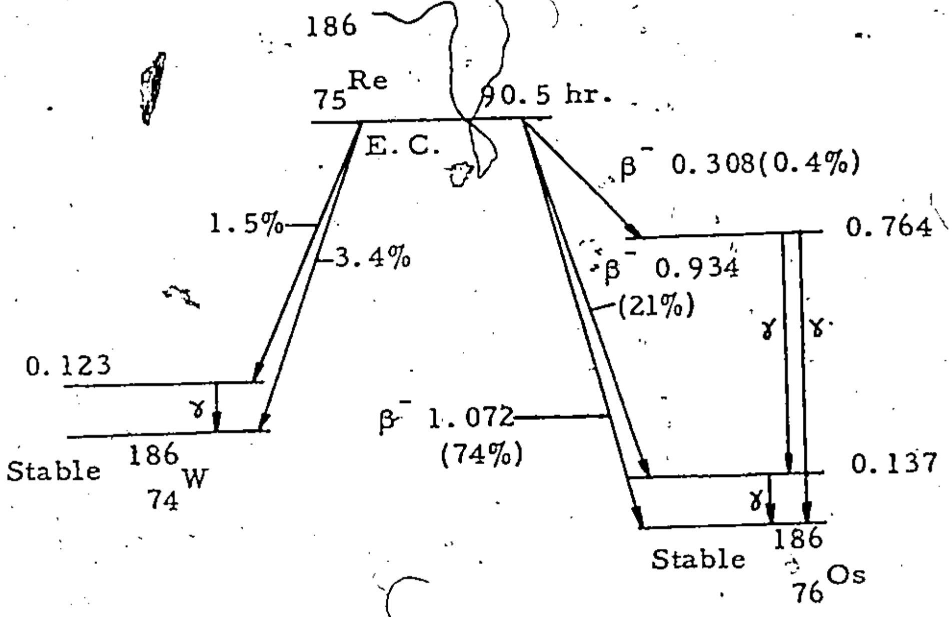
$$^{186}W(n,\gamma)^{187}W \xrightarrow[t_{\frac{1}{2}} = 24 \text{ hrs}]{\beta^-} {}^{187}Re(n,\gamma)^{188}Re \quad \ldots\ldots \quad (3)$$

In this work the radionuclide ^{186}Re was used because of its more favourable production and half-life characteristics. The competing reaction represented by equation (2) can occur with fast neutrons. However, in view of the fast neutron flux of the McMaster Reactor and the low abundance of ^{186}Os in the samples analyzed ($\gtrsim 10^{-11}$ gm), this interference may be neglected. Similarly, for the competing reaction in sequence (1), Morris and Fifield (1961) indicate that for 50 ppm tungsten a neutron flux of 1×10^{12} n/cm^2/sec and a two week irradiation, the ^{186}Re generated is equivalent to ~ 3 picogram/gm. Therefore, this source of error may also be neglected.

The decay scheme of ^{186}Re is given in Figure 1-1.

Figure 1-1

Decay Scheme of ^{186}Re.



Nuclear decay scheme for ^{186}Re Energies in MeV. Morris and Fifield (1961a) – Modified after Lederer et al. (1967).

Another possible source of error in the radioanalysis of rhenium is the presence of ^{99m}Tc ($t_{\frac{1}{2}}$ hr: I. T. 0.0018 MeV; γ 0.1403 MeV). This nuclide is produced in neutron irradiations as follows:

$$^{98}Mo(n,\gamma)^{99}Mo \xrightarrow[t_{\frac{1}{2}} = 66 \text{ hr.}]{\beta^-} {}^{99m}Tc \quad \ldots\ldots \quad (4)$$

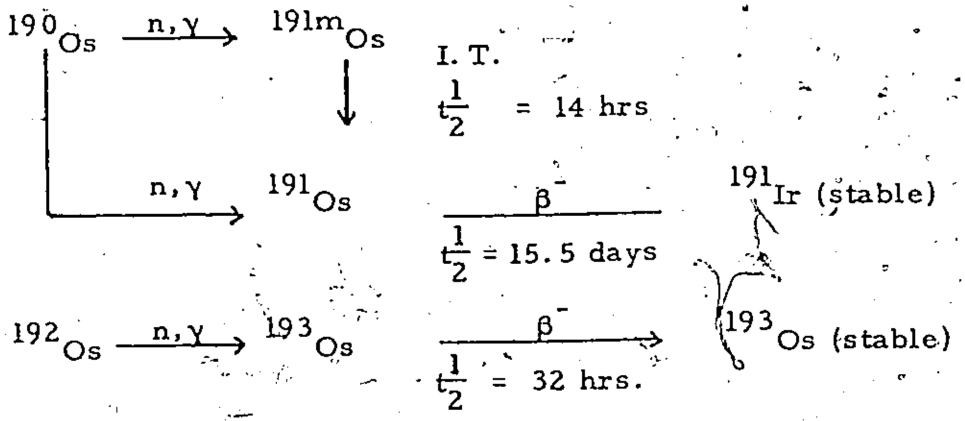
$$^{98}Tc(n,\gamma)^{99m}Tc \quad \ldots\ldots \quad (5)$$

$$^{99}Tc(n,n')^{99m}Tc \quad \ldots\ldots \quad (6)$$

$$^{99}Ru(n,p)^{99m}Tc \quad \ldots\ldots \quad (7)$$

Technetium closely resembles rhenium in its properties and it is necessary to eliminate it during the radiochemical purification. This was done by means of solvent extraction involving methyl ethyl ketone.

Crocket _et al_. (1968) present the nuclear data of osmium in detail. The nuclides most useful for determination of osmium in natural materials are ^{191}Os and ^{193}Os. These nuclides are produced by irradiation of osmium with thermal neutrons according to the following sequences,



^{191}Os was used in this work because of its more favourable production factor and its longer half-life.

Competing reactions which produce Os radionuclides (by fast neutron reaction on iridium and platinum) are

$$^{191}Ir(n,p)^{191}Os \qquad \ldots\ldots \qquad (1)$$

$$^{193}Ir(n,p)^{193}Os \qquad \ldots\ldots \qquad (2)$$

$$^{194}Pt(n,\alpha)^{191}Os \qquad \ldots\ldots \qquad (3)$$

$$^{196}Pt(n,\alpha)^{193}Os \qquad \ldots\ldots \qquad (4)$$

The reactions represented by equations (1) and (3) are of particular interest because of the production of ^{191}Os. Calculations based on a fast neutron flux of 2.5×10^{12} neutrons/cm^2/sec for the McMaster Reactor, indicate that the interferences resulting from fast neutron reactions are insignificant under the conditions of this work.

CHAPTER 2

SAMPLE PREPARATION

The materials analyzed in this research include pure minerals, namely sulphides and oxides, and whole rock samples. The latter category include rocks comprised essentially of either silicates or sulphides.

In the case of material prepared by the author, care was taken to ensure that only unaltered materials were incorporated in the sample. Final purity of the samples was controlled using light transmitting and reflecting microscopes, until a minimum of 98% was achieved. The flowsheets for the separation procedures are given in Figures 2-1 and 2-2.

Samples used in this research, which were previously prepared at McMaster University with standard separation techniques, are listed below.

Samples of pyrite and magnetite from Craigmont, B.C. and of pyrite from the Adams Mine were prepared by Lakefield Research of Canada Ltd., Lakefield, Ontario, using a combination of magnetic and flotation methods.

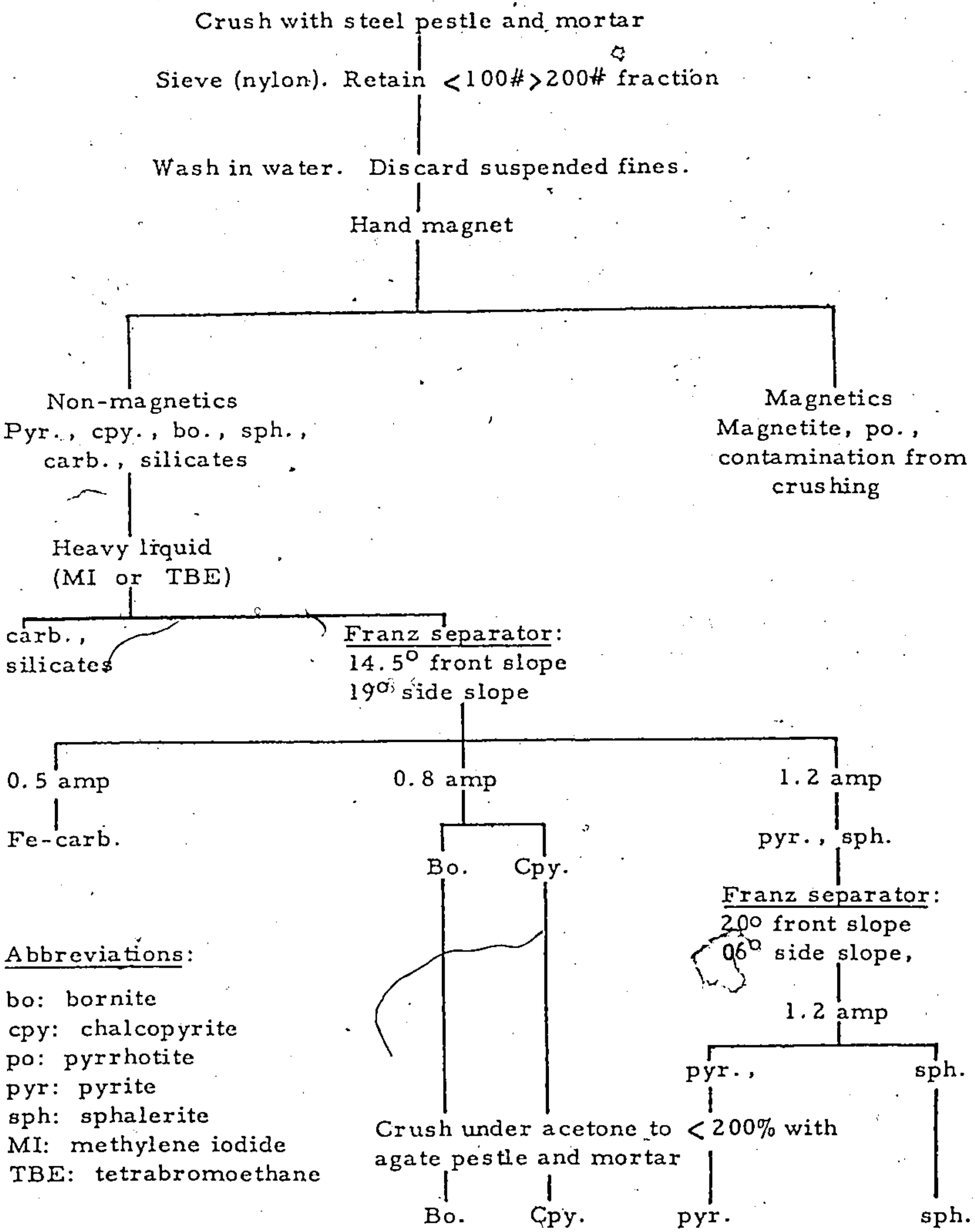


FIGURE 2-1: FLOW SHEET FOR PREPARATION OF BASE METAL SULPHIDES

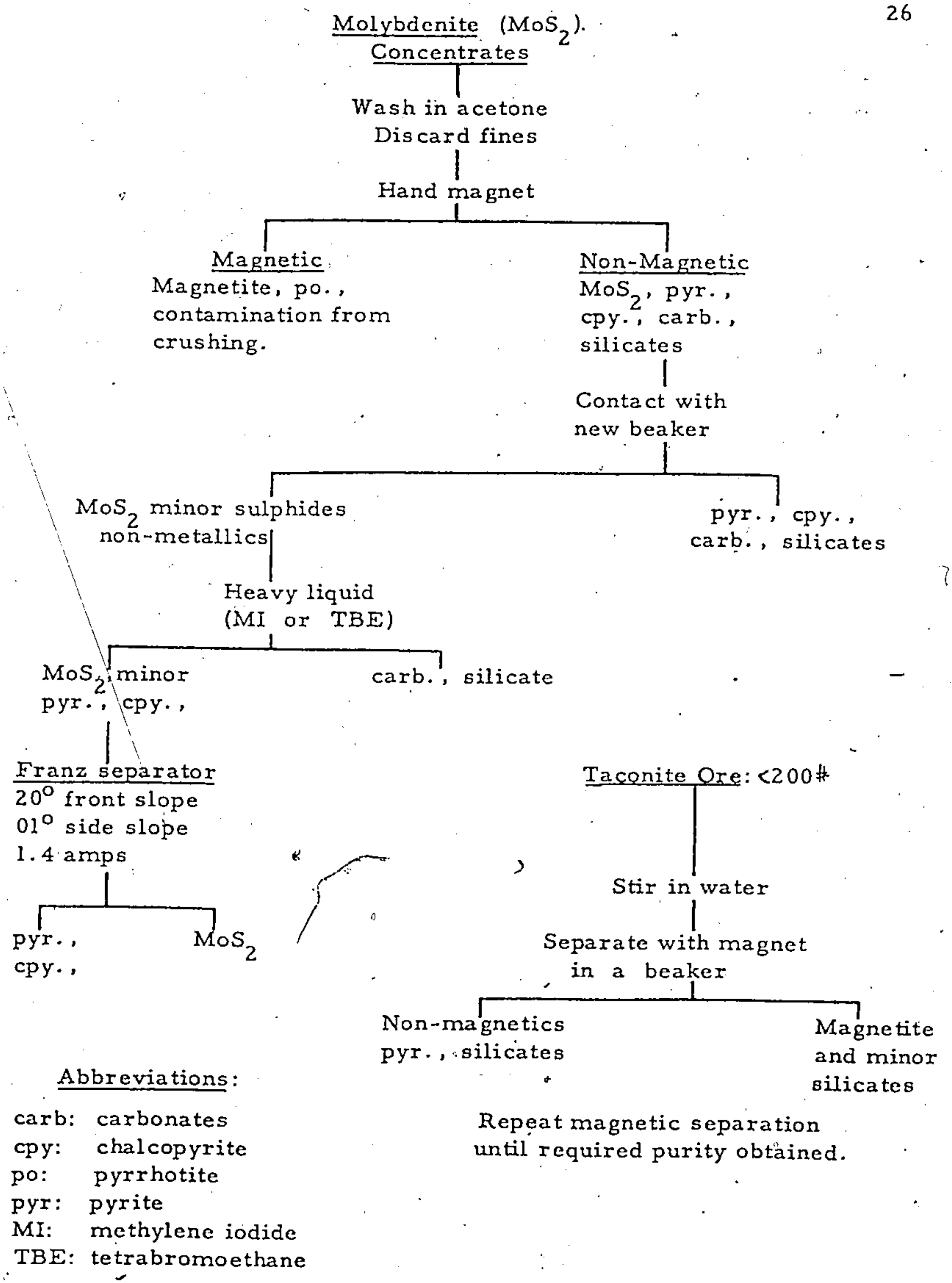


FIGURE 2-2: FLOW SHEET FOR SAMPLE PREPARATION OF MOLYBDENITE CONCENTRATES AND MAGNETITE

Table 2-1

Localities from which Previously Prepared Samples were Obtained

Locality	Material Used	Reference
Bathurst, N.B.	Whole rock, pyrite, sphalerite	Lusk (1968)
Adams Mine, Kirkland Lake, Ont.	Whole rock	Alcock (1971)
Sudbury, Ontario	Chalcopyrite, pyrrhotite	Chyi (1972)

< 100# > 200# fraction. This fraction was then crushed under acetone to < 200# with an agate pestle and mortar.

Prepared samples were stored under acetone.

CHAPTER 3

NEUTRON ACTIVATION METHOD

FLUX MONITOR AND CARRIER PREPARATION

1. General Statement

The determination of elemental abundances by the technique of neutron activation analysis used in this work requires the use of a flux monitor standard and a carrier solution. The abundance of the element sought is known in the flux monitor standard, and the specific activity of the standard is used to determine the content of the same element in the irradiated sample. The carrier, a non-radioactive milligram quantity of osmium or rhenium, is mixed and chemically equilibrated with the activated sample osmium or rhenium in a high temperature fusion. Thereafter, non-quantitative, conventional analytical procedures, suitable for milligram rather than microgram quantities, may be used for the determination of rhenium or osmium.

2. Standard Stock Solutions

Separate standard stock solutions of rhenium and osmium were prepared using Johnson, Matthey Chemical Co. Ltd. "Specpure" potassium perrhenate and ammonium chlorosmate. Quantities of these salts, weighed[1] to dryness, were used such that when diluted with 2M HCl to 500 mls the concentrations of the solutions were 26.67 μgm Re/ml and 17.57 μgm Os/ml respectively.

3. Diluted Standard Solutions

Volumetric aliquots from the standard stock solutions were diluted to 500 mls with 2M HCl to yield diluted standard solutions with metal concentrations of the order of 1.333 μgm Re/ml and 0.8785 μgm Os/ml, either as combined or as separate solutions.

The density of this standard was determined by weighing 1 ml aliquots taken with a calibrated pipette.

4. Flux Monitor Standards

Approximately 25 μgms of the diluted standard solution was used to prepare each flux monitor standard. The inside of the ampoule was wiped dry above the level of the liquid and the weight of the ampoule and standard solution was determined. Finely divided Reagent Grade aluminum oxide powder was then inserted into the ampoule to absorb the standard solution. The powder was dried by heating at 70°C for twelve hours, and the ampoules were sealed. Those to be irradiated for more than five days were sealed in an oxygen-natural gas flame, and the remainder were sealed with polyethylene caps.

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[1] using a 5 place Mettler Balance

Ampoules of different dimensions were used during the course of this work, depending on the nature of the samples to be analyzed. In all cases the dimensions of the ampoules used for the samples and the flux standards were identical.

The metal content of each standard was calculated knowing the concentration and density of the standard solution and the weight of this solution in each ampoule.

5. Carrier Solutions

Separate or combined carrier solutions of rhenium and osmium were prepared using "Specpure" potassium perrhenate and ammonium chlorosmate from Johnson, Matthey Chemical Company. The salts were weighed to dryness, taken into solution in 2M HCl, transferred quantitatively to a 100 ml volumetric flask and diluted to volume with 2M HCl. The metal concentration of these solutions was of the order of 2.367 μgm Re/ml and 2.380 μgm Os/ml.

CHEMICAL SEPARATION OF RHENIUM AND OSMIUM

1. Osmium

One of the most effective methods for the quantitative separation of osmium from other elements, including most of the platinum metals, is by distillation based on the volatility of osmium tetroxide under acid, oxidizing conditions. Boiling nitric acid, perchloric acid or sulphuric acid used in conjunction with an airstream, are most frequently employed. For quantitative distillation of osmium a strong oxidizing agent, such as dichromate, potassium permanganate or sodium bismuthate, must be present during the distillation to ensure that the osmium is in the octavalent state. Ruthenium tetroxide is also volatilized under these conditions. Osmium tetroxide is very volatile (B.P. 130°C) and is extremely toxic. It can cause damage to the eyes, lungs and skin when it is present in concentrations as low as 10^{-7} grams/cubic metre (Hammond, 1972), and should therefore be handled with care. Caution should also be exercised in the storage of powdered or spongy osmium metal which slowly gives off osmium tetroxide at room temperature.

The procedure adopted for the purification of radioactive osmium samples in this work was essentially a double distillation method utilizing nitrogen sweeper gas and solvent extraction prior to precipitation of osmium metal, and is a synthesis of the methods of Crocket _et al._ (1968) and of Bate and Huizenga (1963).

Primary purification of osmium is achieved by a sulphuric acid-hydrogen peroxide distillation effected at a maximum temperature of 90°C. Under these conditions, osmium is selectively and virtually quantitatively distilled from ruthenium which is in a reduced state (Korkisch, 1969a). Osmium is retained in the distillate as sodium osmate.

The secondary purification of osmium consists of an initial sodium bismuthate-concentrated nitric acid distillation followed by a sodium-bismuthate-sulphuric acid distillation using the procedure of Bate and Huizenga (1963). Osmium tetroxide is again absorbed into sodium hydroxide.

After acidification with nitric acid the osmium is further purified by solvent extraction into chloroform, followed by back extraction into sodium hydroxide. The pure aqueous osmium phase is acidified with hydrochloric acid and osmium is precipitated as the metal with zinc powder. Finally, the osmium metal is heated in boiling hydrochloric acid, to eliminate any zinc still present, washed with water and plated out in ethanol. The final osmium metal precipitate, for both standards and samples, contains between 3 and 8% osmium oxides (Hsieh, 1967).

All apparatus used for samples and standards was kept separate, and to avoid inter-experiment contamination, extensive cleaning procedures were used. Chung and Beamish (1968) have shown that a 10% solution of potassium hydroxide in ethanol is an effective agent in removing osmium from glassware. Cleaning procedures used in this work include an initial soaking immediately after the experiment, hot water wash, three-hour soak in 10% KOH-Etoh solution, water rinse, chromic acid soak and a final water rinse. An experiment to determine the effectiveness of this cleaning procedure was carried out. Four blank osmium samples were distilled using apparatus which had been cleaned as described above. The apparatus had previously been used for the analyses of four Cu-Ni sulphide matte samples with osmium contents in the 6 ppm range. This is roughly three orders of magnitude greater than the highest osmium value from geological material obtained in this work. Three of the blank samples gave background counts and one yielded counts 1-1/2 times background.

The apparatus used for the distillation of osmium is shown in Plate A-1. A flowsheet for the radiochemical procedures used for the purification of osmium is given in Figure 3-1, and a detailed description of the method is given in Appendix A-2.

2. Rhenium

Leddicotte (1961) has summarized the salient features of the radiochemistry of rhenium, including the determination of rhenium in a variety of materials using neutron activation analysis. The chemistry of rhenium and methods of separating rhenium with possible radiochemical applications are dealt with by Rulfs (1961) and Korkisch (1969b). Little is known about the toxicity of rhenium and therefore it should be handled accordingly.

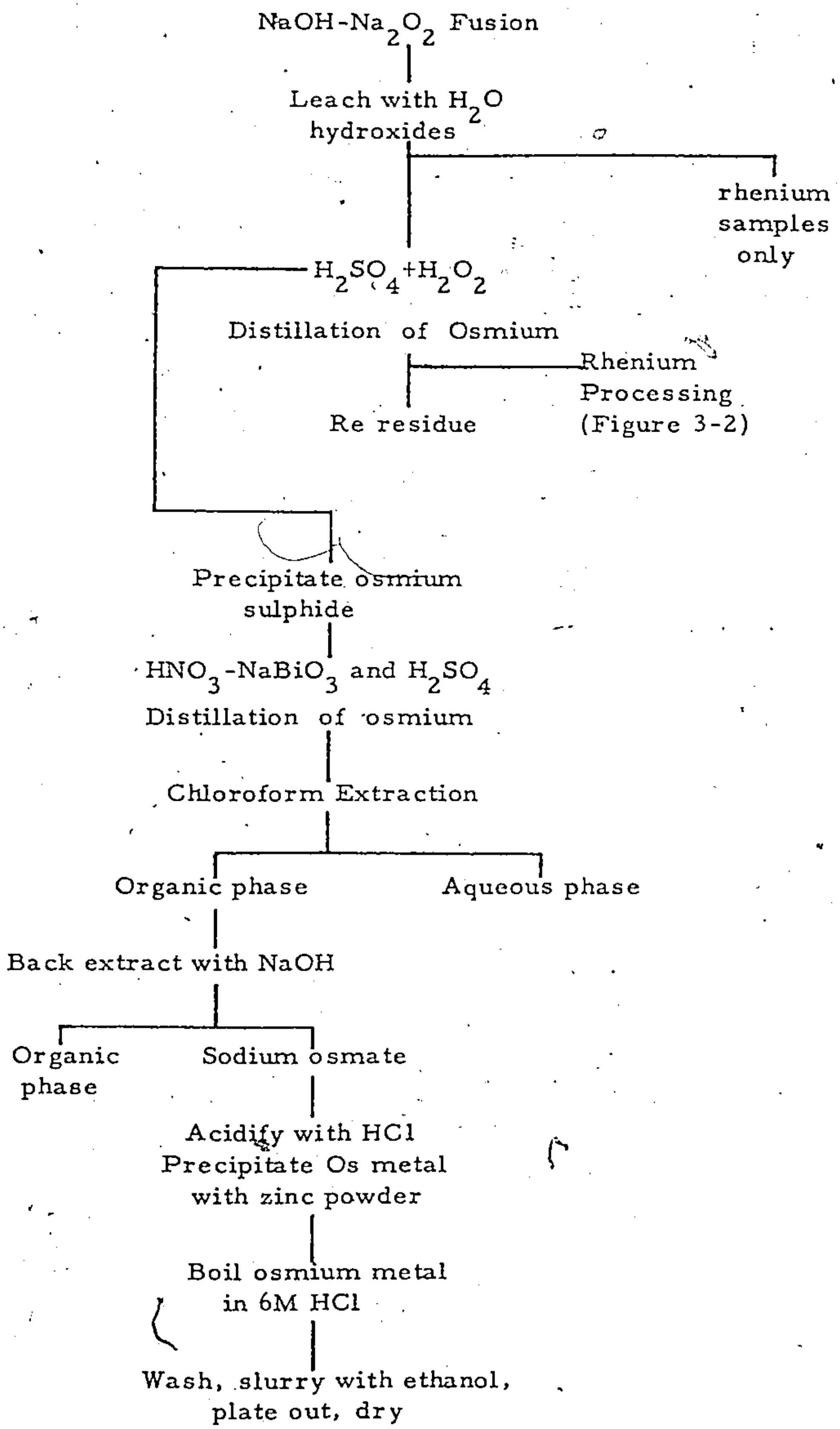


FIGURE 3-1: FLOW SHEET FOR RADIO-PURIFICATION OF OSMIUM

Two properties of rhenium are particularly useful in effecting its separation from radio-contaminants. The first is the volatility of rhenium oxyhalides and rhenium heptoxide, which form the basis for the distillation techniques, and secondly the tendency of rhenium in the plus seven valence state to form anion complexes, thereby enabling it to be separated from contaminants by either cationic or anionic ion exchange resins.

In this work, radiochemical purification of rhenium was initially based on a method involving a primary purification by distillation and a final purification by means of anion exchange resin. Later the procedure was based essentially on anion exchange resins. A generalised flowsheet for the radio-purification of rhenium is given in Figure 3-2.

(a) Separation of Rhenium by Distillation

Volatilization of rhenium heptoxide, Re_2O_7, from hot, strongly oxidizing acids using air, steam or carbon dioxide sweeper gases has been used effectively in separating rhenium from a large number of elements (Noddack and Noddack (1930), Geilman and Weibke (1931), Hiskey and Meloche (1940), Goldberg and Brown (1950). Herr et al. (1960) also determined the rhenium content of iron meteorites utilizing the separation of rhenium heptoxide from a concentrated sulphuric acid solution as a radio-purification technique.

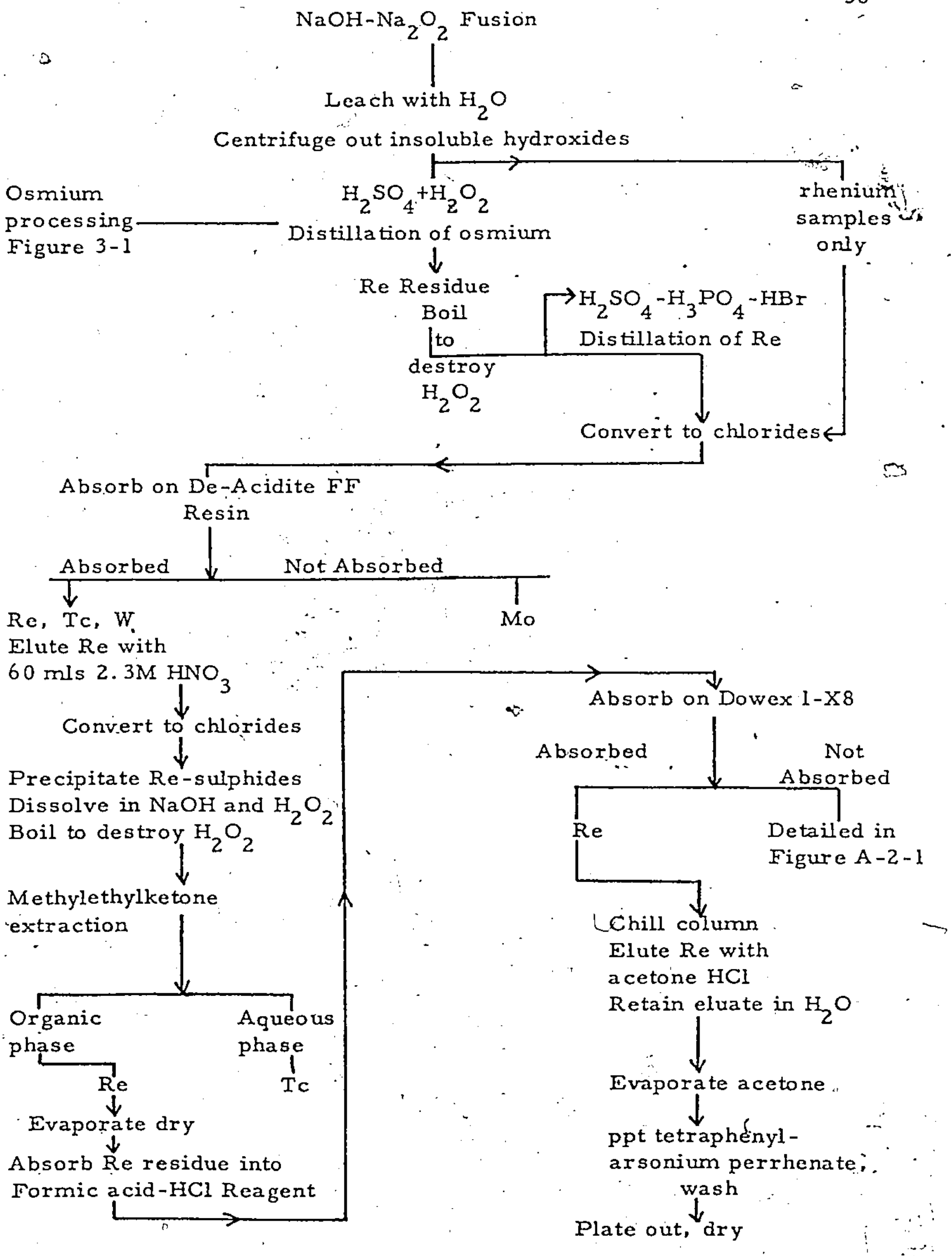


FIGURE 3-2: FLOW SHEET FOR RADIO-PURIFICATION OF RHENIUM

The volatility of rhenium trioxybromide (ReO_3Br) and rhenium trioxychloride (ReO_3Cl) is the basis of additional distillation techniques. Hoffman and Lundell (1939) volatilized rhenium by dripping either concentrated hydrobromic or concentrated hydrochloric acid into either concentrated sulphuric or perchloric acid solutions at 200 to 220°C using carbon dioxide as the sweeper gas.

(b) H_2SO_4-H_3PO_4-HBr Distillation Procedure

The distillation procedure used initially in this work as the primary step in the radiochemical purification of rhenium, was based on the method of Hoffman and Lundell (1939). The procedure consists of volatilizing rhenium, as ReO_3Br, from a concentrated H_2SO_4-H_3PO_4 acid solution, containing holdback carriers, at 200°C by the dropwise addition of concentrated hydrobromic acid.

The following metals were used as holdback carriers; Ag, Co, Cu, Fe, Mn, Mo, Ni and Zn. Nitrogen gas was used as the sweeper. The apparatus (see Plate A2-2) is designed so that cold concentrated HBr can be introduced dropwise, at a controlled rate, into the bottom of the distillation flask, ensuring efficient mixing of the reactants.

A detailed description of the distillation procedure is included in Appendix A-2.

(c) Rhenium Purification by Anion Exchange Resin

In the latter stages of this work radiochemical purity of rhenium was obtained through the use of strong base anion exchange resins. The results of tracer experiments carried out in conjunction with this work are given in Appendix A-4. The procedure adopted for the radiochemical purification of rhenium is based on methods developed by Morgan (1965) and by Matthews and Riley (1970). Essentially, the method consists of purification steps involving the use of De Acidite FF and Dowex 1-X8, and the removal of technetium by solvent extraction with methylethylketone. Rhenium is plated out as tetraphenyl arsonium perrhenate.

Double use of ion exchange resins was necessary to obtain radiochemical purity of the rhenium. Some previous workers, Morgan (1965) and Ishida et al. (1966) obtained radiochemically pure rhenium using a single strong base anion exchange step in a relatively simple purification procedure. These procedures were found to be insufficient to provide radiochemically pure rhenium in this study.

COUNTING AND CALCULATIONS

1. β^- Counting

(a) Counting Equipment

β^- counting was carried out using a Nuclear Chicago planchet counting system comprised essentially of: a gas-flow Geiger-Mueller end-window counting tube with coincidence shielding, automatic sample changer, scaler-timer and a paper tape print out. The counting gas was a 98.7:1.3 mixture of helium:butane. Thickness of the aluminum window was 150 μgm/cm^2. The average background of the detector was 2.0 counts/minute. Electronic drift in the counter was monitored using three uranium acetate standards.

(b) Decay Curves

The β^- radiation of the nuclides ^{186}Re and ^{191}Os, with half-lives of 90.5 hours and 15.5 days respectively, was counted. Radio-purity was established on the basis of decay curves. Typical β^- decay curves are shown in Figures 3-3 and 3-4.

Samples and standards were counted until they had decayed to background. In virtually all instances the samples were radiochemically pure. In the few cases where small quantities of long-lived contaminants were present, graphical corrections were applied to obtain the initial uncontaminated counting rates.

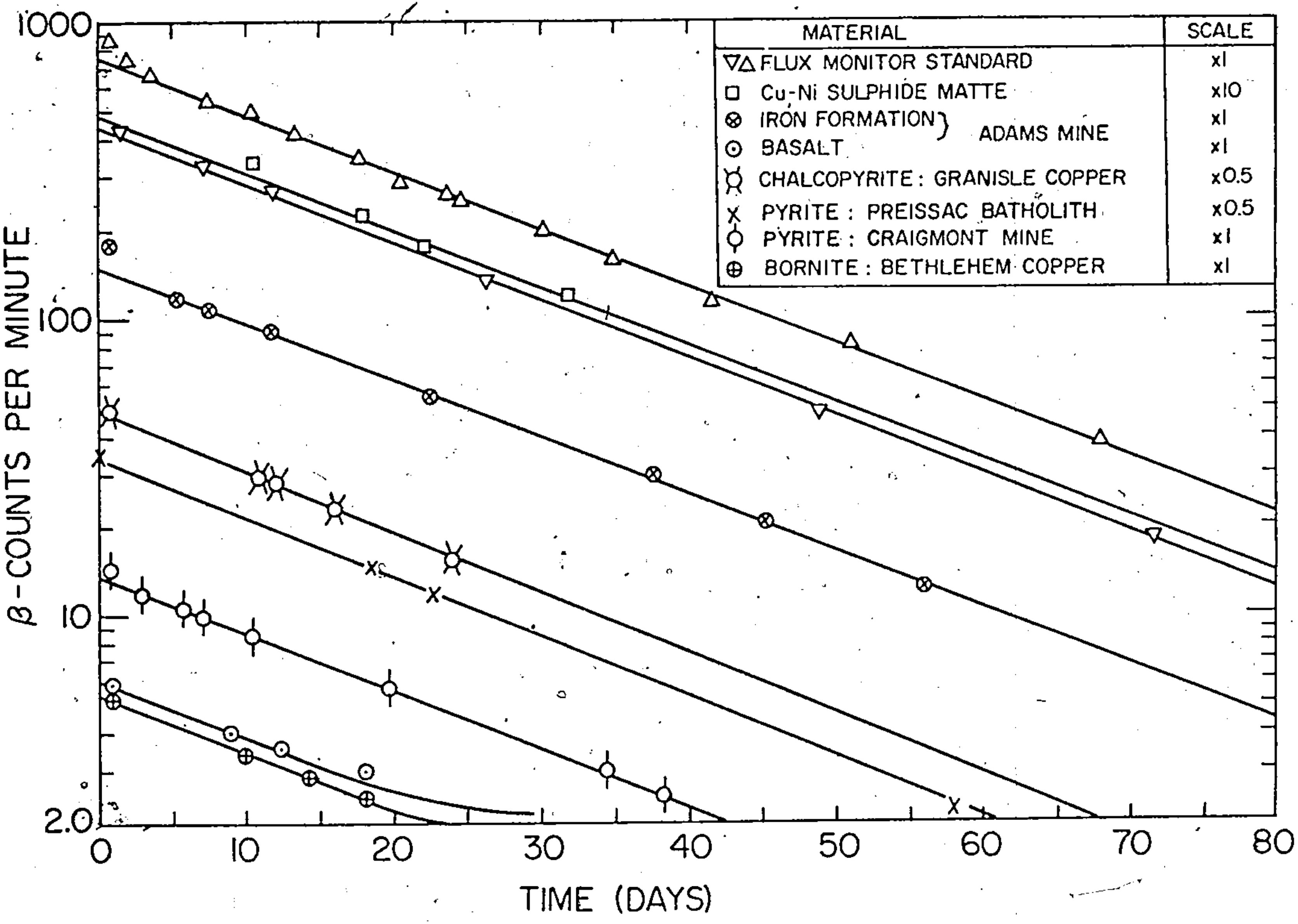


FIGURE 3-4 : β-DECAY CURVES FOR 15.5 DAY ^{191}Os and 31 HOUR ^{193}Os.

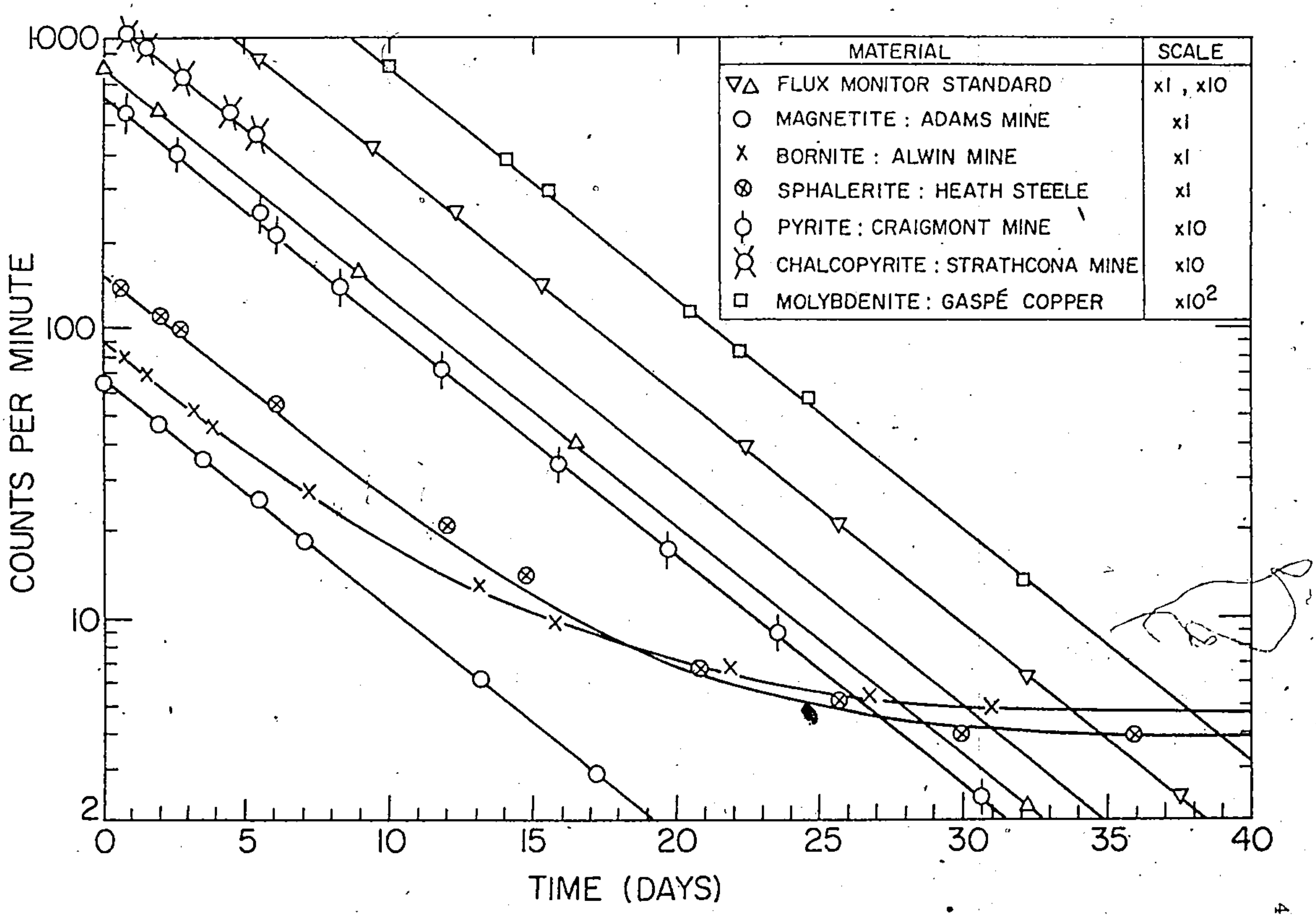


FIGURE 3-3 : β-DECAY CURVES FOR 90.5 HOUR ^{186}Re

Abundance calculations were made on the basis of comparisons of the counting rates of the samples and standards recalculated to an equivalent time, namely, the end of the irradiation.

In some instances the initial activity of osmium samples was very low, 5 counts/min. or less after background subtraction, and it was not possible to draw decay curves. In such cases the sample was counted again after approximately one half-life, and this count rate was compared with the calculated activity, A_2, assuming the sample to be pure osmium and using the relationship

$$A_2 = A_1 e^{-\lambda t}$$

where A_1 = initial activity in counts/min.

λ = decay constant for ^{191}Os

t = time elapsed between counts in the same units as the half-life of ^{191}Os.

If the measured activity agreed within 8% of the calculated activity, A_2, the sample was considered to be pure. Abundances based on count rates differing by more than 8% from the calculated activity were considered as maxima.

(c) Source Geometry

When comparing the activities of several samples it is necessary to ensure the same counting geometry for all the samples. This is necessary because the sample emits radiation in all directions and hence the counting rate is a function of the solid angle subtended by the counter window at the sample. To minimize the errors due to source geometry it is essential to plate out a uniformly distributed sample in the planchet. No problem was encountered with the rhenium precipitate, tetraphenyl-arsoniumperrhenate. The osmium, however, is counted as the metal and though extremely fine grained it was not possible to achieve an even precipitate over the width of the planchet. Further, considerable care must be exercised in handling and storing the finely divided osmium powder because it is very friable, and is also susceptible to disaggregation by static electricity. Spraying the osmium with krylon as a means of fixing it to the planchet did not prove satisfactory, because the precipitate tended to peel off in large flakes.

Where possible, the osmium samples were all counted in the same orientation.

2. γ Counting

(a) Equipment

γ counting was carried out on a Nuclear Chicago system incorporating (i) a detector, either a 130 gm Ge(Li) crystal with an active area of 8 cm^2 facing the window, or a 3"x3" well-type thallium-doped NaI crystal; (ii) high voltage supply; (iii) pre-amplifier; (iv) amplifier; (v) 1600 channel pulse-height analyzer; (vi) readout including a teletype print out and a display oscilloscope.

Most of the γ counting in this work was carried out on the NaI(Tl) detector because its sensitivity is greater than that of the Ge(Li) detector. A typical gamma ray spectrum for ^{186}Re is shown in Figure 3-5.

(b) Evaluation of Photopeaks

The ^{186}Re 137 keV γ-ray photopeak activities of rhenium samples and standards were evaluated, where possible, by the half peak full width method (HPFW) using the procedure of Denechaud et al. (1970). Peak half-widths between standards and samples in the same experiment differed by less than 7%. The net counts (N) for the integrated value of the peak for the selected channels are given by the difference between the sum of the gross counts and the estimated background (B) for the same channels (see Figure 3-6).

The background contribution was determined by first of all drawing an accurate graph showing counts/channel versus channel number for the photopeak and the adjacent parts of the spectrum. A straight line

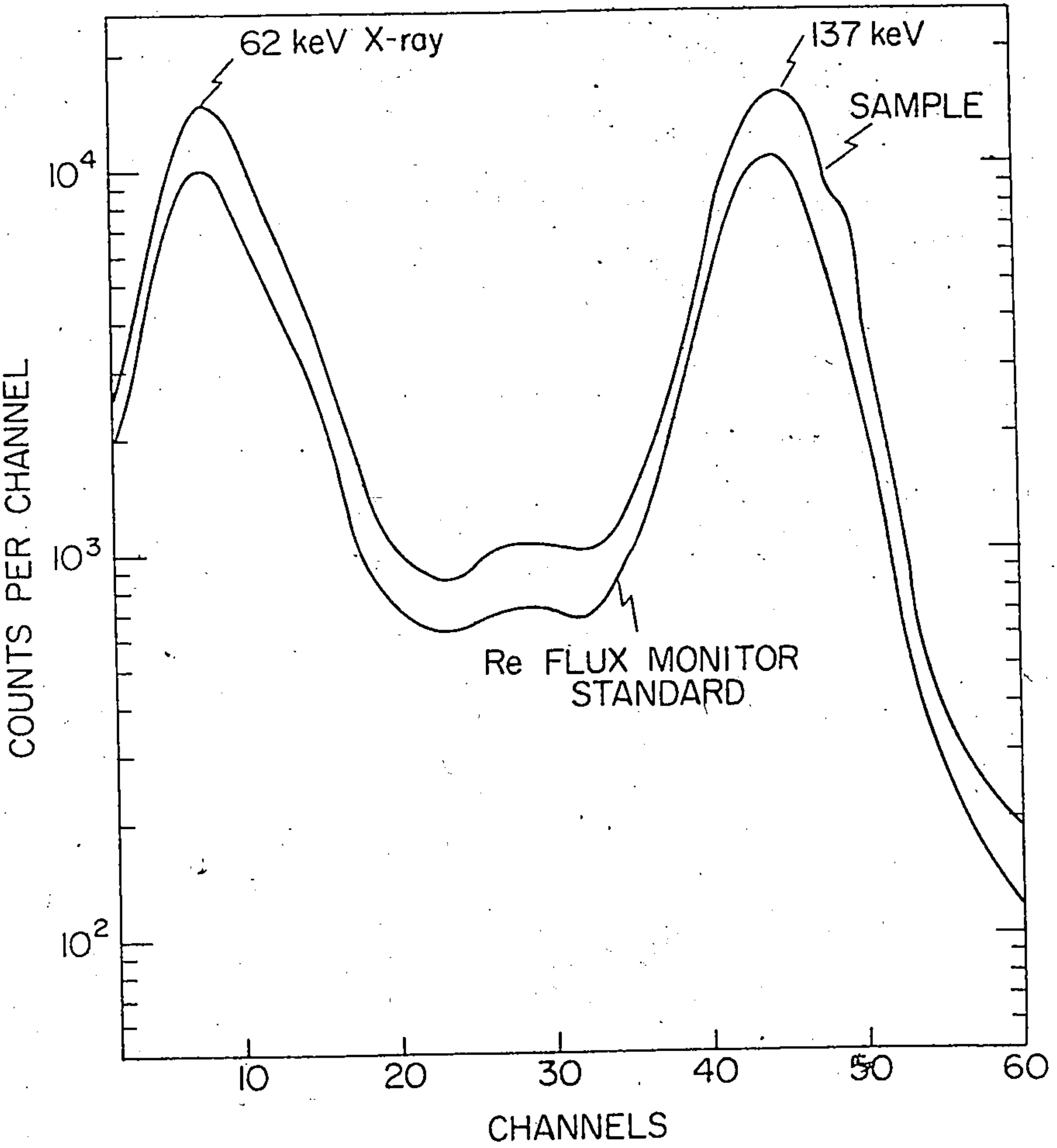


FIGURE 3-5: Gamma-ray spectra for rhenium flux monitor standard and for rhenium separated from molybdenite. NaI (Tl) Detector

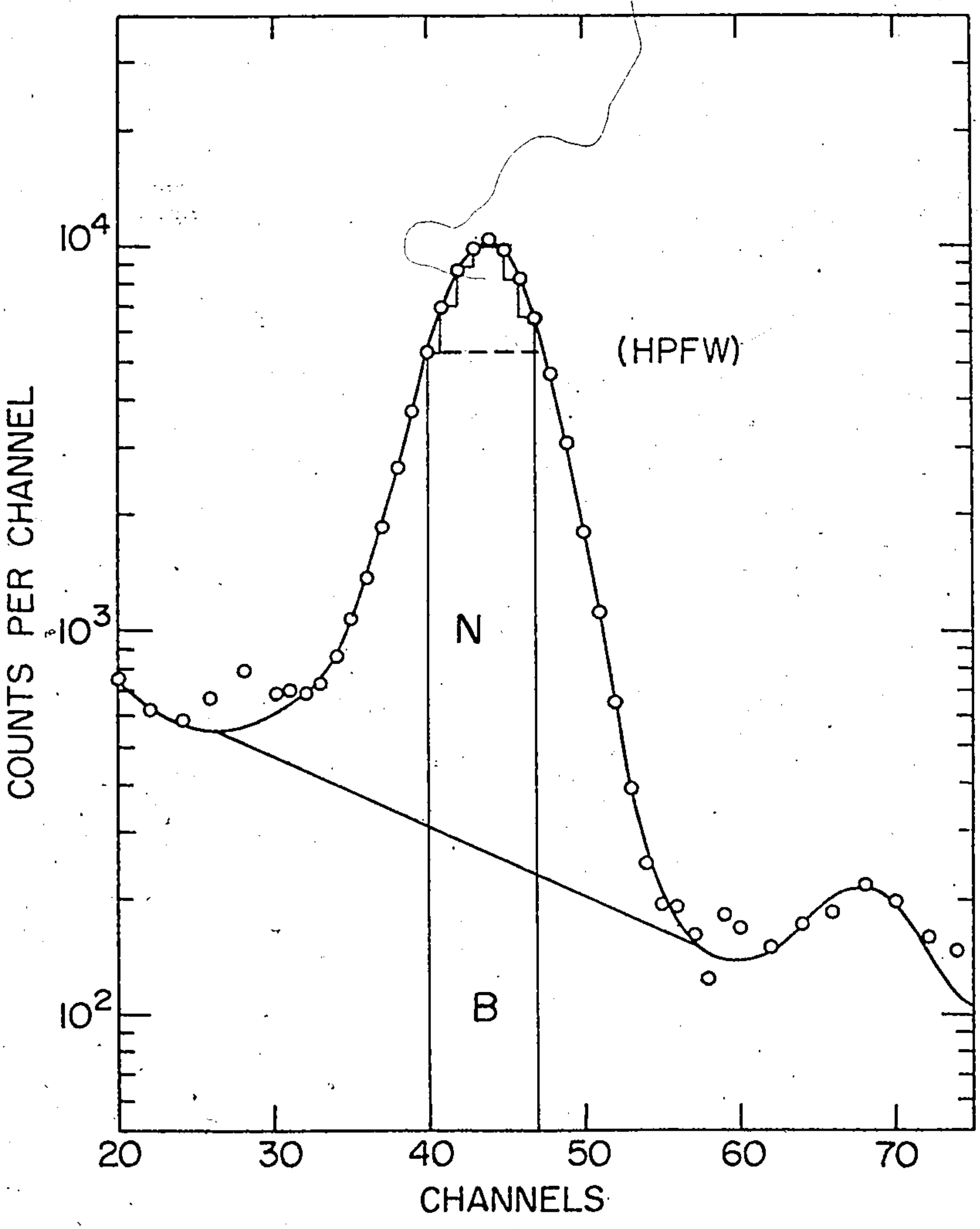


FIGURE 3-6. γ Spectrum Photopeak Evaluation.

representing the base line was then drawn between the valleys on either side of the photopeak. The total background contribution to the photopeak is given by summing the baseline values for each channel to be summed for peak integration.

The error for the integrated net peak counts is given by:

$$\sigma_{net} = (\sigma^2_{gross} + \sigma^2_{background})^{1/2}$$

where $\sigma = (\text{total counts})^{1/2}$ and where background and sample count periods are equal.

3. Element Abundance Calculations

$\frac{C_s}{Y_s} = \frac{\text{counts}}{\text{min.}}$ (at the end of irradiation) of the sample corrected to 100% yield

where Y_s is the observed sample yield with $0 < Y_s < 1$.

W_s = weight of sample irradiated in grams

$\frac{C}{Y} = \frac{\text{counts}}{\text{min.}}$ (at the end of irradiation) of standard corrected to 100% yield

where Y is the observed standard yield with $0 < Y < 1$.

W = weight of metal in standard in μgms.

Element abundances, M, in ppm (ppm = 10^3 ppb) can be calculated from the expression

$$M = \frac{C_s \; Y \; W}{C \; Y_s \; W_s}$$

which is valid for data obtained both by β^- and γ counting.

CHAPTER 4

EVALUATION OF ANALYTICAL METHODS

GENERAL STATEMENT

Appraisal of experimentally derived data can be achieved by examining the accuracy, precision, and sensitivity attainable with the method. The accuracy of the experimental methods used in this work is indicated by comparison of analytical results for standard materials with data obtained by other workers.

Precision is indicated by the internal consistency of results on individual samples of the same material. The limits of sensitivity depend on the analytical conditions and are governed mainly by the weight of sample irradiated, neutron flux, the irradiation time, and counting conditions.

ACCURACY AND PRECISION

1. Osmium

Copper nickel matte samples previously analyzed by several other workers using different analytical techniques, were used as standards for the determination of the accuracy of the osmium method.

The osmium content of the matte samples analyzed in Falconbridge's Thornhill laboratories was determined by a method based on a modification of that used at the Department of Energy, Mines and Resources (DEMR) Laboratory, Ottawa (Faye, 1965). The DEMR method includes collecting the platinum metals in tin during fire assay, followed by dissolution of the tin button. Osmium is separated by distillation of the tetroxide and determined colorimetrically. Hsieh's (1967) method involved neutron activation analysis and included alkaline fusion followed by distillation, precipitation of osmium metal, and β^- counting.

The osmium abundances of the matte samples obtained in this work are compared with the results of previous workers in Table 4-1.

Table 4-1

Osmium Abundances in Cu-Ni Matte Samples

Matte Number	This Work			Previous Work	
	Osmium	Std. Deviation (σ)	Nuclide and Radiation Counted	Osmium (ppm)	Analyst
3572	0.35 0.38 0.37	±0.02	^{191}Os, β^-	0.3	Mineral Sciences Division DMER, Ottawa
				0.33±0.02	Crocket (1968)
8083	0.33 0.37 0.35	±0.03	^{191}Os, β^-	N.D.*	
7517	5.91 7.88 6.90	±1.39	^{191}Os, β^-	6.3±0.3	Falconbridge Nickel Mines Limited Metallurgical Laboratories

* Matte #8083 is similar, but not identical, to Matte #3572.

2. Rhenium

The accuracy of the rhenium method is indicated by the results obtained for the rhenium abundances of molybdenite powders which were supplied by Professor W. Herr of Cologne University, West Germany (see Table 4-2).

Table 4-2

Rhenium Abundances in Standard Molybdenites

Method	Isotope Dilution	Neutron Activation Analysis Nuclide and Radiation Counted				Sample Locality
		^{186}Re	β^-	^{186}Re 137 keV γ		
Worker Date	Riley 1967	Hirt et al. 1963	Morgan 1965	This work	Std. Dev'n. (σ)	
Re	65.0	71.4	63±1	66.5		Yetholme, N.S.W. Australia
(ppm)	65.9	±3.6	65±1	66.3		
				61.1		
				61.7		
				60.7		
	65.5±0.5	71.4±3.6	64±1	63.3	±2.90	
Re (ppm)	-	2.02	-	2.18		Topland, Norway

Rhenium abundances of molybdenites from several British Columbia molybdenite deposits were determined colorimetrically by Giles and Schilling (1972). The arithmetic means they obtained for rhenium abundances in hand specimen-sized samples are in good agreement with the results obtained in this work for molybdenite concentrates from the same deposits. Terada et al. (1971), using neutron activation analysis, determined the rhenium content of molybdenite concentrates from two of the deposits analysed in this work. These results are compared in Table 4-3.

Table 4-3

Comparison of the Rhenium Contents of Some British Columbia Molybdenites obtained by Different Analysts.

Deposit (or Mine)	Giles and Schilling (1972)	Terada* et al. (1971)	This work*
Bethlehem Copper, Ltd.	430	190, 490, 980	211, 234, 335 1162
B.C. Molybdenum	69	-	77.8
Endako	32	24, 27	36.1
Boss Mountain	61	-	54.0

* MoS_2 concentrate

Note: All values in ppm.

CHAPTER 5

GEOCHEMISTRY OF RHENIUM AND OSMIUM

INTRODUCTION

Rhenium, atomic number 75, and osmium, atomic number 76 are transition elements and belong to Groups VIIb and VIII, respectively, of the Periodic Table. Abundance data for rhenium in rocks is still extremely limited and for osmium, the situation is only slightly better. Both elements exhibit siderophile and chalcophile tendencies. The siderophilic tendencies of rhenium and osmium are best illustrated by the high concentrations of the two elements in iron meteorites, where there is also relatively little fractionation between them. The pronounced chalcophilic characteristics of rhenium and osmium are manifest by the association of rhenium with sulphide ores of molybdenum and copper, and by the association of osmium with nickeliferous sulphide ores. The limited abundance data currently available for osmium in igneous rocks suggest that osmium is concentrated in ultramafic rocks relative to felsic rocks (Tables 5-9 and 5-10). Generally, the abundance of osmium in primary silicates is low and this results in its concentrating in residual fluids such as pegmatites. Iridium is known to be highly enriched in thortveitite and gadolinite (Noddack and Noddack,1931), minerals which are characteristically found in granitic pegmatites. By virtue of its geochemical coherence with iridium, osmium may be expected to be similarly enhanced in these minerals.

In the following sections, some physical-chemical parameters of rhenium and osmium are dealt with and their relevance to the geochemistry of these two elements is considered. Even though technetium is an artificial element, it has been included both because of its similarity to rhenium and in order to preserve the chemical continuity of the discussion.

NATURAL ISOTOPES

1. Rhenium

Rhenium is composed of two naturally occurring isotopes, ^{185}Re with an isotopic abundance of 37.07%, and ^{187}Re with an isotopic abundance of 62.93%. The radioactivity of ^{187}Re was discovered by Naldrett and Libby (1948) using counting experiments on rhenium samples of diverse origins. The decay of ^{187}Re to ^{187}Os has been dealt with in Chapter 1.

2. Osmium

The isotopic abundances of the seven naturally occurring isotopes which comprise "normal" osmium are given in Table 5-1.

Table 5-1

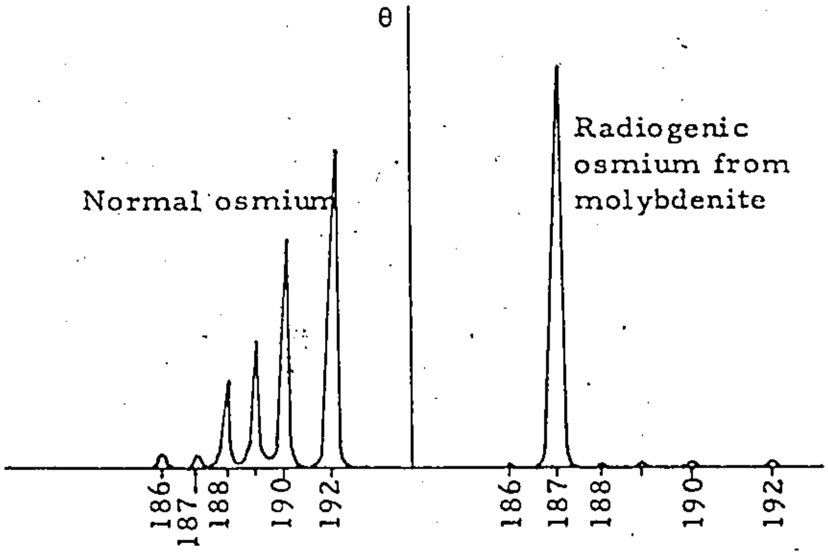
Stable Isotopes of Natural Osmium
After Lederer *et al*. (1967)

Mass Number	184	186	187	188	189	190	192
Isotopic Abundance (Atom %)	0.0018	1.59	1.64	13.3	16.1	26.4	41.0

However, significant differences in the isotopic composition of natural osmium can result from the production of radiogenic $^{187}Os^*$. The amount of radiogenic $^{187}Os^*$ in any sample is a direct function both of the initial ^{187}Re content and the age of the sample. Molybdenites, by virtue of their low common osmium content and their high rhenium abundances, may contain virtually monoisotopic radiogenic $^{187}Os^*$ (see Figure 5-1).

Figure 5-1

Mass Spectra of Osmium (after Hinterberger et al. 1954)



The high osmium content of certain molybdenites is particularly well illustrated by the molybdenites initially used by Herr and his co-workers (1955) for age dating. These provided milligram quantities of ^{187}Os for mass spectrometry. Similarly for the much younger molybdenites of the Guichon Batholith (200 my) calculations indicate a radiogenic ^{187}Os content of several hundred ppb. These are particularly high values even when compared with the common osmium content of the Strathcona ores, Sudbury, with a range of 0.68 to 68 ppb common osmium (Keays and Crocket, 1970).

It should be noted that neutron activation analysis, which is currently the most sensitive analytical method for common osmium, does not detect radiogenic ^{187}Os*. This results from the fact that only four of the seven stable isotopes of osmium, namely ^{184}Os, ^{189}Os, ^{190}Os and ^{192}Os, produce unstable nuclides, when bombarded with thermal neutrons. Hence the specific activity of neutron-irradiated natural osmium varies inversely as its radiogenic ^{187}Os content. Using this relationship and the technique of neutron activation analysis, Herr and Merz (1955) determined the radiogenic ^{187}Os* content in milligram quantities of osmium separated from molybdenites.

PHYSICAL CHEMICAL PROPERTIES OF RHENIUM AND OSMIUM

1. Electronic Configurations

The electronic configurations of rhenium and osmium and some other transition elements are given in Table 5-2. Rhenium resembles manganese in its electron configuration in that it has seven valence electrons of which five are d electrons and two are spin-paired s electrons.

Table 5-2

Electron Configurations of Some Transition Elements

(Electron Core)	Group						
	IVb	Vb	VIb	VIIb	VIII		
(Argon)	Ti $3d^2 4s^2$	V $3d^3 4s^2$	Cr $3d^5 4s^1$	Mn $3d^5 4s^2$	Fe $3d^6 4s^2$	Co $3d^7 4s^2$	Ni $3d^8 4s^2$
(Krypton)	Zr $4d^2 5s^2$	Nb $4d^4 5s^1$	Mo $4d^5 5s^1$	Tc $4d^6 5s^1$	Ru $4d^7 5s^1$	Rh $4d^8 5s^1$	Pd $4d^{10} s^0$
(Xenon)	Hf $4f^{14} 5d^2 6s^2$	Ta $4f^{14} 5d^3 6s^2$	W $4f^{14} 5d^4 6s^2$	Re $4f^{14} 5d^5 6s^2$	Os $4f^{14} 5d^6 6s^2$	Ir $4f^{14} 5d^7 6s^2$	Pt $4f^{14} 5d^9 6s^1$

2. Oxidation States

For the transition metals the highest oxidation state increases regularly from left to right across each period to the vicinity of the manganese and iron triads. To the right of this point oxidation states of the transition elements decrease in value. Elements in this vicinity of the Periodic Table are characterized by a wide range of oxidation states as well as by the highest oxidation states of the transition elements..

These features are exemplified by rhenium which exhibits oxidation states from -1 to +7, and by osmium, which like ruthenium, has a maximum oxidation state of +8.

The trend toward increasing stability of the higher oxidation states from top to bottom of a transition metal group is shown by manganese, technetium and rhenium. In this respect therefore, rhenium, with stable oxidation states of +4 to +7, resembles more closely technetium (most stable oxidation states also +4 and +7), than it does manganese, which is characterized by a most stable oxidation state of +2.

Rhenium is chemically similar to osmium and ruthenium in that it forms stable compounds in its highest oxidation state. This chemical similarity is further underlined by the stability of these elements in the +4 and 0 oxidation states. Further, the stability of rhenium in metallic form is a general characteristic of the platinum group elements as a whole.

(a) Rhenium

All members of the manganese triad exhibit oxidation states of +7, but only the compounds of rhenium and technitium are stable. The radicals MnO_5^-, TcO_5 and ReO_4^-, the heptoxides Mn_2O_7, Tc_2O_7 and Re_2O_7, the heptasulphides Tc_2S_7 and Re_2S_7 and the heptafluoride, ReF_7, are all known.

The heptoxides of the cogeners of manganese differ markedly in stability from that of Mn_2O_7 which decomposes rapidly at room temperature. In fact, the +7 state is the most stable oxidation state in which rhenium occurs.

Rhenium heptoxide, Re_2O_7, is a volatile yellow solid with a melting point of 296°C (Ivanov <u>et al</u>., 1972). It is noted for its high volatility and in this respect resembles osmium tetroxide more closely than the oxides of molybdenum and tungsten. Vapour pressure data for Re_2O_7 is given in Table 5-3.

Table 5-3

Vapour Pressure Data for Re_2O_7. (After Tylkina and Savitskii (1961) in Ivanov <u>et al</u>. (1969))

Temperature °C	Vapour Pressure mm Hg
212	1
289	100
386	400
462	760

Re_2O_7 is slightly less oxidizing than technetium heptoxide and is very stable. It dissolves readily in water to form a colourless strong acid, perrhenic acid, $HReO_4$. Several authors have reported occurrences of water-soluble rhenium which is associated with sedimentary uranium and molybdenum deposits from arid localities. Petersen et al. (1959) conclude that rhenium, which occurs in concentrations from 50 to 1000 ppm at the Sun Valley Mine, Coconino County, Arizona, is present as Re_2O_7. Similarly, Malouf and Zimmerley (1962) report water-soluble rhenium, in concentrations as great as 2000 ppm based on a 100% molybdenite equivalent, associated with ilsemmanite at the Ouray Indian Reserve on the Colorado Plateau. The association of water-soluble rhenium with uranium, molybdenum and vanadium at the Runge Mine, South Dakota, has alao been reported by Myers et al. (1960). Here the rhenium content of a particular sandstone, and of ore veinlets within it, is as high as 70 ppm. However, after water-leaching these samples the evaporate yielded as much as 7000 ppm rhenium.

The +4 state is another important oxidation state in regard to the geochemistry of rhenium. The dioxides, disulphides, tetrahalides and oxyhalides in which rhenium is in the +4 state are all known. Of these rhenium disulphide, ReS_2 is the most important. Actually, rhenium forms a wide range of sulphides, namely, Re_2S, Re_2S_7, ReS_2 and ReS_7 which are among its more stable compounds. ReS_2 and ReS_7

are precipitated under acid conditions from aqueous solution. ReS_2 is of particular interest because of the rhenium content of molybdenites. Synthetic molybdenites containing up to 10% rhenium have been reported and the occurrence of rhenium diselenide, $ReSe_2$, is also known (Vlasov, 1966).

Fluorides in which rhenium exhibit oxidation states ranging from +4 to +7 are also known. Of these, rhenium heptafluoride, ReF_7, is the most stable. Rhenium also forms halides with the remainder of the halogens, characteristically in the +4 state but also in complexes in the +2 state (Mackay and Mackay, 1970). The halogen compounds of rhenium are of particular interest because of the association of chlorine and fluorine with certain ore forming processes.

Naturally-occurring native rhenium is not known, however, either in the elemental form or alloyed with other metals. In this respect rhenium differs from osmium which has long been known to occur in nature, both as the metal and as a constituent of alloys within the Os-Ir-Ru system. The requirements for the formation of alloys between metals are the similarity of oxidation state and the equivalence of radius. Further, for complete solid solution the metals should possess the same crystal structure.

The similarity between rhenium, osmium and ruthenium with regard to these parameters (see Table 5-4) is compatible with the occurrence of natural alloys between these elements. Further,

Table 5-4

Some Physical-chemical Constants of the Transition Elements

1		2	3	4	5	6
	Crystal Structure	(r) Atomic Radius (Å)	$\left(\frac{r_x - r_{Re}}{r_{Re}}\right)100$	S.G.	Melting Point °C	Boiling Point °C
Ti	HCP/BCC	1.462	+ 6.33	4.54	1660	3287
Zr	HCP/BCC	1.602	+16.51	6.51	1852	4377
Hf	HCP/BCC	1.580	+14.91	13.31	2227	4602
V	BCC	1.346	- 2.11	6.11	1890	3380
Nb	BCC	1.468	+ 6.76	8.57	2468	4742
Ta	BCC	1.467	+ 6.69	16.65	2996	5425
Cr	BCC	1.282	- 6.76	7.18-7.20	1857	2672
Mo	BCC	1.400	+ 1.82	10.22	2617	4612
W	BCC	1.408	+ 2.40	19.3	3410	5660
Mn	Cub/Cub/Tet	1.264	- 8.07	7.21	1244	1962
Tc	HCP	1.360	- 1.09	11.5	2172	4877
Re	HCP	1.375	0	21.02	3180	5267 (est.)
Fe	BCC/FCC/BCC	1.274	- 7.35	7.874	1535	2750
Ru	HCP	1.339	- 2.62	12.41	2310	3900
Os	HCP	1.353	- 1.60	22.57	3045	5027
Ni	FCC	1.246	- 9.38	8.902	1453	2732
Rh	HCP	1.345	- 2.18	12.41	1966	3727
Ir	FCC	1.357	- 1.31	22.42	2410	4130
Co	HCP/FCC	1.252	- 8.95	8.9	1495	2870
Pd	FCC	1.376	0.07	12.02	1552	3140
Pt	FCC	1.387	0.87	21.45	1772	3827
Cu	FCC	1.278	- 7.65	8.96	1083	2567
Ag	FCC	1.445	+ 5.09	10.50	962	2212
Au	FCC	1.442	+ 4.87	19.32	1064	2807

Note:

(a) Data in columns 1, 2 and 3 from Savitskii *et al.* (1965).

(b) Data in columns 4, 5 and 6 from 1973-1974 Handbook of Chemistry and Physics, 54th ed., CRC Press.

(c) Abbreviations used:
BCC = body centred cubic
FCC = face centred cubic
HCP = hexagonal close packed
Cub = cubic
Tet = tetragonal.

(d) Column 3: r_x = atomic radius (Å), 12 fold coordination for a given element
r_{Re} = atomic radius (Å), 12 fold coordination, for rhenium.

Savitskii et al. (1965) have demonstrated limited solid solution between rhenium and iridium, and that complete miscibility, in the solid state, exists at elevated temperatures for each of the binary systems rhenium-ruthenium and rhenium-osmium. It is likely, therefore, that rhenium, which reaches concentrations between 100 and 1000 ppb in osmiridium (I. and W. Noddack, 1935) is in elemental form alloyed with the platinum metals.

(b) Osmium

In minerals, osmium commonly exhibits a zero and +4 oxidation state. Also, osmium resembles ruthenium in that both elements occur in the +8 state, which is the highest oxidation state of the transition elements. The most common compound in which osmium exhibits a valence of +8 is osmium tetroxide, which is very volatile and which can be produced by direct oxidation of metallic osmium (Mackay and Mackay, 1970). Under only mildly reducing conditions, OsO_4 alters to form osmium dioxide.

In contrast to rhenium, which occurs in nature in the +7 oxidation state, little is known about osmium in natural systems under surficial conditions. In fact, there is still disagreement about the volatility of osmium metal at room temperatures. Hammond (1973) considers that solid osmium is unaffected by air at room temperature, but that the metal will volatilize slowly under the same conditions when in sponge or powdered form. According to Beamish (1966), however, the oxidation of solid osmium to osmium tetroxide at normal temperatures has long been known. He states that there are reports of iridosmine from Siberia emitting sufficient quantities of the tetroxide at ordinary temperatures to stain a label sealed within the tube containing the iridosmine. Further, he reports that whereas osmium from Ethiopia could be volatilized directly from a native osmium metal, Tasmanian iridosmine consistently failed to yield the tetroxide, even after the most strenuous heating. However, it seems that formation of osmium tetroxide may be expected from metallic osmium under conditions in a supergene environment. Osmium which is in higher oxidation states, for example, where it is chemically bound in osmium-rich minerals such as erlichmanite, a sulphide, or osarsite, a sulpharsenide can be expected to yield osmium tetroxide as an initial product of weathering. The tendency for the tetroxide to become altered to the dioxide under mildly reducing conditions would be strongly enhanced by the presence of organic material.

Osmium also occurs in the +8 state in complexes such as $OsO_4F_2^{2-}$, but osmium octafluoride is not known.

The +4, +5 and +6 valence states of osmium are exemplified by the fluorides OsF_4, OsF_5 and OsF_6 respectively. Of these, osmium tetrafluoride is the most stable. Stable trivalent osmium compounds of the remaining halides are known.

Osmium disulphide is another compound in which osmium exhibits a valence of +4. In contrast to the disulphide and heptasulphide of rhenium, it is precipitated from aqueous solutions under alkaline conditions. Two minerals in which osmium exhibits an oxidation state of +4 are erlichmanite $(Os, Ir, Rh, Ru, Pd)S_2$ and laurite $(Ru, Ir, Os)S_2$.

MINERALS OF RHENIUM AND OSMIUM

1. Rhenium

Controversy still surrounds the question as to whether or not rhenium exists as an independent mineral species. Poplavko et al. (1962) claim to have discovered a sulphide of rhenium associated with the cupriferous sandstone ores of Dzhezkazgan, Kazakhstan, where rhenium is widespread but is not associated with molybdenum. Dzhezkazganite, as the rhenium sulphide has been named, is generally associated with bornite, chalcocite and galena in the Dzezkazgan ores. Repeated reference to dzhezkazganite, sometimes spelled "jeskasganite", is made in the literature (Satpayev, 1965; Vlasov, 1966; Herr et al. 1967;

Sutulov, 1970; Ivanov et al., 1972). The crystallographic parameters of dzhezkazganite have not been completely defined, and there is wide disagreement concerning its composition (Table 5-5), although the formula $CuReS_4$ has been proposed.

The most serious obstacle to establishing the true identity of dzhezkazganite is its mode of occurrence. In the dzhezkazgan ores, for example, it is intimately associated with sulphides with a maximum grain size of 0.15 to 0.2 mm. The dzhezkazganite occurs as thin veins along the margins of bornite and as thin stringers within it. According to Satpayev (1965), grains of dzhezkazganite in bornite, which exhibit optical homogeneity at magnifications of two thousand times, are resolved by electron microscopy into bornite with inclusions of dzhezkazganite exhibiting a variety of textures.

Results of X-ray microprofile analyses of dzhezkazganite are given in Table 5-6.

Table 5-5

Physical and Chemical Properties of Dzhezkazganite Obtained by Various Authors

(Source: Ivanov *et al.* (1972))

Properties	Author
Color in reflected light:	
brownish-gray	Poplavko *et al.*, 1962
pinkish-cream to brown	Satpaeva *et al.*, 1962[1*]
Reflecting power (%):	
wave length, mμ 525 25.76	Poplavko *et al.*, 1962
590 27.20	
650 27.42	
479 to 26.6 to 29.5	Satpaeva *et al.*, 1962
Microhardness:	
230 kg/mm^2 (load 20 g)	Poplavko *et al.*, 1962
208.7-281.0 kg/mm^2 (load not indicated)	Satpaeva *et al.*, 1961
Reaction to etching by:	
NHO_3 (long duration) - etched surface remains brownish-gray	Poplavko *et al.*, 1962
NHO_3 (long duration) - dark areas turn gray	Satpaeva *et al.*, 1962
KCN (20%) - hardly visible darkening	Poplavko *et al*, 1962
KCN (20%) - turns brownish somewhat	Satpaeva *et al.*, 1962
HNO_3 (1:1) - browns slightly	Poplavko *et al.*, 1962
H_2SO_4 (1:4), KOH (20%), $FeCl_3$, HgCl - no reaction	Poplavko *et al.*, 1962
Quantitative determination of composition by spectral optical analyses:	
rhenium, copper, lead, silver	Poplavko *et al.*, 1962
rhenium, copper, lead, molybdenum, iron, silver	Satpaeva *et al.*, 1962
Determination of composition by X-ray spectral method (wt. %):	
Re - 40-77	Poplavko et al., 1962[2*] Poplavko, Troneva, 1966[2*]
Re - base, not determined quantitatively	Kosyak, 1965[3*]
Cu - 8-26	Poplavko *et al.*, 1962
Cu - not established	Poplavko, Troneva, 1966
Mo - 9-12	Kosyak, 1965
Mo - present in amounts appreciably less than rhenium	Kosyak, 1965
Pb - correlates with rhenium	Kosyak, 1965
S - 13-20	Poplavko and Troneva, 1966
S - 25.6	Kosyak, 1965
X-ray diffraction studies:	
Mineral amorphous	Poplavko *et al.*, 1962
Highly dispersed substance with structure of ReS_2	Polyakova, 1965

[1*] - Dzhezkazganite described as rhenium mineral from Dzhezkazgan (Satpaeva *et al.*, 1962).

[2*] - Dzhezkazganite treated with potassium cyanide to remove inclusions of bornite and chalcocite (Poplavko *et al.*, 1962; Poplavko, Troneva, 1966)

[3*] - Dzhezkazganite was analyzed in an intimate intergrowth with bornite (Kosyak, 1966)

Table 5-6

Composition of Dzhezkazganite Based on X-ray Spectral Analysis (Source: Ivanov <u>et al</u>. (1972))

Element	Content, wt. %	Number of Measurements	Content Average
Rhenium	40-77	11	55
Copper	8-26	9	16
Molybdenum	9-12	3	10
Iron	0-1	3	-
Silver	1	1	-
Sulfur	13-20	6	15
Arsenic	1	1	-
Selenium	1	1	-
Cobalt	-	1	-
Nickel	-	1	-
Zinc	-	1	-
Lead	Approximately 0-10	2	5

Capitant <u>et al</u>. (1963) report the occurrence of rhenium-rich inclusions containing "several tens of percent rhenium" in a suite of sulphide minerals from the Prince Leopold Mine, Kipushi, Katanga in Zaire. The major minerals were molybdenite, tennantite and bornite, in that order of abundance, with accessory chalcocite, covellite, pyrite and sphalerite. Distribution of rhenium was studied by means of an electron microprobe. In the molybdenite, rhenium was found to be variable and the presence of local concentrations suggested the existence of a specific rhenium mineral. "The species was located as some small areas on a grey-brown mineral found adjacent to molybdenite in contact with covellite"[1] and is shown in Figure 5-2.

(a) Concentrator Minerals of Rhenium

Rhenium is concentrated in relatively few minerals. Noddack and Noddack (1931) using an X-ray spectrographic method with a sensitivity of 1×10^{-8} detected rhenium in only 100 minerals during the course of their comprehensive study of rhenium in geologic materials. Vlasov (1966) lists 55 minerals with enhanced rhenium contents including native metals and intermetallic compounds, sulphides, oxides, silicates and tungstates. His compilation is based largely on the results of Noddack and Noddack (op. cit.), supplemented by more recent data from various Russian workers. Table 5-7 lists carrier minerals notable for their high rhenium abundances.

From this table it is obvious that the sulphides constitute, numerically, the most important group of rhenium carrier minerals. This group is also by far the most important of the rhenium carriers on the basis of absolute rhenium content. The table also illustrates the association of rhenium with silicate and primary oxide minerals known to have pegmatitic and pneumatolytic affiliations. These rela-

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[1] Capitant et al. (1963)

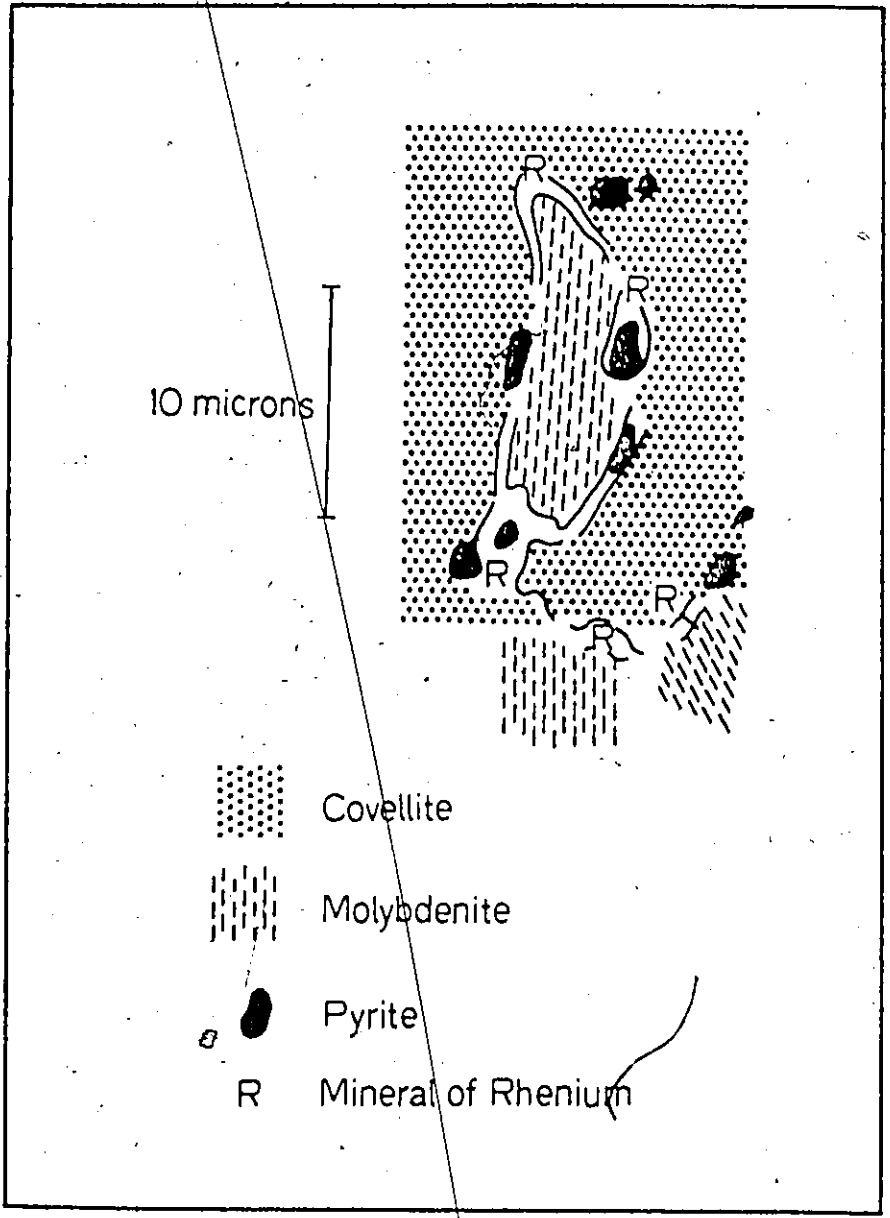


FIGURE 5-2. Distribution of a Rhenium-rich Mineral in Sulphide Ore, Zaire. [After Capitant et al (1963)]

Table 5-7

Minerals Known to Have High Rhenium Contents

Mineral	Composition	Re (ppb)	Reference
		I. Silicates	
Alvite	$(Zr,Hf)SiO_4$	200 to 600	1
Gadolinite	$(Fe,Be)_2Y_2Si_2O_{10}$	30 to 1,100	1
Thortveitite	$Y_2Si_2O_7$	600	1
Zircon	$ZrSiO_4$	up to 50	1
		II. Oxides	
Cassiterite	SnO_2	10	1
Chromite	$FeCr_2O_4$	10 to 20	1
Columbite	$(Fe,Mn)Nb_2O_6$	50 to 200; 260	1; 2
		400	3
Tantalite	$(Fe,Mn)Ta_2O_6$	30 to 80	1
Fergusonite	$Y(Nb,Ta)O_4$	20	1
Samarskite	$Y_2(Nb,Ta)_2O_7$	20	1
		III. Molybdates and Tungstates	
Powellite	$CaMoO_4$	5000 to 170,000	4
Wulfenite	$PbMoO_4$	300 to 11,000	4
Scheelite	$CaWO_4$	20	1
Wolframite	$(Fe,Mn)WO_4$	20	1

Table 5-7 (continued)

Mineral	Composition	Re (ppb)	Reference
	IV. Sulphides, Sulpharsenides, Selenides and Tellurides		
Argentite	Ag_2S	70	1
Bismuthinite	Bi_2S_3	20	1
Bornite	Cu_5FeS_4	20 to 98	1, 5
Chalcocite	Cu_2S	40	1
Chalcopyrite	$CuFeS_2$	80 to 20,000	1, 4, 5
Galena	PbS	3	5
Marcasite	FeS_2	30	1
Molybdenite	MoS_2	10 ppb to 18,800 ppm	5 4, 6
Pyrite	FeS_2	Up to 20 68,000	1, 4, 5 7
Pyrrhotite	$Fe_{1-x}S$	20 to 30	1
Berzelianite	Cu_2Se	20	1
Clausthalite	PbSe	800	1
Enargite	Cu_3AsS_4	20	1
Gersdorffite	NiAsS	50	1
	V. Native Metals and Alloys		
Osmiridium	(Ir, Os)	100 to 1,000	1
Platinum	Pt	30 to 800	1

References:
(1) Noddack and Noddack (1931); (2) Sen (1958); (3) Meshri _et al_. (1963); (4) Vlasov (1966); (5) Morgan _et al_. (1968); (6) Herr _et al_. (1967); (7) Ivanov _et al_. (1972).

tions have led several authors (Rankama and Sahama, 1950; Malouf and Zimmerley, 1962; Morris and Short, 1965, and Vlasov, 1966) to suggest that in the course of magmatic crystallization, rhenium is generally fractionated from the early crystallizing oxide and silicate phases, and is concentrated in the early magmatic sulphides. With progressive crystallization, rhenium becomes increasingly enriched in the residual fluids. This view is supported by the data, albeit very sparse, of Noddack and Noddack (1931) who determined the rhenium content of pyrrhotite and pentlandite from Norwegian copper-nickel deposits to be 30 ppb and 10 ppb, respectively, and by the values of 100 ppb rhenium in pyrrhotite from the magmatic copper-nickel ores as reported by Ivanov et al. (1972). However, rhenium may also be enriched in the early-separated oxide phases of crystallizing mafic or ultramafic magmas, as exemplified by chromites with 10 to 20 ppb rhenium (Noddack and Noddack, op. cit.) and it is also concentrated in osmiridium and platinum (Table 5-7). The tendency for rhenium to be enriched in the residual fluids resulting from the fractional crystallization of magma is apparently substantiated by rhenium abundances of aplite-pegmatite associated with granitoid massifs in northeast Yakutiya, U.S.S.R. Here the rhenium content of the granodiorite, which is of batholithic dimensions, is given as 0.5 ppm and for the pegmatites it is 4.2 ppm (Ivanov et al., 1972). These values are considered to be too high in view of the neutron activation results of Morris and Fifield (1961), Morgan (1965) and Morgan and Lovering (1967). The trend of the values, however, may be significant.

Table 5-7 also serves to illustrate the affiliation between rhenium and those elements closely associated with it in the Periodic Table, especially columbium, tantalum, molybdenum, iron, the platinum metal group and to a lesser extent, chromium and manganese. The association of rhenium with molybdenum is by far the most important. This geochemical association between molybdenum and rhenium is not unexpected in view of their similar properties. For example, the ionic radius of Mo^{+4} in octahedral coordination is 0.70Å and that of Re^{+4} is 0.72Å (Krauskopf, 1967). Also, the electronegativities of the two elements are very similar, 1.30 for molybdenum and 1.46 for rhenium (Morris and Short, 1969). These factors, together with the close resemblance of the crystal structures of MoS_2 and ReS_2 (Morris and Short, 1969), combine to make molybdenite the most important carrier-mineral of rhenium.

Molybdenite occurs in two polymorphs, hexagonal (2H) and rhombohedral (3R). Hexagonal MoS_2 is the most common form, but recently recognition of rhombohedral MoS_2 has become increasingly common. Deposits in which rhombohedral molybdenite is the dominant polytype are generally characterised by low sulphur environments, for example, greisens and carbonatites (Giles and Schillings, 1972). Hexagonal molybdenite is comprised of layers of molybdenum and sulphur in the order - S - Mo - S - S - Mo - S - (Figure 5-3), in which molybdenum atoms are octahedrally coordinated with sulphur, and each sulphur atom is surrounded by three molybdenum atoms (Fyfe, 1964). Each layer in the crystal is composed of a two-dimensional sheet with the composition (MoS_2). Opposing layers of weakly bound sulphur atoms between the sheets result in perfect cleavage parallel to (0001).

Rhenium disulphide was formerly thought to crystallise with a CdI_2 or the hexagonal MoS_2 structure, but is now known to crystallise with a triclinic $ReSe_2$ structure (Alcock and Kjekshus, 1965; Hulliger, 1968). On the basis of this evidence, therefore, it would appear that the rhenium content of MoS_2 is independent of molybdenite polymorphism. Analytical evidence which indicates no direct relationship between the content of molybdenite and MoS_2 polymorphism is cited by Ivanov _et al_. (1972). Giles and Schilling (1972) reached a similar conclusion during the course of their study on the rhenium content of molybdenites.

Rhenium accompanies molybdenum through a wide range of pneumatolytic and hydrothermal processes resulting in appreciable concentrations of rhenium in a wide variety of molybdenum deposits.

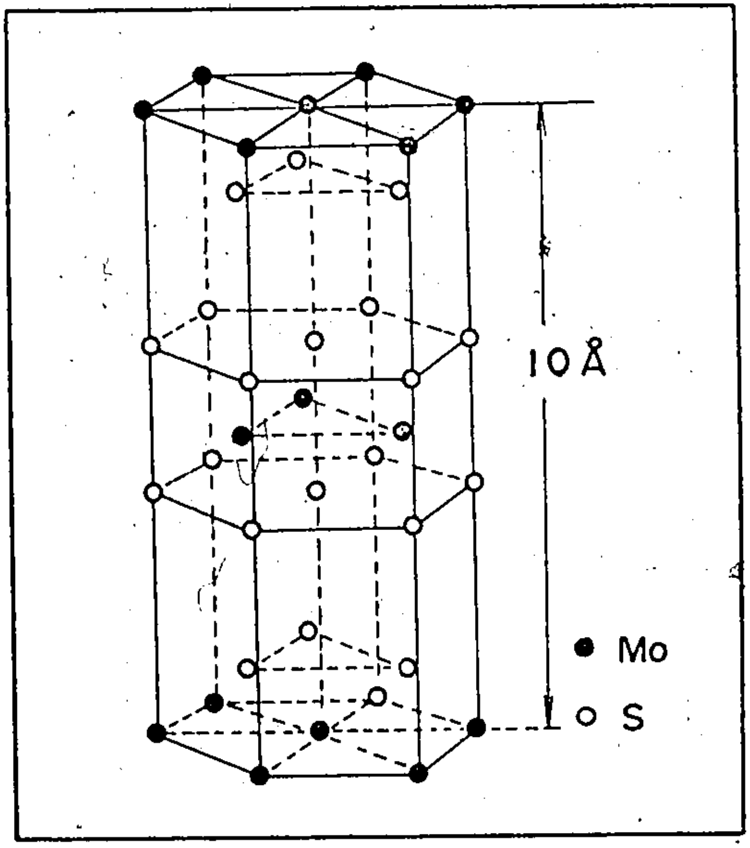


FIGURE 5-3: Structure of Hexagonal Molybdenite (MoS_2)
(After Fyfe, 1964.)

The range in rhenium abundances of molybdenites is very large and varies from 10 ppb (Morgan et al., 1968) to 18,000 ppm (Vlasov, 1966). Herr et al. (1967) cite an example of a molybdenite carrying 5,500 ppm rhenium and the compilation of Fleischer (1959) contains several examples of Scandinavian molybdenites with exceptionally high rhenium contents, ranging from 1,400 ppm to 3,130 ppm. In general, though, molybdenites contain about 1 ppm to 600 ppm rhenium.

Since the work of Fleischer (op. cit.) numerous investigations into the rhenium content of molybdenites have been published (See Table 1-1). The results of systematic researches into the rhenium content of molybdenites from genetically different molybdenite deposits in the U.S.S.R. are reported by Ivanov et al. (1972). The results of these works indicate that hydrothermal molybdenites associated with copper iron sulphides, particularly in the porphyry copper environment, constitute the richest source of rhenium. However, Morgan et al. (1968) in their study of Australian molybdenites found no evidence indicating that high rhenium-bearing molybdenites are associated with copper mineralization.

An affinity between rhenium and selenium has been noted by several authors. Morris and Short (1969) cite the results of Russian workers as evidence for the sympathetic relationship between rhenium and selenium abundances in molybdenites, and the association of rhenium in the selenide minerals berzelianite and clausthalite can be seen from Table 5-7. However, Ivanov et al. (1972) contend that the relationship between rhenium and selenium in molybdenites is complex and that the rhenium content may vary either directly or inversely as the selenium content. This contention is supported by the results of Tischendorf et al. (1968) who established a weak negative correlation between rhenium and selenium in Erzgeberg and Thuringen molybdenites of West Germany. The structure of $ReSe_2$ has been discussed by Alcock and Kjekshus (1965) and Hulliger (1968).

2. Osmium

In contrast to rhenium which occurs essentially as a minor element in host minerals, osmium occurs in three main forms. These are, in the metallic form, either native or as alloys, in osmium compounds, and as a trace element in other minerals.

The equivalence of metallic radii and the similarity of crystal structure of osmium and ruthenium result in extensive solid solution between these elements. There is also complete solid solution between osmium and iron, and osmium and nickel, but both ruthenium and osmium show only limited solid solution with iridium.

Recently, Harris and Cabri (1973) reviewed the nomenclature of the natural alloys of osmium, iridium and ruthenium. The essence of their proposals concerning classifications within this system are contained in Figure 5-4.

Osmium is the principal cation in the sulphide mineral erlichmanite (Os, Ir, Rh, Ru, Pd)S and the sulpharsenide osarsite (Os, Ru, Ni, Pd, Pt, Rh)AsS. Osmium also occurs in irarsite, which is an iridium-rich sulpharsenide of the platinum metals, cobalt and nickel. It is also found in laurite (Ru, Ir, Os)S_2. The crystal structures of the disulphides of osmium have been discussed by Sutarno et al. (1967) and the mineralogy of the platinum metal group as a whole has recently been reviewed by Cabri (1972) (see Table 5-8).

DISTRIBUTION OF RHENIUM AND OSMIUM

Recently there has been considerable interest in the abundances of siderophile and volatile elements in meteorites, and the rhenium content of lunar materials. However, there is still a paucity of information concerning rhenium and osmium in common rocks, and very little is known of their biogeochemical distribution or of their distribution in the hydrosphere and zone of weathering.

With the exception of Table 5-12, all abundance data presented in Tables 5-9 to Table 5-14 inclusive have been obtained by neutron activation analysis. The arithmetic means for osmium and rhenium values, together with the number of samples (N), and the standard deviation (σ) are also reported in these tables.

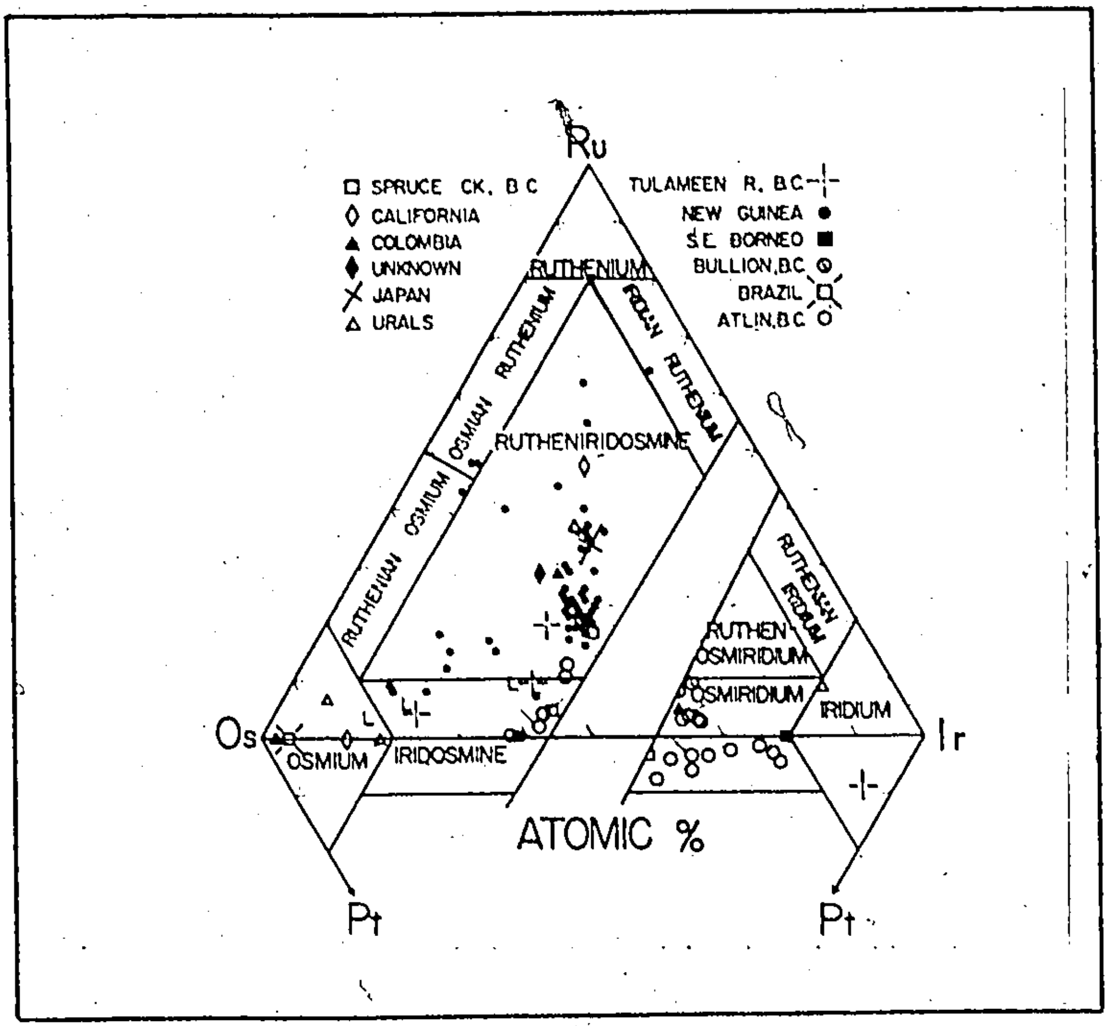


FIGURE 5-4: The Nomenclature of Natural Alloys of Osmium (After Harris and Cabri, 1973)

Table 5-8

Compositional and Unit Cell Data for Osmium-bearing Minerals. After Cabri (1972)

Mineral	Composition	Synthetic Equivalent or End Member	System and Space Group	Cell Parameters Å Natural	Synthetic
Erlichmanite	(Os, Ir, Rh, Ru, Pd)S_2 with Os> other Pt group	OsS_2	Cubic Pa3	No data	a=5.6193
Irarsite	(Ir, Rh, Ru, Pt, Pd, Os, Ni, Co) AsS with Ir> other metals	IrAsS	Cubic Pa3	a=5.777-8	a-5.791
Irodsmine (Iridosmium)	(Os, Ir) Ir 68.20 wt. % Os 32-80 wt. %	?	Hexagonal	No data	a=2.7361, c=4.3417 for $Os_{65}Ir_{35}$
Laurite	(Ru, Ir, Os)S_2 with Ru>Ir, Os	RuS_2	Cubic Pa3	a=5.6135 for Ir, Os rich composition	a=5.6095
Osarsite	Ru, Ni, Ir, Pd, Pt, Rh) AsS with Os> others	OsAsS	Monoclinic	a=5.933 b=5.916 c=6.009 β=112°21′	a=5.922 b=5.944 c=6.044 β=113°05′ for $Os_{0.5}Ru_{0.5}AsS$
Osmiridium	(Ir, Os), Os<32 wt. %	?	Cubic	No data	a=3.8358 for $Ir_{80}Os_{20}$
Palladium	Pd, Rb, Rh, Pt, Os, Ir, Ru with Pd principal metal	Pd	Cubic Fm3m	a=3.91	a=3.8898
Platinum	Pt, Fe, Cu, Ni, Rh, Ir, Os, Ag, Sn with Pt principal metal	Pt	Cubic Fm3m		a=3.9321
Ruthenosmiridium	Ru, Os, Ir, Rh with Ru≃Os≃Ir, Rh minor	RuOsIr	Hexagonal	No data	No data

1. Terrestrial

(a) Igneous Rocks

Abundance data for rhenium and osmium in USGS Standard Rocks and in common igneous rocks are presented in Tables 5-9 and 5-10. In two out of three cases there is good agreement between the osmium values recommended by Flanagan (1973) for USGS Standard Igneous Rocks and the averages presented in Table 5-9. However, there is substantial disagreement in the case of the osmium content of standard peridotite PCC-1. It should also be noted that there is a ten-fold difference in the rhenium content of the standard peridotite, PCC-1, and the only other peridotite which has been analysed. Further, ultramafic rocks contain the lowest rhenium abundances reported to date for all rocks.

Although the significance of averages is obviously limited by the small number of available analyses, the inference may be drawn that rhenium is concentrated in felsic rocks relative to mafic and ultramafic rocks, whereas osmium shows the reverse tendency. This fractionation results in osmium:rhenium ratios which increase from felsic to ultramafic rocks by a factor of about 10^3 in the case of the USGS Standard Rocks. In a study of rhenium and osmium abundances in igneous and metamorphic rocks, Morgan and Lovering (1967) noted a

Table 5-9

Rhenium and Osmium Abundances in Standard Igneous Rocks

Sample	Rhenium N	Rhenium $\frac{gm}{gm} \times 10^{-10}$	Rhenium σ	Rhenium Source(s)	Osmium N	Osmium $\frac{gm}{gm} \times 10^{-10}$	Osmium σ	Osmium Source(s)	$\frac{Os}{Re}$
G-1 (Granite)	8	6.4	1.68	a,b	4	$\leq$ 0.65	-	b,c*,e	$\leq$ 0.1
AGV-1 (Andesite)	2	3.35	0.21	b	2	$\leq$ 0.2	-	d	$\leq$ 0.1
W-1 (Diabase)	10	6.0	1.46	a,b,d*,k	4	2.6	0.27	b,c*,e	0.4
						[2.5]		h	
BCR-1 (Tholeiitic Basalt)	21	8.2	0.85	b,t,z,al,an	4	$\leq$ 0.96	-	b,t	
	4	10.1	0.37	z†					
Average Values	25	8.5	1.02		4	$\leq$ ~~0.95~~	-		$\leq$ 0.1
PCC-1 (Peridotite)	4	0.58	0.30	b,t	8	73	33.8	d,f,g,j,t	127
						[110]		h	
DTS-1 (Dunite)		0.13		b	3	10.8	2.24	b,g	83
						[10]		h	

Sources

a = Morris and Fifield (1961)a
b = Morgan (1965)
c = Bate and Huizenga (1963)
d = Morgan and Lovering (1967)
e = Crocket et al. (1968)
f = Nadkarni and Morrison (1974)
g = Gijbels et al. (1971)
h = Flanagan (1973)
j = Millard and Bartel (1971)
k = Tereda et al. (1974)
t = Lovering and Hughes (1971)
z = Keays et al. (1974)
al = Krahenbuhl et al. (1973)
an = Morgan et al. (1973)
* = Values omitted
† = Different sample split
[ ] = Recommended values

Table 5-10

Rhenium and Osmium Abundances in Common Igneous Rocks

Type	Locality	N	Rhenium $\frac{gm}{gm} \times 10^{-10}$	σ	Sources	Type and Locality	N	Osmium $\frac{gm}{gm} \times 10^{-10}$	σ	Sources	$\frac{Os}{Re}$
I. Felsic: (Includes Na-K rich granite, rhyolite, comendite and quartz-pyroxenes-fayalite porphyry)	Liruei, Nigeria	7	5.1	4.29	m		-	-			-
II. Intermediate (Hybridised diorite)	Insch Mass, Scotland	1	1.6	-	m		-	-			-
III. Mafic: (Syenogabbro, troctolite)	Insch Mass, Scotland	4	3.0	0.43	m		-	-			-
Nephelinite	N.S.W., Australia	2	2.7	0.14	d	same	2	2.7	1.20	d	1.0
IV. Ultramafic:											
(a) Kimberlite	Kimberley Mine, S.A.	4	0.84	0.19	d,t	same	4	16.2	4.70	d,t	19
(b) Peridotite	Snowy Mts., Australia	2	4.3	0.21	d	same	2	53	10.6	d	12
			-			Dunite and peridotite, Mt. Albert, Que.	5	66.6	24.0	n	-
						Serpentinite	6	64.5	48.8	n	-
Average Values		6	2.0	1.8		Average values	17	53.4	47.1		27

Source: b=Morgan (1965), d=Morgan and Lovering (1967), m=Morris and Fifield (1961b), n=Crocket and Chyi (1972), t=Lovering and Hughes (1971).

similar negative correlation between the abundances of these two elements. However, considerably more information is necessary in order to evaluate the statistical significance of this trend.

(b) Sedimentary Rocks

Substantial quantities of osmiridium are recovered as by-products from the lithified placers of the Witwatersrand. The osmiridium occurs as very fine-grained, discrete particles with an average diameter of 0.12 mm(Mertie, 1969). The average grade of the platinum group metals recovered is about 3.5 ppb, but the percentage recovery is known for only one mine, Geduld, where it is about 60% (Cousins, 1973). The grade of osmium in the platinoid mineral concentrates ranges from about 36 to 45 per cent. The only reliable abundance data for osmium and rhenium in common sedimentary rocks is restricted to the neutron activation analysis of three sedimentary rocks by Lovering and Morgan (1964). In addition to low elemental abundances in two of the samples (see Table 5-11), they found a marked depletion of osmium relative to rhenium in a pyritised dark shale.

Considerably more is known about rhenium in sedimentary rocks because sedimentary ores constitute several important sources of rhenium. Rhenium-bearing sedimentary ores are characteristically polymetallic. In the U.S.S.R., copper-bearing sandstones with rhenium contents ranging from 0.8 to 100 ppm are known. The most notable of

Table 5-11

Rhenium and Osmium Abundances in Sedimentary and Metamorphic Rocks and Tektites

Type	Locality	Rhenium N	Rhenium $\frac{gm}{gm} \times 10^{-10}$	Rhenium σ	Rhenium Sources	Osmium Type and Locality	Osmium N	Osmium $\frac{gm}{gm} \times 10^{-10}$	Osmium σ	Osmium Sources	$\frac{Os}{Re}$
(A) SEDIMENTARY											
Sandstone (quartz-rich)	Wilpena Pound, S. Australia	2	0.35	0.11	p	same as for Re	2	$\leq$ 0.60	-	p°	$\leq$1.7
Shale (State Circle Shale)	Ethridge Cr. A. C. T., Australia	2	0.51	0.04	p	same	2	4.54	1.49	p	8.9
Dark shale (with pyrite)	Captain's Flat Railway Station N. S. W., Australia	2	826	47.4	p	same	2	3.45	1.32	p	0.004
(B) METAMORPHIC ROCKS											
Granulite	Delegate, N. S. W. Australia	2	3.7	0.0	d	same	2	1.6	1.0	d	0.4
Eclogite	Africa and Australia	8	8.7	9.57	d	same	8	3.0	2.8	d	0.3
(C) TEKTITES											
All types except Billitonites and Ivory Coast tektites	Australia and Far East	12	0.56	0.34	p°	same as for Re	12	7.66	6.29	p°	14

Source: d=Morgan and Lovering (1967); p=Lovering and Morgan (1964)

°Maxima omitted from calculations

these are the cupriferous sandstone deposits of Kazakhstan. Also, the Kupferschiefer has long been a producer of rhenium. The association of rhenium with the uranium-copper sandstone ores of the Colorado plateau has already been referred to in connection with the oxidation of rhenium.

The cupriferous deposits of Kazakhstan have been described by Ivanov et al. (1972). In these polymetallic deposits, rhenium is associated with the sulphide minerals and there is generally a direct correlation between the rhenium content and the total Cu, Pb, Zn and Fe content. The rhenium and molybdenum content of these ores is approximately equal, and in some areas the rhenium content exceeds that of molybdenum. Therefore, the rhenium in these ores cannot be viewed solely as an impurity of molybdenite, and it is reasonable to expect that the rhenium was precipitated as an independent sulphide mineral. An especially rhenium-rich zone, 3-4 metres thick, occurs in the Pokro-7 deposit at the boundary between a bornite-chalcopyrite rich zone and a galena ore. It is in this zone that dzhezkazganite is said to have been discovered. Rhenium abundances in several other cupriferous sandstones in the U.S.S.R. are presented in Table 5-12.

Tischendorf et al. (1968) have described the occurrence of rhenium in the bituminous shales of the Kupferschiefer and give the rhenium content to be about 22 ppm. This is substantially lower than the values of 23 to 235 ppm rhenium quoted by Morris and Fifield (1969) which are based on older literature results. There is a positive correlation between rhenium and molybdenum in the copper-bearing marls overlying the bituminous shale and this correlation is more pronounced in the ore horizon itself. In these rocks there is also a strong positive correlation between rhenium and the organic content, and a strong negative correlation between rhenium and the calcium content. The exact form in which rhenium occurs in the Kupferschiefer-type deposit is not yet known (Wojciechowska and Serkies, 1966).

The rhenium content of sedimentary ores is given in Table 5-12.

(c) Metamorphic Rocks and Tektites

There is only limited information available on rhenium and osmium abundances in metamorphic rocks and tektites (see Table 5-11). Rhenium and osmium values in four eclogites show large variations. For example, the rhenium content of these rocks varies by a factor of 27 and for osmium it varies by a factor ≥ 35 (Morgan and Lovering, 1967). On the basis of their rhenium and osmium abundances, Lovering and Morgan (1964) concluded that tektites could be derived from either felsic or sedimentary rocks.

Table 5-12

Rhenium Content of Sedimentary Ores (After Morris and Fifield (1969) - Modified)

Type of Deposit	Locality	Rhenium (ppm)	Characteristic ore formers
Copper sandstones	Dzhezkazgan, Kazakhstan, USSR	0.5-85 5-100	Copper and rhenium
	Kop-Kazgan, Kazakhstan, USSR	0.8-35	Copper
	Dalenskoye, Kirghiziya, USSR	2	Insignificant ore development
	Gul'chinskoye, Kirghiziya, USSR	2-5	Insignificant ore development
	Spasskoye, Kazakhstan, USSR	2	Insignificant ore development
	Udokan, East Siberia USSR	Traces-3	Copper
Coal-bearing deposits	Central Asia, USSR	0.095-0.327	Brown coals with high molybdenum content and other rare elements
Bituminous copper-bearing shales	Kupferschiefer, Mansfield, E. Germany	≃ 22	Copper, lead, zinc, vanadium, nickel, molybdenum, rhenium and other rare elements
	Kupferschiefer, W. Germany	0.75-1.1	
Uranium-copper deposits in sandstones	Sun Valley, N. Arizona, USA	50-700	The richest uranium-vanadium region of USA. Supplementary source of rhenium and other rare metals.

(d) Zone of Weathering

Under oxidizing conditions it is likely that rhenium in molybdenite is oxidized from the +4 state to the +7 state to form rhenium heptoxide Re_2O_7. Under extremely arid conditions Re_2O_7 would be stable as, for example, in the previously cited cases of the uranium-molybdenum sandstone ores of the Colorado Plateau. Re_2O_7 readily dissolves in water and under humid conditions perrhenic acid, $HReO_4$, could be expected. Perrhenates, with the exception of the perrhenates of the alkali metals and thallium, are readily soluble in water. Therefore, oxidation and leaching of rhenium-bearing molybdenites can be expected to result in chemical alteration and hydrological dispersion of significant quantities of dissolved rhenium in the perrhenate from.

Further, several authors (Morris and Fifield, 1969; Vlasov 1966 and Ivanov, 1972), on the basis of field observations and experimental work, conclude that during the course of progressive oxidation of rhenium-bearing molybdenite, rhenium may be preferentially oxidized and removed with respect to molybdenum. Hence, increase of rhenium:molybdenum ratios in surface waters relative to molybdenite is to be expected. Ivanov et al. (1972) report, for example, that in the slightly alkaline mine waters of the Katzharan deposit, U.S.S.R., the rhenium:molybdenum ratio is greater by a factor of 200 relative to molybdenite in the deposit.

The primary association of rhenium and molybdenum is also reflected in the zone of oxidation where rhenium is associated with the oxidation products of molybdenite. Wulfenites contain up to 1.25 ppm rhenium (Fleischer, 1959) and powellites with rhenium contents ranging from 0.5 to 170 ppm have been reported by Ivanov et al. (1972).

(e) Oceans

The data currently available on rhenium and osmium in ocean waters and sediments have been summarized in Table 5-13. As a result of their work on eleven North Atlantic deep sea sediments, Olafsson and Riley (1972) suggest that the rhenium content of these sediments results from adsorption of perrhenate ion during the formation of authigenic clay minerals with subsequent incorporation of the adsorbed perrhenate into the lattice of the clay minerals.

(f) Ores

The most important sources of rhenium are molybdenites associated with porphyry copper deposits and, to a lesser degree, the sedimentary ores of which the cupriferous sandstone class is most important. The recovery of rhenium from porphyry copper deposits has been dealt with by Sutulov (1970). In contrast to the granitoid affiliations of rhenium, primary osmium ores are associated with mafic and ultramafic rocks. Osmium-bearing platinum group placers are of secondary importance.

Table 5-13

Rhenium and Osmium Abundances in Oceanic Environment

Type	Locality	N	Rhenium ngm/litre	σ	Sources	Sample Type and Locality	N	Osmium ngm/litre	σ	Sources	$\frac{Os}{Re}$
I. WATERS											
Surface	North Pacific	12	8.4	1.19	af			-			-
Profile samples to 1250 metres	Atlantic	6	5.8	1.40	ag, ah			-			-
Profile samples to 1000 metres	Arctic Waters	3	3.2	0.50	ah			-			-
II. SEDIMENTS			ppb					ppb			
Deep sea	Atlantic	9	3.7	1.72	ah	Pacific	13	0.17	0.11	aj	-

Source: af = Scadden (1969)
ag = Matthews and Riley (1970)
ah = Olafsson and Riley (1972)
aj = Barker and Anders (1968)

Notable advances in the knowledge of platinum metal deposits have been made recently and are summarized by Stumpfl (1974). These developments have resulted largely from progress in the mineralogy of the platinum group metals, and from the application of electron microprobe and neutron activation methods to the study of platinum metal deposits. However, the relative distribution of osmium between the various mineral components of ore deposits is still not well known.

In igneous rocks, concentrations of the platinum group elements may be sufficiently high as to constitute ores in their own right , as in the case of the deposits of the Bushveld Igneous Complex, South Africa, or they may be present in lower concentrations associated with copper-nickel sulphides and recovered as byproducts as, for example, at Sudbury and at Noril'sk, in the U.S.S.R.

Primary platinum deposits fall into two main classes, those associated with chromite-bearing mafic and ultramafic rocks, and those associated with copper nickel sulphide ores in gabbroic rocks. The deposits affiliated with chromite-bearing rocks are further classified according to those associated with large, layered intrusions (for example, the Bushveld Igneous Complex and the Stillwater Complex, Montana), or those in podiform ultramafic rocks situated in orogenic belts (for example the Nizhniy-Tagilsk deposit in the Urals).

The most important primary source of platinum metals are the deposits associated with the layered intrusions exemplified by the Bushveld Igneous Complex. Here the platinum areas occur in the Merensky Reef, a pegmatitic pyroxenite bounded by two thin chromite seams, situated at the top of the Critical Zone. The platinum group metals are associated with nickel, copper, iron sulphides spatially associated with the chromite seams, and occur as native alloys and as compounds of platinum and palladium with arsenic, antimony, bismuth and tellurium (Stumpfl, 1974). Platinum metal values are also found in sulphides, but the relative distribution of the platinum metal group between the various minerals is not yet known. The average tenor of the total platinum group metals in the Merensky Reef is 4 to 8 ppm (Stumpfl, 1974). High iridium values in these ores and the widespread geochemical coherence between osmium and iridium suggests that a similar enrichment may be expected for osmium in these sulphides. A preliminary study of chromites in the Upper Critical Zone below the Merensky Reef has revealed high osmium values ranging from 50 to 114 ppb, with an average of 90 ppb osmium (Gijbels *et al.*, 1974).

Three platinum-bearing dunite pipes occur in the eastern part of the Bushveld Igneous Complex. Two of these pipes, Onverwacht and Mooihoek, are characterized by iron-rich hortonolite cores which are notably enriched in platinum metal values. The role of magmatically derived fluids in the formation of these deposits, indicated by phlogopite, hornblende and fluorapatite associated with the hortonolite dunite, is generally accepted (Crocket, 1969; Stumpfl, 1974), and is emphasized by the even distribution of platinum values in the third pipe, Driekop, which is relatively unzoned petrologically. The platinum group mineral assemblage of these pipes is notably different from that of the Merensky Reef and consists of iron-bearing platinum and a complex association of sulpharsenides, arsenates and antimonide platinoid minerals (Stumpfl, 1974). Osmium is present as laurite, osmiridium and iridosmine (Crocket, 1969) and irarsite (Cabri, 1972).

In the Stillwater Complex, platinum group minerals are associated with nickel, copper and iron sulphides in chromite-rich zones of the peridotite member. The platinum minerals present include merenskyite ($PdTe_2$) and kotulskite (PdTe), as well as iron-bearing platinum, cooperite and the osmium-bearing mineral laurite (Stumpfl, 1974).

The association of the platinum metals with chromite in the "alpine" ultramafics is best illustrated by the deposits of the Ural Mountains, where osmiridium-bearing platinum placers have been noted in ten districts (Quiring, 1962). In the Nizhniy-Tagilsk district, which is typical of the rest, the platinum placers are derived from a body comprised essentially of serpentinized dunite and pyroxenite. The platinum group metals occur in the dunite in irregular masses of chromite of pegmatitic and hydrothermal origin (Mertie, 1969).

In the Inaglinsk deposit, which is of the Urals type (Razin *et al.*, 1965), platinum metal values are associated with a concentrically-zoned pipe-like intrusion comprised of a dunite core surrounded by a suite of alkali-rich rocks. The platinoid minerals are concentrated in the dunite and include ~~native~~ alloys, sperrylite and cooperite. Osmium is present as iridosmine.

The only platinoid minerals identified to date in the pyrrhotite-pentlandite-chalcopyrite ores of Sudbury are compounds of either platinum or palladium with arsenic, antimony, bismuth and tellurium. Niggliite (Pt Sn) has also been tentatively identified by Cabri and LaFlamme (1974). At the Strathcona Mine, osmium values range from 0.68 to 68 ppb. Further, osmium is closely associated with ruthenium and iridium, and is slightly concentrated in pyrrhotite relative to coexisting chalcopyrite (Keays and Crocket, 1970).

In placer deposits, osmium is commonly in the form of osmiridium but is now also known to persist as the sulphide and sulpharsenide forms (Stumpfl, 1974).

2. Extraterrestrial

The published data on rhenium and osmium abundances in meteorites and lunar materials have been summarized and are presented in Tables 5-14 and 5-15. The average class values for rhenium in chondrites and achondrites agree closely with the values of Morris and Short (1969). However, the average for rhenium in irons cited by these authors and which is based on values in two papers, is about 25 percent higher than the corresponding value in Table 5-14. This table illustrates the strong depletion of rhenium and osmium in chondrites and achondrites relative to irons. The lack of fractionation between rhenium and osmium is shown by the similarity of osmium:rhenium ratios for the different classes of chondrites. The Os:Re ratio of 13.0 for achondrites is considerably lower than the value of 19.8 obtained by Morgan and Lovering (1964) for an enstatite achondrite. However, Krahenbuhl et al. (1973) have recently demonstrated that carbonaceous chondrites are more homogeneous than formerly thought, and further adjustments to the Os:Re ratios of chondrites will undoubtedly result from additional analytical data and with the refinement of procedures. With the exception of the nickel-rich and nickel-poor ataxites, the iron meteorites show very consistent Os:Re ratios. The variation between the ataxites is probably a sampling bias.

Table 5-14

Rhenium and Osmium Abundances in Meteorites

	Rhenium				Osmium				
Type	N	$\frac{gm}{gm} \times 10^{-9}$	σ	Source(s)	N	$\frac{gm}{gm} \times 10^{-9}$	σ	Source(s)	$\frac{Os}{Re}$
I. Chondrites									
(i) H-type	15	69.9	16.8	u*, v, x, *am	4	789	88.6	b, v	11.3
(ii) L-type	11	42.8	19.7	v, x, *am	2	568	311	b, w*	13.3
Carbonaceous	20	40.0	8.95	v, x, z, al, *am	4	571	141	b, v	14.3
Average Values	46	51.1	195		10	657	181		12.8
II. Achondrites		71		u*		-			
	12	0.22	0.34	ak	11	2.87	4.94	ak	13.0
		$\frac{gm}{gm} \times 10^{-6}$				$\frac{gm}{gm} \times 10^{-6}$			
III. Irons									
(i) Hexahedrites	14	0.97	1.57	aa, ab, y	14	9.92	19.10	aa, ab, y	10.4
(ii) Octahedrites	111	0.30	0.33	aa, ab, ac, y	95	3.20	4.86	aa, ab, y	10.6
(iii) Ni-rich ataxites	6	1.45	1.29	ab, y	6	19.5	17.6	ab, y	13.4
(iv) Ni-poor ataxites	6	0.17	0.27	ab, y	6	1.34	1.95	ab, y	7.9
Average Values	137	0.43	0.70		121	4.70	9.3		10.9

Source:

u = Perzehogin (1965) cited in Morris and Short (1969)
v = Morgan and Lovering (1964)
w = Vinogradov et al. (1972)
x = Fouché and Smales (1967)
y = Crocket et al. (1974)
z = Keays et al. (1974)
aa = Herr et al. (1960)
ab = Herr et al. (1961)
ac = Goldberg and Brown (1950)
ak = Morgan (1965b) cited in Lovering and Butterfield (1970)
al = Krahenbuhl et al. (1973)
am = Case et al. (1973)
* = Values not included.

Table 5-15

Some Rhenium and Osmium Abundances of Lunar Materials

Sample Type	Sample Number	N	Rhenium $\frac{gm}{gm} \times 10^{-10}$	σ	N	Osmium $\frac{gm}{gm} \times 10^{-10}$	σ	Source	$\frac{Os}{Re}$
I Breccia	Luna 20		10.5					ap	
	14305 BDI interior		6.2					ad	
	14305 AEI surface		8.34					ad	
	14321 b		0.21					ad	
	c		0.37					ad	
	10019,12		7.3			78		t	
	10046,20		6.7			76		t	
	10084,53		8.5			81		t	
	Average Values	8	7.8	0.10	3	78	2.52		10
II Soils	14163		13.16					ad,	
	1416,57		10					z	
	14259		14.1					ad	
			11.6					ad	
	10084.49		7.1					z	
	Average Values	5	11.2	2.7	-	-			—
III Rocks	12021		0.78					ad,	
			0.77					ad	
	12053		0.33					ad	
	15401,26		0.30					ad	
			0.26						
	Average Values	5	0.50	0.26	-	-		ae*	-
	Pristine Highlands								
	Anorthosites		0.085	-		-		az	
	Norites		0.47	-		-			

Source: t = Lovering and Hughes (1971); z = Keays et al. (1974); ad = Michel et al. (1972); ae = Lovering and Butterfield (1970); ap = Morgan et al. (1973); az = Ganapathy et al. (1973); * = values omitted.

In addition to abundance determinations of rhenium in lunar materials, recent interest has also been focussed on anomalies in the isotopic composition of rhenium as a result of bombardment of the lunar surface by epithermal neutrons (Michel et al., 1972). Table 5-15 illustrates the enrichment of rhenium in lunar soils with respect to lunar rocks as a result of meteoric contamination. The abundance of rhenium in lunar rocks is similar to the abundance of rhenium in achondrites and some terrestrial ultramafic rocks (see Tables 5-9, 5-10 and 5-15).

CHAPTER 6

DISCUSSION OF THE MAIN DEPOSITS SAMPLED AND ANALYTICAL RESULTS

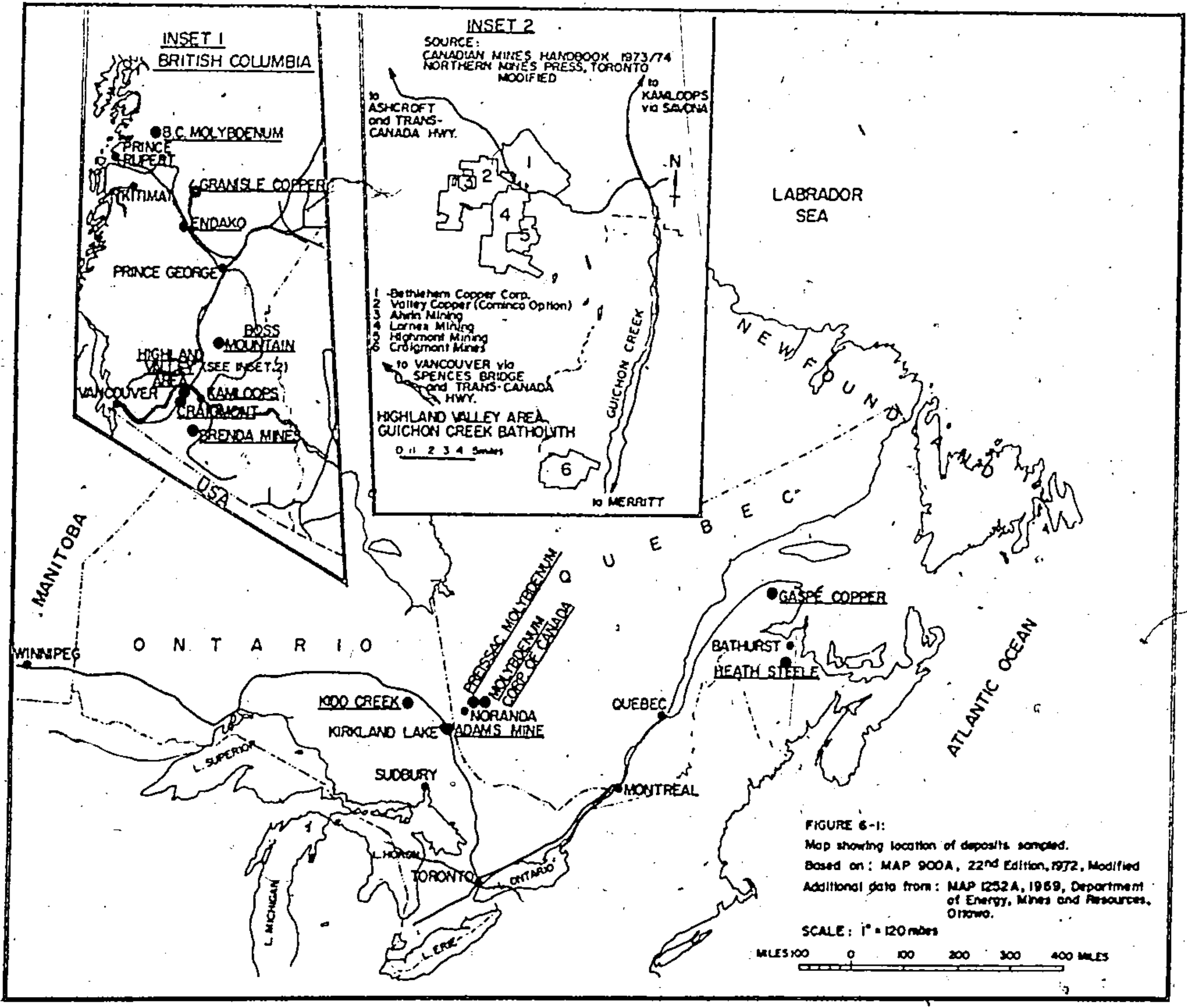
STRATHCONA MINE

At Strathcona Mine, situated near Sudbury (Figure 6-1), recoverable quantities of the platinum group metals are associated with nickel-copper ores which are spatially and genetically related to the Sudbury Nickel Irruptive. The Irruptive is composed essentially of granophyre overlying norite and a discontinuous ore-bearing unit called the sub-layer (Souch et al., 1969). The Irruptive, together with the overlying stratified rocks, form the Sudbury Basin. The regional setting of the Sudbury Basin is discussed by Card and Hutchinson (1972), and the chronology of the metamorphic history of the area has been dealt with by Gibbins and McNutt (1975). Sub-layer breccias which host many of the Ni-Cu ores of the area have been described by Naldrett et al. (1972).

FIGURE 6-1: MAP SHOWING LOCATION OF DEPOSITS SAMPLED

Based on: Map 900A, 22nd Edition, 1972, Modified

Additional data from: Map 1252A, 1969, Department of Energy, Mines and Resources, Ottawa.



SOURCE:
CANADIAN MINES HANDBOOK 1973/74
NORTHERN MINES PRESS, TORONTO
MODIFIED

FIGURE 6-1:
Map showing location of deposits sampled.
Based on: MAP 900A, 22nd Edition, 1972, Modified
Additional data from: MAP 1252A, 1969, Department of Energy, Mines and Resources, Ottawa.
SCALE: 1" = 120 miles

The ores at Strathcona have been described by Cowan (1968). The principal metallic minerals of these magmatic ores are pyrrhotite, magnetite, pentlandite, chalcopyrite and pyrite (Naldrett and Kullerud, 1967). The parageneses of these minerals are now well known and have been thoroughly discussed by Naldrett and Kullerud (1967) on the basis of experimental work by Kullerud (1963, 1967) and Craig and Kullerud (1967).

Platinum group metals are distributed in the Sudbury ores in two main forms: (1) as discrete minerals and (2) as minor constituents in metallic minerals.

(1) The occurrence of discrete platinum-group minerals such as sperrylite, michenerite and froodite in the Sudbury ores is well established (Hawley, 1962), and recently, platinum and palladium minerals of As, Bi, Sb, Sn and Te have also been identified in these ores (Cabri and LaFlamme, 1974). No osmium minerals have been reported to date either in the Sudbury ores in general, or in the particular case of the Strathcona ores. Therefore, the most important mode of occurrence of osmium in the Sudbury ores is as an impurity in the metallic minerals.

(2) The distribution of the platinum group elements in Strathcona ore minerals is influenced by two main controls. First, by fractionation between ore minerals at high temperatures. Second, by partitioning between metallic minerals at sub-solidus temperatures. In addition to these primary controls, distribution of the platinum metals at Strathcona has also been affected by the more complex history of the lower two ore zones.

The first minerals to crystallise from the sulphide melt at Strathcona were Fe-monosulphide (pyrrhotite) solid solution and magnetite. These minerals persisted until at least 700 °C (Naldrett and Kullerud, 1967). The initial distribution of the platinum group metals at sub-liquidus temperatures is therefore controlled by this high temperature event. Chyi (1972) dealt with the distribution of platinum, palladium and iridium in the Strathcona ores under these conditions. He found iridium to be concentrated in pyrrhotite relative to magnetite by a factor of 2 in the Deep Ore Zone. Osmium, by virtue of its coherence with iridium, may likewise be expected to concentrate in pyrrhotite relative to magnetite. This contention is supported by the concentration of osmium in high temperature pyrrhotites noted by Keays and Crocket (1970) during their study of precious metals in Sudbury ores.

Sub-solidus distribution of the platinum metals in these ores is controlled mainly by exsolution processes. Pyrite exsolves from hexagonal pyrrhotite solid solution below 700°C, followed by chalcopyrite below 450°C and pentlandite below 300°C (Naldrett and Kullerud, 1967). The osmium content of Strathcona pyrites is not known. In their study of the Sudbury ores, including Strathcona, Keays and Crocket (1970) found a general lack of fractionation of osmium between pyrrhotite and chalcopyrite. This they interpreted as being a consequence of osmium in solid solution in high temperature pyrrhotite. Chyi (1972) found iridium in the Deep Ore Zone at Strathcona to be enriched in chalcopyrite relative to pentlandite, magnetite and pyrrhotite by factors of 3.5, 5.7 and 5.3 respectively.

There is no published information concerning rhenium in the Sudbury ores. The samples analysed include massive sulphides, chalcopyrite and pyrrhotite separates from the Deep Ore Zone, and massive pyritic banded ore from the footwall of the Main Ore Zone. The analytical results are given in Table 6-1.

Table 6-1

Analytical Results: Strathcona Mine

Material* Sample No.	Rhenium (ppb)	Osmium (ppb)	$\frac{\text{Os}}{\text{Re}}$
Pyrrhotite(DIC)**	24.7 26.4 Av. 25.6±0.9 ppb	3.06	0.12
Chalcopyrite (DIC)	17.0 19.0 Av. 18.0±1.0 ppb	6.15	0.34
Massive Banded Sulphides (Main Zone: 1875 Level)	251 260 Av. 255±5 ppb	34.7	0.13
Massive Sulphides (Deep Zone: 2625 Level)	29.9	N.S.***	-

* For sample descriptions, see Appendix C.

** DI refers to the stope from which the sample was collected (see Figure 6-2). The letter C indicates a particular sample from this stope.

*** N.S. Not sought.

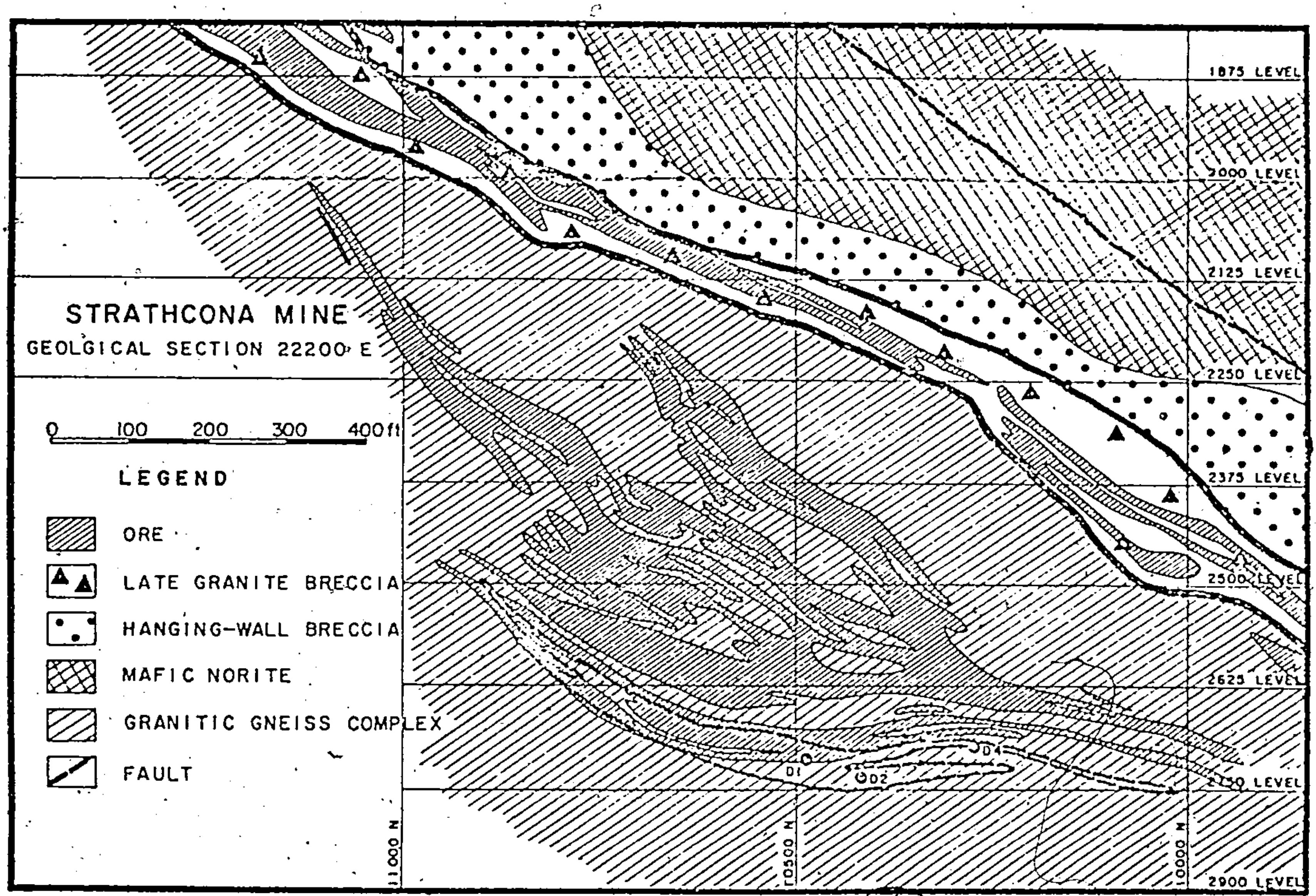


FIGURE 6-2: STRATHCONA MINE, GEOLOGICAL SECTION SHOWING LOCATION OF D1 STOPE.

HEATH STEELE MINE

The orebodies of Heath Steele Mine are characteristic of a group of volcanogenic, stratiform, massive sulphide deposits which occur in the vicinity of Newcastle, near Bathurst, New Brunswick (see Figure 6-1). Ore deposits of this class are world-wide in their distribution and occur through a wide range of geologic time. In the Bathurst-Newcastle area, they are associated with felsic rocks in a volcanic complex of Ordovician Age (Helmstaedt, 1971).

The geology of the Heath Steele Mine has been described by McFarlane and Gates (1966). The samples analysed are from the B-1 orezone. The orebody exhibits metal zoning and macroscopic banding and is comprised essentially of very fine-grained sulphides in two distinct assemblages (i) pyrrhotite-chalcopyrite, (ii) pyrite-galena-sphalerite. The footwall of the orebody is copper-rich and the hanging wall is rich in lead and zinc. The textures of the ore minerals have been discussed by Stanton (1960) and Roy (1961). The only previous work dealing with platinum group metals of Heath Steele is a study by Mercer and Crocket (1972) concerned with the distribution of palladium and gold in the B-1 orebody and its wallrocks.

The locations of the samples analysed in this work are shown in Figure 6-3 and the analytical results are shown in Table 6-2.

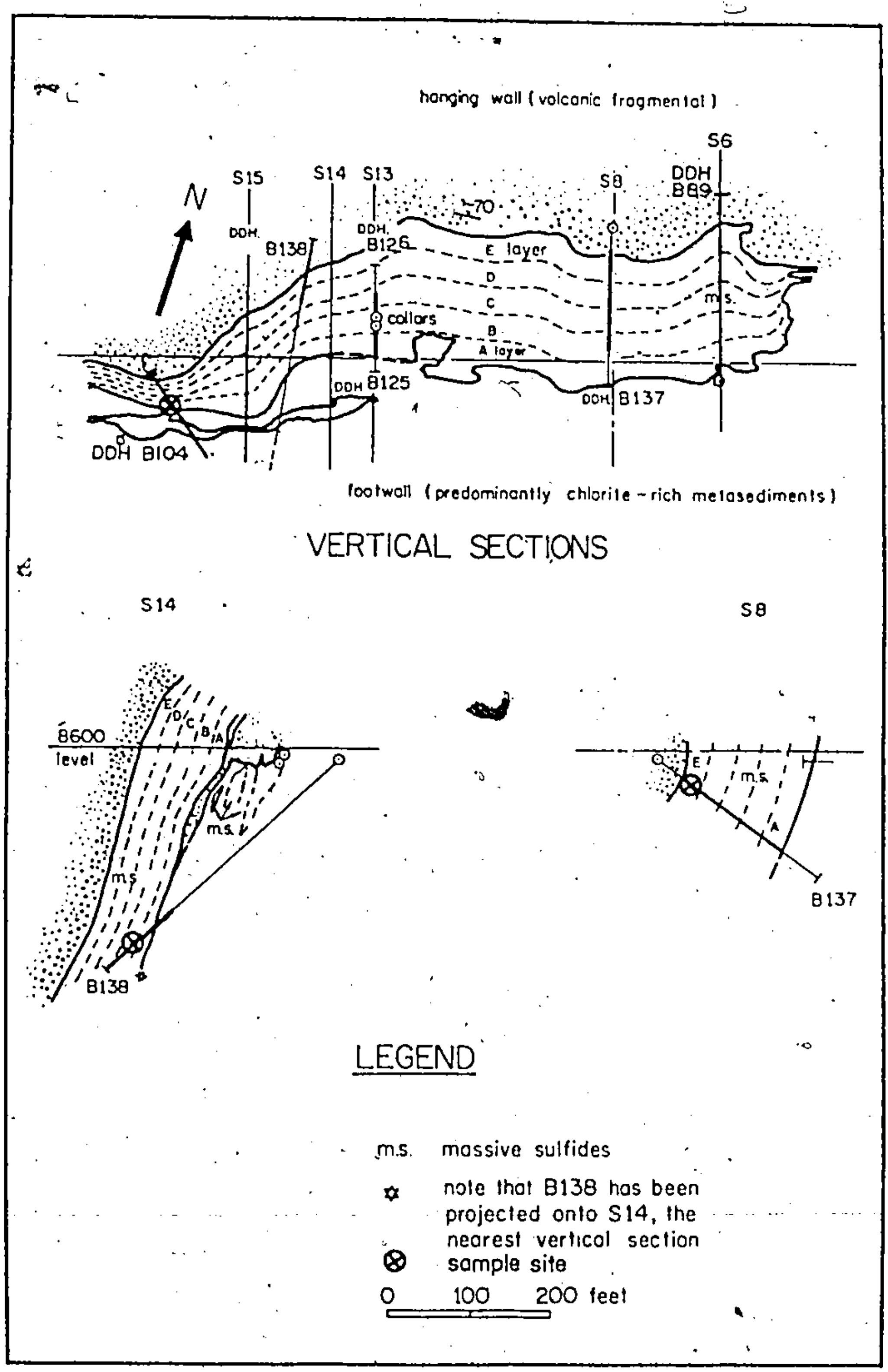


FIGURE 6-3: HEATH STEELE, GEOLOGY and SAMPLE SITES

Table 6-2

Analytical Results: Heath Steele Mine

Material* (Sample No.)	Rhenium (ppb)	Osmium (ppb)	Os/Re
Massive sulphides (No. A4049)	3.83 3.54 Av 3.68±0.14 ppb	0.05 (Max.)	≤ 0.01
Massive sulphides (No. A4093)	0.75	0.07 (Max.) 0.17 (Max.)	≲ 0.16
Sphalerite (No. B89-3)	0.20	0.03 (Max.) 0.03 (Max.)	≤ 0.15
Chalcopyrite (No. B104-5-1)	3.00	0.04 (Max.)	≤ 0.01

* For sample descriptions see Appendix C.

ADAMS MINE (BOSTON IRON FORMATION)

1. Location and Regional Geology

The Adams Mine is located at the eastern margin of the Boston Iron Formation about 7-1/2 miles southeast of Kirkland Lake, Ontario (see Figure 6-1). The Kirkland Lake area is situated at the southwestern extremity of the Abitibi greenstone belt. All exposed bedrock in the area is of Archean Age.

In the vicinity of Kirkland Lake the greenstone belt is composed of a Keewatin "volcanic" assemblage overlain by a Timiskaming "sedimentary" assemblage which is intruded by granites, batholiths and syenite stocks and appears to represent the central sediment of an Archean volcano-tectonic basin (Pyc et al., 1972). An alkaline volcanic suite within the Timiskaming assemblage (Ridler, 1970) is notable for its high potassium content (Cooke and Moorehouse, 1969) and is associated with the Boston Iron Formation. Ridler (1970) has characterized the Archean stratigraphy in this area by three sequential volcanic cycles trending from an older sub-alkalic and saturated suite (tholeiites, andesites, and dacites) to a hyperalkaline undersaturated suite (alkaline trachytes, feldspathoidal lavas, and syenites). He assigns the Boston Iron Formation to the upper portion of the second volcanic cycle, and a Timiskaming Age.

Whole rock ages by the Rb-Sr isochron method indicate absolute ages of 2358 my and 2508 my for the Timiskaming and Keewatin volcanics respectively (Fairbairn et al., 1965).

2. Local Geology

The Adams Mine is situated at the eastern extremity of the Boston Iron Range which is about six miles long with a width of 3,000 to 4,000 feet. The iron range is arc-shaped and conforms approximately with the boundary of a syenite stock immediately to the north. In the vicinity of the Adams Mine it is composed essentially of iron formation, cherty quartzites, and volcanic rocks, mainly trachybasalts. At least three major iron-bearing horizons have been recognized in the eastern portion of the range (Dubuc, 1965). Locally, these iron-rich units merge, but generally they are separated by the basic lava flows. These flows occupy increasingly larger volumes of the stratigraphic column as one proceeds in a westerly direction, until in the western portions the basin of deposition is occupied almost entirely by volcanic rocks.

The iron deposits are typical of the "Algoma-type" iron-formation and are comprised essentially of well defined, alternating thin bands of chert and magnetite and are generally 100 to 150 feet thick, though they may be thicker as a result of deformation. Locally, jasper, specular hematite, and pods of chlorite with or without magnetite and containing small quantities of pyrite are important.

The locations of the mine and of the samples analyzed are given in Figures 6-4 and 6-5. Analytical results are presented in Table 6-3.

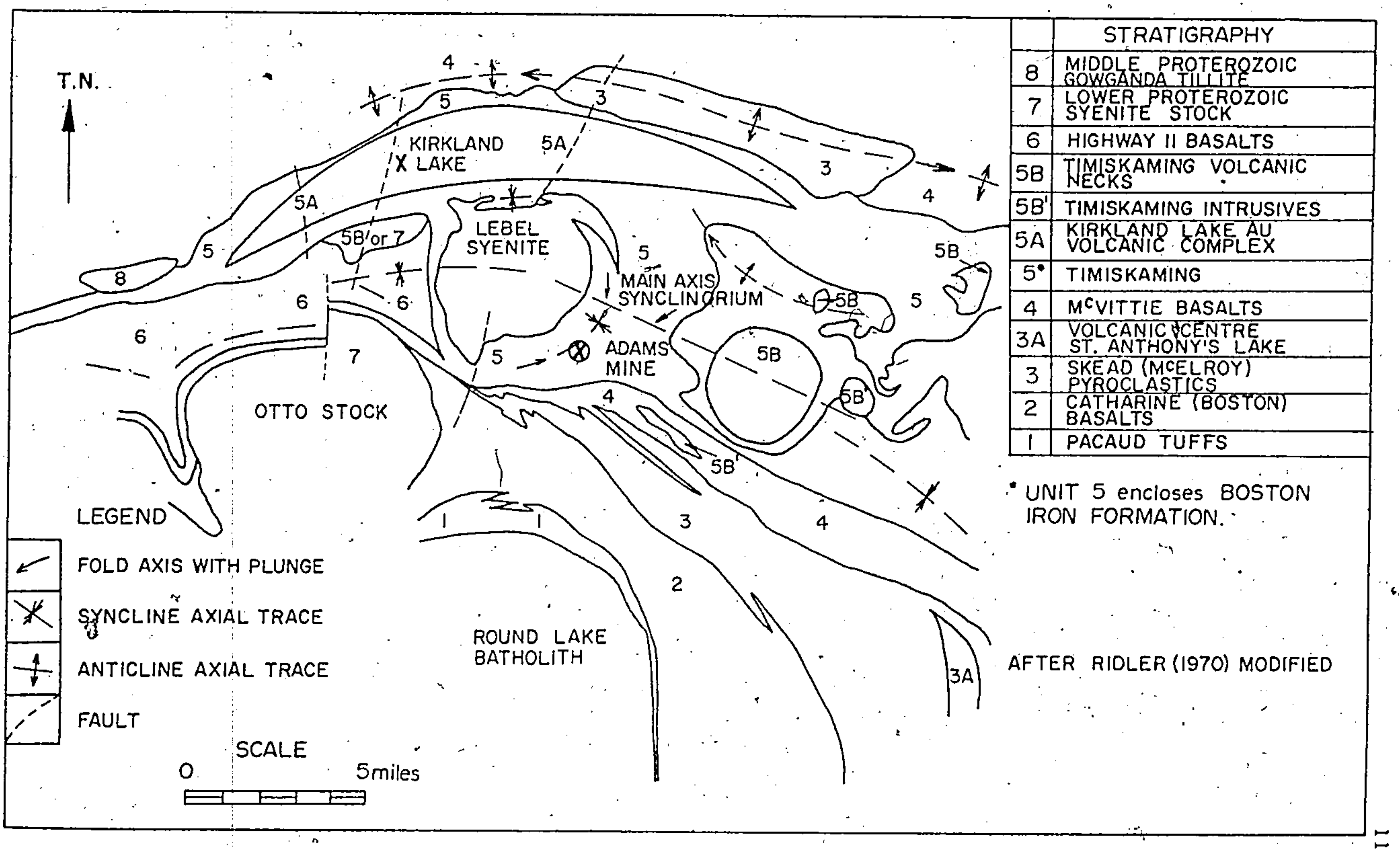
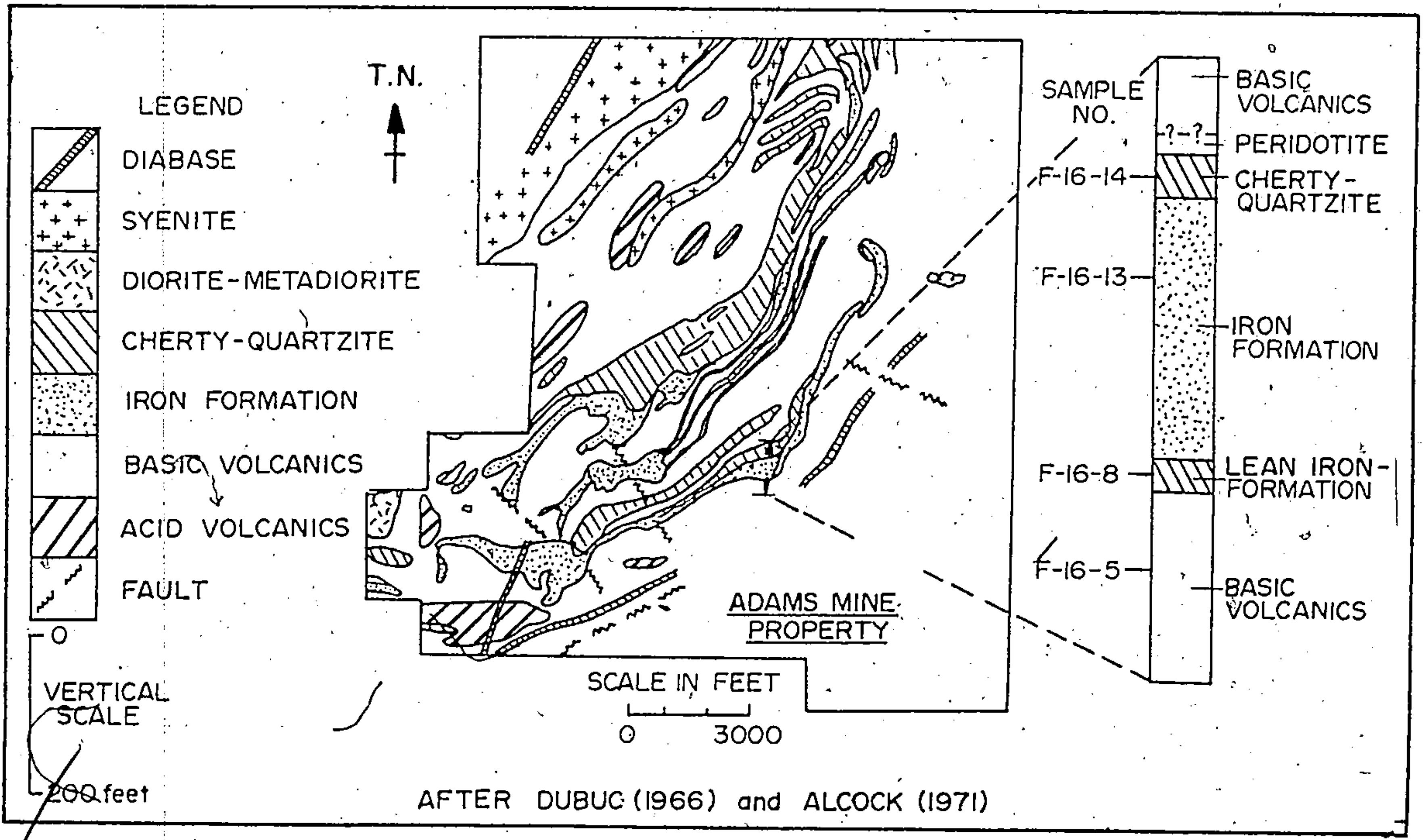


FIGURE 6-4 : Map showing regional geology of the ADAMS MINE.



AFTER DUBUC (1966) and ALCOCK (1971)

FIGURE 6-5: Geology of the ADAMS MINE.

Table 6-3

Analytical Results: Adams Mine

Material* (Sample No.)	Rhenium (ppb)	Osmium (ppb)	$\frac{Os}{Re}$
Banded Iron Formation (F-16-13)	N.S.**	3.04 3.35 3.20±0.15 ppb	
Magnetite (F-16-13)	0.21 0.17 0.41 0.40 0.30+0.13 ppb	1.76 3.31 2.53±0.78 ppb	8.43
Pyrite	2.10 2.08 2.09±0.01 ppb	0.16 0.11 0.13±0.03 ppb	0.06
Basalt (F-16-5)	N.S.**	0.14 0.13 0.13_5±0.00_5 ppb	
Lean Iron Formation (F-16-8)	N.S.	0.02 0.06 0.04±0.02 ppb	
Cherty Quartzite (F-16-14)	N.S.	0.03 0.06 0.05±0.02 ppb	

* Sample descriptions in Appendix C

** Not sought.

GUICHON CREEK BATHOLITH

1. General Statement

The Guichon Creek Batholith is located in the southern portion of the Intermontane Belt of the Canadian Cordillera and is known for its associated copper deposits. These deposits include the porphyry copper and high grade vein deposits of the Highland Valley area in the northern part of the batholith, and the contact metasomatic deposit at Craigmont Mines located on the southern margin of the batholith (see Figure 6-1). Molybdenites from the Guichon Batholith were analyzed from Bethlehem Copper, Highmont, Lornex, and Valley Copper. Additional metallic minerals were also analyzed from Alwin Mining, Bethlehem Copper, and Craigmont Mines.

2. Regional Geology

The Guichon Creek Batholith is an elongate, composite, semiconcordant, pluton which intrudes sedimentary and volcanic rocks of Permian Age (Cache Creek Group) and Upper Triassic Age (Nicola Group). Aeger et al. (1972) have discussed the results of a preliminary gravimetric survey over the batholith, and the geology of the batholith has been dealt with by McMillan (1972).

Petrologically, the batholith is composed of a series of nearly concentric phases which grade from older and more mafic at the margins, to younger and more felsic at the core. From margin to core these phases are: The Hybrid (Border) Phase (predominantly quartz diorite), the Highland Valley and Bethlehem Phases (granodiorites) and the Bethsaida Phase (quartz monzonite). Breccia pipes near the contacts of the inner three phases are closely associated with small granitic masses, and are indicative of sub-volcanic explosions during the final stages of crystallisation of the batholith (Carr, 1967 and Northcote, 1969). Deuteric alteration is widespread throughout the batholith.

Radiometric dating of biotites and hornblendes in the constituent phases of the batholith by the K/Ar method gave an average age of 200±5 my (White et al., 1967). K/Ar dating of biotites from these phases gave an average age of 198±8 my (Northcote, 1969). There is no difference between the radiometric ages of the petrological phases of the batholith.

3. Ore Deposits

Copper is widespread throughout the batholith. It occurs as chalcopyrite and bornite in accessory amounts in large volumes of the older phases of the batholith and is sufficiently concentrated in the younger phases to constitute numerous metallic deposits, some of which are currently viable. The copper deposits within the batholith are of two types; high grade small tonnage vein deposits such as those found at Alwin Mines, and the porphyry copper deposits of the Highland Valley area, e.g. Bethlehem Copper Corp., Highmont, Lornex and Valley Copper. All the porphyry copper deposits occur near the northern part of the core of the batholith associated with the contacts of either the Guichon and Bethlehem or the Bethlehem and Bethsaida Phases. The ores are further characterised by their association with major faults, for example, Valley Copper, Lornex, and the J.A. Zone of Bethlehem Copper (see Figure 6-6), and by their association with breccia pipes, as at Bethlehem and Highmont. The main metallic minerals of the porphyry copper deposits are chalcopyrite, bornite and pyrite. Molybdenite is recovered where it occurs in sufficient quantity, for example, at Lornex. The ores are associated with widespread hydrothermal alteration (McMillan, 1972), and are considered to constitute part of the late stages of crystallisation of the batholith because of their close affiliation with the younger phases.

The high grade (2.5%) copper deposit at Alwin is localized in the Bethsaida phase and is associated with a weakly mineralized quartz plagioclase porphyry. The deposit is composed of sharp-walled veins of bornite, chalcopyrite and locally primary chalcocite, which occur along permeable fault zones up to 30 feet wide. The gangue minerals

FIGURE 6-6: GEOLOGY OF THE GUICHON CREEK BATHOLITH

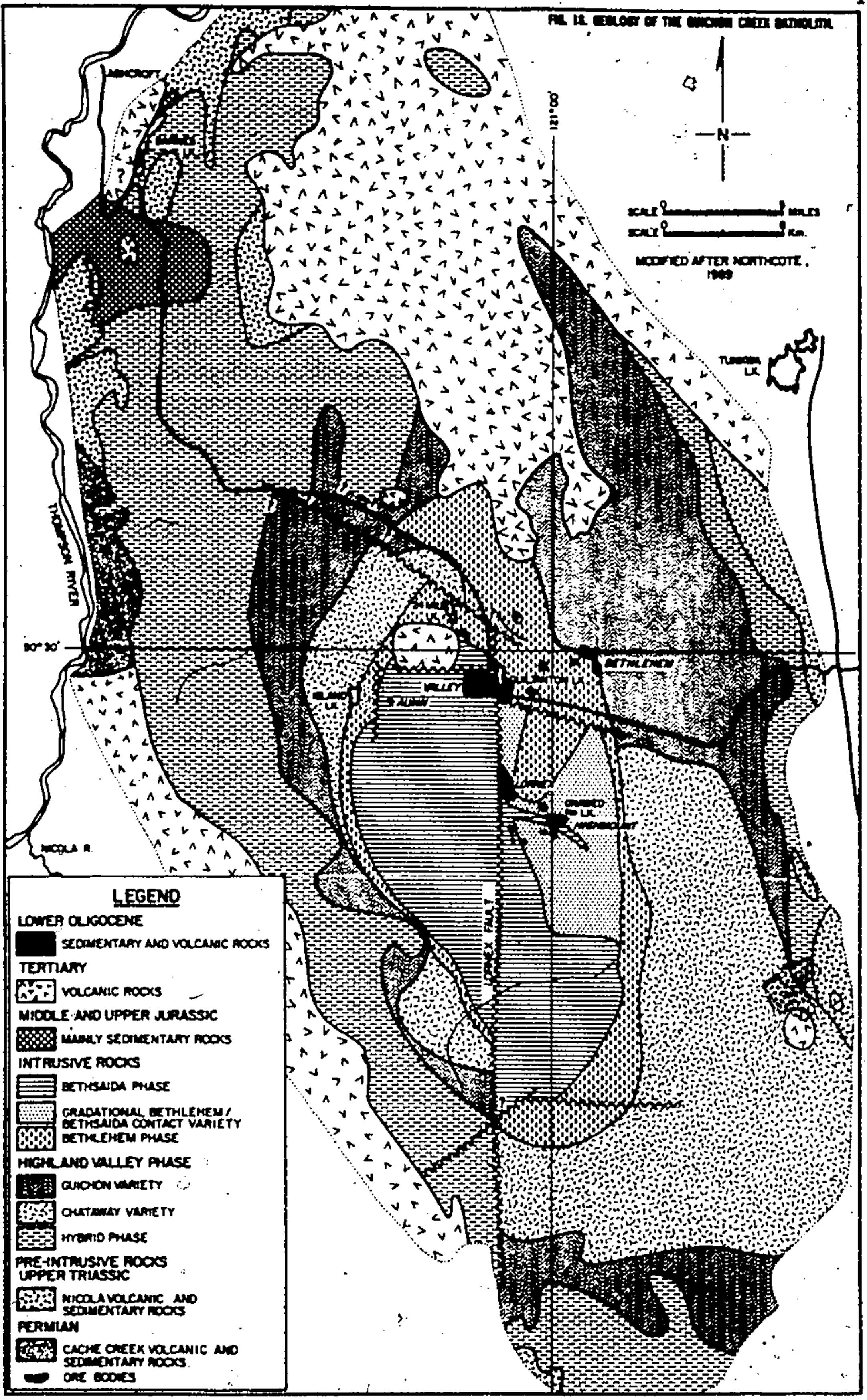


FIG. 13. GEOLOGY OF THE GUICHON CREEK BATHOLITH

MODIFIED AFTER NORTHCOTE, 1969

within the veins are mainly quartz and sericite and lesser quantities of feldspar, calcite, chlorite, hematite and clay minerals. The country rock adjacent to the veins has been only slightly altered.

Rhenium and osmium abundances in hypogene sulphides from the central portions of the Guichon Batholith, were determined in primary copper minerals from Alwin Mining (chalcopyrite) and Bethlehem Copper Corporation (bornite) and in molybdenites from Lornex, Highmont, and Valley Copper. The results are given in Table 6-4.

The property of Bethlehem Copper Corporation straddles the contact between the Bethlehem and Guichon Quartz diorites and contains five separate but closely associated orebodies including the Jersey Zone, the deposit analyzed in this work. Molybdenites were also analyzed from the J.A. Zone, located in the Highland Valley proper on the Bethlehem property.

The contact zone between the Bethlehem and Guichon quartz-diorites in the vicinity of the Jersey pit is very complex. The ore is typical of the porphyry copper deposits in this area and is composed essentially of chalcopyrite and bornite localized mainly in structurally controlled sites. Molybdenite is associated with chalcopyrite. Biotite and tourmaline, and hematite are present in small quantities.

Table 6-4

Analytical Results: Central Guichon Batholith

Material Sample Location	Rhenium (ppb)	Osmium (ppb)	$\frac{\text{Os}}{\text{Re}}$
CHALCOPYRITE Alwin	1.95	0.19	0.10
BORNITE Bethlehem	0.76	0.07 0.05 Av. 0.06±0.01 ppb	0.08
	(ppm)	(ppb)	
MOLYBDENITES* Lornex (L-1)	257	0.08 (Max.)	3.1×10^{-7}
Highmont (H/S)	95.7	0.14	1.5×10^{-6}
Valley Copper (H/S)	288 297 Av. 293±5 ppm	0.19	6.5×10^{-7}
Bethlehem Copper No. B-1	1171 1153 1162±9 ppm	N.S.	-
No. B-3	335 340 338±2.5 ppm	N.S.	-
J.A. Zone No. 2	222 200 211±11 ppm	N.S.	-
No. 3	246 221 234±13 ppm	N.S.	-

* MoS_2 concentrates unless otherwise specified.

H/S: Hand specimen

N.S.: Not sought

Sample Descriptions in Appendix C.

Three zones of hydrothermal alteration are associated with the Jersey orebody; a central argillic assemblage consisting of chlorite, sericite and clay, an epidote-bearing zone, and a poorly defined pyrite halo. At Valley Copper argillic and phyllic alteration is well developed, whereas at Lornex and the J.A. Zone, prophylitic alteration is better developed. The hydrothermal alteration associated with the porphyry copper deposits of the area has been discussed by Lowell and Guilbert (1970) and by Rowe (1973).

CRAIGMONT MINE

The contact metasomatic copper deposits at Craigmont Mine occur in a geologically complex area near the south contact of the Guichon Batholith (see Figure 6-1). The ore is localized in an altered impure limestone unit within the Nicola Group (Upper Triassic). In the mine area the Nicola Group is comprised of tuffs, greywacke, limestone, and argillite (Rennie et al., 1960).

The ore occurs as five ore zones in a copper, magnesium, iron, and silica-rich skarn associated with an anticline. Chalcopyrite is the only ore mineral in these massive pyrometasomatic replacement deposits, and was introduced in two main stages: the first, in which it is associated with magnetite, and the second in which it accompanies hematite. Magnetite and hematite account for about 25%, by weight, of the orebody. Other metallic minerals associated with the ore include pyrite, pyrrhotite and bornite.

The locations of the samples are not accurately known because they were, of necessity, collected from dump material. The results of samples analysed from Craigmont are presented in Table 6-5.

Table 6-5

Analytical Results: Craigmont Mine

Material	Rhenium (ppb)	Osmium (ppb)	Os/Re
Pyrite	37.4 37.3 Av. 37.4±0.1 ppb	0.10	0.003
Chalcopyrite	3.72	0.01	0.003
Magnetite	1.86 2.35 Av. 2.11±0.25 ppb	0.09	0.04

Sample descriptions in Appendix C.

GRANISLE COPPER MINE

1. Location and Regional Geology

Granisle Copper Mine is also situated in the Intermontane Belt of British Columbia and is located at the north end of Babine Lake

(Latitude 56°56.5'N, Longitude 125°00'W), 6.5 km. northeast of Smithers. The Granisle deposit is representative of several porphyry copper deposits which occur in the area. These deposits are associated with small Tertiary dykes and stocks of biotite-feldspar porphyry which are of quartz dioritic composition. The porphyries are associated with northwest-trending faults of regional extent and intrude Mesozoic volcanic and sedimentary rocks. The following summary of the geology of the mine area is based on papers by Fahrni (1967) and Carter (1965, 1972).

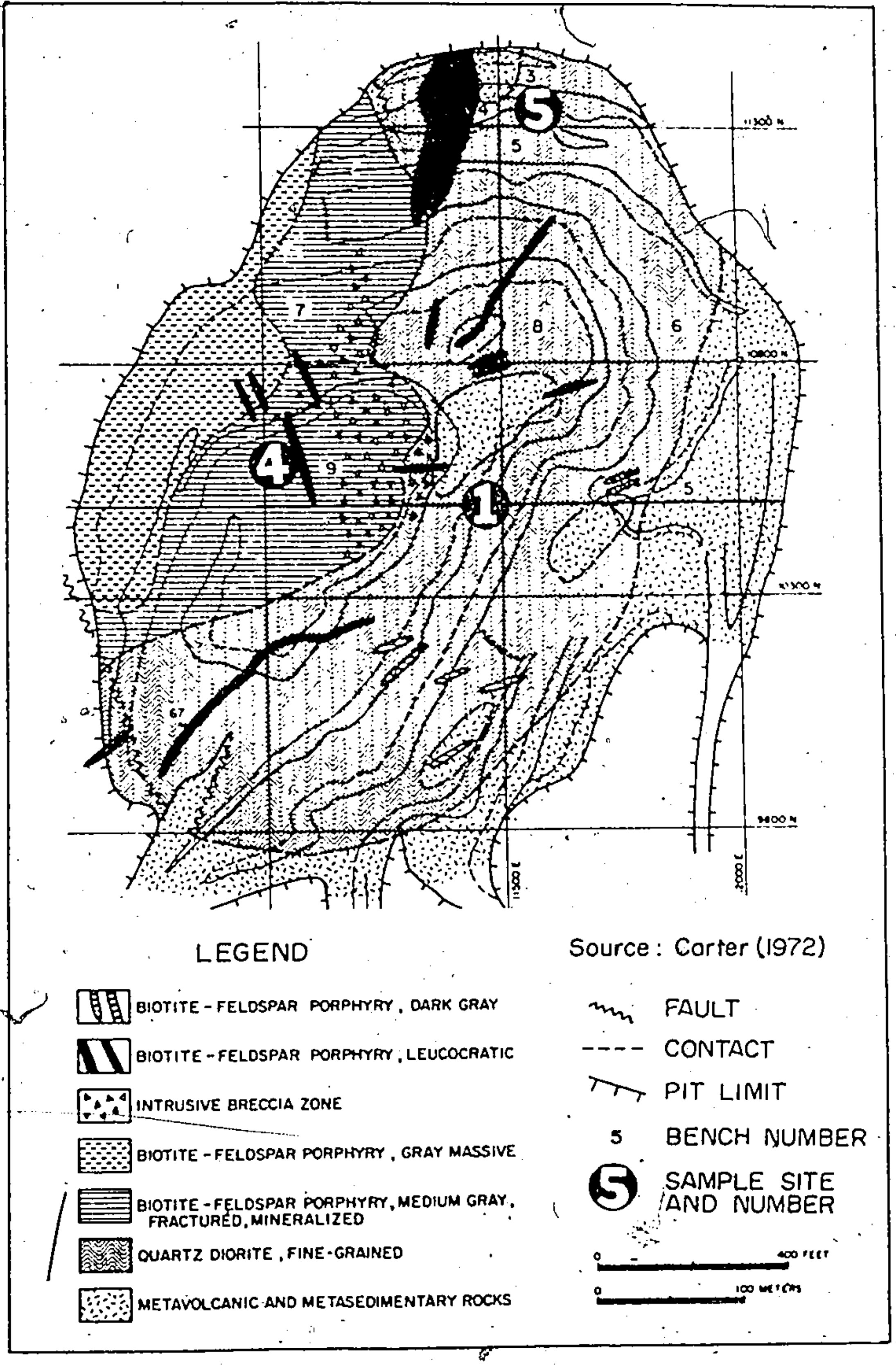
2. Local Geology

McDonald Island, upon which the mine is located, is underlain by rocks of the Hazelton Group (Lower Jurassic) comprised essentially of andesitic volcanic rocks and lesser quantities of sedimentary rocks. The copper mineralization is associated with a set of multiple-intruded porphyries. The most notable of these is a dyke of biotite-feldspar porphyry 120 to 200 metres wide which strikes north easterly across the island. K/Ar age determinations on four biotites within, and in close proximity to the orebody have a mean age of 51.2±2 my and indicate close time relationships between intrusive, hydrothermal and mineralizing activity (Carter, 1972).

3. Ore Deposit

The ore consists essentially of chalcopyrite, bornite and minor pyrite. Medium to coarse-grained chalcopyrite is the most common ore mineral. It generally occupies narrow quartz-filled fractures but also occurs as disseminations in quartz diorite and in metavolcanic and metasedimentary rocks. Bornite is most common in the southern part of the orebody and is associated with chalcopyrite and quartz in fractures. Magnetite and specular hematite are common in the northern part of the deposit. Drusy quartz veins thought to be later than the main mineralization contain some molybdenite. A zone of potassic alteration coincides approximately with the limits of the ore zone. The association between hydrothermal alteration and the porphyry copper deposits in the area has been discussed by Carson and Jambor (1974).

The location of samples analyzed is shown in Figure 6-7. The analytical results are given in Table 6-6.



Source: Carter (1972)

FIGURE 6-7 : Geology of GRANISLE COPPER MINE and sample sites.

Table 6-6

Analytical Results: Granisle Copper

Material (Sample No.)	Rhenium (ppb)	Osmium (ppb)	$\frac{\text{Os}}{\text{Re}}$
Chalcopyrite (No. 1)	0.91	0.08	
	1.31	0.04	
	1.00	0.07	
	Av. 1.08±0.23 ppb	Av. 0.06±0.02 ppb	0.06
Pyrite (No. 5)	0.57	0.014	
	0.38	0.016	
	Av. 0.47±0.09 ppb	0.095	
		Av. 0.042±0.053 ppb	0.09
Bornite (No. 4)	0.09	0.36	
	0.19	0.26	
	Av. 0.14±0.05 ppb	0.39	
		Av. 0.34±0.08 ppb	2.43

Sample Descriptions in Appendix C.

KIDD CREEK MINE

The Kidd Creek deposit is an example of the volcanogenic stratiform massive sulphide deposits which are associated with felsic volcanic rocks in the Canadian Precambrian Shield. The deposit is mined by Ecstall Mining, a subsidiary of Texasgulf Inc., and is located 16 miles north of Timmins, Ontario (see Figure 6-1).

The deposit is located at the western extremity of the Abitibi greenstone belt. The geology of the mine area is complex and is incompletely known. Brief descriptions of the local geology have been given by Pyke and Middleton (1970), Pye et al. (1972) and Matulich et al. (1974). Recently the nature of the ores and their geological setting have been dealt with more definitively by Walker and Mannard (1974) and by Walker et al. (1975).

A wide variety of rock types is exposed in the immediate vicinity of the mine and includes Archean mafic, intermediate and felsic volcanic rocks, tuffaceous sedimentary rocks, and ultramafic and mafic intrusions. These rocks have been regionally metamorphosed to the greenschist facies, and have been assigned an age of 2750 my on the basis of U-Pb determinations in zircons by Krogh and Davis (1971).

1. Local Geology

The massive sulphides which constitute the ore deposit are situated concordantly near the top of a rhyolitic volcaniclastic pile. Approximately 60% of the pit area is underlain by felsic extrusive rocks which include rhyolitic tuffs, agglomerates and massive rhyolite flows, as well as chert and carbonaceous argillite. The massive sulphides which exhibit metal zoning and banding occur in three forms, distinguishable on the basis of megascopic texture, and are distributed into five distinct ore zones (Walker and Mannard, 1974).

The locations of samples analysed for rhenium and osmium are shown in Figure 6-8, and the analytical results are given in Table 6-7.

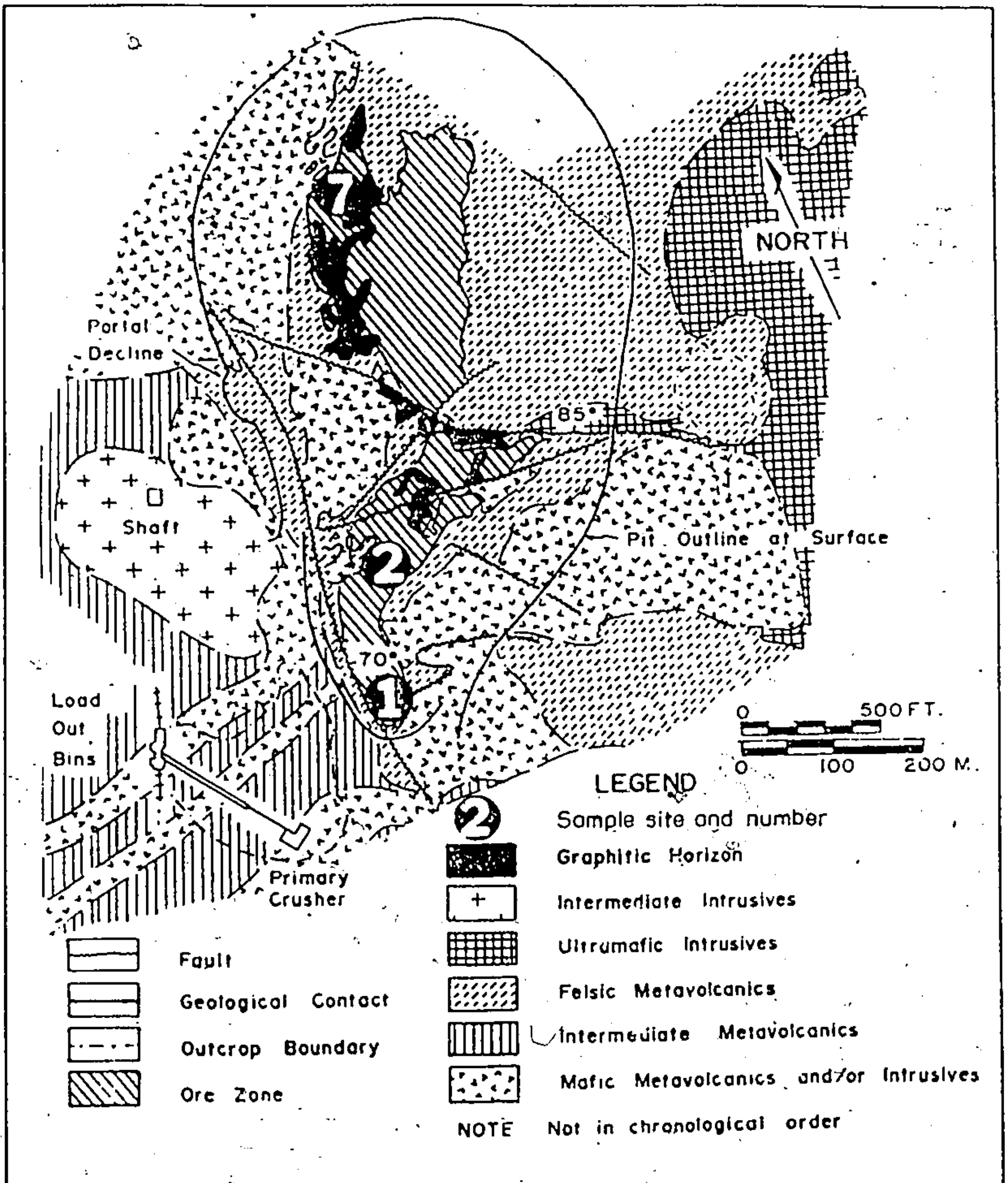
Table 6-7

Analytical Results: Kidd Creek

Material (Sample No.)	Ore Zone*	Rhenium (ppb)	Osmium (ppb)	$\frac{Os}{Re}$
Pyrite	2	0.85	0.06	
(No. 7)		0.85	0.08	
		Av. 0.85±0.00 ppb	Av. 0.07±0.01 ppb	0.08
Chalcopyrite	3	0.12	0.09	
(No. 1)		0.12	0.08	
		0.12	Av. $0.08_5 \pm 0.01_5$ ppb	0.71
		Av. 0.12±0.00 ppb		
Sphalerite	3	0.06	0.033	
(No. 2)			0.062	
			Av. 0.048±0.02 ppb	0.80

* After Walker and Mannard (1974).

N.B. Sample Descriptions in Appendix C.



SOURCE : PYE E.G. et al (1972), p74

FIGURE 6-8 : General geology and sample sites, KIDD CREEK MINE.

OTHER ANALYTICAL RESULTS

Analytical results for molybdenites from MoS_2 producers are given in Table 6-8. The locations of these deposits are shown in Figure 6-1.

Table 6-8

Rhenium Content of Molybdenite Concentrates from MoS_2 Producers

Mine	Location	Rhenium (ppm)
Brenda Mine (H/S)	B.C.	63.4
Lornex Mine	B.C.	221 227 224±3 ppm
Molybdenum Corp. of Canada	P.Q.	24.4
Preissac Molybdenum Preissac LaCorne Batholith(1)	P.Q.	28.0 26.2
Gaspé Copper	P.Q.	145 190 168±22 ppm 84

H/S = Hand specimen

Reference: (1) = Vokes (1963)

CHAPTER 7

DISCUSSION

THE CURRENT FEASIBILITY OF DATING METALLIC MINERAL DEPOSITS BY THE RHENIUM-OSMIUM METHOD

1. General Statement

In order to evaluate the feasibility of dating metallic ore deposits by the rhenium-osmium method, it is necessary to discuss both the elemental abundances and the isotopic ratios of rhenium and osmium in terms of current techniques. The rhenium and common osmium abundances obtained in this work for metallic minerals from a variety of ore deposits have been presented in Chapter 6. These results have been used to obtain information on the isotopic composition of rhenium and osmium in the metallic minerals of a number of Canadian ore deposits. These data have been used to define model rhenium-osmium isochrons which are comparable to isochrons obtained by the rubidium-strontium method. The study furnishes information on the feasibility of rhenium-osmium dating of metallic deposits from seven major mining camps. These deposits are representative of a wide variety of ore types, and are located in areas of widely different age and geological setting.

2. Assumptions

Calculation of the isotopic data and the subsequent derivation of the model isochrons have been based on the following assumptions.

It is assumed that all samples, including both minerals and whole rocks have remained closed systems with respect to rhenium and osmium since their crystallization. If the age of the deposit is known, the quantity of radiogenic $^{187}Os^*$ derived from its ^{187}Re parent can be calculated. Using the general law of radioactive decay, the decay of ^{187}Re atoms may be written as

$$^{187}Re_{now} = {}^{187}Re_{init.}\ e^{-\lambda t} \tag{1}$$

and

$$^{187}Os^* = {}^{187}Re_{now}\ (e^{\lambda t} - 1) \tag{2}$$

The total ^{187}Os atoms in the sample are given by

$$^{187}Os_{total} = {}^{187}Os^* + {}^{187}Os_{common} \tag{3}$$

$$\therefore\ {}^{187}Os_{total} = {}^{187}Os_{common} + {}^{187}Re(e^{\lambda t} - 1) \tag{4}$$

and $\therefore$

$$\frac{^{187}Os_{total}}{^{186}Os} = \frac{^{187}Os_{common}}{^{186}Os} + \frac{^{187}Re_{now}}{^{186}Os}\ (e^{\lambda t} - 1) \tag{5}$$

Model Re-Os isochrons defined by points with $\frac{^{187}\mathrm{Os}_{\mathrm{total}}}{^{186}\mathrm{Os}}$ as ordinates and $\frac{^{187}\mathrm{Re}}{^{186}\mathrm{Os}}$ as abscissae have been derived using equation (4) as the basis for the calculation of $^{187}\mathrm{Os}_{\mathrm{total}}$, and are presented in Figures 7-1 and 7-6.

No rhenium or osmium isotopic ratios were measured in this work. $^{187}\mathrm{Os}_{\mathrm{total}}$ in equation (4) was calculated on the following assumptions:

(a) There is no inter-sample variation in the isotopic composition of common osmium. Values of 1.59% and 1.64% were used for the isotopic abundance of $^{186}\mathrm{Os}$ and $^{187}\mathrm{Os}$ in common osmium respectively, and are based on the values given by Friedlander et al. (1966). Therefore, the $^{186}\mathrm{Os}$ and $^{187}\mathrm{Os}_{\mathrm{common}}$ are given by

(b)
$$\text{Atoms } ^{186}\mathrm{Os} = \frac{\mathrm{Os(gm)} \mathrm{x} \mathrm{N} \mathrm{x} \text{Atomic Abundance } ^{186}\mathrm{Os}}{\text{Atomic Weight Os (gm)}} \tag{6}$$

where N = Avogadro's Number and Atomic Abundance $^{187}\mathrm{Os}$ = 1.64%.

Similarly

$$\text{Atoms } ^{187}\mathrm{Os}_{\mathrm{common}} = \frac{\mathrm{Os(gm)} \mathrm{x} \mathrm{N} \mathrm{x} \text{Atomic Abundance } ^{187}\mathrm{Os}}{\text{Atomic Weight Os(gm)}} \tag{7}$$

where atomic abundance $^{186}\mathrm{Os}$ = 1.59%.

In the calculation of the radiogenic osmium component $^{187}Os^{*}$, equation (4), it is assumed that

(c) $$^{187}Re = \frac{Re(gm) x N x \text{Atomic Abundance } {}^{187}Re}{\text{Atomic Weight Re (gm)}} \qquad (8)$$

(d) t = age of the deposit. The absolute age of the deposit is based on the radiometric age of the enclosing associated rocks, and assumes age equivalence between these rocks and the metallic deposit. Contemporaneity between the various metallic minerals comprising the ore deposit is also assumed.

The ages used for the metallic deposits are given in Table 7-1.

(e) The half-life of ^{187}Re is taken as $4.3 x 10^{10}$ years (Hirt <u>et al</u>., 1963).

3. Sample Calculation

A sample calculation for the determination of points with ordinates of $^{187}Os_{total}/^{186}Os$ and abscissae of $^{187}Re/^{186}Os$ which were used to define the model isochrons is given below. A sample of massive sulphide from the Strathcona Mine with a content of 34.7 ppb rhenium and 255.4 ppb common osmium is used in this example.

The total ^{187}Os in the sample is given by equation (4). For $t = 1.844 x 10^{9}$ years (Krogh and Davis, 1974) and for a half-life for $^{187}Re = 4.3 x 10^{10}$ years (Hirt <u>et al</u>., 1963).

Table 7-1

Ages Assigned to t in Equations (4) and (5)

Deposit	Absolute age (years) = t in Equations (5) and (6)	Dating Method	Reference
Adams Mine	2,358 ± 74 my	Rb/Sr	Fairbairn _et_ _al_. (1965)
Craigmont Mine	200 ± 5 my	K/Ar Rb/Sr	White _et_ _al_. (1967) Christmas _et_ _al_. (1969)
Granisle Copper	51.2 ± 2 my	K/Ar	Carter (1972)
Highland Valley	200 ± 5 my	K/Ar	White _et_ _al_. (1967)
Kidd Creek Mine	2,750	U-Pb	Krogh _et_ _al_. (1971)
Strathcona Mine	1,844 ± 3 my	U-Pb	Krogh and Davis (1974)

$$\lambda t = 0.029718\ ,\ (e^{\lambda t}-1) = 0.030164$$

$$\therefore\ Os^{*} = {}^{187}Re\,(0.030164) \qquad (9)$$

From (8),

$${}^{187}Re = \frac{255.4x10^{-9}x0.6293xN}{186.2}$$

$$\therefore\ {}^{187}Re = 86.3050x10^{-11}xN \text{ atoms} \qquad (10)$$

Substitute (10) in (9)

$$\therefore\ {}^{187}Os^{*} = 86.3050x10^{-11}xNx0.30164$$

$$\therefore\ {}^{187}Os = 260.34x10^{-13}xN \text{ atoms.} \qquad (11)$$

Measured common osmium is 34.75 ppb, therefore from (6)

$${}^{186}Os = \frac{34.75x10^{-9}xNx1.59x10^{-2}}{190.2}$$

$$\therefore\ {}^{186}Os = 29.046x10^{-13}xN \text{ atoms} \qquad (12)$$

Similarly, from (7)

$${}^{187}Os_{common} = \frac{34.75x10^{-9}xNx1.64x10^{-2}}{190.2}$$

$$\therefore\ {}^{187}Os_{common} = 29.959xNx10^{-13} \qquad (13)$$

From (3)

$${}^{187}Os_{total} = {}^{187}Os^{*} + {}^{187}Os_{common}$$

Substituting values from (11) and (13)

$$\therefore\ {}^{187}\mathrm{Os}_{\mathrm{total}} = 290.29\mathrm{x}10^{-13}\mathrm{xN\ atoms} \qquad (14)$$

From (12) and (14)

$$\frac{{}^{187}\mathrm{Os}_{\mathrm{total}}}{{}^{186}\mathrm{Os}} = \frac{290.29\mathrm{x}10^{-13}\mathrm{xN\ atoms}}{29.046\mathrm{x}10^{-13}\mathrm{xN\ atoms}}$$

$$\frac{{}^{187}\mathrm{Os}_{\mathrm{total}}}{{}^{186}\mathrm{Os}} = 9.994 \qquad (15)$$

Similarly from (10) and (12)

$$\frac{{}^{187}\mathrm{Re}}{{}^{186}\mathrm{Os}} = \frac{86.305\mathrm{x}10^{-11}\mathrm{xN\ atoms}}{29.046\mathrm{x}10^{-13}\mathrm{xN\ atoms}}$$

$$\frac{{}^{187}\mathrm{Re}}{{}^{186}\mathrm{Os}} = 297.1 \qquad (16)$$

The values in (15) and (16) give the ordinate and abscissa respectively of a point used to define the model isochrons. Data for these points are summarised in Table 7-2.

The weight of ^{187}Re in each sample given in Table 7-2 has been calculated directly from the weight of rhenium in the sample. The values for the atomic weights and atomic abundances are those given by Friedlander _et al_. (1966). A similar approach was used to calculate the weight of $^{187}\mathrm{Os}_{\mathrm{common}}$ directly from the experimentally determined weight of osmium.

Table 7-2

Data for Points Used in Model Isochron Diagrams

Deposit	Mineral	MEASURED		CALCULATED				
							Atomic Ratios	
		Re ($\frac{gm}{gm} \times 10^{-9}$)	Os$_{common}$ ($\frac{gm}{gm} \times 10^{-11}$)	^{187}Re $\frac{gm}{gm}$	^{187}Os* $\frac{gm}{gm}$	^{187}Os$_{total}$ $\frac{gm}{gm}$	$\frac{^{187}Os_{total}}{^{186}Os}$	$\frac{^{187}Re}{^{186}Os}$
Adams Mine	Magnetite	0.30±0.13	253.0±78.0	1.88×10^{-10}	7.29×10^{-12}	4.81×10^{-11}	1.22	4.75
	Pyrite	2.09±0.01	13.0± 3.0	1.32×10^{-9}	5.13×10^{-11}	5.34×10^{-11}	2.55	632.
Craigmont	Magnetite	2.11±0.25	8.53	1.33×10^{-9}	4.31×10^{-12}	5.68×10^{-12}	4.26	999.
	Chalcopyrite	3.72	1.48	2.35×10^{-9}	7.58×10^{-12}	7.82×10^{-12}	33.9	10.2×10^{3}
	Pyrite	37.3 ±0.1	9.97	23.6×10^{-9}	7.61×10^{-11}	7.77×10^{-11}	49.7	15.1×10^{3}
Granisle Copper	Bornite	0.14±0.05	33.5±8.0	8.60 ± 10^{-11}	7.10×10^{-14}	5.47×10^{-12}	1.05	16.4
	Chalcopyrite	1.08±0.23	6.41±2.0	6.79×10^{-10}	5.61 ± 10^{-13}	1.59×10^{-12}	1.59	677.
Highmont	Molybdenite	95.7 ppm	13.5	60.4×10^{-6}	$195. \times 10^{-9}$	1.95×10^{-7}	92.4×10^{3}	$286. \times 10^{5}$
Valley Copper	Molybdenite	297. ±5.0 ppm	18.9	$188. \times 10^{-6}$	$606. \times 10^{-9}$	6.06×10^{-7}	$205. \times 10^{3}$	$635. \times 10^{5}$
Lornex	Molybdenite	256. ppm	8.0 (max.)	$162. \times 10^{-6}$	$557. \times 10^{-9}$	5.57×10^{-7}	$445. \times 10^{3}$	$130. \times 10^{5}$
Alwin	Chalcopyrite	1.95	49.4	1.23×10^{-9}	3.97×10^{-12}	7.10×10^{-12}	2.34	405.
Bethlehem	Bornite	0.76	6.33	4.82×10^{-10}	1.56×10^{-12}	2.58×10^{-12}	2.61	488.
Kidd Creek.	Chalcopyrite	0.12±0.00	8.0±1.2	7.50×10^{-11}	3.40×10^{-12}	4.69×10^{-12}	3.74	59.7
	Pyrite	0.85±0.00	7.3±1.3	5.36×10^{-10}	2.43×10^{-11}	2.55×10^{-12}	22.2	466.
	Sphalerite	0.061	4.8±1.5	3.85×10^{-11}	1.75×10^{-12}	2.51×10^{-12}	3.38	51.8
Strathcona	Chalcopyrite	18.0 ±1.0	615.	11.4×10^{-9}	3.43×10^{-10}	4.42×10^{-10}	4.59	118.
	Massive Sulphide	255. ±5.0	3470	161.0×10^{-9}	4.87×10^{-9}	5.43×10^{-9}	9.99	297.
	Pyrrhotite	25.6 ±0.9	306.	16.2×10^{-9}	4.88×10^{-10}	5.38×10^{-10}	11.2	338.

4. Nature of the Data Used

The rhenium and common osmium abundances presented in Chapter 6 for a variety of ore-forming minerals, including pyrite, pyrrhotite, chalcopyrite, bornite, sphalerite, molybdenite, and magnetite, as well as several massive sulphide samples form the basis of the calculations. The massive sulphides may be considered as the Re-Os equivalent of Rb-Sr whole rock samples. Of the eighteen points used to define the model isochrons, eight are based on samples analyzed in replicate for common osmium, and twelve are based on samples analyzed in replicate for rhenium. The remainder are based on single analyses only.

No model isochron plot has been made for Heath Steele because only maxima values were obtained for the common osmium content of this deposit. However, a maximum value of 0.08 ppb common osmium in Lornex molybdenite has been treated as an absolute value for the purpose of the isochron calculations because it approximate the value of common osmium in molybdenites from the Highmont and Valley Copper deposits. The atomic ratios for ^{187}Re/^{186}Os and ^{187}Os$_{total}$/^{186}Os calculated for metallic minerals from various deposits are given in Table 7-2.

5. Some Deliberations

The calculated $^{187}Os_{total}/^{186}Os$ and $^{187}Re/^{186}Os$ ratios presented in Table 7-2 have been used to define points along model isochrons for their respective ore deposits. The intercept on the $^{187}Os_{total}/^{186}Os$ axis, given by $^{187}Os_{common}/^{186}Os$, is of necessity the same for each of the model isochrons (Figures 7-1 to 7-6). A line was fitted by means of a simple linear regression program and use of the HP 2000 time-sharing facilities of the McMaster University Computer Centre. The program, GRGPLT, written by W. F. Sharpe (1971) of the Stanford Graduate School of Business, provides a plot of the data points and the equation of the regression line.

The errors assigned to the points in Figures 7-1 to 7-6 assume a 10% error in the determination of both the $^{187}Os/^{186}Os$ and $^{187}Re/^{186}Os$ ratios. The 10% error in the $^{187}Os/^{186}Os$ ratio is based on the experimental work of Herr et al. (1967), who report that 10^{-7} grams is the minimum amount of $^{187}Os^*$ (radiogenic) which is measurable mass spectrometrically by the $^{187}Os/^{186}Os$ ratio with an accuracy of 10%. These authors report that the detection limit for $^{187}Os^*$ may be increased to 10^{-8} grams by adopting the use of ^{190}Os as a spike and measuring the $^{187}Os/^{186}Os$ ratio. The 10% error assigned to the

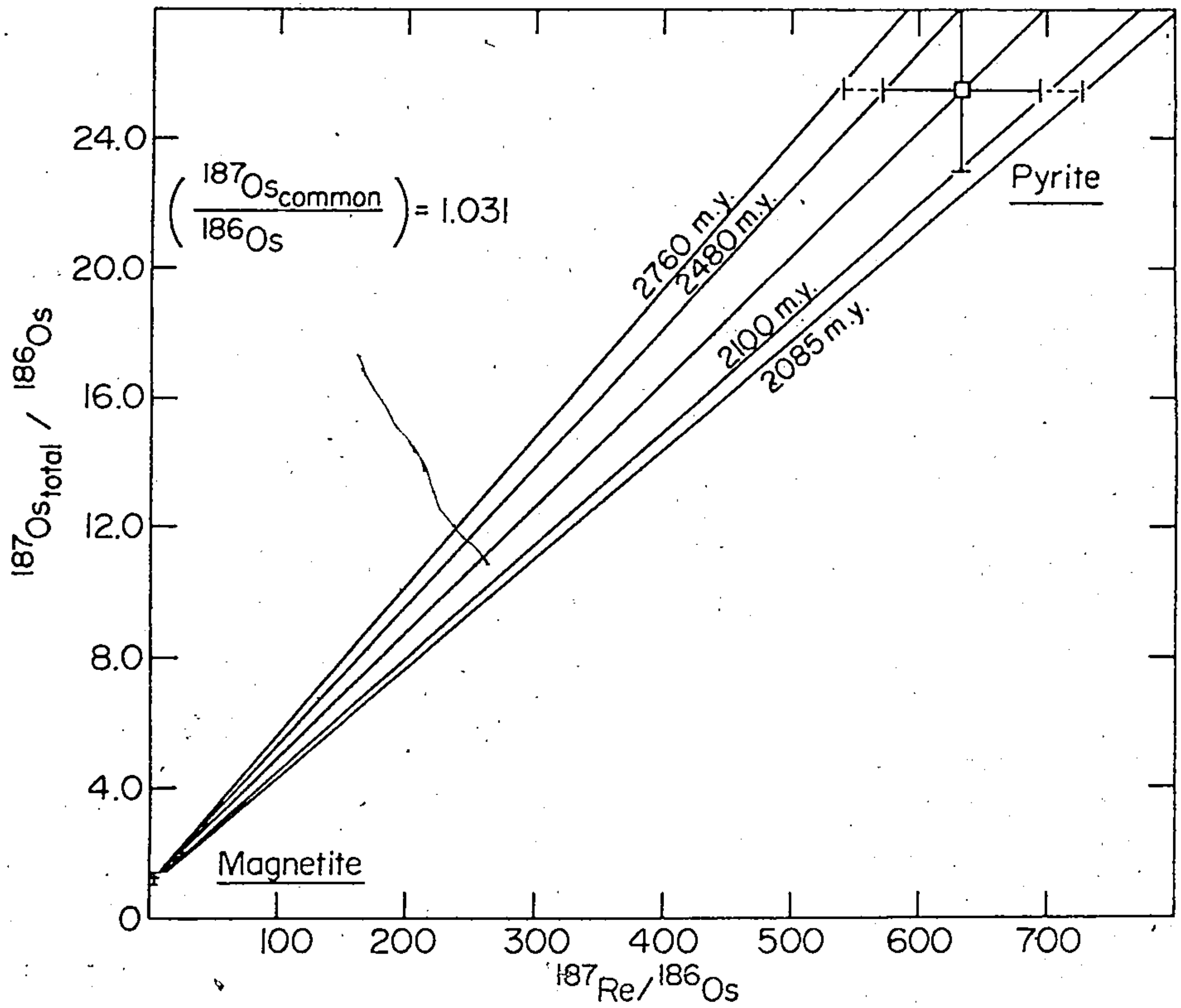


FIGURE 7-1: Model Re-Os Isochron, ADAMS MINE (2,358 m.y.)

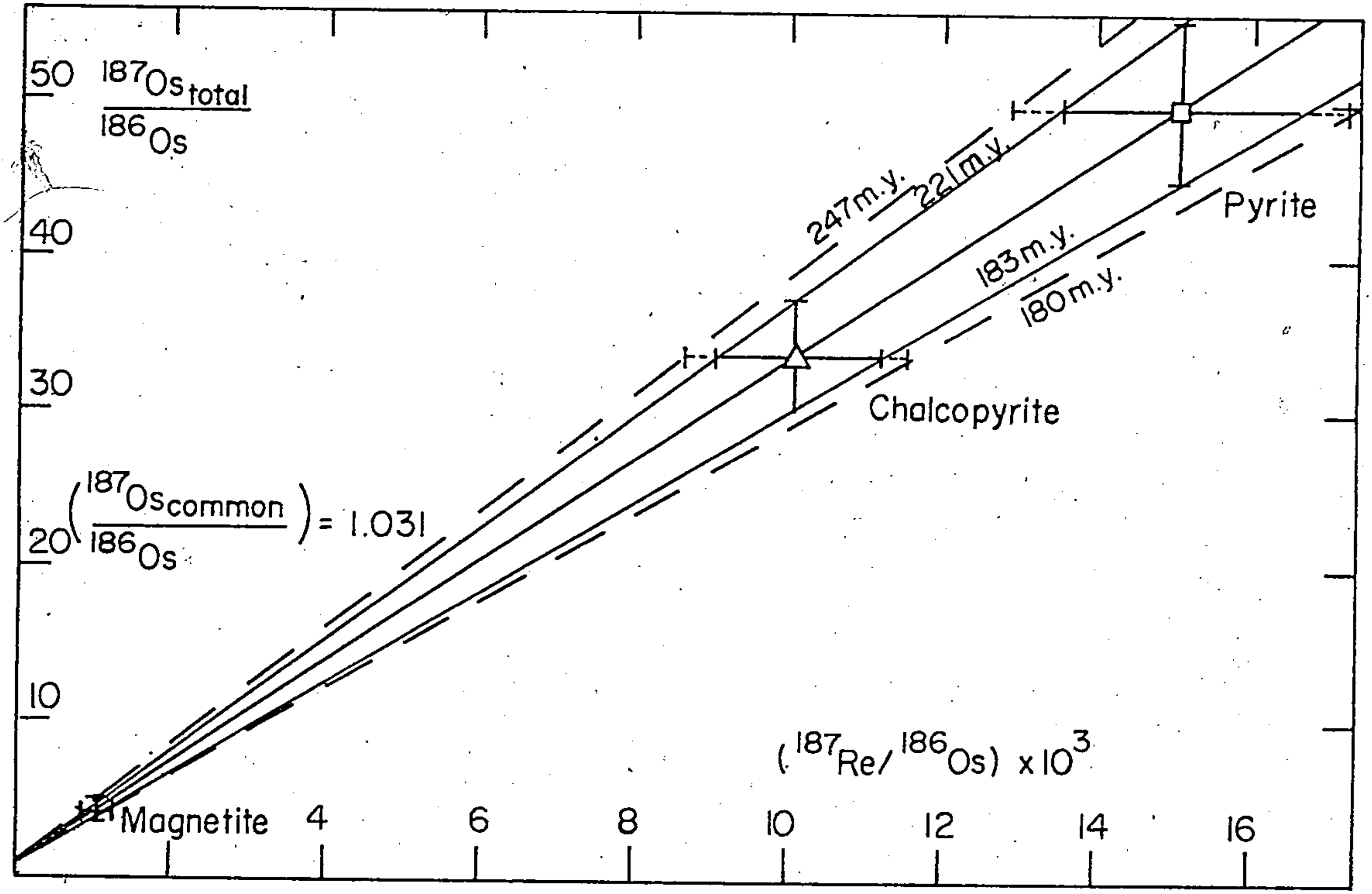


FIGURE 7-2: Model Re-Os Isochron, CRAIGMONT MINE (200 m.y.)

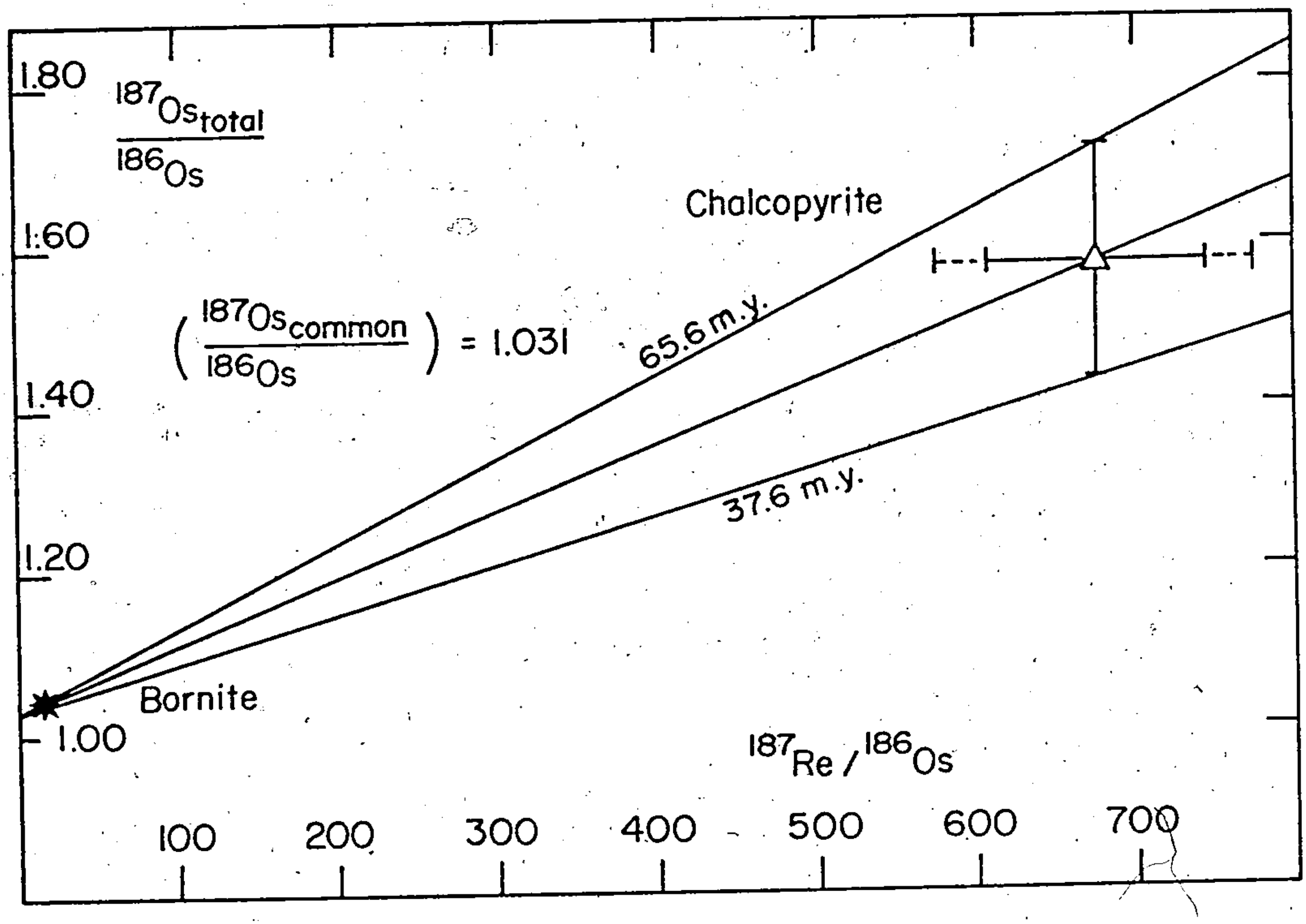


FIGURE 7-3: Model Re-Os Isochron, GRANISLE COPPER (51.2 m.y.)

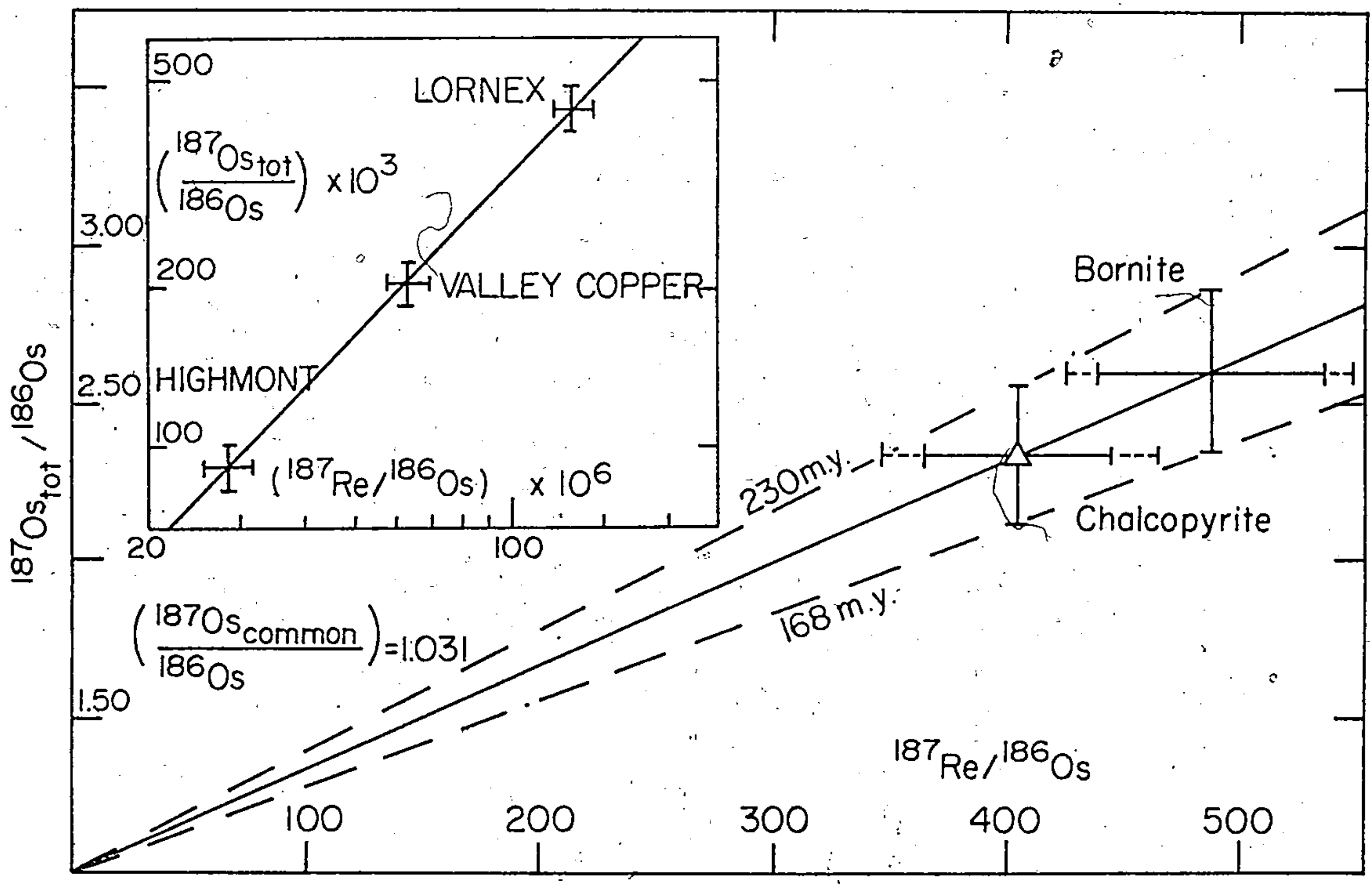


FIGURE 7-4: Model Re-Os Isochron, GUICHON BATHOLITH (200 m.y.)

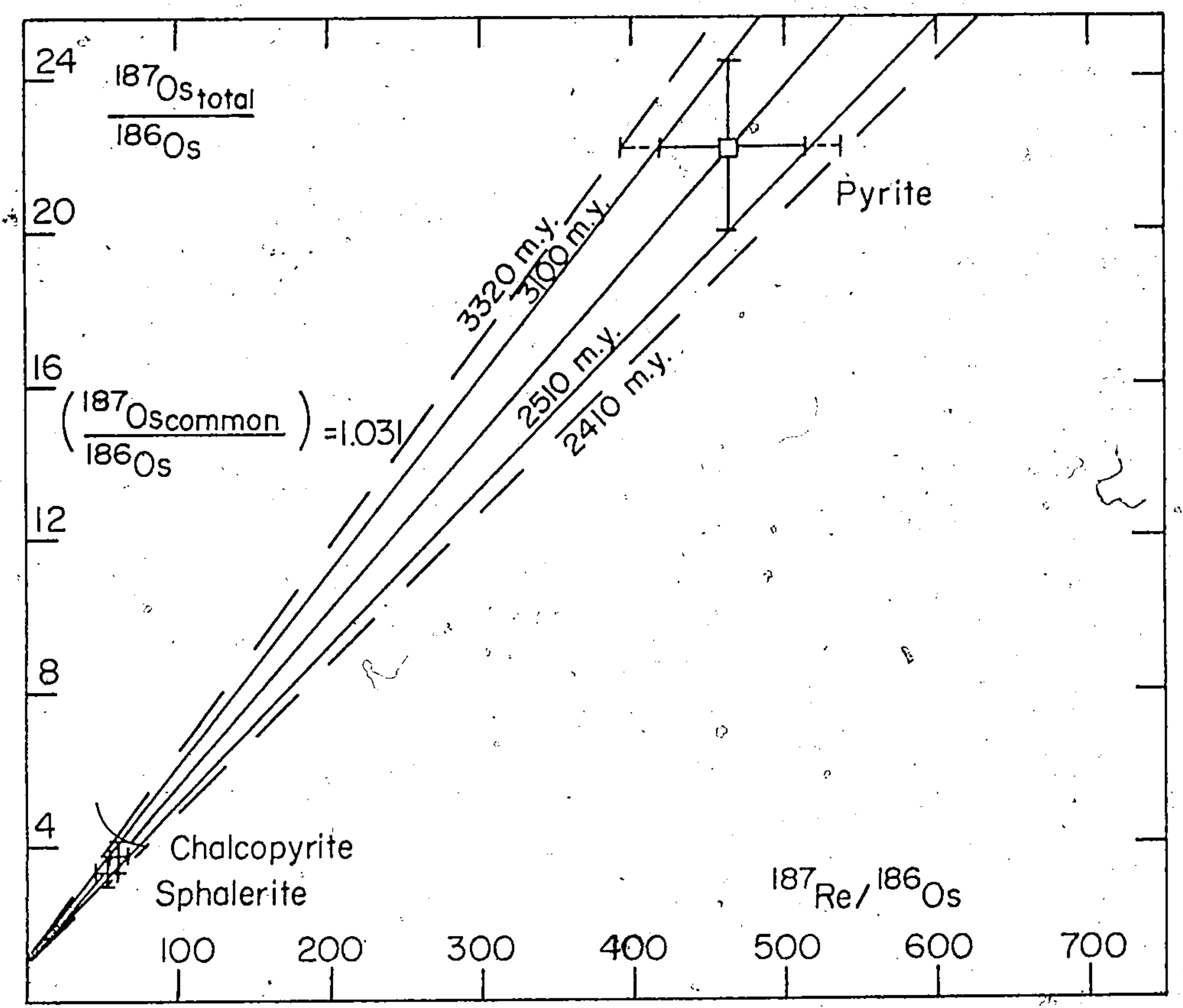


FIGURE 7-5: Model Re-Os Isochron, KIDD CREEK (2750 m.y.)

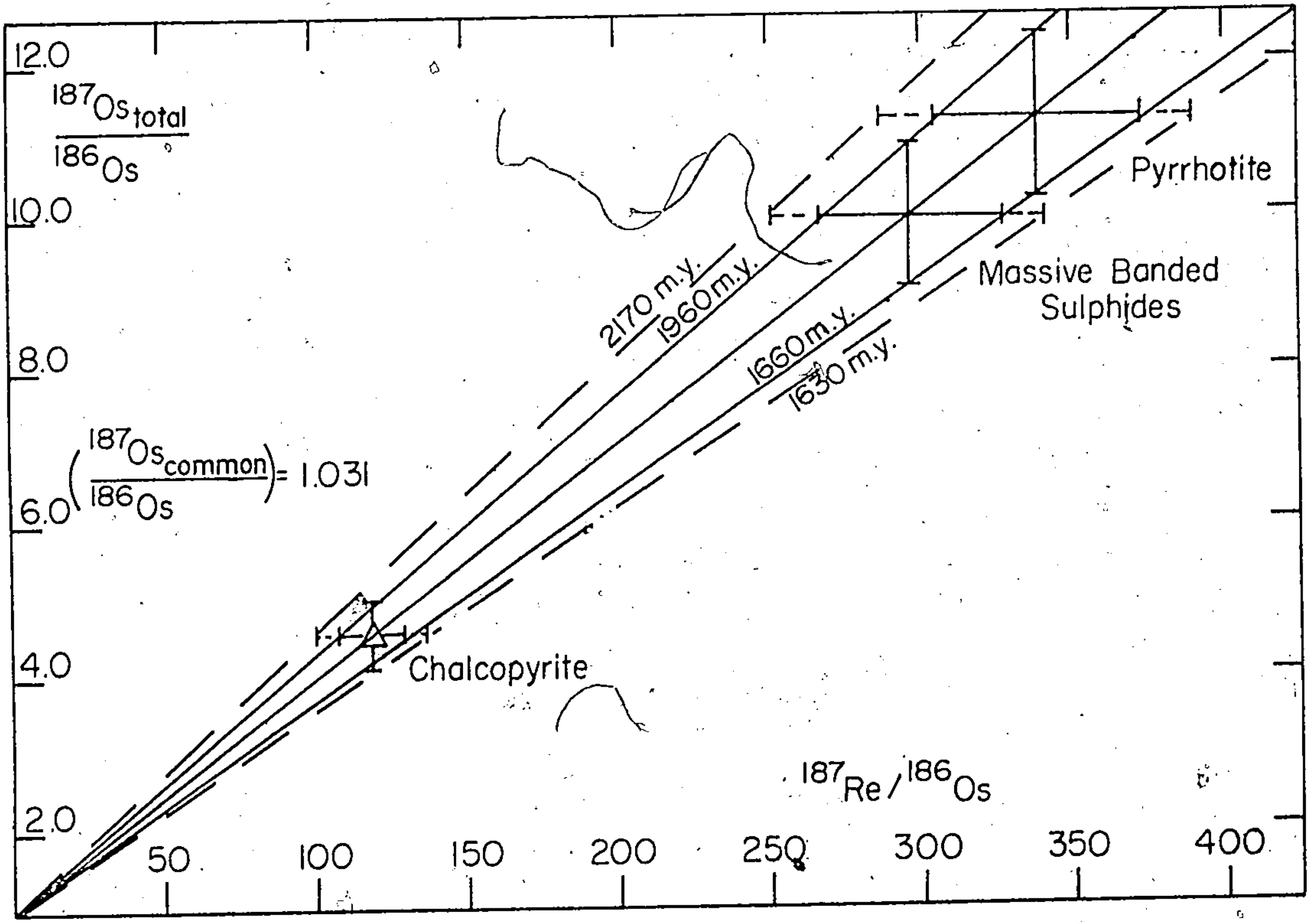


FIGURE 7-6: Model Re-Os Isochron, STRATHCONA MINE (1,844 m.y.)

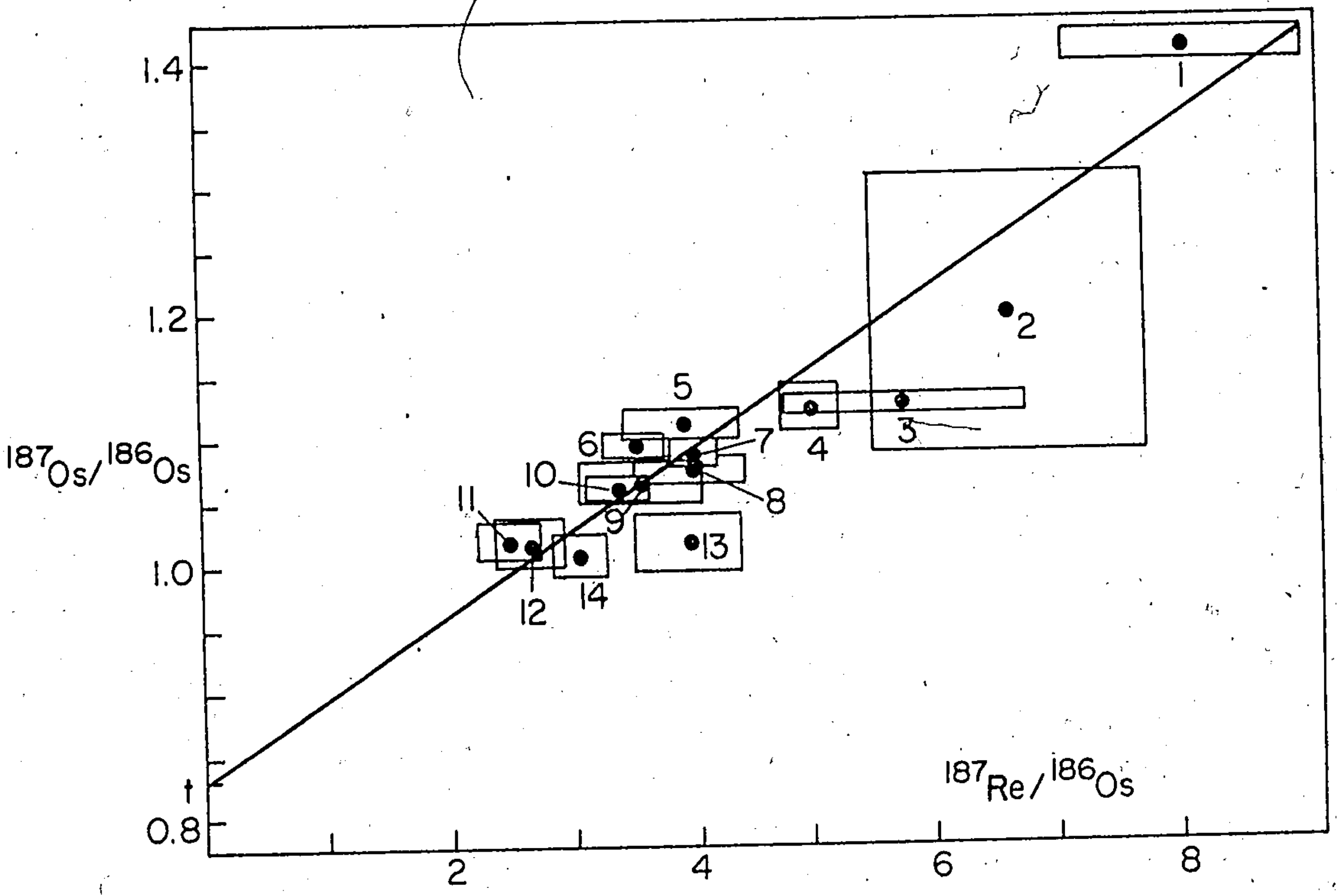


FIGURE 7-7: $^{187}Os/^{186}Os$ vs $^{187}Re/^{186}Os$ in 14 Iron Meteorites (Herr et al, 1961)

^{187}Re/^{186}Os ratios is based on the average experimental error which Herr et al. (1961) obtained in their investigation of iron meteorites.

The uncertainty associated with Re-Os age determinations, assuming sufficient ^{187}Os* can be obtained for analysis, is given by the slope of the limiting isochrons shown in Figures 7-1 to 7-5. In Table 7-3 the range in the Re-Os age from the limiting isochrons, for 10% errors in each of the ^{187}Os$_{total}$/^{186}Os and ^{187}Re/^{186}Os ratios, is compared with the radiometric age of the deposit and with the range in ages expected for an error of 15% in the ^{187}Re/^{186}Os ratio and an error of 10% in the ^{187}Os$_{total}$/^{186}Os ratios. Molybdenites from the Guichon Batholith have not been treated in this manner because of their great distance from the origin (Inset, Figure 7-4). The range in ages assigned to Granisle Copper assumes negligible error for the bornite point.

Of the orebodies studied in this work only the molybdenites from the Guichon Batholith have calculated abundances of ^{187}Os* in substantial excess of 10^{-8} grams (see Table 7-2). Strathcona Mine, with calculated ^{187}Os$_{total}$ values ranging from 5.43 ppb to 0.54 ppb contains sufficient ^{187}Os* to be measurable by current techniques in mass spectrometry by the use of samples of up to 100 grams, assuming 100% yield in the extraction process. The remaining deposits, however, in which the calculated ^{187}Os* is in the range of 10^{-11} to 10^{-14} grams/gram, must be considered beyond the scope of these methods, and therefore undatable by the Re/Os isochron method.

Table 7-3

Range in Ages Expected by Re-Os Method for Six Metallic Deposits

Deposit or Camp	Radiometric Age (my)	Range in age expected in Re-Os method (my) by error in ^{187}Re/^{186}Os of	
		(a) ±10%	(b) ±15%
Adams Mine	2,358	2,100 to 2,480	2,085 to 2,760
Craigmont	200	183 to 221	180 to 247
Granisle	51.2	37.6 to 65.6	37.6 to 65.6
Guichon Batholith (Cu-Fe Sulphides)	200	168 to 230	168 to 230
Kidd Creek	2,750.	2,510 to 3,100	2,410 to 3,320
Strathcona	1,844	1,660 to 1,960	1,630 to 2,170

From Table 7-2 it can be seen that the abundance level of rhenium in the metallic minerals of base metal ore deposits is generally greater than the abundance of common osmium by a factor ranging from two or three to as much as 10^2. In the molybdenites of the Guichon Batholith rhenium is present in quantities which are in excess of the common osmium content by a factor of 10^6. The results also indicate that rhenium can be determined with acceptable errors at the level of 1 to 10 ppb and in some instances, in the 0.1 to 1.0 ppb range. In this regard it is of interest to note that Michel et al. (1972) used neutron activation analysis, combined with extensive radiochemical separations, to determine simultaneously both the isotopic composition and the abundance of rhenium in lunar materials. The abundance of rhenium in these samples is between 0.95 ppb and 1.4 ppb. Herr et al. (1971) using the same procedure determined rhenium abundances in lunar rocks in the range 0.03 to 0.09 ppb. Errors of less than 10% for concentrations of rhenium ranging from 0.03 to 0.10 ppb and errors less than 5% for abundances ranging from 0.1 to 0.9 ppb rhenium are cited by these authors. Together with the results of this work, therefore, these data indicate that current techniques in the field of neutron activation are adequate for the determination of rhenium in the very small quantities with which it occurs in metallic ore deposits.

However, the combination of the long half-life of ^{187}Re and the extremely small concentrations in which ^{187}Re generally occurs in ore deposits, places severe limitations on the applicability of the rhenium-osmium method. A measure of these restrictions is afforded by Figure 7-8 and by Table 7-4. Figure 7-8 denotes the variation in the amount of ^{187}Os* generated by different quantities of rhenium using terrestrial ages ranging from 50 my to 3,000 my and using an age of 4,500 my for meteorites. The diagram also provides a means of assessing the feasibility of applying the Re-Os method to an ore deposit if two of the three parameters are either known, or can be estimated. A similar approach was used by Riley (1967) to evaluate the potential of the rhenium method to date some Australian ores. However, his investigation was restricted, for the most part, to molybdenites with rhenium contents in the ppm range. The ^{187}Os* abundances of more than 50% of these samples was greater than 10^{-7} gm/gm, which is from four to five orders of magnitude greater than the calculated ^{187}Os* content of the minerals analysed from the base metal deposits in this study. The lower limits of ^{187}Os* in the remaining molybdenites studied by Riley (1967), is about 5 ppb, which is roughly equivalent to the upper limits of the ^{187}Os* content of the Strathcona ores.

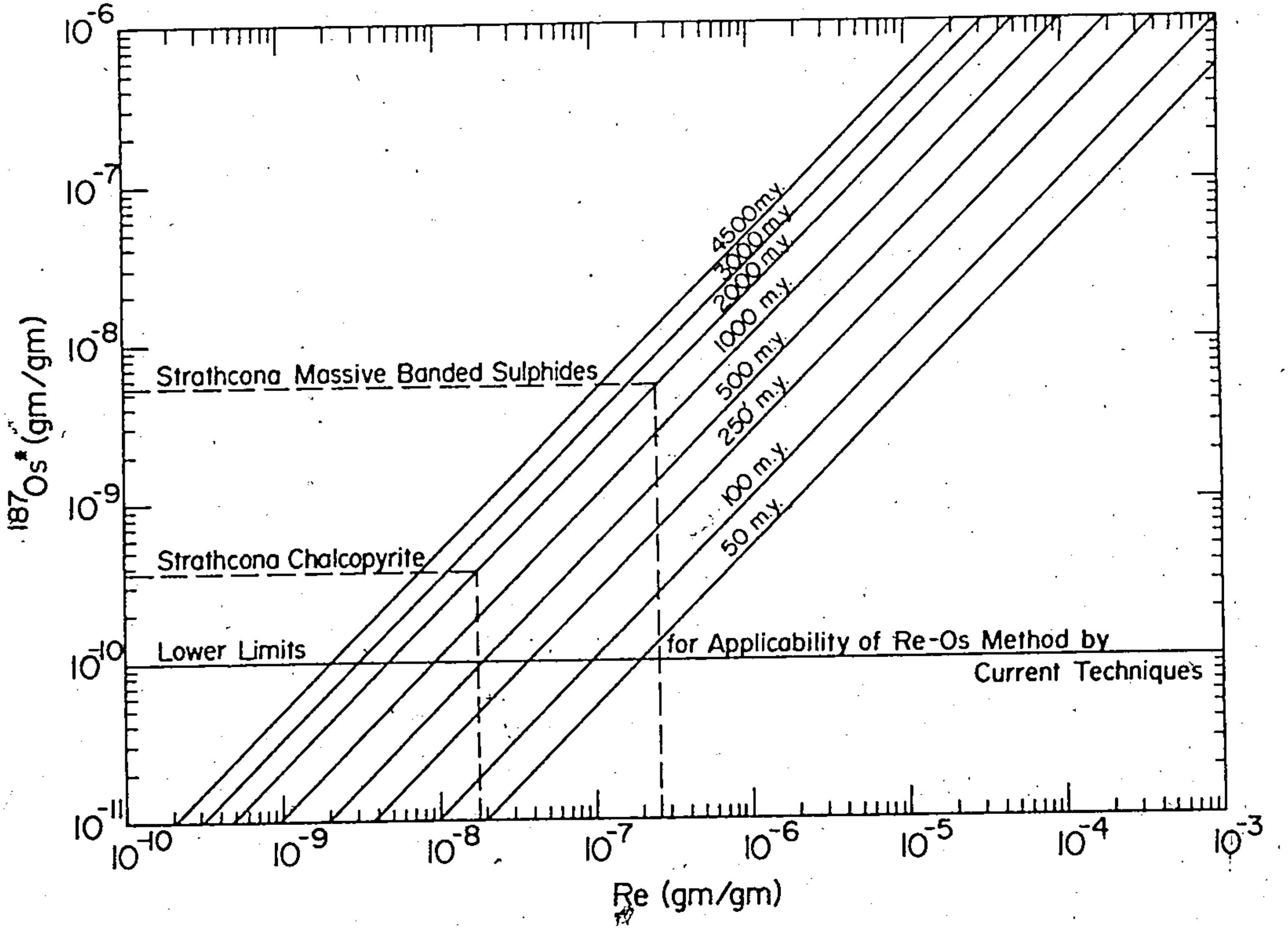


Figure 7-8 : $^{187}Os^*$ Abundance as a Function of Age and Rhenium Abundance.

Table 7-4

^{187}Os* Content of Metallic Deposits

Deposit or Camp	Calculated ^{187}Os* $\frac{gm}{gm}$	Minimum Weight (gm) to give 10^{-8} gm ^{187}Os*
Adams Mine	5×10^{-11} to 7×10^{-12}	10^3 to 10^4
Craigmont	7×10^{-11} to 6×10^{-12}	10^3 to 10^4
Granisle Copper	6×10^{-13} to 7×10^{-14}	10^5 to 10^6
Guichon Creek	$\sim 2\times10^{-12}$ to 4×10^{-7}	10^4
Heath Steele	1×10^{-11} to 7×10^{-13}	10^3 to 10^5
Kidd Creek	2×10^{-11} to 2×10^{-12}	10^3 to 10^4
Strathcona	5×10^{-9} to 4×10^{-10}	10 to 10^2

Table 7-4 indicates the range in concentration of ^{187}Os* calculated in the major ore-forming minerals, exclusive of molybdenites, from seven Canadian ore deposits or mining camps. The table also indicates the minimum weight of pure sample necessary to attain the lower limit of detection of 10^{-8} gm. ^{187}Os* cited by Herr et al. (1967). Pre-analytical concentration of osmium on a substantial scale, involving the use of large quantities of starting material, is obviously necessary to obtain ^{187}Os* in quantities sufficient for isotopic determinations. For example, it is estimated that, in general, chemical treatment of samples weighing from 1 to 10 kilograms, assuming one hundred per cent yield, is obligatory in order to provide the minimum quantity of ^{187}Os* requisite for mass spectrometry. In the extreme case of bornite from Granisle Copper, a minimum of 1000 kgm would be required to yield 10^{-8} gm of ^{187}Os*. With the exception of the molybdenites, Strathcona Mine is the only base metal deposit where relatively small samples, from 10 to 100 gm, are estimated to contain ^{187}Os* in sufficient quantity for isotopic determination by current techniques in mass spectrometry.

However, treatment of large samples is not unknown in geochronological studies. In the uranium-lead method, for example, separation of zircons from samples weighing up to 50 kilograms was routine until Krogh (1971) introduced procedures which enabled the isotopic determination of nanogram quantities of lead in zircon samples as small as 2.5x10^{-4} gm. The sample weights cited as being necessary for the isotopic determination of osmium, however, are the weights of pure, separated, mineral of whole rock required for chemical treatment. The large samples required, which are onerous in their own right, become even more so if alkaline fusion is used for the dissolution of the samples. Direct distillation of osmium using strong oxidizing acids, such as nitric acid or perchloric acid, is an obvious alternative for metallic minerals soluble in these acids.

A more fruitful approach would probably be to develop techniques with increased sensitivity which are capable of analysing extremely small quantities of osmium. For example, the methods developed by Krogh (1971) for U-Pb determinations of zircons. Investigations along these lines have already been initiated. For example, Chung and Beamish (1968) in an attempt to derive a method for the quantitative distillation of nanogram quantities of osmium directly from ores, effected the quantitative, carrier-free, distillation of microgram quantities of osmium from a 12N sulphuric acid - 30% hydrogen peroxide solution at 105°C. Insignificant quantities of ruthenium were distilled under these conditions. The volatility of osmium tetroxide, which readily affords an efficient method of separating osmium from a large number of elements, can therefore be used as a separate technique even when the osmium is present in very limited quantities.

Neutron activation techniques for the determination of osmium abundances have been developed to the stage where concentrations in the sub-nanogram range can be determined with acceptable errors in accuracy and precision. Lovering and Butterfield (1970) and Lovering and Hughes (1971), for example, measured low osmium concentrations in lunar materials by neutron activation analysis. In the latter work reproducibility between replicate samples agreed within 7 to 10% at the 0.1 to 0.9 ppb level. For the majority of the ore deposits analysed in this work the common osmium content is of the order of 10^{-11} gms/gm. Additional refinements in techniques will therefore be necessary to enable these quantities to be measured with the required accuracy on a routine basis.

The major analytical problem confronting the rhenium-osmium method at the present time, however, is the determination of the isotopic composition of osmium for the extremely small concentrations in which osmium is present in metallic ore deposits. In addition to determinations by mass spectrometry, the isotopic abundance of ^{187}Os can also be determined by neutron activation analysis. The method, developed by Herr and Merz (1955), is dependent upon the fact that only three of the seven naturally-occurring isotopes of osmium, namely ^{184}Os, ^{190}Os and ^{192}Os, form radioactive isotopes when irradiated with thermal neutrons. The remaining four isotopes, with mass numbers 186, 187, 188 and 189, merely form more stable nuclei when irradiated under these conditions. ^{187}Os is the only one of these four isotopes whose isotopic abundance has a radiogenic component. Therefore, a sample with a higher ^{187}Os* (radiogenic) content will have a lower specific activity after thermal neutron activation than a reference sample of isotopically "normal osmium". The lowering of specific activity is proportional to the ^{187}Os* in the sample. The lower limit of detection for ^{187}Os* by this method is given as 2 micrograms by Herr and Merz (1955) who used this method to obtain an age of 2.7×10^{9} years for a molybdenite from Lofoten, Norway, with a rhenium content of 509 ppm and a ^{187}Os* content of 7.75 ppm.

In spite of the low concentrations in which rhenium and osmium generally occur in ore deposits, however, the results for the metallic minerals analysed in this study indicate that intradeposit differences between common osmium-rhenium ratios are generally favourable to the application of the Re-Os method. Intradeposit variation between maximum and minimum values of the common osmium-rhenium ratio, range from a factor of 2.8 (Strathcona Mine) to in excess of 3.2×10^{5} for the Guichon Creek Batholith (see Table 7-5). The large factor for the Guichon Creek Batholith is due to the high rhenium content of the molybdenites and their low common osmium content. The intradeposit range in common osmium-rhenium ratios is also reflected by the

Table 7-5

Intradeposit Variation of Common Osmium:Rhenium Ratios

Deposit or Camp	Mineral	$\frac{Os_{common}}{Re} = R$	Intradeposit $\frac{R_{maximum}}{R_{minimum}}$
Adams Mine	Magnetite	8.4	140
	Pyrite	0.06	
Craigmont	Pyrite	$3x10^{-3}$	13
	Chalcopyrite	$3x10^{-3}$	
	Magnetite	$4x10^{-2}$	
		0.04	
Granisle Copper	Chalcopyrite	0.06	40
	Bornite	2.43	
Guichon Creek Batholith	Molybdenite (Lornex)	$\geq 3.1x10^{-7}$	$3.2x10^{5}$
	Bornite (Bethlehem Copper)	0.10	
	Chalcopyrite (Alwin Mine)	0.10	
Heath Steele	Massive Sulphides (A4049)	≤ 0.01	
	Massive Sulphides (A4093)	≤ 0.16	
	Sphalerite	≤ 0.15	
	Chalcopyrite	≤ 0.10	

Table 7-5 (continued)

Deposit or Camp	Mineral	$\frac{Os_{common}}{Re} = R$	Intradeposit $\frac{R_{maximum}}{R_{minimum}}$
Kidd Creek	Pyrite	0.08	
	Chalcopyrite	0.70	9.
	Sphalerite	0.80	
Strathcona	Pyrrhotite	0.12	
	Chalcopyrite	0.34	2.8
	Massive banded sulphide	0.13	

points defining the model isochrons (Figures 7-1 to 7-6). Theoretically, resolution of these points from one another is possible, even admitting the large errors assigned to them. In practice, however, determination of the relevant isotopic ratios of rhenium and osmium is limited to the minerals of relatively few deposits such as the molybdenites of the Guichon Creek Batholith and sulphides from Strathcona Mine. At the Strathcona Mine where rhenium and osmium concentrations are relatively high, the ratio of maximum to minimum values for the common osmium to rhenium ratio is one of the smallest values (see Table 7-5).

The large spread of $^{187}Os_{total}/^{186}Os$ and $^{187}Re/^{186}Os$ ratios expected for metallic ore deposits contrast strongly with the narrow range for these ratios in iron meteorites (compare Figures 7-1 to 7-6 with 7-7). This is a result of the greater fractionation between rhenium and osmium in terrestrial materials, compared with their distribution in iron meteorites, where, in spite of large elemental abundances Os/Re ratios are relatively constant (see Table 5-14).

A summary of $^{187}Os_{total}/^{186}Os$ and $^{187}Re/^{186}Os$ ratios for the metallic minerals analysed in this work is presented in Table 7-6. Median values have been chosen as being representative of the various minerals because of the large variations in these ratios which occur in some minerals.

Table 7-6

$^{187}Os_{tot.}/^{186}Os$ and $^{187}Re/^{186}Os$ in Some Metallic Minerals

Mineral	N	$^{187}Os_{total}/^{186}Os$		$^{187}Re/^{186}Os$	
		Range	Median	Range	Median
Bornite	3	1.14 - 2.57	1.16	34.7 - 477.	160.
Chalcopyrite	5	1.61 - 33.2	3.33	50.7 - 9970.	397.
Magnetite	2	1.21 - 4.19	2.70	4.65 - 978.	491.
Massive Sulphides	2	10.6 - 16.7	13.7	290. - 2700	1495
Molybdenite	3	9.04×10^4 - 2.17×10^5	1.69×10^5	$2.80 - 6.73\times10^7$	5.25×10^7
Pyrite	4	1.40 - 48.9	24.9	$451 - 1.49\times10^4$	538

Note: N = Number of samples.

The large ratios for molybdenites, which result from their high rhenium content, are readily apparent from Table 7-6. An examination of the limited data in this table and Figures 7-1 and 7-2 suggests that magnetites may be useful for defining points near the $^{187}Os_{total}/^{186}Os$ axis when attempting to use the isochron method in rhenium-osmium chronology. Pyrite shows a wide range of values for the deposits analysed, and in view of its ubiquity should probably be included in any rhenium-osmium geochronological study. Massive sulphides, that is "whole rock" sulphides, are of importance to rhenium-osmium geochronology for the same reasons that whole rock samples are to the rubidium-strontium method. At the present stage in rhenium-osmium work, however, analysis of massive sulphides has the additional potential of leading to either the discovery of new minerals or concentrator minerals of osmium and rhenium, or to the identification of minerals previously not reported.

6. The Suitability of Various Ore Types to Re-Os Geochronology

Molybdenite-bearing metallic deposits with direct igneous affiliations are particularly amenable to dating by the rhenium-osmium method. Examples in this class are numerous and include molybdenite-bearing pegmatites and quartz veins, molybdenite-wolframite greisens as well as contact metasomatic deposits and skarn deposits containing molybdenite. Also included in this group are certain types of porphyry deposits, such as the porphyry molybdenums, molybdenite-bearing porphyry copper deposits and molybdenite-bearing porphyry tungsten deposits.

Further, on the basis of this study, it is suggested that the nickel copper sulphide ores, such as are being mined at Strathcona Mine, are amenable to rhenium-osmium geochronology. This is particularly significant in view of the importance of ores of the nickel-copper-platinum group metal class which are associated with mafic and ultramafic rocks. Another type of copper ore which appears to be suitable for the application of the rhenium-osmium method occurs at Messina, Transvaal, South Africa, where platinum group minerals are associated with copper iron sulphides ascribed a hydrothermal origin by Mihalik et al. (1974). Of particular interest in this deposit is the occurrence of abundant clausthalite, a known concentrator mineral of rhenium, which occurs as a seam 8 cm. wide associated with chalcocite and bornite. The age of the sulphide mineralisation, determined by the Pb/Pb method, is at least 2,200 my (P.G. Coomer, personal communication, 1975).

In attempting to assess the applicability of the rhenium-osmium method to primary platinum deposits, however, the situation is confused by two apparently opposing trends. Mineralogical evidence, for example the association of rhenium with chromite, and with iridium and osmium in detrital osmiridium in conglomerates of the Witwatersrand (cf. Chapter 5), suggests that primary platinum deposits warrant investigation for their potential application to the rhenium-osmium method. However, surveys of abundance data suggest that there is an inverse correlation between osmium and rhenium abundances in rocks and that rhenium abundances are low in ultramafic rocks. Consequently, one might predict relatively high, possibly unfavourably high, osmium: rhenium ratios in primary platinum deposits with chromite affiliations.

However, common osmium:rhenium ratios may be acceptable for much older deposits, by virtue of the larger quantities of $^{187}Os^{*}$ generated in the older deposits.

Other ores with igneous affiliations for which dating by the rhenium-osmium method may be feasible include beryllium, yttrium, hafnium and zirconium-bearing granite pegmatites. Also, the results from the Adams Mine suggest that certain volcanogenic iron ores, particularly those associated with alkali basalts, should be investigated in order to evaluate more fully their suitability to direct dating by the rhenium-osmium method.

Sedimentary ores which may have a role in rhenium-osmium geochronology include cupriferous sandstones of the Dzhezkazgan class, as well as copper ores associated with bituminous shales, as for example, the White Pine Mine, in Michigan, U.S.A. Similarly, studies of uranium-copper-vanadian ores of the Colorado Plateau which are known to have high concentrations of rhenium, are worthy of further investigation.

On the basis of this study, it appears that several types of ore deposits are unfavourable to the Re-Os method by virtue of the low rhenium and osmium abundances in their principal metallic minerals. They are: (1) stratabound sulphides of volcanogenic origin, (2) porphyry copper deposits lacking, or containing trace amounts of molybdenite, (3) base metal contact metasomatic deposits.

In (1), exemplified by Heath Steele and Kidd Creek, the principal metallic minerals, chalcopyrite, pyrite and sphalerite, are characterised by extremely low abundances of both rhenium and osmium. If these results are representative, it is likely that the only possibility for the application of Re-Os geochronology to this class of deposit is the presence of rhenium-carrier minerals in the minor metallic mineral assemblage.

Minerals such as clausthalite ($PbSe$) and naummanite (Ag_2Se), which occur in volcanogenic stratabound massive sulphide deposits, are of potential importance to the Re-Os method in this regard. Clausthalite, which occurs in the uranium-vanadium deposits of the Colorado Plateau, has also been reported from the ores of Kidd Creek (Walker and Mannard, 1974) and Rio Tinto (Roberts et al., 1974). However, although there are no data on the rhenium content of naummanite, it is also considered to be a potentially significant mineral in Re-Os chronology because of its association with clausthalite in the Harz Mountains, Germany (Roberts et al., 1974), and because of the positive correlation between rhenium and selenium in some molybdenites. It is interesting to note, therefore, that in addition to clausthalite at Kidd Creek, 4 modal percent naummanite has been reported in a polished section from these ores by Tepedino (1969). Further, at Heath Steele, 3.17 ppb rhenium occurs in an unidentified carrier-mineral in massive sulphides (No. 4049) which assay 7.56 oz. silver/ton. Enrichment of rhenium among the minor mineral suite of this class of ore deposit is further suggested by the presence of molybdenum in the Kuroko ores, where it occurs in sufficient quantity to be manifest as molybdenite (Dr. Takeo-Sato, personal communication, 1975).

Obviously, considerably more data are necessary before a more complete evaluation can be made of the applicability of the Re-Os method to volcanogenic stratabound massive sulphide deposits.

In (2), Granisle Copper is the only deposit characteristic of this class of porphyry copper ore analysed in this work. The low abundance of rhenium in the major metallic minerals of Granisle Copper combined with the relatively young age of the deposit (51.2 my, see Table 7-1), result in the lowest $^{187}Os^*$ calculated in this work, viz. 10^{-13} to 10^{-14} gm/gm. The rhenium content of the molybdenite which occurs in minor quantities at Granisle Copper is not known, but the extremely low $^{187}Os^*$ abundances, combined with the low common osmium contents in the principal metallic minerals, do not favour application of the Re-Os isochron method to this class of ore deposit.

In (3), at Craigmont Mine, the three major metallic minerals, chalcopyrite, magnetite and pyrite, are slightly enriched in rhenium (2 to 37 ppb), compared with the rhenium content of the common metallic minerals comprising the deposits of the previous two classes.

However, the quantities of $^{187}Os^*$ (7.9×10^{-11} to 7.8×10^{-12}) generated in 200×10^6 years, are sufficiently small as to place this, and similar but younger deposits, beyond the current scope of the Re-Os method. Very much older deposits of the base metal contact metasomatic class, which are associated with the margins of igneous rocks with known rhenium affiliations, may, if suitably enriched in rhenium, be amenable to direct dating by the rhenium-osmium isochron method.

7. Assessment of the Half-Life of ^{187}Re

In spite of the inaccuracies built into the currently accepted value for the half-life of ^{187}Re, the figure of $4.3\pm0.5\times10^{10}$ years, which was determined by the geological method, is considered to be a reasonable approximation for the following reasons. The age of iron and stone meteorites given by the rhenium-osmium method as 4 to 5 billion years (Herr et al., 1961), is in reasonable agreement with the age of 4.5 to 4.7 billion years given by the rubidium-strontium method (Faure and Powell, 1972). Also, Herr et al. (op. cit.) obtained ~~an~~ apparent rhenium-osmium age of 3080±70 million years for molybdenite from granulite facies metamorphic rocks in the Fiskenaesset area of southwest Greenland. The granulite metamorphic event in this area has subsequently been dated at 2,800-2,900 million years by the lead method, and 3040±50 million years by the rubidium-strontium whole rock isochron method (Pankhurst et al., 1973). Further, molybdenite from the Shap Granite, England, gave an age of 430±20 million years by the rhenium-osmium method, and the age of the granite has been determined by the rubidium-strontium method as 380±19 million years (Herr et al., 1967).

However, the half-life of ^{187}Re can, undoubtedly, be refined. In view of the very low energy of the β^- decay of ^{187}Re, the geological method, involving use of the isochron technique, would obviously present the most satisfactory approach. Several deposits, or types of deposit, warrant consideration in any experiments aimed at refining the half-life of ^{187}Re. Those most worthy of attention are the Ni-Cu ores of the Sudbury area where, as exemplified by the results from Strathcona Mine, the applicability of the rhenium-osmium method is currently feasible, and where the age of the norite is now well established (Krogh and Davis, 1974; Gibbins and McNutt (in press)). In this context the association between rhenium and selenium in some molybdenites (Ivanov et al., 1972), suggests that a study of the distribution of rhenium and selenium in the Sudbury ores is warranted. This is particularly so in view of the characteristic of selenium to combine with heavy elements, and the fact that no selenium minerals occur at Sudbury (Hawley, 1962). Instead, selenium substitutes for sulphur in the sulphide minerals where it occurs, in increasing order of abundance, in pyrrhotite, pentlandite and chalcopyrite (Hawley, 1962). Therefore, by establishing the relationship between rhenium and selenium in the sulphide minerals, the selenium content of the ores, which is infinitely better known than that of rhenium, could be used as a guide for Re-Os geochronological studies of these deposits.

A second type of deposit to be taken into account are the rhenium-rich uranium-copper-vanadium deposits of the Colorado Plateau (discussed in Chapter 5). The deposits range in age from Carboniferous to Tertiary (Stanton, 1972), and are of particular interest because they afford the opportunity of establishing the age of the rhenium-bearing material directly by another radiometric method.

Thirdly, in the Fiskenaesset area of southwest Greenland where a metamorphic age of about 3.0 billion years has been established, rhenium-rich molybdenite is associated with a chromite-bearing complex. The great age of this area could be significant in terms of rhenium-osmium geochronology, particularly in the light of the general paucity of $^{187}Os^{*}$ in metallic deposits indicated by this study.

THE RHENIUM AND COMMON OSMIUM CONTENT OF THE ORES

1. General Statement

With the exception of molybdenites in the case of rhenium, and the Sudbury ores in the case of osmium(1), generally only very low

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(1) unless otherwise stated in this section, the term "osmium" refers to common osmium.

rhenium and osmium abundances were found in the common metallic minerals of the ores studied. About half of the rhenium abundances are in the 0.1 to 0.9 ppb range (Tables 6-1 to 6-7). This is about three orders of magnitude less than the average values of rhenium for common copper-iron sulphide minerals from a variety of ores cited in the Russian literature. Abundances for rhenium determined colorimetrically in tens of pyrites, chalcopyrites and bornites are given by Ivanov et al. (1972), and are presented in Table 7-7.

Table 7-7

Rhenium in Copper-Iron Sulphides of the USSR
(After Ivanov et al., 1972)

Mineral	Number of Analyses	Rhenium (ppm)
Bornite	65	45.
Chalcopyrite	62	0.86
Galena		0.2
Pyrite	60	0.3
Pyrrhotite		0.15
Sphalerite		0.05

The bulk of the rhenium results obtained here are also less, by one order of magnitude, than the lowest mean value determined by Morgan et al. (1968) in common Australian sulphide minerals by neutron activation analysis. Simultaneous determination of common osmium in these minerals yielded abundances described by Morgan et al. (1968) as, "vanishingly small". This characteristic is also a feature of the osmium content of several Canadian ore deposits. For example, the majority of the common osmium abundances obtained in this study are in the 0.01 to 0.09 ppb range, two orders of magnitude less than lowest mean value determined by Morgan et al. (1968).

2. Contact Metasomatic and Volcanogenic Massive Sulphides

Osmium abundances in the ore samples from Heath Steele and Kidd Creek were among the lowest encountered. At Kidd Creek three mineral separates have an average osmium content of 0.07 ppb, which is similar to the osmium content of tholeiitic basalt, BCR-1 (Table 5-9). At Heath Steele osmium values are exceptionally low. Three samples have a maximum osmium content ranging from ~0.03 to ~0.05 ppb. The highest value is 0.12 ppb. The very low concentrations of osmium in the samples from Heath Steele are consistent with the results of Mercer and Crocket (1972), who noted a significant depletion of palladium in the B-1 orebody relative to both the country rocks and to average crustal rocks.

In addition to their low osmium abundances, the Heath Steele ores also have low Os/Re ratios. Comparisons with Os/Re ratios of crustal rocks are hampered by the paucity of the data (two ratios only). However, at Heath Steele Os/Re ratios appear to be slightly lower than in felsic igneous and metamorphic rocks (Tables 5-9 and 6-2), and are lower than a shale from Australia by a factor of at least 890.

Also, the depletion of osmium relative to rhenium in one of two massive sulphides from Heath Steele is less by a factor of at least 13 compared to the Os/Re ratio of massive sulphide from the Main Ore Zone at Strathcona. The comparison with Strathcona is particularly apt in view of the magmatic nature of the Sudbury ores, and their intimate association with mafic sub-layer rocks of the Irruptive (Souch et al., 1969). These rocks contain ultramafic inclusions (Naldrett and Kullerud, 1967; Cowan, 1968) and are ascribed a mantle origin (Naldrett et al., 1972). Although the quartz-rich nature of the Irruptive and the relatively high initial $^{87}Sr/^{86}Sr$ (0.7063) of the norite (Gibbins, 1973) are evidence against a simple mantle source for the Irruptive, the massive sulphide at Strathcona is the most primitive* of the ores examined, and has therefore been used as a basis of reference in comparing Os-Re fractionation in the various ores.

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* Comparison of the degree of fractionation is made with meteorites where unfractionated Os/Re is taken as ~ 11 (Table 5-14). Ores and other samples are compared against this base.

The lowest Os/Re ratios encountered in this study, with the exception of those of the molybdenites, are values of 0.003 in chalcopyrite and pyrite from Craigmont Mine (Table 6-5). These ratios are considered to be a direct reflection of the influence of rhenium-bearing fluids derived from the Guichon Creek Batholith. This view tends to be supported by the fact that the Craigmont metasomatic deposits are genetically related to the Guichon Creek Batholith (Christmas et al., 1969).

3. Porphyry Cu and Porphyry Mo Deposits

At Granisle Copper there is a paucity of molybdenite and rhenium depleted in the principal metallic minerals. This suggests that molybdenum-deficient porphyry copper deposits are also deficient in rhenium. This is to be expected in view of the geochemical coherence between rhenium and molybdenum, but is in contrast to the situation at Craigmont Mine where there is no molybdenite and the principal metallic minerals are slightly enriched in rhenium (Table 7-2).

In an attempt to evaluate the role of molybdenite in the distribution of rhenium, Os/Re ratios have been calculated for molybdenite concentrate and a "typical" porphyry copper deposit from the Guichon Batholith. Data used for the calculation of the Os/Re ratio for the "typical" porphyry copper deposit from the Highland Valley are given in Table 7-8.

Table 7-8

Data for Calculation of Os/Re Ratio of a Typical Highland Valley Porphyry Copper Deposit

	Re (ppb)	Os (ppb)	Source
Chalcopyrite (H/S) (Alwin Mine)	1.95	0.19	Table 6-4
Bornite (H/S) (Bethlehem)	0.76	0.06	"
	(ppm)	(ppb)	
MoS_2 (concentrate) (Lornex)	257	0.08	"
Valley Copper (H/S)	293	0.19	"
	Av. 275	Av. 0.135	

Total Lornex Cu Metal (tons)	12.5×10^5	Canadian Mines Handbook 1974
Total Lornex Mo Metal (tons)	4.102×10^4	

Bornite/Chalcopyrite = 4/1

H/S = Hand Specimen

Os/Re ratios of 5.90×10^{-5} and 4.91×10^{-7} were calculated for the "typical" prophyry copper deposit and molybdenite, respectively, suggesting that the molybdenite structure results in an enrichment of rhenium with respect to osmium by a factor of 120 relative to the distribution of these elements in the deposit as a whole. Also, the fractionation of osmium and rhenium in the deposit as a whole is very strong, being 2,200 times as great as Os-Re fractionation at Strathcona.

The enrichment of rhenium in the molybdenites of porphyry Cu-Mo deposits compared with its abundance in molybdenites from porphyry Mo ores is well illustrated in Table 7-9, and agrees with the results of Giles and Schilling (1972). Contrary to their views, the bulk rhenium content of molybdenites from porphyry Cu-Mo ores appears to be significantly greater than that of molybdenites from porphyry Mo deposits. This suggests a genetic difference between the two groups in which copper plays an essential role. Possibly, in the ore-forming solutions a copper complex exists which also preferentially complexes rhenium, but which breaks down at the site of metal deposition, thereby enabling rhenium to enter the molybdenite structure (Giles and Schilling, 1972).

Table 7-9

Rhenium Content of Some Porphyry Cu-Mo and Porphyry-Mo Deposits

Deposit	Tons	Reserves[1] Mo (%)	Cu (%)	Re (ppm)[2]	Metal Reserves (Tons) Mo	Cu	Re (Metric tons)	$\frac{Cu}{Mo}$
B.C. Molybdenum	$40.2x10^7$	0.138	-	77.8	$5.5x10^3$	-	7.20	-
Boss Mt.	$2.7x10^6$	0.25	-	54.0	$6.75x10^3$	-	6.08	-
Endako	$1.53x10^8$	0.085	-	36.1	$1.30x10^5$	-	7.84	-
J.A. Zone (Bethlehem Copper)	$2.86x10^8$	0.017	0.43	222.	$4.87x10^4$	$1.23x10^6$	18.1	25.3
Lornex	$2.93x10^8$	0.014	0.43	257.	$4.1x10^4$	$1.25x10^6$	17.6	30.5

(1) Ore Reserve Data from Canadian Mines Handbook (1973-4)

(2) Rhenium content for MoS_2 concentrates

The rhenium contents and geological characteristics of some Canadian molybdenite ores are given in Table 7-10. The complexity of the porphyry intrusives is based on Sutherland-Brown's (1969) classification. In order to minimise intradeposit variations, MoS_2 concentrates were analysed where possible. With the exception of Gaspe Copper and the deposits of the Preissac LaCorne Batholith, all the deposits sampled are in the Intermontane Belt of the Cordillera. The only pattern discerned in the distribution of these deposits is a northwest trending lineament joining the three porphyry molybdenum deposits - Boss Mountain, Endako and B.C. Molybdenum(see Figure 6-1).

The limited data and intradeposit variations in the rhenium content of molybdenites not withstanding, Tables 7-9 and 7-10 indicate generally low rhenium contents for molybdenites of Sutherland-Brown's plutonic porphyry class, e.g. Brenda and Endako Mines in B.C., as well as Molybdenum Corporation and Preissac Molybdenum in Quebec, which are considered by Sawkins (1972) to represent root zones of porphyry deposits. Three of these deposits are copper-poor, and two, the ores of the Preissac LaCorne Batholith, are associated with bismuth. At Brenda Mine, where molybdenum is associated with copper, the rhenium content appears to be higher than in other plutonic molybdenites. This suggests that for the copper-deficient plutonic ores, molybdenite may have

Table 7-10

Geological Features of Rhenium-Bearing MoS_2 Ores

Mine	Rhenium (ppm) in MoS_2	Major Metal(s)	Composition of Intrusive$^{(1)}$	Complexity of Intrusive$^{(2)}$	Age m.y.$^{(2)}$	Tectonic Setting
B.C. Molybdenum	77.8	Mo	Qm^{1a}	Elaborate	53 K/Ar	Cordilleran Intermontane Belt$^{(2)}$
Bethlehem Copper	211, 234, 335, 1162	Cu, Mo	Qm	Complex	200 K/Ar	
Boss Mt.	54.0	Mo	Gd^{1b}	Elaborate	105	
Brenda Mine (H/S)	63.4	Mo, Cu	Gd.	Plutonic	150-180	
Endako	36.1	Mo	Qm	Plutonic	150	
Highmont H/S	95.7	Cu, Mo	Qm, Gd	Complex	200 K/Ar	
Lornex	224, 257	Cu, Mo	Qm, Gd	Complex	200 K/Ar	
Valley Copper (H/S)	293	Cu, Mo	Qm	Complex	200 K/Ar	Cordilleran Intermontane Belt$^{(2)}$
Gaspé Copper	84.4, 168	Cu, Mo	Qm^{1c}	-	346^{1a} K/Ar	Appalachian Orogen
Molybdenum Corporation of Canada	24.4	Bi, Mo	G^{1d}	-	2485 Rb/Sr	Orogenic granite
Preissac Molybdenum Co.	28.0	Bi, Mo	G	-	2485 Rb/Sr	Orogenic granite

Table 7-10 continued

Sources:	(1)	Copper and Molybdenum Deposits of the Western Cordillera, Guidebook A09-C09, 24th International Geological Congress, Montreal.
	(1a)	Clark (1972)
	(1b)	Soregaroli (1975)
	(1c)	Hollister _et al._ (1974)
	(1d)	Vokes (1963)
	(2)	Sutherland Brown (1969)
	H/S	Hand specimen. All other molybdenites are MoS_2 concentrates.

Abbreviations:

Gd: Granodiorite

Qm: Quartz Monzonite

crystallised from rhenium-impoverished fluids. However, Giles and Schilling (1972) have tentatively suggested that at Bingham there is a decrease in the rhenium content of molybdenite with depth. Therefore, if Sawkins' (1972) interpretation is correct, the low rhenium content of the Preissac LaCorne molybdenites may be indicative of a physical control, for example, a temperature gradient. Alternatively, bismuth, which is known to occur in molybdenite in sufficiently high concentrations to crystallise as discrete minerals (R.R. Potter, 1968, personal communication), may have depressed the rhenium content of the molybdenites of the Preissac LaCorne Batholith.

Also, the rhenium content of molybdenite from Gaspé Copper appears to be intermediate between the molybdenites with plutonic affiliations and those associated with porphyry copper ores (Table 7-8). This result tends to substantiate the interpretation of Hollister et al. (1974), who have recently recognised the occurrence of porphyry-type deposits associated with the Appalachian Orogen. They ascribe the differences between these deposits and the porphyry coppers of the Cordillera as mainly due to the greater age and depth of erosion of the deposits of the Appalachian Orogen.

4. Iron Formation

Osmium and rhenium at the Adams Mine are present as trace elements in both the major and minor metallic minerals. The osmium content of a single whole rock sample of banded iron ore from the mine is 3.20 ppb, and in magnetite separated from the same sample is 2.53 ppb. (see Table 6-3). These values are equivalent to the lowermost concentrations of osmium in the sulphide minerals of the Sudbury ores (Keays and Crocket, 1970).

Osmium values from the iron ore at the Adams Mine are higher by a factor of 7 than the highest osmium value reported to date for sedimentary rocks (Table 5-11). In marked contrast to the iron ore, the immediately adjacent country rock horizons are low in osmium. For example, single samples from each of the footwall lean iron formation and the hanging-wall cherty quartzite contain 0.04 ppb and 0.05 ppb osmium respectively. Also, the osmium content of a single sample from the footwall tholeiitic flows is 0.14 ppb (Table 6-3), which is intermediate between the osmium content of diabase, W-1, and tholeiitic basalt, BCR-1 (Table 5-9), but much lower than the ore. The question of the origin of the osmium in the Boston Iron Formation is discussed in a later section.

5. Genetic Considerations

Mention has been made in Chapter 5 of the depletion of osmium and rhenium in achondrites relative to chondrites and iron meteorites. The similarity of osmium abundances in achondrites and terrestrial ultramafic rocks was also noted. The abundance of rhenium in deep seated ultramafic rocks is more problematical, but at least in one instance of a peridotite nodule cited by Morgan and Lovering (1967), it is comparable with that of achondrites.

As a result of their siderophile characteristics osmium and rhenium are undoubtedly highly enriched in the earth's core relative to the upper mantle and crust. The siderophilic character of these metals is shown by their enrichment in iron meteorites, and their partitioning into the metallic phase relative to the silicate and sulphide phases of chondrites (Crocket, 1972; Herr et al., 1961). Further, the depletion of osmium and rhenium in the mantle is probably a reflection of processes which were active during the formative stages of the primitive earth. On the basis of the high boiling points of rhenium and osmium, Crocket (1972) has suggested that significant quantities of both elements condense at temperatures of about 2000°K during the accretionary stage of iron meteorite condensation. In this model, metallic iron probably represents the first important sink for rhenium and osmium, which are thought to alloy directly with the metallic iron. This is not unreasonable in view of the complete solid solution between osmium and iron and the Os/Re ratios of iron meteorites.

Hence, a major fractionation of osmium and rhenium between iron and silicate phases probably occurred in the primordial earth. Formation of the core and consolidation of the mantle, therefore, resulted in osmium and rhenium being highly depleted in the mantle relative to the core.

At Strathcona osmium and rhenium are relatively strongly fractionated compared with their relative abundances in chondrites. For example, the Os/Re ratio at Strathcona is less than that of chondrite meteorites by about 90 (see Table 5-14). As such the value of 0.13 for Os/Re in massive sulphide from Strathcona is probably a reflection of the depletion of osmium relative to rhenium effected during the formation of the mantle-derived initial sulphide melt from which the ores crystallised.

At the Adams Mine iron formation is intimately associated with mafic volcanic rocks (Chapter 6). This spatial association between mafic volcanism and Archean iron-formation is well known, and has been interpreted as evidence for a direct genetic link between the iron formation and volcanic activity (Goodwin, 1973; Hutchinson et al., 1971; Ridler, 1970) although the exact role played by the volcanism is not known.

The apparent homogeneity of rhenium, and particularly that of osmium, in the Boston Iron Formation, and the association of these elements with the iron, suggests that rhenium and osmium were deposited from solution at the time the iron precipitated. Anomalous concentrations of the transition and noble metals associated with sediments of the East Pacific Rise are considered to have been scavenged from solution by iron hydroxide (Crocket _et al._, 1973; Bostrom and Peterson, 1966); therefore, it is likely that the rhenium and osmium in the Boston Iron Formation was precipitated in a similar manner.

Mechanisms capable of providing the metals in solution within the submarine volcanic model include (i) hydrothermal exhalations of magmatic origin (Bostrom and Peterson, 1966; Crocket _et al._, 1973); (ii) creation of metal-enriched hydrothermal solutions by the action of sea water on hot basaltic material (Corliss, 1971 and Piper, 1973); (iii) cold alteration of basaltic rocks by oceanic water (Keen, 1975). The first two mechanisms either individually or in combination are considered adequate to supply the required dissolved metals, although the Corliss model, which allows for a sea water component, provides greater flexibility. However, the relative lack of fractionation between osmium and rhenium in magnetite at the Adams Mine, and the paucity of data indicate that additional data are required to test these models.

Relative to Strathcona progressively smaller Os/Re ratios occur at Heath Steele, Craigmont and the "typical" porphyry copper of the Highland Valley where the ratios are smaller than that at Strathcona by factors of 13, 43 and 2,200 respectively. Volcanogenic, strata bound, massive sulphide deposits and porphyry copper ores are characterized by their close genetic affiliations with felsic derivatives of calc alkaline magmatism (Sangster, 1972; Sillitoe, 1972), and this has led to the development of a plate tectonic model for the origin of these ores (Sawkins, 1972; Sillitoe, 1972). In this model, felsic calc alkaline rocks are considered as typical end products of magmatism generated along subduction zones between compressive lithospheric plates. The role of hydrothermal solutions in the formation of both types of ore is generally accepted.

Several lines of evidence indicate a mantle source for the ores associated with the Guichon Batholith, including the Highland Valley porphyry copper ores and the metasomatic deposits of Craigmont Mine. These include an initial $^{87}Sr/^{86}Sr$ ratio of 0.7037 obtained from a mineral-whole rock isochron (Christmas <u>et al</u>., 1969), and by sulphides with δS^{34} values near zero per mil (Christmas <u>et al</u>., 1969; Jones, 1975). Recently Kesler <u>et al</u>. (1975), on the basis of petrographic, chemical and isotopic data, have reaffirmed the primitive nature of porphyry copper intrusions with island arc affinities, including that of the Guichon Batholith.

Therefore, the low Os/Re ratios of the ores associated with the Guichon Creek Batholith are considered to reflect enrichment of rhenium relative to osmium during the formation of these deposits, starting with a source in the mantle and culminating with ore deposition at a high level in the crust (Sawkins, 1972; Sillitoe, 1972). Enrichment of rhenium relative to osmium may occur during the differentiation from basaltic to granitic magma in which Os/Re show the opposite tendency. Also, in the granitic melt osmium and rhenium are excluded from the common rock forming minerals and are therefore concentrated in the aequeous-rich residual fluids, where they probably exist as chloride complexes. The solubility of osmium and rhenium in hydrothermal solutions may be considered as a function both of the oxidation potential of the solution and the oxidation state of each metal. In this model the ability of both osmium and rhenium to exist in a wide range of oxidation states plays an important role in the fractionation of the two metals in the hydrothermal environment. The response of either metal to increments in the oxidation potential of the solution will be slightly different, resulting in interelement differences in oxidation state and solubility. In this manner significant fractionations between osmium and rhenium could be achieved in hydrothermal solutions, even though the response of both metals to changes in oxidation potential have the same sense.

The role assigned to hydrothermal solutions in effecting fractionation between osmium and rhenium seems reasonable in view of the low Os/Re ratio at Strathcona where water is relatively unimportant in the ore-forming process. However, at the Heath Steele, Craigmont and the Highland Valley deposits in which hydrothermal solutions have played an important role in ore formation, osmium and rhenium are progressively more fractionated.

CHAPTER 8

SUMMARY AND CONCLUSIONS

Prior to this investigation, only very limited data were available on rhenium and osmium in ore deposits. Rhenium was known to be concentrated in molybdenites and osmium was known to occur together with the platinum metal group in mafic and ultramafic rocks. However, no methodical intradeposit studies had been conducted on the two elements and only osmium had been studied systematically at Sudbury.

The results of this work are summarised as follows:

(1) The Strathcona ores are amenable to dating by the Re-Os method with current techniques and could be used to refine the half-life of ^{187}Re by the isochron method. Knowledge of the relationship between rhenium and selenium in the Strathcona ores would assist such a study.

The rhenium content of Strathcona chalcopyrite and pyrrhotite is about 20 ppb, and in one massive sulphide sample it is 255 ppb. The Os/Re ratio at Strathcona is about 0.13. Calculated ^{187}Os* (radiogenic) is in the range 0.5 to 5 ppb. Samples of up to 100 grams would be required to provide sufficient $^{187}Os^*$ for mass spectrometry.

(2) Nickel-copper ores similar to those at Strathcona favour application of the Re-Os isochron method.

(3) By virtue of their high rhenium content molybdenites frequently generate $^{187}Os^*$ in sufficient quantity for mass spectrometric analysis. However, the extremely low common osmium abundances in molybdenite results in the radiogenic osmium being virtually monoisotopic. Extremely high $^{187}Re/^{186}Os$ ratios in molybdenites (of the order 10^7 in the Guichon Batholith) do not favour the use of this mineral in the isochron method.

(4) Very low abundances of rhenium and osmium in the principal metallic minerals of strata bound, volcanogenic massive sulphide deposits, contact metasomatic deposits, molybdenum-deficient porphyry Cu and Precambrian banded iron formation mitigate against application of the Re-Os method to these deposits. These ores, which range in age from 50 to 2750 my, generally contain 0.1 to 0.9 ppb rhenium, 0.01 to 0.09 ppb osmium, and $^{187}Os^*$ calculated to be in the 10^{-12} to 10^{-14} gm/gm range. Hence samples weighing between 10 and 10^3 kgm. would be required to provide the minimum quantity of $^{187}Os^*$ for mass spectrometry.

(5) The only prospect of applying the Re-Os method to volcanogenic, strata bound, massive sulphide ores appears to be the minor metallic mineral assemblage. Selenide minerals such as clausthalite, a known concentrator mineral of rhenium, berzelianite and naummanite warrant investigation, particularly so because of the positive correlation between rhenium and selenium in some molybdenites. Clausthalite occurs at Rio Tinto and Kidd Creek, and four percent naummanite has been reported from Kidd Creek.

(6) Apart from Strathcona, other areas which could be used to refine the half-life of ^{187}Re include the rhenium-rich uranium-copper-vanadium deposits of the Colorado Plateau, and the Fiskenaesset area of southwest Greenland.

(7) Rhenium is enriched in molybdenites associated with porphyry copper ores and the bulk rhenium content of molybdenites in porphyry Cu-Mo ores appears to be significantly larger than that of porphyry Mo ores.

Also, molybdenites associated with porphyry deposits of Sutherland-Brown's plutonic class appear to be impoverished in rhenium.

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APPENDIX A-1

PROCEDURE FOR RHENIUM AND/OR OSMIUM STANDARDS

(A) Preliminary Treatment for All Standards

(1) Pipette 3.0 ml of carrier solution into a 35 ml zirconium crucible.

(2) Freeze ampoules which have been irradiated for long periods (greater than six days) in liquid nitrogen.

(3) Open vial and quantitatively transfer standard powder to crucible containing carrier.

(4) Add small amount of 95% ethanol if any powder floats on surface.

(5) Make carrier solution alkaline by addition of 1.0 mls 3M NaOH. Add 2 mls ethanol and let stand for ten minutes.

(6) Evaporate to incipient dryness under aheat lamp and take to complete dryness using a warm hot plate.

(7) Add 3 gms Na_2O_2 and 3 pellets NaOH to the dry salts and fuse as for sample (Appendix A-2, Step 4).

(8) Quench crucible in water and leach the fusion cake with 30 ml distilled water.

(9) Let stand for 20 minutes then transfer to a 250 ml beaker.

(10) Centrifuge out insoluble hydroxides.

(11) Decant and retain supernatant. Wash the precipitate with 10 ml water and centrifuge.

(12) Add this supernatant to previously retained supernatant. The volume at this point is about 45 mls.

If processing osmium only or rhenium-osmium standards, proceed with step (13).

If processing rhenium-only standards, proceed with step (27).

(B) Osmium-only and Rhenium-Osmium Standards

(13) Admit the supernatant to the distillation flask. The apparatus used for the distillation of osmium standards is essentially the same as that used for the osmium samples up to and including the primary receiver. See plate A2-1. The receiving flask contains 30 mls chilled 3M NaOH. Waste gases from the receiving flask are neutralised in a weak ammonium hydroxide solution prior to venting into the fumehood.

i) Separation of Osmium

(14) Bubble nitrogen sweeper gas through the distillation line at the rate of 2 bubbles/second.

(15) Admit 20 mls 50% H_2SO_4 rapidly to distillation flask and immediately add 10 mls 35% H_2O_2. Immediately close stop-cock to ensure rapid acidification of osmium solution. (This is necessary to prevent hydrolysis of osmium.)

(16) Distil osmium tetroxide at 80° to 90° for thirty minutes. Osmium is retained in the ice-chilled receiving flask as sodium osmate. Retain the solution in the distillation flask.

(17) Transfer osmium distillate to a 250 ml beaker. Acidify with concentrated hydrochloric acid, and heat on a hot plate to just below boiling.

(18) Precipitate osmium metal with addition of slight excess of zinc powder and heat for 15 minutes.

(19) Destroy excess zinc with concentrated hydrochloric acid.

(20) Centrifuge and retain precipitate.

(21) Add 6M hydrochloric acid and boil with electrothermal bunsen for at least three minutes.

(22) Centrifuge and retain precipitate. Wash precipitate with water and centrifuge. Repeat once with water and once with ethanol.

(23) Slurry with ethanol, plate out onto weighed vycor planchet and dry under a heat lamp.

(24) Weigh.

(25) Count.

(26) For rhenium component of rhenium-osmium standards boil the residual liquid in distillation flask (from step 16) to destroy hydrogen peroxide and transfer to 250 ml beaker before proceeding with next step.

ii) General Treatment for Rhenium Standards

(27) Precipitate rhenium sulphides by adding 25 mls concentrated hydrochloric acid and diluting to 100 mls with water. Add one gram of thioacetomide and heat for one hour.

(28) Centrifuge, discard supernatant, wash the precipitate with water, centrifuge and decant supernatant.

(29) Dissolve rhenium sulphides in 5 ml 5M sodium hydroxide and hydrogen peroxide. ~~Heat~~ with electrothermal bunsen to assist dissolution. Destroy hydrogen peroxide by boiling with electrothermal bunsen as for samples.

(30) Make volume up to 15 mls with 5M sodium hydroxide. Transfer to 125 ml separatory funnel. Extract rhenium into 15 mls methylethylketone by shaking for 1-1/2 minutes.

(31) Transfer rhenium-bearing organic phase to 250 ml beaker and evaporate to dryness as for samples.

(32) Dissolve residue in 2 mls concentrated hydrochloric acid and 5 mls water. Add 5 drops ferric chloride and 2 drops lanthanum chloride solution.

(33) Make solution weakly alkaline with concentrated ammonium hydroxide, and heat to boiling.

(34) Cool to room temperature and centrifuge out iron hydroxide. Filter supernatant through Whatman 541 filter paper. Collect filtrate in a 50 ml beaker.

(35) Adjust pH to 8.5 with ammonium hydroxide and/or hydrochloric acid.

(36) Add 3 mls of 1% aqueous tetraphenylarsonium chloride solution. Stir, heat to 70°C for 5 minutes.

(37) Chill for 15 minutes in ice. Centrifuge, discard supernatant.

(38) Wash precipitate with ice cold water and centrifuge. Repeat additional two times.

(39) Slurry with cold water and plate out on a weighed aluminum planchet.

(40) Dry under a heat lamp using an airstream. Dry in an oven at 105°C for 30 minutes to ensure complete dryness of tetraphenylarsonium perrhenate.

(41) Weigh.

(42) Count.

APPENDIX A-2

TREATMENT OF SAMPLES

(A) Preliminary Treatment for All Samples

(1) Add 5.0 mls carrier solution to a 35 ml zirconium crucible followed by 1.7 mls 3M NaOH (also add 2 mls 95% ethanol where osmium carrier is involved).

(2) Let stand for ten minutes, then evaporate to incipient dryness with a heat lamp and finally to complete dryness on a hot plate.

(3) Transfer sample from vial to crucible (samples irradiated for more than 6 days are frozen in liquid nitrogen prior to opening).

(4) Fusion: Add 1.5 grams sodium peroxide, 3 to 5 pellets NaOH (depending on size) followed by 1.5 grams sodium peroxide. Heat at low temperature for four minutes, then to cherry redness for four minutes. Swirl three times during latter heating to obtain homogenization between sample and carrier.

(5) Quench crucible in cold distilled water and place on 5" diameter "Speedy Vap" watch glass.

(6) Leach fusion cake with 30 mls distilled water taking care to avoid splutter.

(7) Allow crucibles to stand for 1/2 hour.

(8) (a) Transfer liquid sample from crucible to 50 ml beaker. Use a policeman to insure quantitative transfer of sample from crucible, lid and any splutter on watch glass.

(b) Add 3 mls concentrated hydrochloric acid to crucible to assist dissolution of any residue. Add 10 mls water and transfer to 100 ml beaker.

(9) (a) Transfer sample to test tube and centrifuge out insoluble hydroxides. (The supernatant contains rhenium and osmium in their highest oxidation states.)

(b) Transfer supernatant to 250 ml beaker. Wash insoluble hydroxides with 10 mls water, centrifuge and add supernatant to sample.

For samples being processed for rhenium only, proceed with step 18(a); otherwise, proceed directly with the next step.

(B) Separation of Osmium

(10) Transfer the supernatant liquid from step (9) to the primary distillation flask (see plate A2-1). Adjust flow rate of nitrogen to two bubbles/sec.

(11) H_2SO_4 - H_2O_2 Distillation.

(a) Add 20 mls 50% H_2SO_4 to the sample through the thistle funnel, followed immediately by 10 mls hydrogen peroxide. (Note:- rapid acidification of the osmium is necessary to prevent hydrolysis.)

(b) Using heating mantles, distill at 85° to 90° for 20 minutes then heat water trap to boiling for 10 minutes.

(c) Osmium is retained in the primary receiver in ice-chilled 3M sodium hydroxide (see Plate A2-1).

(d) Reduce line to room temperature and transfer sodium osmate to 250 ml beaker. Wash primary receiver then return to distillation line.

(12) Precipitate osmium disulphide from chilled sodium osmate in a 250 ml. beaker by:

(a) Adding 10 mls hot H_2O solution containing 1 gram thio-actemide in 25 mls H_2O.

(b) Heat to boiling for 20 minutes (if this step is omitted a good precipitate does not result).

(c) Take to first reddening of litmus with 6M or concentrated HCl (bubbles vigorously near neutral point).

(d) Dilute with water to 125 mls. Boil for 10 minutes.

(e) Cool and centrifuge out osmium sulphide in a test tube.

(13) (a) Shut off nitrogen sweeper gas. Remove the original sample solution from the distillation flask and retain for rhenium processing.

(b) Wash distillation flask and replace in the line.

(14) HNO_3 - $NaBiO_3$ - H_3PO_4 Distillation:

Note:- Prior to the start of this distillation, (i) prepare all glassware required for the purification of the osmium in step 15; (ii) dissolve 0.3 grams $NaBiO_3$ in 5 mls concentrated boiling nitric acid.

(a) Start N_2 gas using 5 to 10 bubbles/second.

(b) Add 10 mls conc. HNO_3 to osmium sulphide precipitate from step 12(e). Stir well and admit to secondary distillation flask immediately.

(c) Add 5.0 mls concentrated HNO_3 in which 0.3 gms $NaBiO_3$ has previously been dissolved.

(d) Add 1.0 ml H_3PO_4 to the secondary distillation flask (D. F.) then wash out test tube which contained osmium sulphide with 2.0 mls conc. HNO_3 and add this to secondary D. F.

(e) Heat secondary D. F. to boiling point. When solution is nearly colourless (~5 mins.), add

(f) 5 mls conc. HNO_3 and 3 mls conc. H_2SO_4. Heat to 3 to 5 mins.

(g) Osmium is retained in 20 mls chilled 6M NaOH as sodium osmate. Proceed immediately with next step.

(15) Purification of Osmium Samples:

(a) Transfer sodium osmate obtained from step 14(g) to 50 ml beaker and place in ice bucket.

(b) Add conc. HNO_3 dropwise using micropipette until near neutral point. (Volume generally 37 to 39 ml at this point.)

(c) Make up volume to 40 mls with conc. chilled HNO_3.

(d) Immediately transfer to 125 ml separatory funnel and shake well.

(e) Immediately add 30 mls chloroform. Shake for 1-1/2 minutes.

(f) Allow phases to separate. Transfer organic phase (bottom layer) to clean 125 ml separatory funnel, add 30 ml 3M NaOH and shake for 1 minute.

(g) Drain off organic phase, transfer aqueous osmium-bearing phase to chilled test tube.

(h) Centrifuge to remove entrained chloroform.

(16) Precipitation of Os:

Proceed via steps 17-23, Standards Procedure, page 218.

(17) Weigh and count.

(C) Purification of Rhenium Samples

(18) Use rhenium solution from step 13(a) for primary purification by either ion exchange (19-1b) or by distillation (19-2).

(19-1) Primary purification of rhenium by ion exchange using De-Acidite FF resin:

(a) Preparation of anion-exchange columns (see Appendix A-3).

(b) Add 20 mls 12M hydrochloric acid to sample solution from step 13(a). Cool and stir well.

(c) Absorb rhenium onto prepared De-acidite FF column.

(d) Wash column with 50 mls 1M hydrochloric acid.

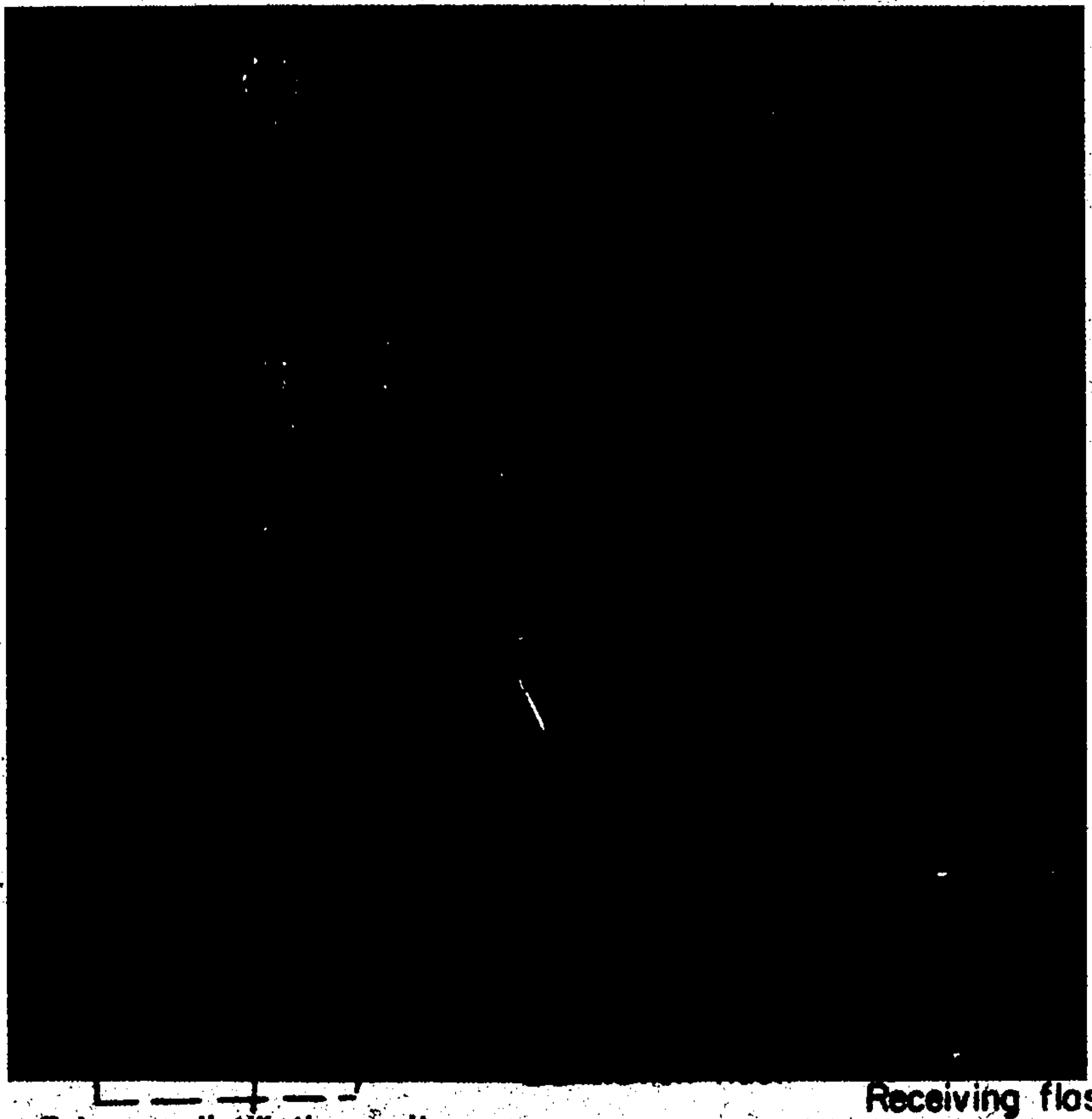
(e) Wash with 30 mls water.

(f) Elute rhenium with 60 mls 2.3M nitric acid at flow rate of 0.5 mls/min. Collect in 500 ml erlenmyer flask. Convert to chlorides as in step 20.

(19-2) Primary purification of rhenium by H_2SO_4-HBr-H_3PO_4 Distillation:

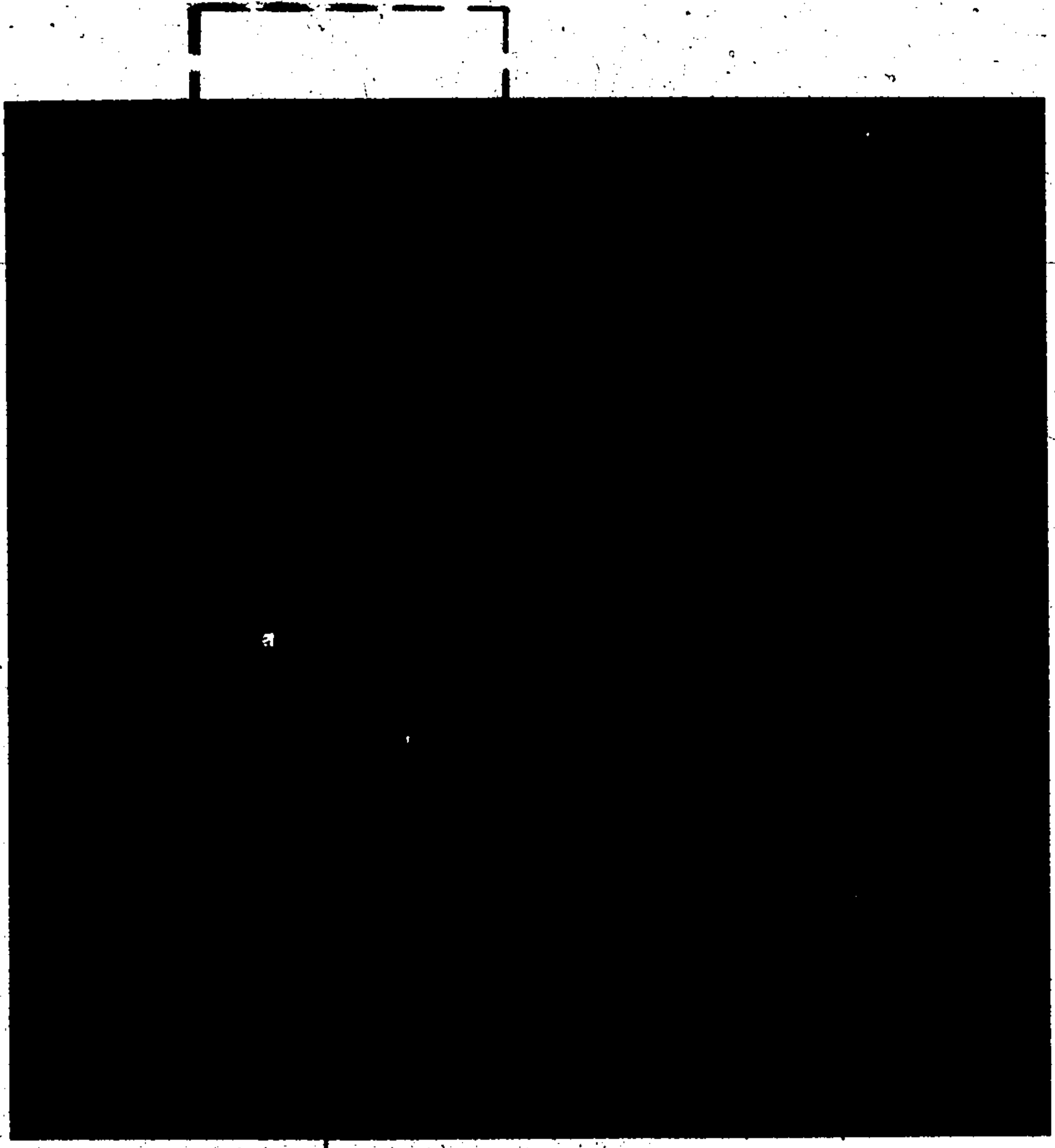
(a) Place rhenium solution in primary distillation flask of apparatus illustrated in Plate A2-2. (Note:

PLATE A2-1: APPARATUS FOR THE DISTILLATION OF OSMIUM



Scale : 1cm. = 4.72cm.

PLATE A2-2: APPARATUS FOR THE DISTILLATION OF RHENIUM



Primary distillation unit

Scale : 1cm = 5.04cm

The chilled receiving flask is initially empty, and waste gases are bubbled through dilute NH_4OH before being vented to the fume hood.)

(b) Start N_2 sweeper gas. Use moderately strong flow (~ 8 bubbles/sec).

(c) Add hold back carriers for Ag, Co, Cu, Fe, Mn, Mo, Ni and Zn to give metal contents of 10 to 40 mgms. (0.25 mgms for Ag.) The holdback carriers were in the form of sulphate solutions except for Mo which was in the form of sodium molybdate.

(d) Add 5 mls H_3PO_4 and 10 mls conc. H_2SO_4, followed by an additional 35 mls conc. H_2SO_4.

(e) Close stopcock. Place 25 mls conc. HBr in thistle funnel.

(f) Boil to drive off water and reduce to conc. H_2SO_4. Take temperature to 155°C.

(g) Drain water from receiving flask, replace with 17 mls chilled 6M NaOH. Replace receiving flask in line. Chill with ice.

(h) Heat distillation flask rapidly to 210° C. Start HBr dripping a few drops at a time. Increase drip rate of HBr until it is between 1.25 to 2.5 ml/min (i.e. distill at 200° to 220° C for 10 to 20 minutes).

(j) Place distillate in 250 ml beaker, add H_2O to 100 mls, precipitate rhenium sulphides as in step 21(b).

(20) Convert nitrates from step (19-1)f to chloride by:

(a) Adding 5 mls conc. HCl, attaching stem (length 5-3/4 inches, internal diameter 0.75 inches) to erlenmyer flask and heating to just boiling. The additional height provided by the stem to the erlenmyer flask is necessary to prevent serious losses of rhenium heptoxide by volatilization.

(b) Reduce volume of solution to about 2 mls. Add several mls concentrated hydrochloric acid to destroy nitrates and boil.

(c) Repeat step (b) until all nitrates are destroyed.

(d) Transfer to 250 ml beaker.

(21) Precipitate rhenium sulphides by:

(a) Adding 25 mls concentrated hydrochloric acid and diluting to 100 mls with water.

(b) Add 0.5 grams thioacetemide, cover with watch glass and heat gently for at least several hours.

(c) Centrifuge out rhenium sulphides.

(22) Dissolve rhenium sulphides by:

(a) Adding 5 mls 5M sodium hydroxide, 10 drops (more if necessary) hydrogen peroxide and heating with electrothermal bunsen.

(b) Add several mls water and boil back down to original volume of 5 mls. Place in 100 ml beaker.

(23) Solvent extraction of technetium:

(a) Dilute volume of rhenium solution to 15 mls with 5M sodium hydroxide.

(b) Dissolve 0.5 grams hydroxylamine hydrochloride in the solution to reduce technetium to the tetravalent state.

(c) First organic contacting:

(i) Transfer rhenium solution to 125 ml separatory funnel, add 15 mls methylethylketone.

(ii) Shake for one minute.

(iii) Drain aqueous phase (bottom) into original beaker. Retain.

(iv) Drain organic phase into clean separatory funnel. Retain.

(v) Replace aqueous phase in beaker back in dirty separatory funnel.

(d) Repeat step (c) and combine the organic phases.

(e) Clean combined organic phases by contacting with 5 mls 5M sodium hydroxide. Discard aqueous phase.

(f) Transfer organic phase to 250 ml beaker and evaporate to dryness on water bath at 70° using an airstream.

(g) Absorb rhenium into 5 mls formic acid hydrochloric acid solution (95/5 vol/vol).

(24) Final ion exchange treatment.

Preparation of Dowex 1-X8 ion exchange resin (see Appendix A-3):

(a) Absorb rhenium solution from (23)g onto prepared Dowex 1-X8 column.

(b) Elute with 35 mls formic acid-hydrochloric acid solution (95/5 vol/vol). Discard eluate.

(c) Elute with 25 mls water. Reject eluate.

(d) Elute with 45 mls 0.5M hydrochloric acid. Discard eluate.

(e) (i) Cool column with ice for ten minutes.

(ii) Elute rhenium with 50 mls acetone-hydrochloric acid solution (95/5 vol/vol) at 0.5 mls/min.

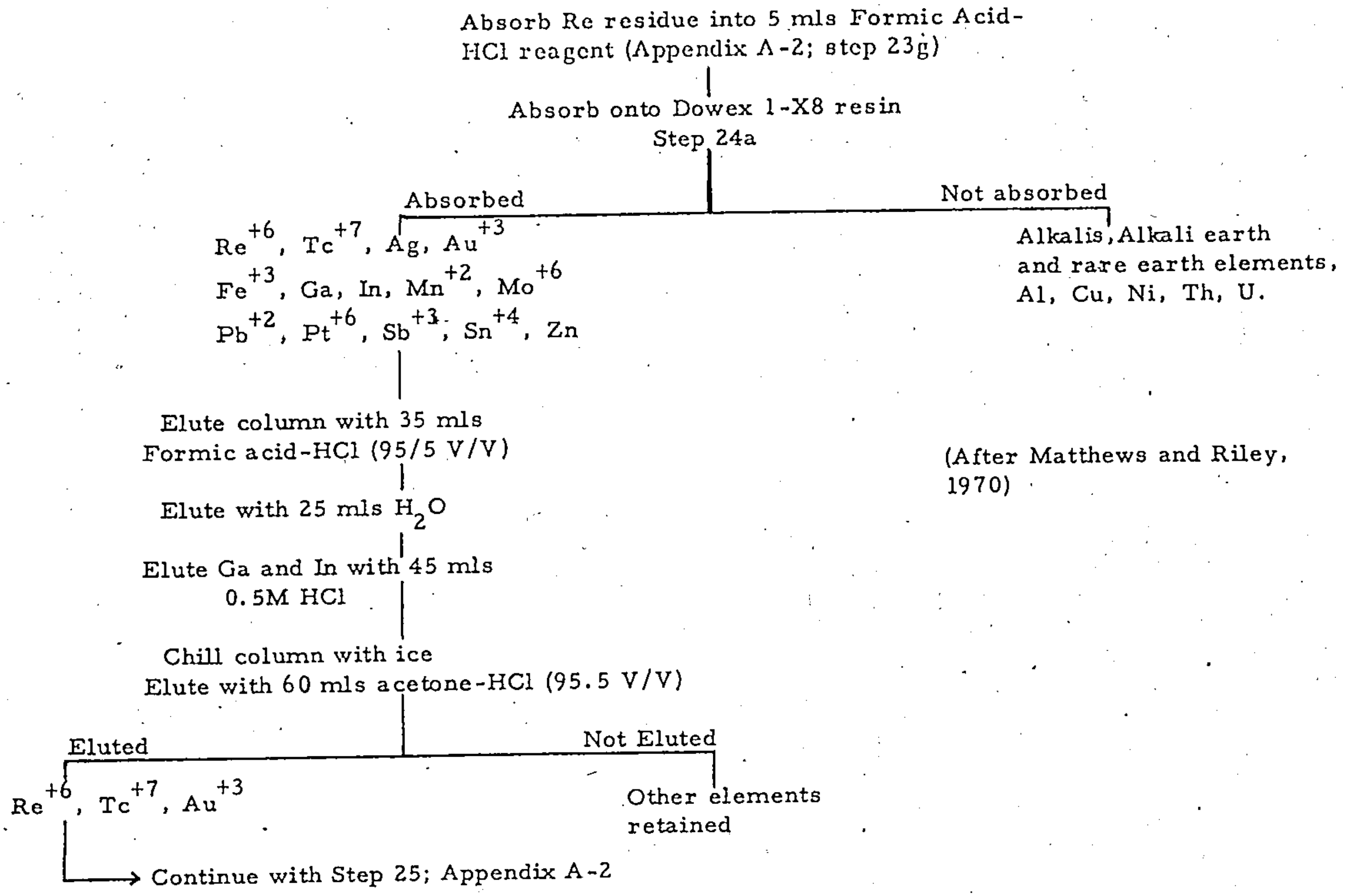
(iii) Collect rhenium in 250 ml beaker containing 10 mls water.

Note: The separation of elements achieved with DOWEX 1-X8 using the procedure outlined in step (24) is given in Figure A2-1.

(25) Evaporate off acetone using water bath at 70°C and air stream.

(26) Adjust pH to 8.5 using weak ammonium hydroxide or hydrochloric acid solutions as required.

(27) Precipitation of tetraphenylarsonium perrhenate:
Proceed via steps 36-42, Standards Procedure, page 220.



(After Matthews and Riley, 1970)

FIGURE A 2-1: SEPARATION OF ELEMENTS WITH DOWEX 1-X8 ANION EXCHANGE RESIN

APPENDIX A-3

PRELIMINARY TREATMENT OF ANION EXCHANGE RESINS

The resins used are De-Acidite FF 100 to 200 mesh, 7 to 9% cross linked, in the chloride form, and Dowex 1-X8, 100 to 200 mesh, chloride form.

1. Elutriate the resin ten times in water using a 1000 ml measuring cylinder. Store the sized resin in 1M hydrochloric acid until required for use.

2. Prepare elution reagents for Dowex 1-X8

   (a) Formic acid-hydrochloric acid reagent:

   Prepare a solution of 90% formic acid-concentrated hydrochloric acid (S.G. 1.18) in proportions of 95:5% (volume: volume).

   (b) Acetone-hydrochloric acid reagent:

   Prepare a solution of acetone-concentrated hydrochloric acid (S.G. 1.18) in proportions of 85:5% (volume:volume).

3. Prepare the ion exchange columns. The columns are identical except that those used for Dowex 1-X8 contain a cooling jacket (see Figure A3-1). Use a resin bed length of 3.0 cms. Insert

a small plug of fine glass fibre wool into the column and position it so as to rest snugly on top of the resin bed.

4. Wash the columns with 60 mls of distilled water.

5. Wash the De-Acidite columns with 60 mls 1M hydrochloric acid and the Dowex 1-X8 columns with 50 mls of the formic acid-hydrochloric acid reagent.

The columns are now ready for absorption of the rhenium. That is, for the De-Acidite continue with step 19(b) and for the Dowex 1-X8 continue with step 24(a) of Radiochemical Purification of Rhenium Samples.

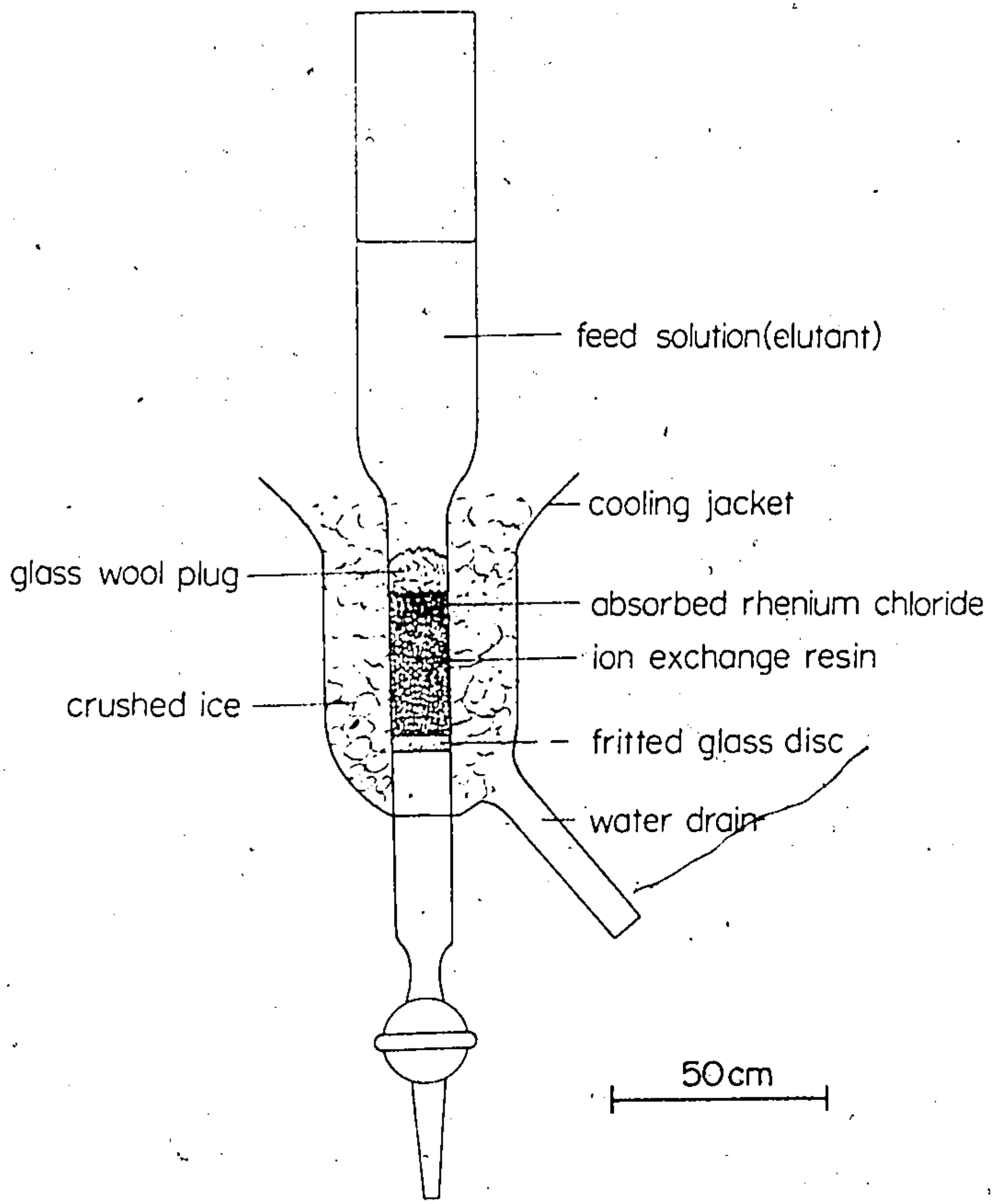


Figure A3-1: Diagram of ion exchange column equipped with cooling jacket.

APPENDIX A-4

TRACER EXPERIMENTS ON ANION EXCHANGE RESINS

Tracer experiments were conducted on the strong base anion exchange resins De-Acidite FF and Dowex 1-X8, to evaluate their elution characteristics for rhenium. The De-Acidite FF was prepared in the manner described in Appendix A-3. For Dowex 1-X8 in the $^{-}$SCN form, preparation of the resin, absorption and elution of rhenium was according to the methods of Kawabuchi (1965) and Ishida (1966). In both cases a resin bed 3 cms in length was used. The columns used are identical to that shown in Figure A3-1, except that they lack the cooling jacket. An elution rate of 0.5 mls/min. was used throughout this work.

In these experiments ^{186}Re tracer was added to approximately 15 milligrams of rhenium in suitable form. This initial aliquot was made up to volume in a 10 ml volumetric flask, and the initial radioactivity determined by γ counting. Having been absorbed onto the resin, the radioactive rhenium was eluted with 2.3M nitric acid from the De-Acidite FF and with a standardized 0.5M thiocyanate - 0.5M hydrochloric acid solution from the Dowex 1-X8. The eluate was collected as 10 ml fractions in volumetric flasks identical to the one used initially. The 10 ml eluates were γ counted and a correction for decay applied. The results presented in Figures A4-1 and A4-2 indicate that for De-Acidite FF 98.5% of the rhenium recovered is eluted in the 20 to 70 ml fraction of the eluate, while for Dowex 1-X8 99.2% of the rhenium recovered is eluted in the 30 to 90 ml portion of the eluate. Thus, the tailings effect is minimal for both resins.

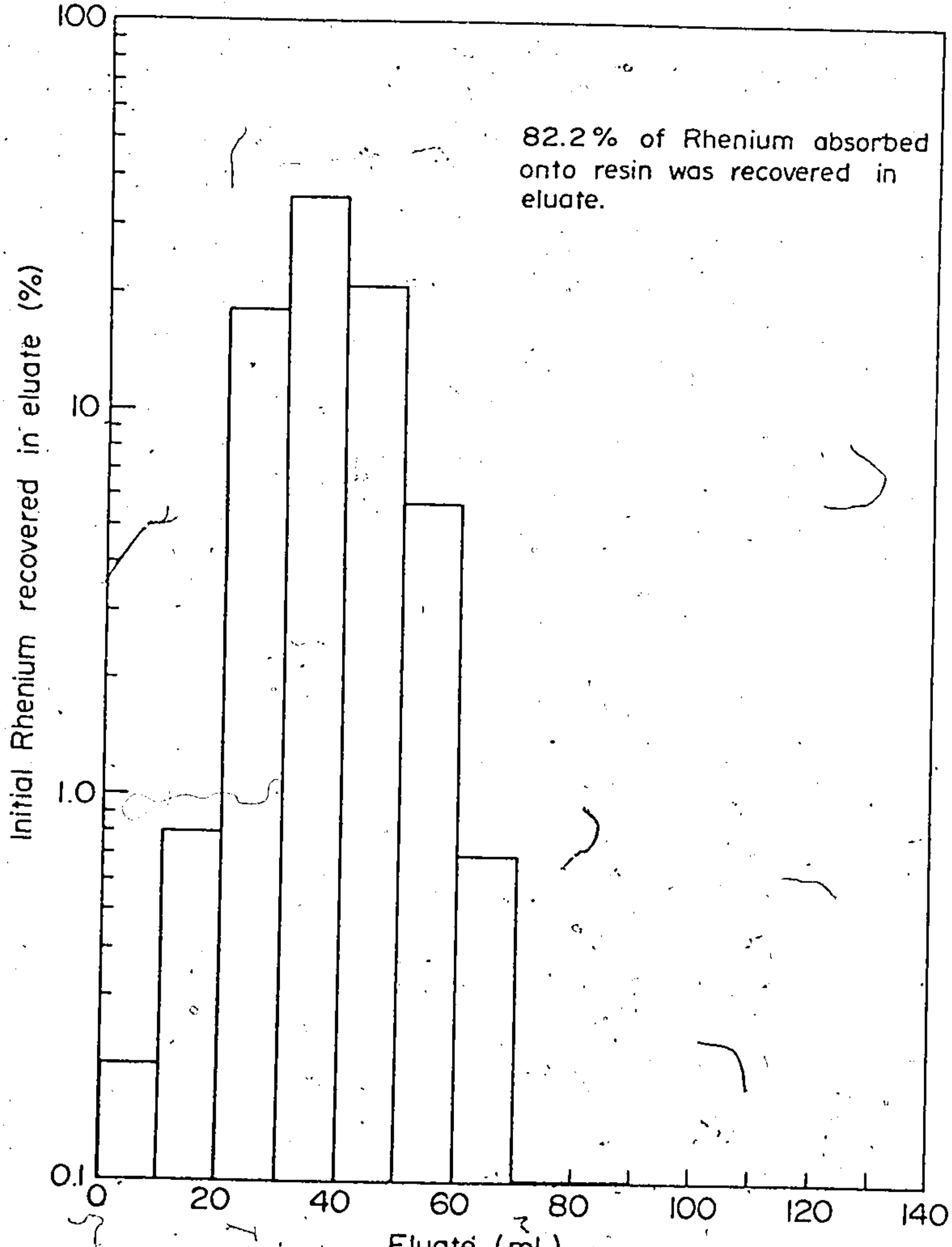


Figure A4-1: Elution characteristics of DE-ACIDITE FF (Cl$^-$ form) using 2.3M HNO_3

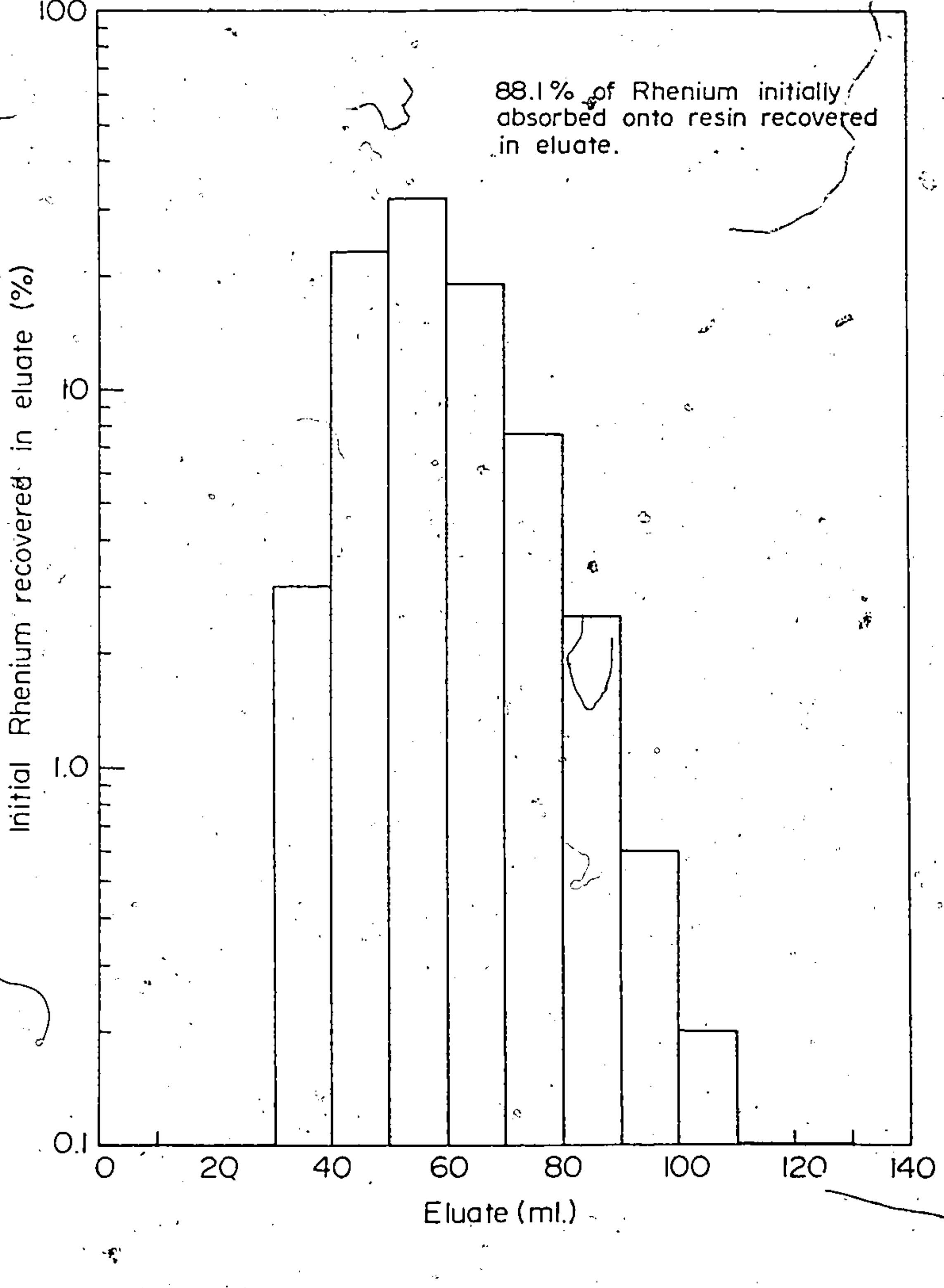


Figure A4-2: Elution characteristics of DOWEX 1-X8 ⁻SCN form eluted with 0.5M thiocyanate - 0.5M HCl solution.

APPENDIX B

EVALUATION OF SELF-ABSORPTION OF ^{186}Re AND ^{191}Os β^- ACTIVITY IN RHENIUM AND OSMIUM PRECIPITATES

In radioactive samples of finite thickness the β^-'s originate both at the top surface and from within the source. With increasing thickness, a greater proportion of the β^- activity is absorbed within the source, and if the source is sufficiently thick, β^- particles originating in the lower layers of the sample will be totally absorbed. This phenomenon is known as self absorption. It results in decreasing apparent specific activity (count rate divided by the mass of the source) with increasing sample weight, and must therefore be evaluated as a source of error in β^- comparative counting methods.

Two experiments were performed to determine if there is any absorption effect of ^{186}Re and ^{191}Os β^- radiation over the weight ranges of rhenium and osmium samples counted. The following is the procedure used in these experiments.

Irradiate sufficient rhenium and osmium to yield about 0.7μ Curies activity of the respective radionuclides. Cool for about 12 hours. Flush the irradiated osmium and rhenium salts into two separate 100 ml beakers with 6M HCl. Dilute to 30 mls with 2M HCl. Pipette 1 ml of the radioactive rhenium and osmium solutions into each of several beakers containing different amounts of their respective carrier solutions. Homogenize by heating on a hot plate for two hours. Precipitate osmium as the metal and rhenium as tetraphenylarsonium perrhenate as described in Appendix A-1. Plate out the osmium and rhenium precipitates onto pre-weighed planchets, using a capillary pipette to obtain as evenly distributed a precipitate as possible. Dry the precipitates slowly, weigh to determine their respective chemical yields and count.

The results are presented in Tables B-1 and B-2 and Figures B-1 and B-2. They indicate that there is no significant self-absorption effect of β^- particles by the rhenium or osmium precipitates in the weight range used in this research. This conclusion is supported by data from Bowen and Gibbons (1963) on the self-absorption of β particles for ^{35}S in which they indicate the self-absorption effect to be insignificant for thicknesses less than about 1.9 mg/cm^2. The maximum precipitate thickness counted in the self-absorption experiments is 1.32 mg Re metal/cm^2 and 2.5 mg Os metal/cm^2 which is two to three times the thicknesses of precipitates used in the abundance determinations. Therefore, no corrections for self-absorption were made in this work.

Table B-1

Results of ^{191}Os Self-Absorption Experiment

Sample No.	Carrier Recovered (mgm)	$\frac{\beta^- \text{ counts}}{\text{min}}$	Chemical Yield	Counts/ min. 100% C.Y. (a)	Carrier Taken (mgm) (b)	CPM 100% C.Y. x Initial Wt. (a) x (b)
1	0.46	606.3	93.95	645.4	0.4896	316.0
2	0.93	789.0	94.8	830.7	0.9792	813.4
3	1.30	834.4	88.5	942.8	1.4689	1384.9
4	1.84	818.2	94.0	870.9	1.9585	1706.0
5	2.29	849.1	93.5	907.7	2.4481	2222.0
6	2.72	858.4	92.58	927.2	2.9377	2522.0
7	3.23	848.4	94.24	898.1	3.4273	3078.0
8	3.70	753.2	94.46	797.3	3.9169	3123.0
9	4.30	908.1	97.6	930.6	4.4066	4101.0
10	4.58	862.1	93.6	921.5	4.8962	4511.8
11	6.26	799.2	91.3	875.2	6.8547	5999.0
12	9.62	859.7	98.2	875.1	9.7924	8569.3

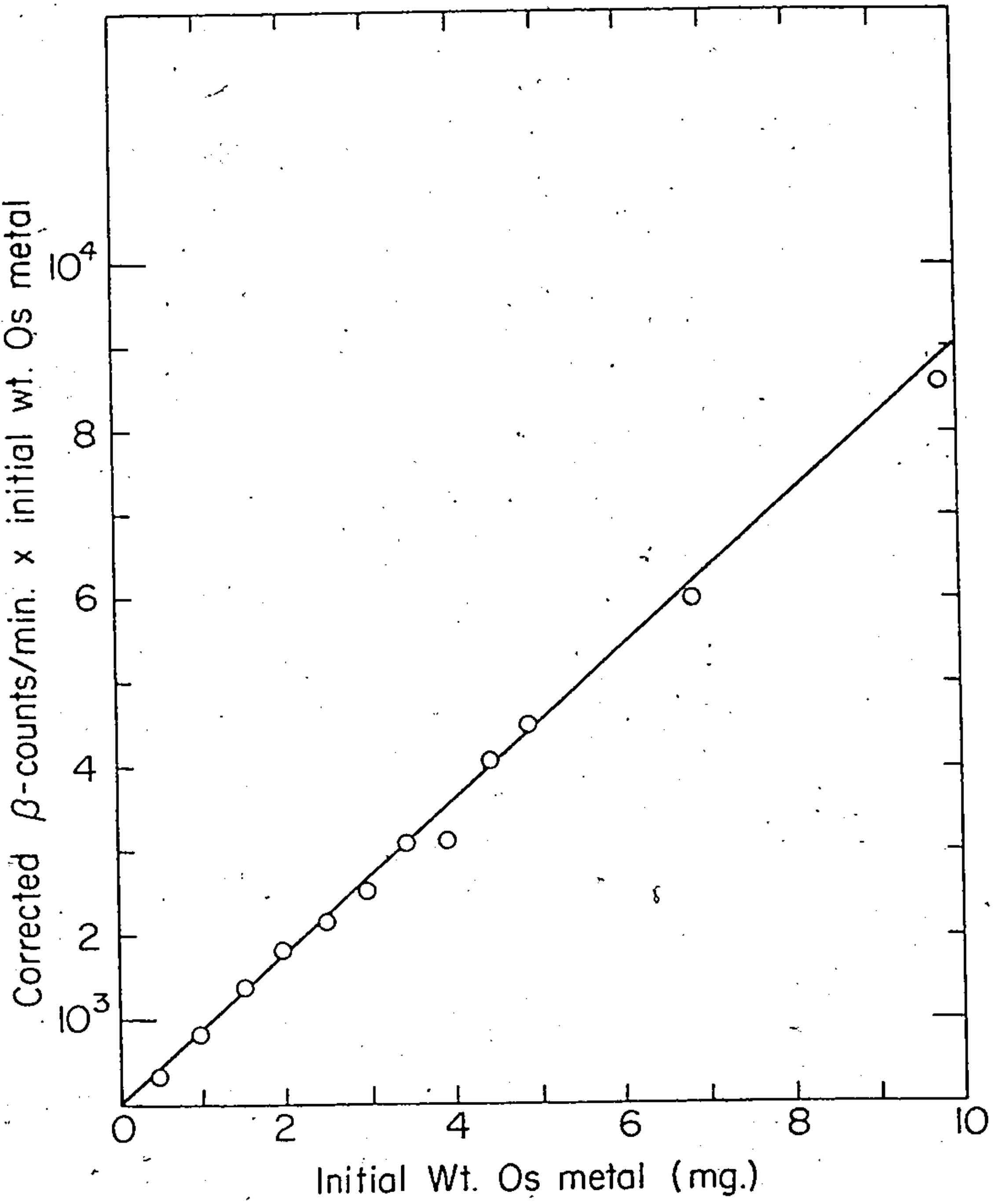


FIGURE B-1 : 0.14 MeV/β^- ^{191}Os SELF ABSORPTION

Table B-2

Results of ^{186}Re Self-Absorption Experiment

Sample No.	Weight Counted	β^- Activity CPM (a)	Chemical Yield	β^- Activity 100% C.Y. (b)	Initial	CPM 100% C.Y. x Initial Wt. (a) x (b)
1	1.69	192.5	70.31	273.8	2.405	658.5
2	4.03	193.2	83.74	230.7	4.8102	1110.0
3	6.07	198.0	84.11	235.4	7.215	1698.0
4	9.66	198.9	80.30	247.0	12.026	2970.0

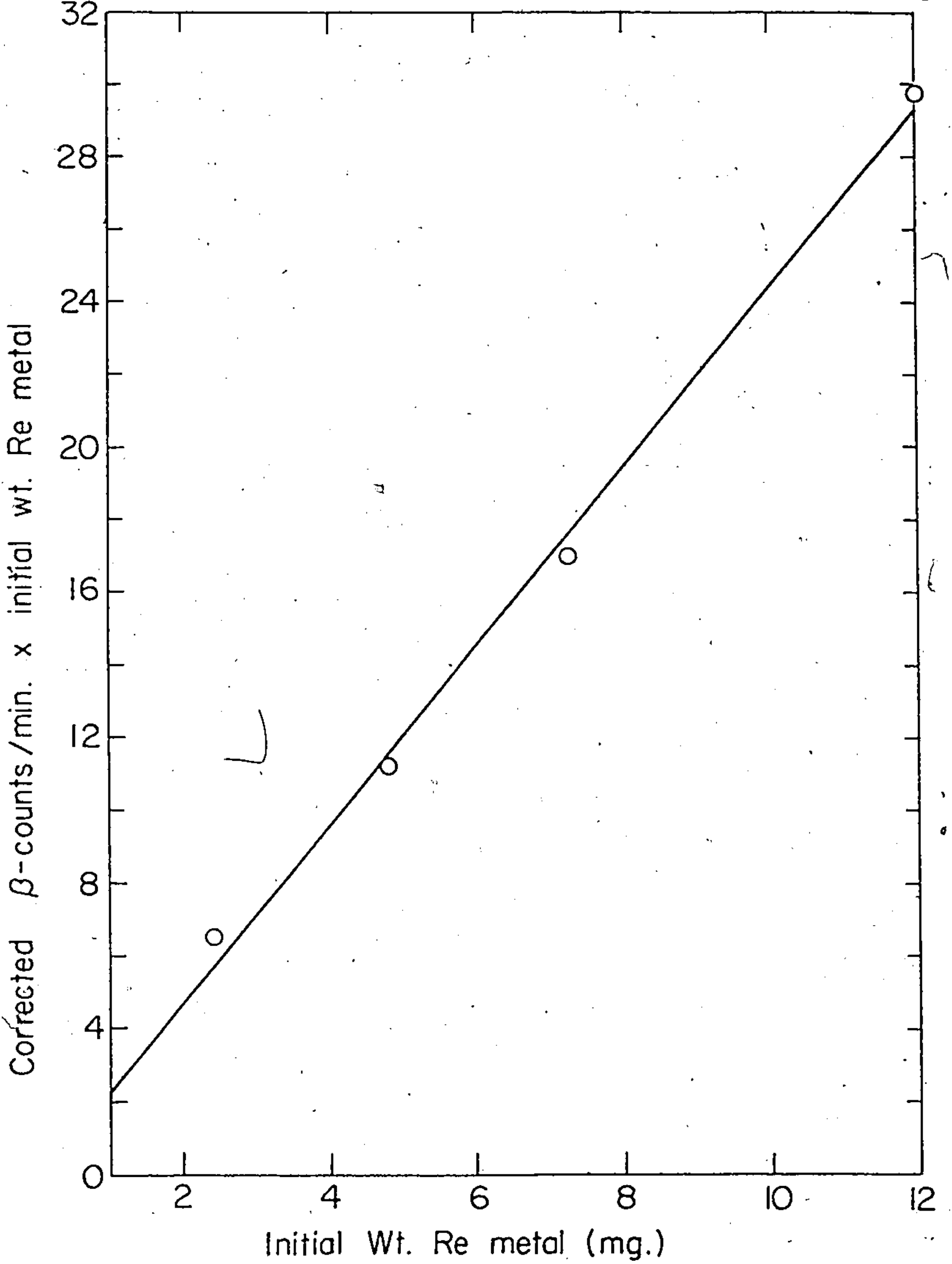


FIGURE B-2 : 0.93, 1.07 MeV β^{-} ^{186}Re SELF ABSORPTION

APPENDIX C

SAMPLE DESCRIPTIONS

1. MAIN DEPOSITS

Adams Mine

With the exception of the pyrite, all samples analysed from this deposit were collected by Alcock (1971). The following sample descriptions are taken directly from his work.

F-16-5: Tholeiitic basalt: Massive, fine-grained, dark green lava. Mineralogy includes quartz, actinolite, feldspar and traces of sulphides (thin section). For normative composition see Alcock (1971).

F-16-8: Lean I. F.: Non-banded, very fine-grained (< 1 mm), magnetite occurs as disseminations in chert.

Mode - 24.9% quartz/chert
15.4% magnetite
55.0% fine-grained magnetite-chert matrix
4.7% chlorite/actinolite

F-16-13: Oxide Iron Formation: 1/4 to 1/2 in. thick alternating bands of magnetite and chert; disseminated sulphides; complexly folded.

F-16-14: Cherty Quartzite: Massive chert bed containing disseminated graphite, which imparts black color to outcrop. Aggregates of actinolite needles rim occasional bleb of magnetite (T/S).

Mode - 84.0% quartz/chert
12.3% actinolite/chlorite
3.7% magnetite

Pyrite: Approximately 3% disseminated, banded pyrite is associated with oxide iron formation comprised of 1/4 to 1/2 inch thick alternating bands of magnetite (40%) and greyish-green chert (57%). The pyrite varies from fine to medium-grained and frequently occurs as discrete cubes.

Craigmont

Chalcopyrite: From ore composed of chalcopyrite (15 to 20%), coarse grained magnetite (20%), fine-grained chlorite (60 to 55%) and potash feldspar (5%).

Magnetite: From similar material as for chalcopyrite

Pyrite: 15 to 20% massive pyrite associated with carbonate (calcite) vein in altered limestone.

Granisle Copper

Chalcopyrite (No. 1): Chalcopyrite (10 to 15%) with quartz as fissure-filling in altered quartz-diorite. The fissure quartz charaterised by incipient cockscomb texture and by small vugs. Associated with bornite (< 0.5%) and fine-grained cubes of pyrite (< 0.1%).

Bornite (No. 4): Essentially massive bornite associated with small amounts of chalcopyrite (5 to 7%) in quartz. The bornite is either from a fault zone or a fissure because of the vuggy nature of the quartz. Minor manganese carbonate.

Pyrite (No. 5): Essentially massive pyrite from fault zone. Associated with dolomite and calcite. Pyrite has light surface tarnish in part.

Heath Steele

Massive Sulphides: 5-foot massive sulphide pulp sample from diamond
(No. A4049) drill Hole (DDH) B137. Footage interval 66 to 71.

Assay results:	Pb	Zn	Cu	Ag
	3.38%	2.05%	0.86%	7.56 oz/ton

Massive Sulphides: 5-foot massive sulphide pulp sample from DDH B138.
(No. A4093) Footage interval, 375 to 380. Less than 20% silicate.

Assay results:	Pb	Zn	Cu	Ag
	0.16%	0.28%	1.86%	0.55 oz/ton

Sphalerite: DDH: B89-3. Sample 111 feet from collar. Sphalerite-
(No. B89-3) pyrite-galena ore band with appreciable chlorite. Sample purity 98%. Layer C.

Chalcopyrite: DDH: B104-5. Sample 349 from collar. Massive
(No. B104-5-1) sulphides, less than 20% silicates impurities. Sample purity 90 to 95%.

<u>Guichon Batholith</u> (Highland Valley Area)

Bornite: (Alwin Mining)	Pure massive bornite
Chalcopyrite: (Bethlehem Copper)	From chalcopyrite-rich 1" wide quartz vein
Molybdenites:	
(1) Highmont Mining	Molybdenite-rich quartz vein material from dump in front of adit.
(2) Lornex Mining (L-1)	Daily Molybdenite concentrate
(3) Valley Copper	Molybdenite-rich quartz pyrite vein (formerly the Tamarak Showing). Weathered surface stained with limonite and ferrimolybdite.

Kidd Creek

Chalcopyrite (No.1): Massive chalcopyrite (93 to 95%). Largest single impurity is sphalerite (~3%).

Pyrite (No. 7): Mainly pyrite (85%), but with lesser quantities of "carbon-rich" material (12%) and sphalerite (3%). Pyrite is either with "buckshot" texture, massive, or very fine-grained. Small amounts of cubic pyrite also present. Pyrite spherules reach approximately 1/8" diameter. Sample striated on one face.

Sphalerite (No. 2): From 1/2" thick massive sphalerite band in massive sphalerite and galena ore. Minor (about 5%) carbonate and silicate impurities.

Strathcona

Pyrrhotite: Pyrrhotite separate containing 2.3 modal percent pentlandite,
(DIC) obtained from massive sulphides comprised of pyrrhotite (~75%), magnetite (~8%), chalcopyrite (~15%). From D1 stope, 2750 level. Chyi's Sample C.

Chalcopyrite: Chalcopyrite separate from same sample as that from
(DIC) which pyrrhotite obtained.

Massive Banded Sulphides: Massive sulphides > 99%. Composed of pyrite (54 to 49%), pyrrhotite (20%), chalcopyrite (15 to 20%), pentlandite (3%). From Main Ore Zone, Stope J. Footwall side of ore. Collected by R. Wright.

Massive Sulphides: From massive sulphide vein in footwall gneisses. Vein composed of nickeliferous pyrrhotite (80%), chalcopyrite (12%), and magnetite (8%). Deep ore zone 2625 level. R. Wright's No. 3 sample.

2. OTHER DEPOSITS

Anglo American Molybdenite Co.:

Pyrite: Pure material from a pyrite cube measuring 35 mm along its edges.

Denison Mines:

Pyrite: Mineral separate prepared by R. Martindale.

Molybdenites

Bethlehem Copper:

B-1 (Laboratory concentrates from Jersey Pit molybdenite
(
B-3 (

B-4 MoS_2 concentrate. J.A. Zone. Representative of $\sim 10^9$ ft.^{3}

B-5 MoS_2 concentrate. J.A. Zone. Representative of ~ 5×10^8 ft^3.

Boss Mountain:

Daily mill MoS_2 concentrate

Brenda Mines:

Molybdenite associated with chalcopyrite in 1/4" quartz vein in granodiorite.

B.C. Molybdenum:

Monthly mill MoS_2 composite concentrate.

Endako Mines:

Monthly mill MoS_2 composite concentrate.

Gaspé Copper:

MoS_2 concentrate.

Molybdenite Corp. of Canada:

Daily mill MoS_2 concentrate.