

EVALUATION AND APPLICATION
OF
RADIOCHEMICAL NEUTRON ACTIVATION TO
NOBLE METAL ANALYSIS

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NOBLE METAL ANALYSIS

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ABSTRACT

A rapid and simple radiochemical neutron activation technique involving tellurium coprecipitation of Au, Ir, Pd and Pt was evaluated using the U.S.G.S. standards PCC-1 (peridotite) and DTS-1 (dunite) as well as a house standard, JHC-6 (spinifex zone of a komatiitic peridotite). It was then applied to the analysis of samples of Archean greenstone from the Red Lake area.

The technique gives detection limits of 0.01-0.02, 0.02, 0.1-0.4 and 1-2 ppb for Au, Ir, Pd and Pt respectively and precisions of <25-35%. The method can be successfully applied to the analysis of PGE levels in sulphur-poor rocks, and large numbers of samples can be processed in a short period of time.

A comparison of PGE content between several types of mafic rocks was made as well as an investigation of possible secular trends (Archean vs. Phanerozoic) in PGE concentration.

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CHAPTER 1

INTRODUCTION

The noble metals are the six platinum group elements (PGE; Ru, Rh, Os, Ir, Pd, and Pt), Au and Ag. In the metallic state, they are relatively inert and are not easily oxidized. Although noble metal concentrations may reach part per million (ppm) levels in ore deposits (Crocket et al., 1968; Crocket, 1979; Hertogen et al., 1980), the noble metal contents of the earth's crust and upper mantle are generally at part per billion (ppb) levels. Techniques employed for noble metal lithogeochemical analysis must therefore be very sensitive. Several suitable techniques may be found in the literature (see the reviews by Crocket and Cabri, 1981 and Beamish and Van Loon, 1972, 1977). Instrumental neutron activation has been used directly only for the determination of one or two noble metals (i.e., Au and Ir in ores and meteorites, where their concentrations are on the level of ppm; Crocket, 1971; Hoffman et al., 1978), but several radiochemical neutron activation techniques can successfully determine up to six platinum group elements with sensitivities, under ideal conditions, that are several orders of magnitude lower than those obtainable

by other approaches.

Crocket et al. (1968) developed a neutron activation procedure for noble metal analysis in silicate rocks, meteorites and sulphide ores involving alkali peroxide fusion, with subsequent separation and purification of individual elements by distillation, ion exchange and solvent extraction. Gamma and beta (Pd only) radiation was counted in radiochemically pure sources. Average precisions of $\pm 13\%$ for replicate analysis of Au, Ir and Pd in W-1 were attained. The sensitivities for Au, Ir, Pd and Pt (0.05, 0.01, 0.1 and 0.5 ppb respectively) are very good, but the technique is time consuming (two days of radiochemistry for up to 12 samples) and hence the method is inappropriate for large scale lithogeochemical surveys (large numbers of samples). Hoffman et al. (1978) developed a technique for analysis of all PGE, including 4 minute ^{104}Rh and gold, in rocks and ores by employing instrumental neutron activation after preconcentration by nickel sulphide fire-assay. The great advantage of this procedure is its ability to analyse for all six PGE and to process large samples (50 grams), thereby avoiding problems associated with the inhomogeneity of noble metal distribution. It is the pre-irradiation nickel sulphide fire-assay which allows larger samples to be analysed. Although pre-irradiation contamination is not a major problem in the processing of ore samples, it may be for

unmineralized rock samples. The detection limits reported for Au, Ir, Pd and Pt are 0.1, 0.1, 50 and 5 ppb respectively (Hoffman et al, 1978). Difficulty must be expected in the application of this technique to sulphide-poor rocks where picogram levels of PGE may be expected. Nadkarni and Morrison (1974) developed a simple radiochemical group separation technique based on a noble metal-selective chelating resin (Safrion NMRR). Stockman (1982,1983) was unable to duplicate their reported results after numerous attempts. Ahmad et al. (1977) reported average precisions of $\pm 6\%$ for analyses of Au, Pd, Pt and Ir in U.S.G.S. standards W-1 and PCC-1 for a technique employing isotope carriers, hold-back carriers and liquid-liquid extraction.

A simple and rapid, carrier-based radiochemical procedure for the determination of Au, Ir, Pd and Pt, based on classical tellurium coprecipitation methods (Feigl, 1949; Rodden, 1950; Marhenke and Sandell, 1963) and high resolution γ -ray spectroscopy was developed by Stockman (1982, 1983) at the Massachusetts Institute of Technology. The method was successfully applied to the analysis of ultramafic standard rocks (W-1 and PCC-1) on which good accuracy and precision were obtained (Stockman, 1982), and chromites (Rhonda Ultramafic Complex, Spain and Josephine Peridotite, Oregon).

Stockman's technique has several advantages over existing radiochemical activation methods for noble metals. It is a very rapid procedure, (radiochemical processing of five samples can be accomplished within two hours) and analytically simple, involving the coprecipitation of the PGEs in a single precipitate. The high resolution of modern Ge(Li) detectors allows individual elemental analysis of the precipitate and the non-discriminatory β^- -counting of Pd (Crocket et al., 1968) is avoided. Although sample sizes are limited to ≤ 0.5 grams and the procedure is not suitable for 4 minute ^{104}Rh , nor tested for Os or Ru, potential sensitivities as good or better than Hoffman et al. (1978) are attained (detection limits are 0.01-0.02 ppb Au; 0.1-0.4 ppb Pd; 1-2 ppb Pt and 0.02 ppb Ir; Stockman, 1983) for low sulphur rocks. All samples, including the chromites and U.S.G.S. standards were low in Na (a required parameter for successful application of the method under the present irradiation-decay conditions; PCC-1 and W-1 contain 0.006 and 2.15 wt. % Na_2O respectively; Flanagan, 1976; Na_2O values range from 0.03 to 0.29 wt. % in the Rhonda Peridotite and 0.006 to 0.06 wt. % in the Josephine Peridotite; Stockman, 1982), and relatively rich in noble metals (literature values for Au, Ir, Pd and Pt in PCC-1 are given in Table 5.1a). Consensus values of 5.4 ± 3.1 ppb Au, 0.28 ± 0.05 ppb Ir, 13.5 ± 4.1 ppb Pt (Govindaraju, 1983)

and 11.5 ± 0.3 ppb Pd (Crocket et al., 1968)¹ have been determined for NAA analysis of W-1. Concentrations of these metals in the ultramafic complexes studied by Stockman (1982) are 0.2 to 2.2 ppb Au, 3.4 to 14.8 ppb Ir, <0.5 to 9.3 ppb Pd and 3.5 to 15 ppb Pt.

The objectives of this work are to establish the procedure developed by Stockman (1983) by analysis of well known international ultramafic rock standards, and to test the procedure, for its applicability to mafic rocks, particularly greenstones. No large scale surveys for PGE, and Pt in particular, have been made on mafic rocks. Other questions of geochemical interest include variations in PGE content between the major classes of basalts and between mafic rocks from different tectonic environments. Also, an investigation of possible secular trends (Phanerozoic vs. Archean) in PGE concentration is of interest.

The scope of the study was somewhat limited by practical and instrumental problems. It was discovered early in the work that rocks with $>0.5\%$ Na_2O were too radioactive to safely handle after a six hour irradiation ($8 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ flux) and a 12 hour cooling period. Increased cooling time resulted in ^{109}Pd activities that

1. Govindaraju (1983) consensus value of 17 ± 7.8 ppb Pd in W-1 is misleadingly high and was therefore not included.

were too low to detect, and decreased irradiation time substantially diminished Ir, Au and Pt activities. It was also determined that a very well shielded coaxial detector was needed to reduce external background from U-Th series daughter products to sufficiently low levels to obtain good net count rates on 88 KeV ^{109}Pd and 158 KeV $^{199}\text{Au(Pt)}$.

CHAPTER 2

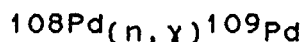
PRINCIPLES OF NEUTRON ACTIVATION ANALYSIS

2.1 General Theory of Neutron Activation Analysis

Neutron Activation Analysis (NAA) involves bombarding samples with neutrons, at or near the core of a nuclear reactor. Some of the sample atoms interact with the bombarding neutrons, commonly by absorption in an (n,γ) reaction. A typical reaction is;



or



where the γ-rays result from the transition of a nucleus from an excited state to a lower energy state. These reactions are dependent on neutron energy and, in general, are more efficient for low kinetic energy neutrons. Many of the isotopes thus produced are radioactive. Spontaneous decay to stable nuclides is accompanied by release of characteristic β⁻ or γ-rays. These radiations are used to identify and quantify the elements present, as a direct proportionality exists between the number of decays detected and the original quantity of parent element in the sample.

The limit of detection for a given analytical technique is the minimum amount of the element of interest that can be reliably detected by that procedure (MacDougall and Crummett, 1980). For neutron activation, it is dependent upon neutron flux, neutron cross-section, irradiation parameters (irradiation and decay times) and detector efficiency.

Neutron activation analysis requires the irradiation of a sample (elemental concentration unknown), with a standard (known elemental concentration), and subsequent comparison of the induced radioactivity of a specific nuclide in each. A proportionality exists between the sample and standard such that;

$$A_{\text{samp}} = A_{\text{std}}(X_{\text{samp}}/X_{\text{std}})$$

where A_{samp} = radioactivity induced in the sample,

A_{std} = radioactivity induced in the standard,

X_{samp} = concentration of analysis element in the sample,

and, X_{std} = concentration of the same element in the standard.

For elements yielding only small amounts of the desired radiation (ie; elements present in trace amounts, <0.1%, with no efficiently activated isotope), against

high backgrounds of other radiations of similar energy, chemical processing is necessary. Wet chemical extraction of a specific element or group of elements from a solution (produced by dissolution of the bulk sample), is referred to as radiochemical neutron activation or RNAA.

Instrumental neutron activation analysis (INAA) involves the counting of all of the radiation produced by neutron activation with no chemical treatment of the samples after irradiation. It is effective for analysis of many elements present in larger abundances, and minor elements which are efficiently activated and easily detectable above background levels. Isolation of the desired elements from an interfering matrix, either individually (Crocket et al., 1968) or as a group (Stockman, 1982, 1983), yields a γ -ray spectrum free of interfering peaks, with lower background, such that the sensitivity and accuracy of analyses are improved.

In RNAA the sample is taken into solution, after a pre-determined cooling time, in the presence of a carrier (non-radioactive chemical compound containing known amounts of the elements of interest). Complete mixing (isotopic exchange) of radioactive sample and inactive carrier isotopes is required, and can be achieved by alkali peroxide fusions or acid dissolution.

Subsequent analytical steps involve working with milligram rather than microgram (or lower) amounts of the desired elements. Elements are selectively identified by measurement of the emitted characteristic γ -, β - or x-rays, the intensities of which are directly proportional to the amount of that element in the sample. After radioassay, the fraction of carrier recovered in the chemical separation is determined to correct for non-quantitative chemical yield of the analysis element. Note that an inherent assumption in carrier procedures of this nature is that the mass of radioactive analysis element is negligible in comparison with the mass of carrier added.

2.2 Radioactive Decay

The fundamental law of radioactive decay is based on the observation that the number of atoms that decay per unit time is proportional to the total number of radioactive atoms present (N), or:

$$dN/dt = -\lambda N \quad (1)$$

where λ (time^{-1}) is the radioactive decay constant (the fraction of radioisotopes to decay per unit time), which has a unique value for a given radionuclide. Integration of (1) yields:

$$N = N_0 e^{-\lambda t} \quad \text{or} \quad N_0 = N e^{\lambda t} \quad (2)$$

where N_0 is the number of radioactive parent atoms present at some original time ($t=0$), and N is the number present now. If t is the time required for half of the initial number of radioisotopes to decay (half-life), then;

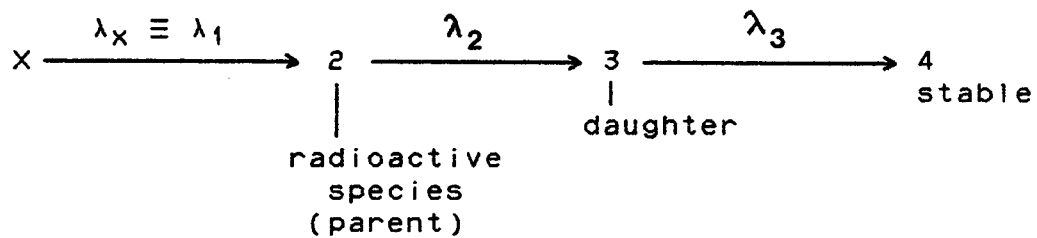
$$N = 1/2 N_0 = N_0 e^{-\lambda t_{1/2}} \quad (3)$$

from which $t_{1/2} = 0.693/\lambda \quad (4)$

where $t_{1/2}$ is the characteristic half life for a given nuclide.

2.3 Production of Radioisotopes by a Nuclear Reactor

If it is assumed that a nuclear reactor (X) produces neutrons at a constant rate, then formally the reactor can be regarded as having an infinite half-life; that is, $t_{1/2}(X)$ is ∞ and $\lambda_X=0$. Production of neutrons will continue indefinitely, until the reactor is shut down. In addition, it can usually be assumed that the target element is not appreciably used up during a nuclear reaction (practically speaking, a valid assumption in this work). These approximations allow simplifications to be made in the development of equations which describe the production of radionuclides by neutron irradiation in a constant flux reactor. Consider a case where a reactor generates radioactive species (2) which decays to a daughter (3);



Formally, X is considered of infinite half-life, and able to produce (2) at a constant rate. Therefore, $\lambda_X \equiv 0$ because $t_{1/2}(X) \longrightarrow \infty$ and $\lambda_X N_X = R$, where R is the constant production rate of nuclide (2). For a neutron irradiation;

$$R = (nv) (\sigma) (a) (N)$$

where, nv is the neutron flux in $n \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$,

σ is the thermal neutron absorption cross-section in 10^{-24} cm^2 ,

a is the fractional atomic abundance of the target nuclide

and N is the number of target nuclide atoms.

The activity induced by the decay of two nuclides in series is given as;

$$A_2 = c_2 \lambda_2 N_2 \quad (5)$$

where c_2 is the proportionality factor between the number of decays and the number of particles counted by the detector for each nuclide (the counting efficiency). For the decay of two radionuclides in series, it can be

shown that (Friedlander and Kennedy, 1981, equation 5-2);

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + N_2^0 e^{-\lambda_2 t} \quad (6)$$

In the case of growth of species (2) from irradiation by reactor neutrons, equation 6 can be modified by setting

$$\lambda_1 \equiv \lambda_x = 0$$

$$\text{and } \lambda_1 N_1^0 \equiv \lambda_x N_x = R,$$

$$\text{so that, } N_2 = R/\lambda_2 (1 - e^{-\lambda_2 t}), \quad (6a)$$

assuming $N_2^0 = 0$ or that there is no daughter activity in a sample at the beginning of an irradiation, and that t is the irradiation time, t_{ir} . Substitution of 6a into 5 gives the activity induced in species (2) as;

$$A_2 = c_2 R (1 - e^{-\lambda_2 t_{ir}}) \quad (7)$$

where t_{ir} is the time of irradiation. At $t = 0$, $A_2 = A_2^0 = 0$, and as $t \rightarrow \infty$, $A_2 \rightarrow c_2 R$, a constant value referred to as "saturation activity". By differentiation of equation 7, the initial growth of A_2 is found;

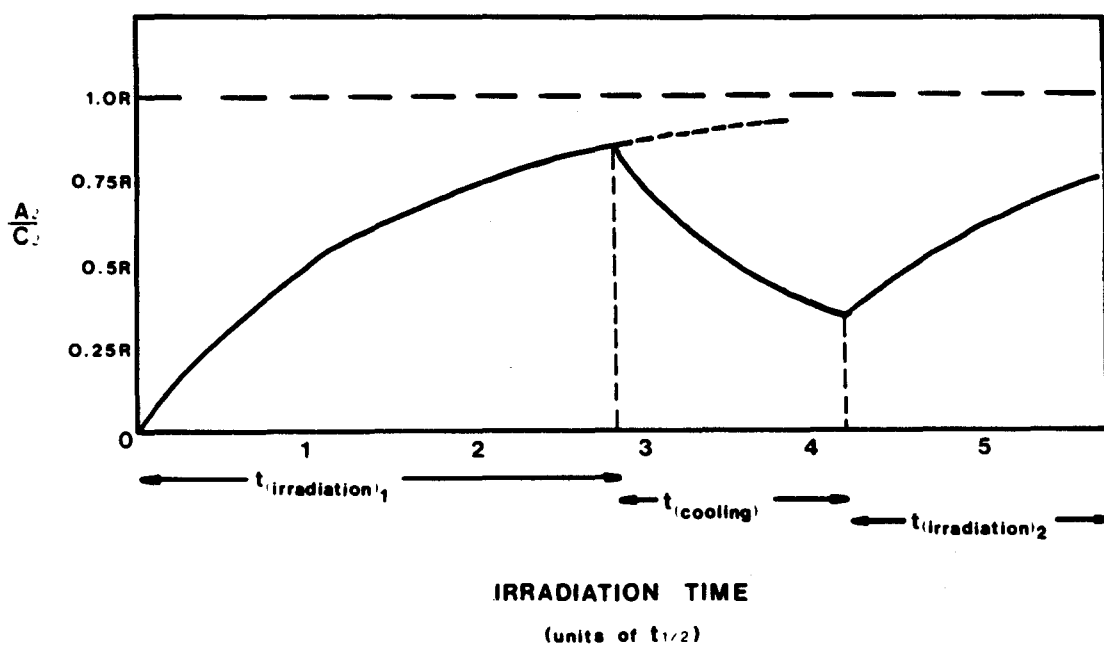
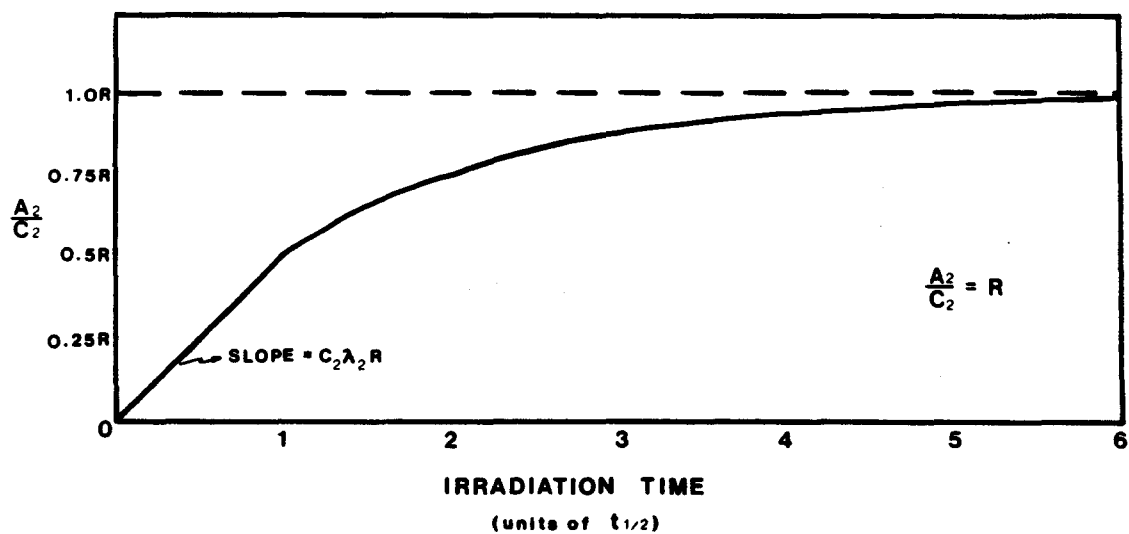
$$\left[\frac{dA_2}{dt} \right]_{t=0} = \left[c_2 R \lambda_2 e^{-\lambda_2 t_{ir}} \right]_{t=0} = c_2 R \lambda_2 \quad (8)$$

Therefore the initial growth of activity of 2 is a constant, inversely dependent on the mean life, τ ($\tau = 1/\lambda$). A saturation activity is asymptotically approached as irradiation times become long compared to the half-life. At saturation, production rate of activity

by neutrons and decay rates are equal. The saturation activity depends only on the production rate (R) and the counting efficiency (c_2), and is independent of the half-life of the nuclide produced.

Figure 2.1 illustrates the properties of equation 7. Activity is plotted against irradiation time, given in units of half-lives. As activation proceeds, there is an increase in induced activity, but the rate of growth of the activity diminishes with time. Irradiation times are often limited to one half-life which produces one half the maximum activity possible for a given nuclide. Since saturation activity is approached asymptotically, irradiation times of about six half-lives are required to obtain the effective maximum saturation activity. Figure 2.2 also illustrates the change in activity with time, where the irradiation has been interrupted by a cooling period, and then resumed. During the second irradiation stage, the activity grows according to a curve exactly parallel to the original growth curve. This demonstrates the independence of radioactive decay from the previous history of the nuclide; that is, the growth of new activity (irradiation 2) is independent of the activity produced in irradiation 1.

The activity induced for a second daughter product of an (n,γ) reaction can be derived by applying the



assumptions and simplifications used to develop equation 7;

$$A_3 = c_3 R \left(1 - \frac{\lambda_3}{\lambda_3 - \lambda_2} e^{-\lambda_2 t_{ir}} + \frac{\lambda_2}{\lambda_3 - \lambda_2} e^{-\lambda_3 t_{ir}} \right) \quad (9)$$

where A_3 is the activity of species (3) in disintegrations per second, λ_2 and λ_3 are the decay constants of species (2) and (3) respectively in s^{-1} and c_3 is the counting efficiency for species (3). After long irradiations, $t \rightarrow \infty$ and $A_3 \rightarrow c_3 R$, so that the decay rate is equal to the production rate from the immediate parent (2) and ultimately from the initial nuclear reaction. At $t=0$;

$$\left[\frac{dA_3}{dt} \right]_{t=0} = \left[c_3 R \left(\frac{\lambda_2 \lambda_3}{\lambda_3 - \lambda_2} e^{-\lambda_2 t_{ir}} - \frac{\lambda_2 \lambda_3}{\lambda_3 - \lambda_2} e^{-\lambda_2 t_{ir}} \right) \right]_{t=0} = 0 \quad (10)$$

which follows since $A_3=0$ at $t_{ir}=0$, at the start of the irradiation.

2.4 Production Factor

The production factor (PF) is a convenient parameter for comparison of relative activities per unit weight of the target element in samples irradiated simultaneously (Crocket, 1971). It is given by;

$$PF = \frac{\sigma a}{w} (1 - e^{-\lambda t_{ir}}) \quad (11)$$

for direct products of (n,γ) reactions and by;

$$PF = \frac{\sigma a}{W} \left(1 - \frac{\lambda_3}{\lambda_3 - \lambda_2} e^{-\lambda_2 t_{ir}} + \frac{\lambda_2}{\lambda_3 - \lambda_2} e^{-\lambda_3 t_{ir}} \right) \quad (12)$$

for daughter products of the (n,γ) reaction, where W is the atomic weight and all other factors are as defined in sections 2.2 and 2.3. The production factor is directly proportional to induced activity (equation 7) and compares relative activities per unit weight of the target element for irradiations of equal time and neutron flux. It is derived from equation 7 by replacing $c_2 R = c_2 (nv) (\sigma) (a) (N)$ by $\frac{\sigma a}{W}$.

CHAPTER 3

APPLICATION OF RNAA TO PGE ANALYSIS OF LOW SULPHUR MAFIC AND ULTRAMAFIC ROCKS

NAA is very sensitive for platinum group elements¹ (to the 0.01 ppb range for some elements such as Ir) and is capable of determining Au, Ir, Pd and Pt in a 100 milligram (or less) sample of most unmineralized, low-sulphur mafic rocks, with no preconcentration of the metals. Problems are normally encountered with other PGE. Special pre-concentration procedures are required to measure Rh due to the short half-life of 4 minute ^{104}Rh . For Ru, fission product interference from ^{235}U is often a problem, and in the case of Os, volatilization must be avoided. NAA is as sensitive a procedure as Induced Coupled Plasma Mass Spectrometry, and the possible contamination from reagents associated with sample dissolution for ICP-MS is avoided in NAA. As the method depends on induced radioactivity, post-irradiation contamination can only occur by the accidental addition of specific radioisotopes. Therefore, procedures which do not use pre-concentration methods avoid the risks of

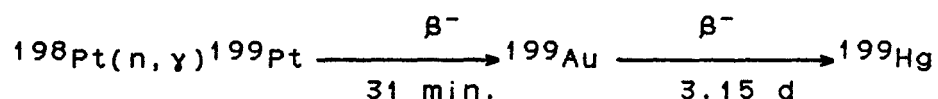
1. For the sake of brevity and convenience, Au is included in the term PGE.

contamination by trace elements inadvertently added after irradiation. One particular problem with using RNAA for PGE determination is that the maximum sample size possible is 2-3 grams. Heterogeneity of PGE distribution, particularly if a sulphide phase is present may present a serious problem in conjunction with the above size limitation.

Equation 7 applies to the production of radionuclides by direct (n,γ) reactions; for example,



It is applicable to the determination of all PGEs considered in this study, except Pt. For Pt, the relevant reaction is one involving a daughter product of a (n,γ) reaction;



The half-life of ^{199}Pt is 31 minutes, so for decay periods of ca. 300 minutes (10 half-lives of ^{199}Pt), total decay of ^{199}Pt will have occurred. The ^{199}Au activity is therefore directly proportional to the Pt concentration. For such a reaction, equation 9 applies.

Analytical sensitivity is mainly dependent on maximizing the induced activity A, as defined in equation 7. Sensitivity is therefore optimized when the neutron

flux, irradiation time and sample weight are maximized. The latter factor is somewhat limited by the maximum 2-3 gram sample size of rock powder samples.¹ Preconcentration (Hoffman et al., 1978) can considerably increase the sample size (to 50 grams). The flux is normally $10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ in a reactor such as the McMaster University Reactor, but can be as high as $10^{14} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Irradiation times are chosen to maximize the activity of the radioisotopes of interest, and minimize the activity of potential interfering radionuclides. Production factors for Au, Pt, Pd and Ir are given in Table 3.1 for a seven day versus a one day irradiation. For a 7 day irradiation, the relative PGE activities are $\text{Au} > \text{Ir} \gg \text{Pd} > \text{Pt}$.² The longer lived radioisotopes are favoured and are most active. Typically, samples must decay before they can be safely handled, and if, for example, silicate rocks are irradiated, a decay period of ca. 7 days is required. This will leave only radioisotopes of longer half-lives with sufficient activity for detection. For shorter irradiation times, one day for example, the relative sensitivities remain about the same; $\text{Au} > \text{Ir} \gg \text{Pd} > \text{Pt}$, but the absolute sensitivities are lower than when a longer irradiation time is employed,

1. High Na concentrations limited sample sizes in the present work to 0.1 grams in some cases.

2. Where \gg designates a factor of 10.

TABLE 3.1. PRODUCTION FACTORS FOR Au, Ir, Pd and Pt.

Element	Stable Target Isotope	Isotopic Abundance (%)	σ Activity (barns)	Radionuclide	Production Factor $t(ir)=1$ wk	Factor $t(ir)=1$ day
Pd	^{102}Pd	8.96	5	17d ^{103}Pd	0.012	0.0019
	^{108}Pd	26.71	12.2	13.4h ^{109}Pd	3.0	2.15
Ir	^{191}Ir	37.3	1050	74d ^{192}Ir	11.4	1.7
	^{193}Ir	62.7	110	19.2h ^{194}Ir	36	20
Pt	^{196}Pt	25.3	0.75	18.3h ^{197}Pt	0.10	0.06
	^{198}Pt	7.2	3.7	3.14d ^{199}Au	0.11	0.03
Au	^{197}Au	100	98.8	2.7d ^{198}Au	82.42	22.36

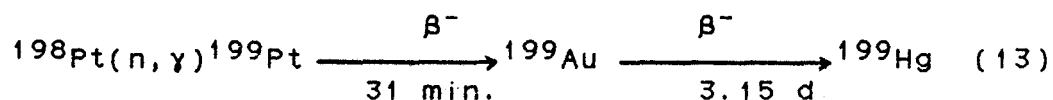
Taken from Crocket and Cabri, (1981) and Crocket, (1971).
d = day; wk = week; h = hours.

and wet chemistry should be performed as soon as possible. Since cooling times are short, shorter half-life products may be detected. Production factors give relative activities at the end of the irradiation and it must be noted that, although ^{109}Pd activity is increased by 30% when a longer (seven day) irradiation time is employed, by the end of the extensive decay period required after longer irradiations, Pd will have almost totally decayed away. Although an increased irradiation time increases induced activity (to a certain limit, as discussed), it can also produce practical problems, for example high Na activity. ^{24}Na ($t_{1/2}=15$ hours) has a high efficiency of activation and is present in most rock samples. As it has a slightly longer half-life than ^{109}Pd , excessive cooling times intended to reduce the Na activity will all but eliminate the ^{109}Pd activity. To optimize analytical conditions for ^{109}Pd (13.4 hour half-life) a 13.4 hour irradiation is practical (if there is no Na present in sample), and one half of saturation activity is generated by a one half-life irradiation. The incremental value of additional irradiation to ^{109}Pd activity decreases rapidly as saturation is approached (ie., with longer irradiation times; fig. 2.2). In this work irradiations lasted six hours (approximately one half the ^{109}Pd half-life), and decay time, including laboratory processing, was 24 hours (before actual

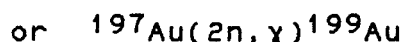
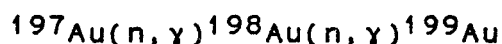
counting began). After cooling, 7-8% of the potential saturation activity of ^{109}Pd activity remains. The longest lived isotope analysed here was 74 day ^{192}Ir . Under these conditions, only 0.2% of the maximum Ir activity remained when counting started. In order to optimize conditions for Ir, a longer irradiation time could be employed. However, this was unnecessary because the sensitivity for Ir ($\sigma = 1050$ barns, abundance of ^{191}Ir parent is 37.3%) is very high. Further, a long irradiation is impractical due to ^{24}Na activity levels. A possible compromise practiced by Crocket et al. (1968) is a 24 hour irradiation at a thermal neutron flux of $10^{13} \text{ n.cm}^{-2}.\text{s}^{-1}$, (to generate high levels of long-lived isotopes), followed by a one week cooling, with a 12 hour re-irradiation for Pd, followed by a 48 hour cooling period. In the present work, the conditions of irradiation are governed by ^{109}Pd optimization and the minimization of ^{24}Na activity.

3.1 Interference from Gold on Platinum Determination

The determination of Pt is made via the



reaction.¹ The 3.14 day ^{199}Au has a prominent γ -ray at 158 KeV, and is easily distinguished from the 2.65 day ^{198}Au γ -ray peak at 412 KeV produced from the $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$ reaction. Gold and Pt are both determined from photopeaks in the gold γ -ray spectrum. There is, however, a competing reaction which produces ^{199}Au .



This reaction also generates 158 KeV radiation, but in this case, from gold. Therefore, the 158 KeV peak of ^{199}Au is not solely a measure of Pt content. The ^{199}Au activity produced from ^{198}Pt is given by equation 9, while ^{199}Au activity produced from ^{197}Au is given by (Friedlander et al., 1981);

$$A_3 = \frac{(nv)^2 \sigma_1 \sigma_2 N}{\lambda^*} \left(1 - \frac{\lambda_3}{\lambda_3 - \lambda^*} e^{-\lambda t_{ir}} + \frac{\lambda^*}{\lambda_3 - \lambda^*} e^{-\lambda^* t_{ir}} \right) \quad (14)$$

1. The direct determination of Pt by the reaction $^{196}\text{Pt}(n,\gamma)^{197}\text{Pt}$ is roughly of the same sensitivity as (14) above for a 1 week irradiation and twice as sensitive for a 1 day irradiation. However, radiochemical separation and purification of Pt is much more exacting and tedious than that of gold (Crocket, 1972).

where A_3 is the activity of ^{199}Au in disintegrations per second, σ_1 and σ_2 are the neutron absorption cross-sections for ^{197}Au and ^{198}Au respectively in 10^{-24} cm^2 , N is the number of ^{197}Au atoms, and λ_3 is the decay constant of ^{199}Au in s^{-1} and $\lambda^* = \lambda_2 + n\nu\sigma_2$, where λ_2 and σ_2 are the decay constant and neutron absorption cross-section of ^{198}Au . From equations 9 and 14, it is noted that the amount of ^{199}Au arising from the $(2n,\gamma)$ reaction on ^{197}Au is proportional to the Pt/Au value of the sample, and the neutron flux density, and increases with irradiation time. Crocket (1981) calculated that in a sample with $\text{Pt} = \text{Au}$, a 24 hour irradiation at a flux of $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ results in the production of approximately 80% of the ^{199}Au activity from the $(2n,\gamma)$ reaction on gold.

The Pt/Au value of the samples varies greatly from ultramafic (3 to 15) to mafic (usually <3) rocks. Larger corrections are usually required for Pt determination in mafic rocks by the ^{199}Au method. In this work the extent of ^{199}Au production from the $(2n,\gamma)$ reaction was estimated at 9% for DTS-1 ($\text{Pt}/\text{Au} = 4$), 8% for JHC-6 ($\text{Pt}/\text{Au} = 5$) and 4% for PCC-1 ($\text{Pt}/\text{Au} = 9$). In the mafic rocks, the correction varied from $<3\%$ (basaltic komatiite with Pt/Au of 76) to 60% (high iron tholeiite with Pt/Au of 0.78).

The correction is based on determination of the 158

KeV activity generated in a pure gold source (the gold-iridium standard) which gives a quantitative measure of the $(2n, \gamma)$ reaction, and a determination of the gold content of each sample. The calculation (adapted from Oshin, 1981) is shown below;

Let A_T = total activity at 158 KeV

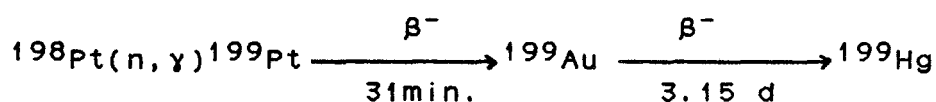
and B_T = total activity at 412 KeV.

From figure 3.1, it is seen that;

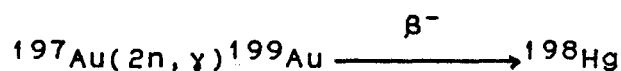
$$A_T = A_1 + A_2 \quad (\text{Fig. 3.1b inset}) \quad (1)$$

$$\text{and } B_T = B_1 \quad (2)$$

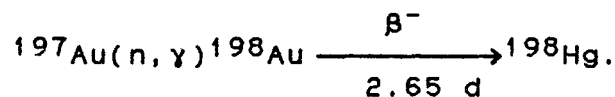
where A_1 is the activity at 158 KeV from the reaction,



and A_2 is the activity at 158 KeV from the reaction,



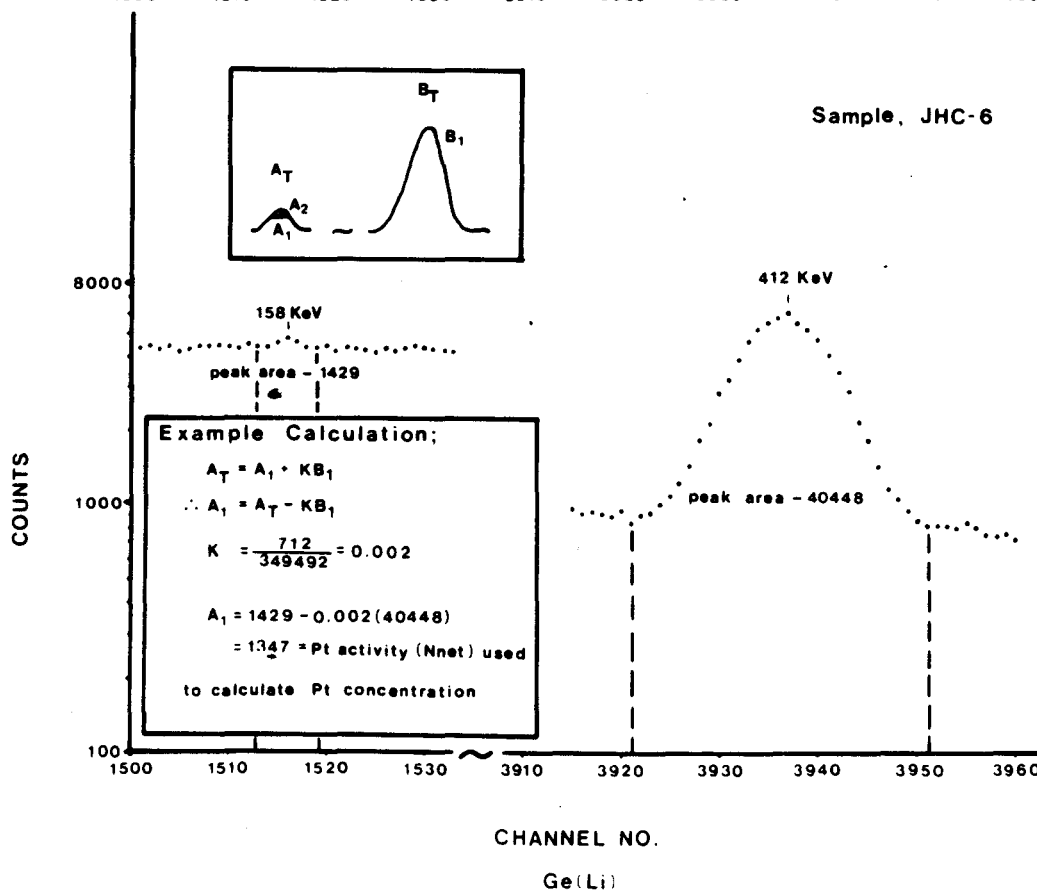
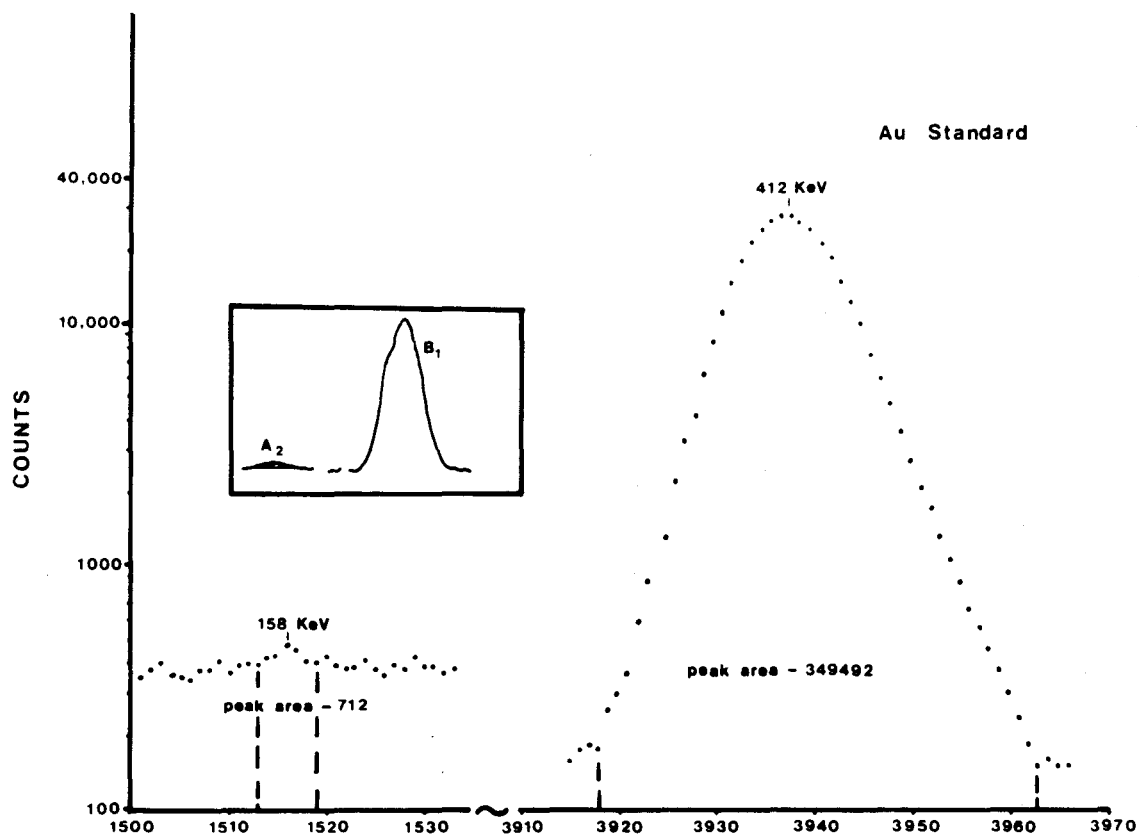
and B_1 is the activity at 412 KeV from the reaction,



The ratio of the activity produced by the (n, γ)

and $(2n, \gamma)$ reactions on ^{197}Au at 412 KeV (B_1)

and at 158 KeV (A_2) respectively may be expressed as;



$$K = A_2/B_1 \quad (3)$$

Substituting for A_2 in equation 1,

$$A_T = A_1 + KB_1 \quad (4)$$

The observed activity at 158 KeV (A_T) is, therefore, the sum of the activity due to ^{198}Pt (A_1) and the (n, γ) reaction on ^{197}Au (B_1), multiplied by a factor, K. K is determined by measuring the 158 KeV and 412 KeV activity on a pure Au standard (no Pt present), and using equation 3;

$$K = \frac{\text{activity of Au standard at 158 KeV}}{\text{activity of Au standard at 412 KeV}}$$

It is assumed that for all standards and samples irradiated under the same conditions (same irradiation package),

$$K(\text{std}) = K(\text{samp})$$

If $K(\text{std})$ is known, the activity at 158 KeV due solely to the ^{198}Pt reaction (A_1) can be determined from equation 4 (see figure 3.1 for an example).

CHAPTER 4

ANALYTICAL PROCEDURE

The following is a description of the analytical procedure followed in the present work. The procedure is adapted from Stockman (1982, 1983). Changes with respect to his procedure are detailed in Appendix 1.

4.1 Brief Description of the Radiochemical Tellurium Coprecipitation Technique

The analytical technique adapted and tested in this work is a carrier-based RNAA procedure, involving a rapid group separation of Au, Ir, Pd and Pt, with subsequent use of γ -ray spectrometry on high resolution Ge(Li) and intrinsic Ge detectors to identify individual elements. A 0.1 to 0.5 gram sample is irradiated in a thermal neutron flux of $8 \times 10^{12} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ for six hours, cooled for 12-18 hours and then fused with carriers in a Na_2O_2 -NaOH flux. The fusion cake is dissolved in HCl. The carrier and activated noble metals are coprecipitated with 3 mg of Te using Sn^{2+} as a reducing agent. The precipitate is washed, sealed in a compact counting form, and counted for 1000 to 50000 seconds (refer to Table 4.1 for details on counting times). Radiochemistry on five samples can be completed in 2 hours.

After PGE activities have been counted and allowed to decay for at least 18 days, the samples are re-irradiated for 4 minutes at $8 \times 10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, and the relative chemical yield on the carriers in the samples and standards are determined by direct counting of the appropriate γ -rays on a Ge(Li) detector. Stockman (1982) reports absolute yields (determined by radioactive tracer experiments) of 90-100% for Au, Pd and Pt and 60% for Ir. Typical detection limits for analysis of a 0.5 gram sample of peridotite are 0.01-0.02 ppb Au; 0.1-0.4 ppb Pd; 1-2 ppb Pt and 0.02 ppb Ir.

4.2 Detailed Analytical Procedures

A. Stock Solutions

1. PGE Carrier Solutions

Iridium - Prepare a stock solution containing ca. 0.200 mg/g Ir by weighing 0.114 g of ammonium chloroiridate ($(\text{NH}_4)_2\text{IrCl}_6$, 44% Ir) into a 250 ml erlenmeyer flask containing ca. 100ml of 2M HCl.¹ Warm the solution on a hot plate, swirling to dissolve the Ir salt. Cool to room temperature, and transfer quantitatively to a 250 ml volumetric flask, using 2M HCl, not water to rinse the flask.²

1. All carrier solutions were prepared from Johnson-Matthey Spec-Pure grade chemicals.

2. A gelatinous precipitate may form when solutions are diluted with distilled H_2O rather than 2M HCl.

Bring to volume with 2M HCl, and then rapidly suction filter the solution through a pre-weighed 1 cm diameter acid-resistant filter paper (Whatman-541) in a Hirsch funnel. Transfer the solution to a polyethylene bottle with a tight fitting lid. Rinse, dry and weigh the filter paper to verify that < 1% of the Ir salt remained undissolved.

Palladium - Prepare a stock solution containing ca. 0.700 mg/g Pd by weighing 0.140 g of pure Pd sponge into a 250 ml beaker. Add 15 ml of aqua regia (1 HNO₃:3 HCl by volume) and warm the covered solution very gently on a hot plate until the effervescence subsides and dissolution is complete. Evaporate the solution under a stream of filtered air, and swirl the beaker occasionally until a thick syrup is formed at incipient dryness. Add 2 ml conc. HCl and again bring the solution to incipient dryness; repeat five times (this procedure is required for the destruction of unstable Pd⁴⁺-NO₃ complexes).¹ Dissolve the syrup in ca. 10 ml conc. HCl and quantitatively transfer to a 250 ml volumetric flask, using 2M HCl to rinse the beaker. Bring to volume with 2M HCl and filter (as with Ir solution) to check for complete dissolution of Pd and to remove any

1. Avoid evaporation to dryness at any stage of nitrate-complex elimination which may result in the formation of Pd-metal, which is effectively insoluble in conc. HCl.

organic dust which may induce precipitation of Pd metal. Transfer the Pd stock solution to a tightly capped polyethylene bottle.

Platinum - The Pt stock solution containing ca. 0.34 mg/g Pt is prepared by weighing ca. 0.1 g of Pt sponge into a 250 ml beaker and proceeding as for Pd, above.

Gold - The Au stock solution of ca. 0.500 mg/g Au is prepared by weighing 0.100 g of Au sponge into a 250 ml beaker, and proceeding as for Pd, above. Care must be taken to heat the Au solution slowly and to avoid evaporation of the solution to complete dryness, as precipitation of Au metal (insoluble in HCl) will result. In addition, the final Au stock solution must be stored in a dark place to prevent photoreduction.

Prepare a carrier solution containing ca. 0.0500 mg/g Ir, 0.20 mg/g Pd, 0.10 mg/g Pt and 0.125 mg/g Au by pipetting 25 ml of each stock solution into a capped polyethylene bottle.

II. Tellurium Solution

To prepare a stock solution of 1.0 mg/g Te, weigh 0.1 g of Te metal powder (BDH Chemicals Ltd.) into a 250 ml beaker. Add 5 ml conc. HCl and 5 ml conc. HNO₃. Allow effervescence to subside, and evaporate the yellow-orange solution to incipient dryness. Add 2 - 5 ml conc.

HCl to the white-yellow Te chloro-nitrate precipitate, and again bring the solution to incipient dryness; repeat five times. After the second or third time, the precipitate will dissolve and be replaced by an orange-yellow syrup. Dissolve the solution in 10 ml HCl, and bring to 100 ml volume with distilled water.

III. Stannous Chloride Solution

To prepare a 1 M stannous chloride solution, weigh 22.5 g of stannous chloride dihydrate (BDH Chemicals Ltd.) into a 250 ml beaker. Add 16 ml conc. HCl and warm the solution to completely dissolve the salt. Bring to 100 ml with distilled water, and store in a tightly capped amber bottle. Prepare fresh every 2 months.

IV. Lithium Chloride Solution

Prepare a 10 mg/ml solution of LiCl by dissolving 1.0 gram of salt (Fisher Scientific Company.) in 100 ml of distilled water.

V. Dilute Acid

Prepare 500 ml of 2:1 (v/v) HCl:H₂O (ca. 8N) and 1000 ml of 1:11 (v/v) HCl:H₂O (ca. 1 N). For each sample processed, 25 ml of 2:1 and 200 ml of 1:11 is used. About 150 ml of 1:11 is used for each standard.

B. PREPARATION OF STANDARDS

I. Preparation of Poly Vials

Clean ca. 40 (20 Au-Ir and 20 Pd-Pt standards) 2/5 dram polyvials (approximately 1 cm inner diameter; flip-top or with separate lids) by soaking them in a 2:1 (v/v) HCl:HClO₄ solution. Rinse the vials with H₂O, distilled water and then pure acetone. Dry the vials at ca. 70 °C for a few minutes in an oven and allow vials to cool. Add SiO₂ powder, prepared by crushing ultrahigh purity, zone refined quartz tubing, to fill about 1/2 of the volume in each vial.¹

II. Standard Solutions

i) Au-Ir (ca. 500 ng/ml Au; 200 ng/ml Ir)

Pipette 1 ml of each of the Au and Ir solutions into a 1000 ml volumetric flask containing ca. 500 ml of 2M HCl, and bring to volume with 2M HCl.

ii) Pd-Pt (ca. 3500 ng/ml Pt; ca. 7000 ng/ml Pd)

Pipette 1 ml of each of the Pd and Pt stock

1. The quartz tubing is crushed sufficiently to pass a 100 mesh nylon screen. If the quartz powder is discoloured, some contamination has been introduced in crushing from the iron mortar and pestle. To remove such material, wash the powder in warm aqua regia, followed by several distilled-demineralized water rinses.

solutions into a 100 ml volumetric flask containing ca. 50 ml 2M HCl and bring to volume with 2 M HCl.

Standard solutions should be prepared fresh before buretting into poly vials.

III. Final Preparation of Standards

i) Au-Ir standards (ca. 150 ng Au; 60 ng Ir)

Using a microburette, deliver 0.300 ml of the Au-Ir standard solution to a pre-weighed poly vial containing silica powder (weight includes silica powder). Quickly weigh the vial and solution, and label each. When ca. 20 standards are prepared, calculate the mean weight of the solutions delivered to the vials, and discard any which deviate more than 0.5% from the mean. Dry the solutions onto the SiO₂ powder by placing the remaining standards in an oven at ca. 70 °C. After drying, all poly vials should be capped and sealed with a soldering iron. Verify that the seal is tight by squeezing each gently with pliers under water. Discard any vials which leak.

ii) Pd-Pt (1050 ng Pt; 2100 ng Pd)

Deliver 0.300 ml of Pd-Pt standard solution to pre-weighed poly vials and proceed as for Au-Ir standards.

C. PREPARATION OF SAMPLE CRUCIBLES AND STANDARD BEAKERS

I. Sample Crucibles

Nickel sample crucibles (CANLAB, 25 ml, 3.5 cm diameter, shown in plate 1) were chosen over zirconium for several reasons; Zr crucibles corrode just as rapidly as Ni crucibles at dull red heat, and therefore are of no advantage; Zr crucibles yield an insoluble zirconia precipitate which must be removed after fusion; and Ni crucibles are 1/4 the price of Zr crucibles.

To prepare the sample crucibles for irradiated rock powder, melt three pellets of NaOH in each crucible over a meeker flame and swirl the waxy liquid to coat the sides of the crucible about 1/3 of the way up. Set the crucibles to cool on a Pb brick. Pipette 1 ml of Au-Ir-Pt-Pd carrier into each crucible, making sure the pipette does not touch the bare metal, only the coating. Gently dry the carrier onto the NaOH on a hotplate (set on low heat), under a flow of filtered air and a heat lamp. Place the crucibles in an oven at ca. 50 ° C overnight to avoid rehydration of dry NaOH.

II. Standard Beakers

The 250 ml standard beakers are prepared for radiochemistry by pipetting 1 ml of Au-Ir-Pt-Pd carrier

into each. Add a few milligrams of NaCl ¹ and two drops of conc. HNO_3 ². Cover the beakers with parafilm and label.

D. PREPARATION OF SAMPLES

All work surfaces, including microbalance pan should be kept clean, and no jewelry should be worn during sample handling. Poly vials are cleaned by soaking in 2:1 (v/v) $\text{HCl}:\text{HClO}_4$, rinsing with H_2O , distilled water and finally, pure acetone.

Weigh 0.1 to 0.5 grams of ultrabasic rock (weight varies inversely with sodium content ³) or 0.3 grams of mafic or intermediate rock into each vial. Seal the lid with a soldering iron and verify the seal by gently squeezing each vial with pliers under water. Rinse the vials with distilled water and dry them.

E. IRRADIATION

Irradiate 1-5 rock powder samples and 4 standards (2 Au-Ir and 2 Pd-Pt), sealed in poly vials, and grouped in a petri dish (plate 1) for 6 hours at a thermal neutron flux of $8 \times 10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$. In the McMaster pool-type nuclear research reactor, variation of neutron flux with position required that the same loading

1. Avoids plating of metal onto glass, and possible metal reduction which could impede complete dissolution.

2. Avoids metal reduction (HNO_3 is an oxidant)

3. For $\text{Na}_2\text{O} < 0.05\%$ use 0.5 grams; for $\text{Na}_2\text{O} > 0.05\%$ use ca. 0.1 grams.

position (9C) be utilized for each irradiation.¹ This was necessary to obtain a reproducible total package radiation dose at the end of irradiation. Cool the package for 12 to 18 hours. After decay the most active species will be ^{24}Na ($\gamma + \beta^-$), followed by ^{31}Si (β^-), ^{198}Au ($\gamma + \beta^-$) and perhaps ^{82}Br , and $^{80\text{m}}\text{Br}$ (from HCl). The standard dose rates are negligible compared to sample dose rates. At the surface of unshielded samples, dose rates are 450 mR/hr (γ) to 5 R/hr ($\gamma + \beta^-$). At one meter from five unshielded samples, dose rates ($\gamma + \beta^-$) are from 5.5 mR/hr ($\gamma + \beta^-$) to 4.5 mR/hr (γ). Shielded behind 3 cm of Pb, maximum dose rates at the surface of the Pb are ca. 4.0 mR/hr. At the surface of two cm of Pb shielding, the standards give dose rates of 20 mR/hr.

Inclusion of flux wires is recommended by Stockman (1982) as a possible improvement on the technique. Small Co flux wires were included in each irradiation package to monitor flux variations across the irradiation container and between different irradiations. It was determined that the flux varied by a maximum of 1% across the container.

1. Samples should never be inverted and should be rotated during radiation.

F. RADIOCHEMISTRY: SAMPLES

A flow chart of the procedure is given in figure 4.1. All processing of radioactive samples must take place behind 3-5 centimeters of lead brick shielding. Samples should be handled with long handled tongs (20 cm) at all times. The procedure below describes the processing of one sample which takes 1.5 to 2 hours; however, 5 samples may easily be processed simultaneously in 2 - 2.5 hours.

Sample Transfer and Fusion

Remove a crucible from the oven. Add 7 NaOH pellets and ca. 3 grams of Na_2O_2 . Rinse the outside of the sample vial with acetone to remove possible contaminants. Tap the vial against a Pb brick to knock all the irradiated rock powder to the bottom. Place the vial in a Pb vial holder (plate 1) and with a scalpel (extended handle, ca. 20 cm long) quickly cut off the top of the vial. Pour rock powder over the flux mix in the crucible. Add another 3 grams of Na_2O_2 and gently tap the crucible against a Pb brick to even out the mixture. Cover the crucible with a labelled Ni lid and place it on a low bunsen flame for ca. 5 minutes, or until the fusion cake has nearly melted. Turn up the flame and continue heating until the fusion cake is at dull

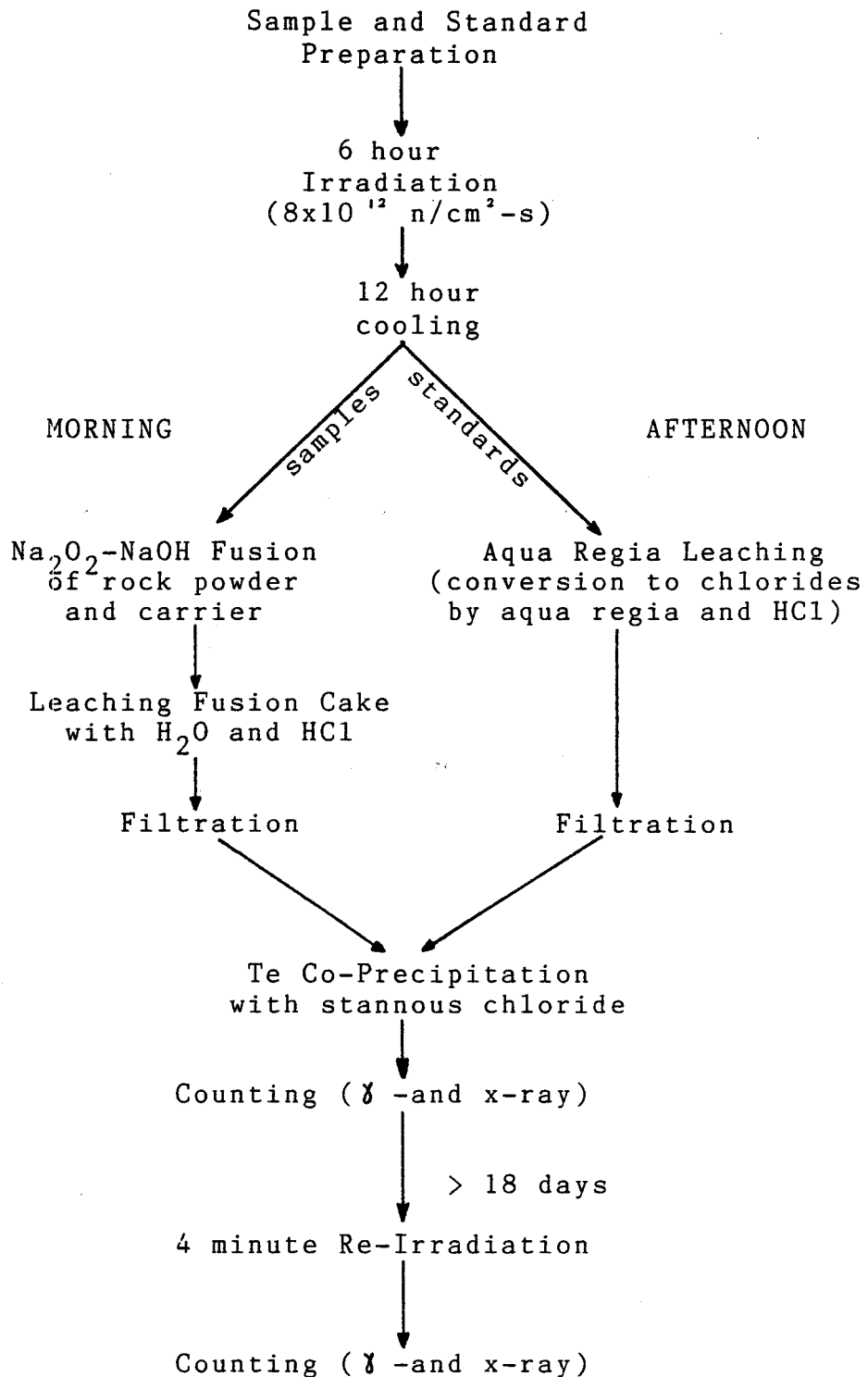
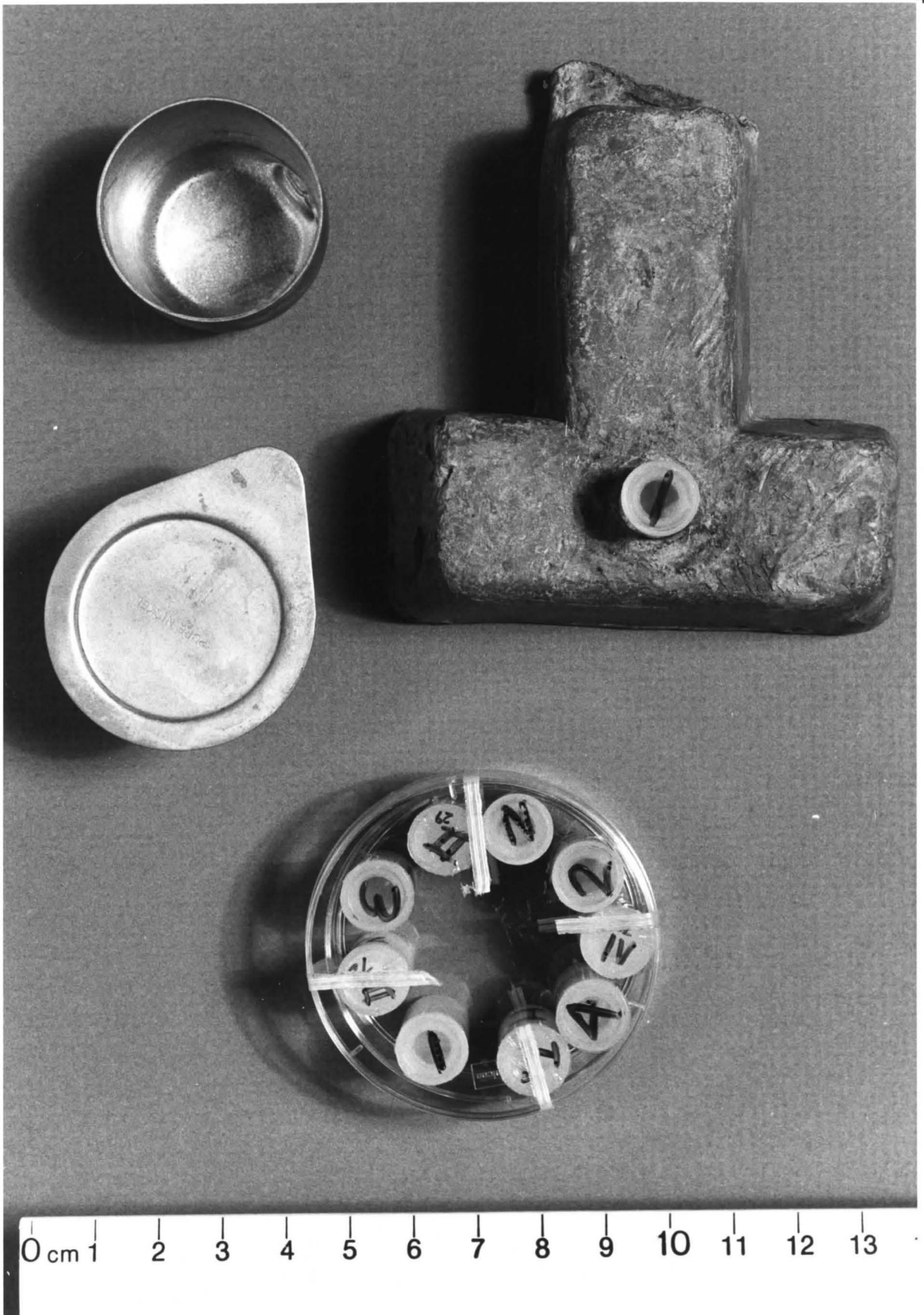


Figure 4.1 . Flow chart for group separation of Au, Ir, Pd and Pt by the tellurium co-precipitation technique.



red heat (ca. 600 ° C; at higher temperatures, insoluble Ni oxides form which are difficult to remove when fusion cake is leached). The crucible corrodes after only a few fusions if higher temperatures are used. Continue heating for 5 to 10 minutes, swirling occasionally. When fusion is complete, place the crucible on a Pb brick to speed cooling. Place the lid so it is half covering the crucible to facilitate transfer in the leaching stage. After ca. 3 minutes a "ping" will be heard as the fusion cake cracks and pulls away from the sides of the crucible.

Leaching the Fusion Cake

Immediately after the 3 minute cooling, place the crucible on its side in a 250 ml beaker containing 60 ml distilled water and 3 silicate boiling chips. The beaker should be on a hotplate, set on low. Cover immediately with a watch glass. After effervescence subsides, rinse the watch glass into the beaker with 5 ml 2:1 dilute HCl acid. Rinse the inside and outside of the crucible with 20 ml 2:1 HCl:H₂O, then with 15 ml conc. HCl to dissolve any remaining black oxides. Measure the proportions of acids carefully, as pH

is critical to the precipitation step.¹ Transfer the cleaned crucible to a large beaker of distilled water to soak. Rinse the lid with a small amount of 2:1 dilute acid and remove to soak. Add any rinsings to the beaker. Replace the watch glass and turn up the hot plate to boil the solution gently for ca. 10 minutes, to convert H_2O_2 (produced by the reaction of Na_2O_2 and H_2O) to H_2O and O_2 . The solution is ca. $2.1M^2$ in H^+ and ca. $3.8 M$ in Cl^- . The solution should be clear, without traces of colloidal silica or undissolved rock. Solutions of peridotite (PCC-1) will be green (partly due to Ni^{+2} from dissolution of the crucible) while solutions of more Fe-rich siliceous rocks (high Fe tholeiite 78-34) will be yellow-green (from $FeCl$ complexes), and chromites will be orange (from dichromate; Stockman, 1982). Dose rates at surface are now on the order of 20 mR/hr per sample.

When the solution has boiled, pass it through a fast acid-resistant filter paper (Whatman 1) into a 250 ml erlenmeyer flask containing 3 silicate boiling chips. Rinse the watch glass, beaker and filter paper with ca. 40 ml 1:11 $HCl:H_2O$. This step is a

1. The Te-precipitation is a reduction process ($Te^{+4} \rightarrow Te^0$) and consequently depends on H^+ availability or pH.
2. Accounting for the neutralization of alkali from Na_2O_2 and OH^- .

precaution against the presence of unseen rock powder or silica gel which may inhibit Te precipitation. If complete dissolution is always attained, the filtration step may be eliminated. Add 2 ml Te solution to the erlenmeyer flask, cover with watch glass, and set on a hot plate to boil. The solution should be 140 to 150 ml. Dose rates at the surface of one sample are now approximately 10 mR/hr.

Te Precipitation

When the solution in the erlenmeyer is at a rolling, but not violent boil, add (dropwise at first) 10-15 ml stannous chloride solution (Sn^{2+}) to reduce Te to the metal. Black clouds of fine precipitate should appear immediately. Boil the solution ca. 5-10 minutes, until the precipitate is well coagulated, and the solution is clear. The PGE are co-precipitated by the Te metal. Add 1 ml Te solution and boil again until the precipitate is well coagulated. Heat a volume of 1:11 dilute HCl equivalent to 120 ml per sample.

Filtering and Washing the Precipitate

Place a 4.2 cm diameter circle of acid-resistant filter paper (Whatman 1) into a 300 ml capacity millipore filter holder. Place the holder on a 2000 ml side-arm filter flask, attached to a vacuum pump. Pour a

small amount of distilled water into the holder reservoir and turn on the pump to verify the seal. Pour the Te precipitate and solution into the holder. Rinse the erlenmeyer with 1:11 HCl:H₂O and transfer the rinsings to the reservoir. Apply suction only after the sample has been added to the reservoir or uneven settling will result. Rinse the sides of the reservoir with 1:11 HCl:H₂O and wash the precipitate by passing 10 ml of hot 1:11 HCl:H₂O through the filter apparatus 10 times. Break down the apparatus, and transfer the filter paper with the precipitate outside the fume hood. The dose rate of the precipitate will be very low (< 2 mR/hr).

Counting Form

Allow the papers to dry 15 - 20 minutes, then quarter the paper (fold paper in half, with the precipitate in the middle, then fold again). Seal the quartered paper by wrapping it in a small piece of thin plastic wrap (Saran Wrap), then place the sample in a polyethylene envelope and heat seal the open end. Label the envelope, center it on the counting tray, and tape it down. (plate 2).



G. RADIOCHEMISTRY: STANDARDS

The procedure described below is for the processing of a single standard. In practice, 4 standards (2, Au-Ir and 2, Pd-Pt) may be processed simultaneously. The procedure takes ca. 3 hours. Standard processing should take place after processing of samples is completed, preferably in another room, to avoid contamination.

Equilibration with Carrier

Rinse the standard vial with acetone, and tap the vial to bring all the SiO_2 powder to one end. Place the vial into the Pb vial holder, and snip off the end with a long handled scalpel. Pour the SiO_2 powder into the prepared standard beaker. Add 1 ml of aqua regia to the vial and pour the vial contents into the beaker. Repeat twice. Add another 1 ml of aqua regia to the vial and set aside. Add 1 ml LiCl to the beaker (to help prevent metal reduction upon drying), cover, and gently warm the solution on a hot plate, until effervescence subsides. Add the contents of the vial to the beaker, discard the vial and set the beaker to warm until incipient dryness is reached. Keep hot plate on low or the silica powder will spit and contamination between standards will occur. Add 2 ml conc. HCl , and again bring the solution to incipient dryness. Repeat 5

times. (the repeated addition of HCl converts noble metal nitrates to chlorides). Add 10 ml conc. HCl and 90 ml 1:11 HCl:H₂O to the beaker. Filter the solution through a fast filter paper (Whatman 541) into a 250 ml erlenmeyer flask containing 3 silicate boiling chips. Wash the filter paper and SiO₂ powder with 40 ml 1:11 HCl:H₂O), and add rinsings to the flask. Add 2 ml Te solution, cover and set flask to boil on a hot plate. The solution should be clear and at 140-150 ml volume. Discard the filter paper and SiO₂ powder to active waste storage.

Te Precipitation

When the solution is at a rolling ,but not violent boil, add 10 ml of Sn⁺² solution, dropwise at first. Boil the solution 5-10 minutes until the precipitate coagulates, then add 1 ml Te solution, and boil again. Continue processing the standards exactly as the samples were processed.

H. COUNTING

Count the samples for the 22 KeV Ag K x-ray (from ¹⁰⁹Pd decay) and the 88 KeV ¹⁰⁹Pd γ-ray on an intrinsic Ge low energy photon spectrometer for 2,000 to 10,000 seconds (5,000 seconds usually give adequate counting statistics). The samples should be counted flush against the detector cap. Count the Pd-Pt standards for

1,000 seconds in the same position. Dead times for the samples are 0% and <1% for the standards.

Count the samples for the 158 KeV $^{199}\text{Au(Pt)}$ γ -ray, the 328 KeV ^{194}Ir γ -ray, the 317 KeV ^{192}Ir γ -ray and the 412 KeV ^{198}Au γ -ray on a coaxial Ge(Li) detector. Count the samples for 20,000 to 50,000 seconds and the standards for 1,000 seconds. Count all samples and standards flush against the detector cap. Dead times will be 0% for most samples, and 1-3% for the Au-Ir standards.

The following three passivated hyperpure germanium detectors were used for the work reported here.

1. A planar intrinsic germanium detector (APTEC) with 500 mm² active area, 0.005 inch window thickness, 10 mm sensitive depth and energy resolution of less than 0.37 KeV (FWHM) at 5.9 KeV and 0.6 KeV (FWHM) at 122 KeV.

2. A coaxial intrinsic germanium spectrometer (APTEC) with 18.4 cm² active area, 55 cm³ active volume, 0.02 inch window thickness, energy resolution of less than 0.85 KeV (FWHM) at 122 KeV and 1.8 KeV (FWHM) at 1.332 MeV, relative efficiency of greater than 10% and peak to compton ratio of 35:1.

These two detectors were connected with a Canberra Industries Series 80 multichannel gamma-ray spectrometer including model 8623 pulse height analyser/live time

corrector, including a 100 MHz analogue to digital converter with 8192 channel conversion gain and model 861 peak analyser option.

3. A coaxial intrinsic germanium spectrometer (APTEC S90) with 83.6 cm^3 active volume, 0.5 mm window thickness, energy resolution of 1.17 KeV (FWHM) at 122 KeV and 1.9 KeV (FWHM) at 1333 KeV, relative efficiency, of >20 %, and a peak to compton ratio of 46:1. This detector was connected with a Canberra Industries Series 90 multichannel analyser with model 8075 analogue digital converter.

Properties of relevant γ -rays and counting parameters are outlined in Table 4.1. As sensitivity is dependant on induced activity, the nuclide with the highest yield is generally counted. Those counted here are the 22 and 88 KeV x- and γ -rays of ^{109}Pd , 158.4 KeV of $^{199}\text{Au}(\text{Pt})$, 411.8 KeV of ^{198}Au , 316.5 KeV of ^{192}Ir and 328.5 KeV of ^{194}Ir . ^{192}Ir values were generally chosen over ^{194}Ir as a 74 day half-life gave more reliable results on international rock standards after 50,000 second counts.

The pertinent nuclear reactions for ^{109}Pd production and decay are;

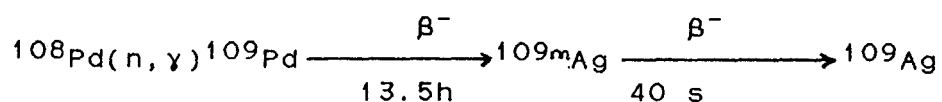


Table 4.1.

CHARACTERISTICS OF NOBLE METAL SPECTRA AND COUNTING TIMES

ISOTOPE	T1/2	KeV	RELATIVE INTENSITY	WHEN COUNTED (HOURS AFTER RADIOCHEM.)	DETECTOR	COUNT LENGTH (Kilosec.)
¹⁰⁹ Pd	13.5hr	22	100	0-12	planar	2-10
		25	20	/		
		88	/	0-12	coaxial**	10-20
					coaxial***	5-10
¹⁹⁷ Pt	19hr	77.4	/	/	/	/
¹⁹⁹ Au	3.15d	158.4	100	24-48	coaxial**	20-50
					coaxial***	>15-50
		208.2	20	/	/	/
¹⁹⁸ Au	2.65d	411.8	100	0-48	coaxial**	20-50
					coaxial***	5-10
		675.9	/	/	/	/
¹⁹² Ir	74d	65-78	/	/	/	/
		295.9	30	/	/	/
		308.4	30	/	/	/
		316.5	100	24-48	coaxial**	20-50
					coaxial***	20-40
		468.1	50	/	/	/
		604.1	/	/	/	/
¹⁹⁴ Ir	19hr	29.4	/	/	/	/
		328.5	100	0-24	coaxial**	5-50
					coaxial***	5-10

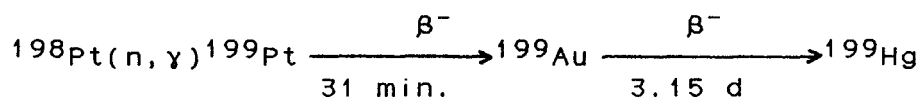
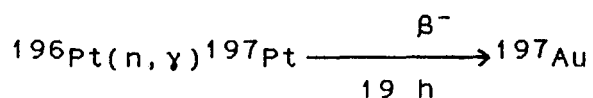
a) Most intense peak of each isotope taken as 100.

b) Count length for adequate counting statistics of 10,000 counts above background

c) ** = 15% efficient coaxial Ge(Li),
 *** = >20% efficient coaxial Ge(Li).

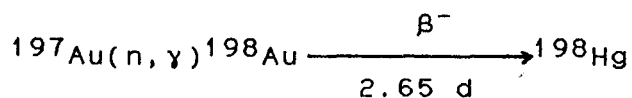
Decay of ^{109m}Ag gives an 88 KeV γ -ray with relatively poor yield (5%) and internal conversion Ag K x-rays (22 KeV) with good yield (ca. 50%). Pd determinations on the lower energy peak should be very sensitive as the thin LEPS detector picks up little Compton background from high energy radiation.

The important reactions for Pt are;

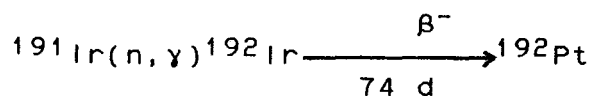


Although the 77 KeV γ -ray of ^{197}Pt was used by Nadkarni and Morrison (1974), it is not recommended because of interference from Pt K x-rays of approximately this energy generated by ^{192}Ir decay (Stockman, 1982). The second reaction produces a 158 KeV γ -ray via ^{199}Au decay, which was used for Pt determination in this study.

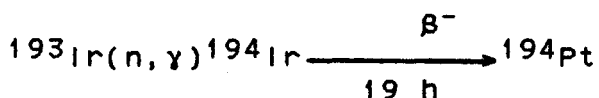
Gold is determined via;



and Ir by;



and,



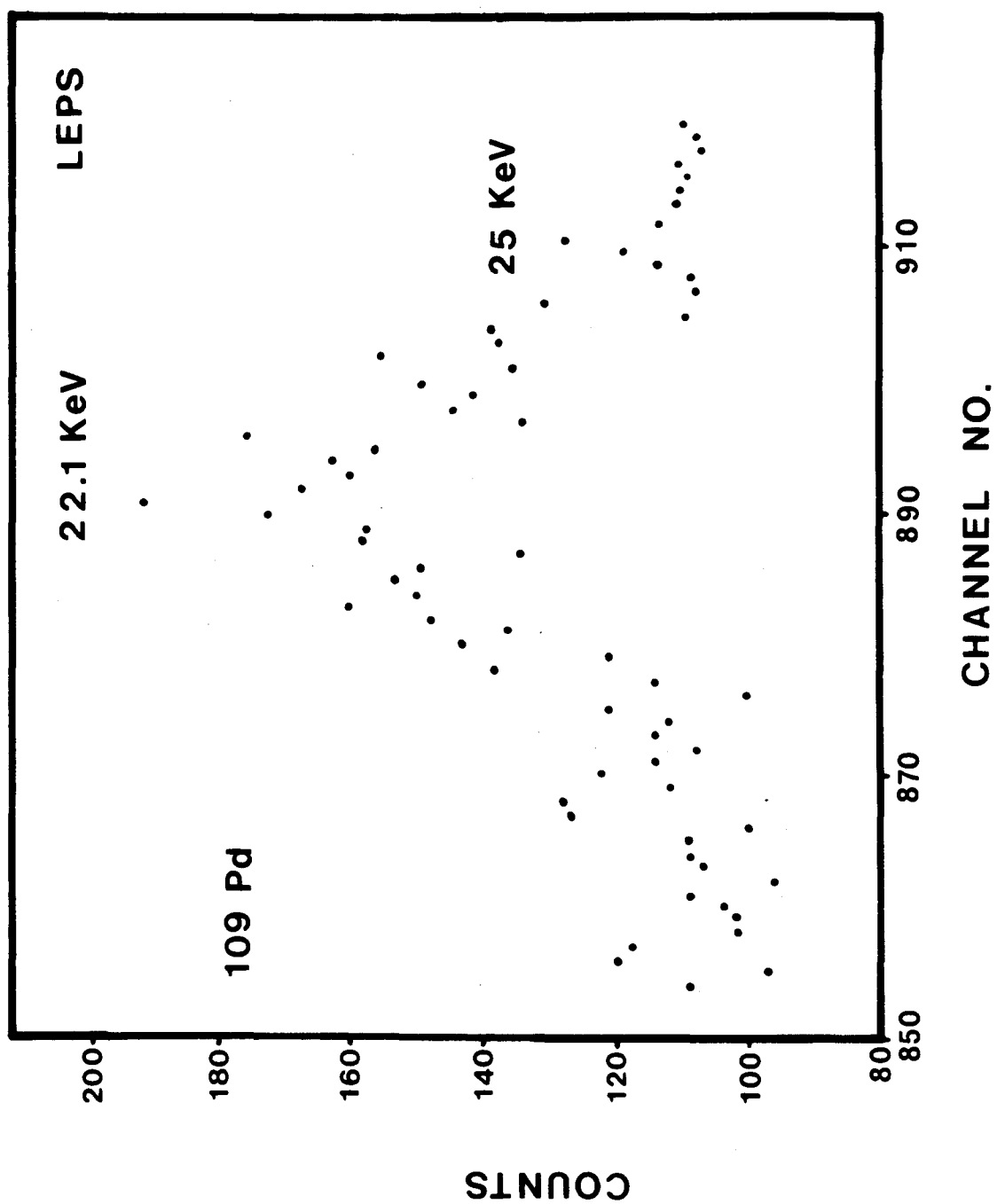
^{192}Ir has a peak at 316.5 KeV which is most prominent after long, high flux irradiations and long decay periods. ^{194}Ir has a 328 KeV γ -ray and provides the most intense Ir peaks immediately after irradiation. A typical gamma spectrum for JHC-6 (house standard, fine grained olivine spinifex zone of a Komatiitic peridotite) is given in figure 4.2.

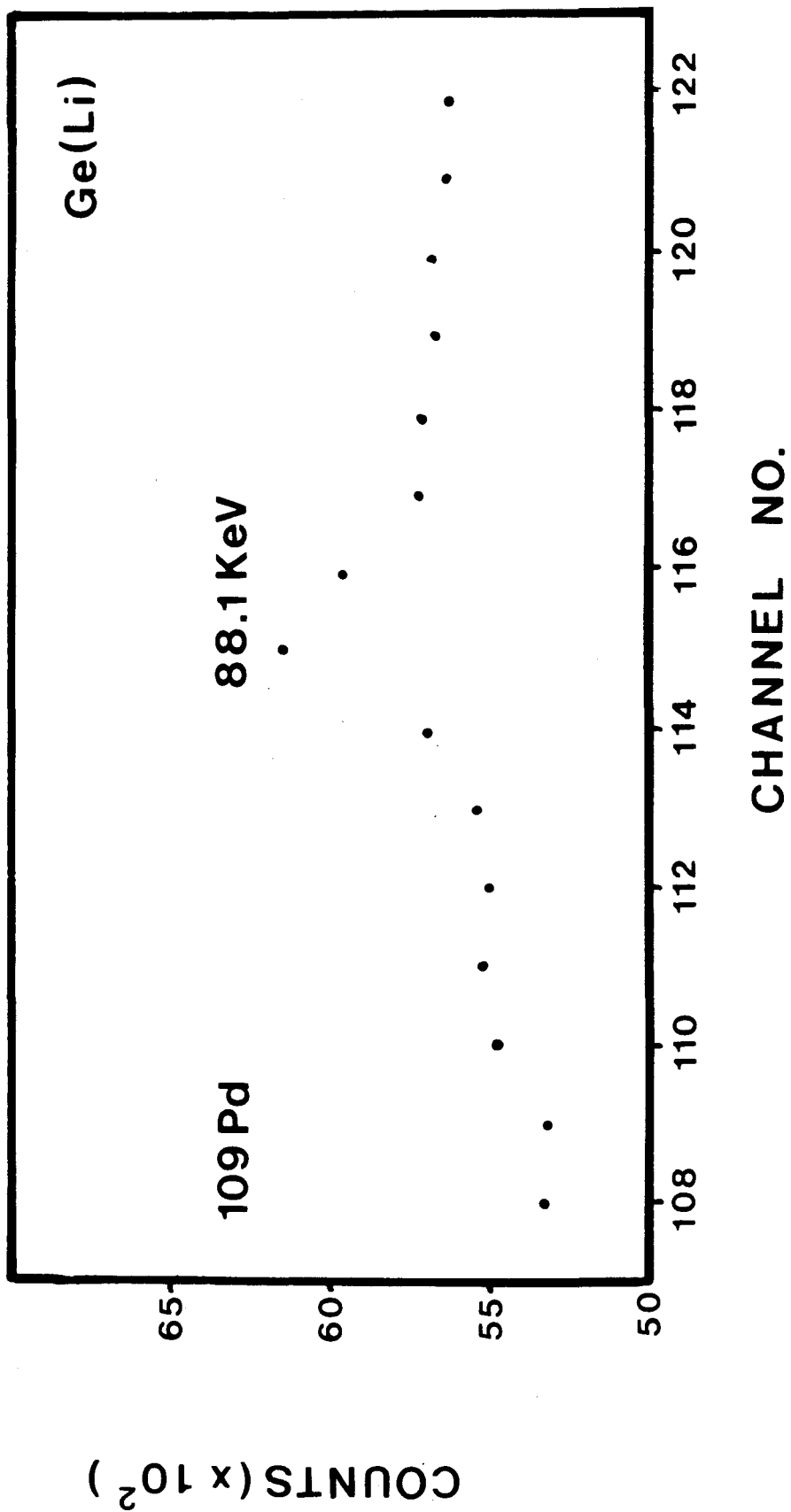
1. RE-IRRADIATION FOR CHEMICAL YIELD DETERMINATION

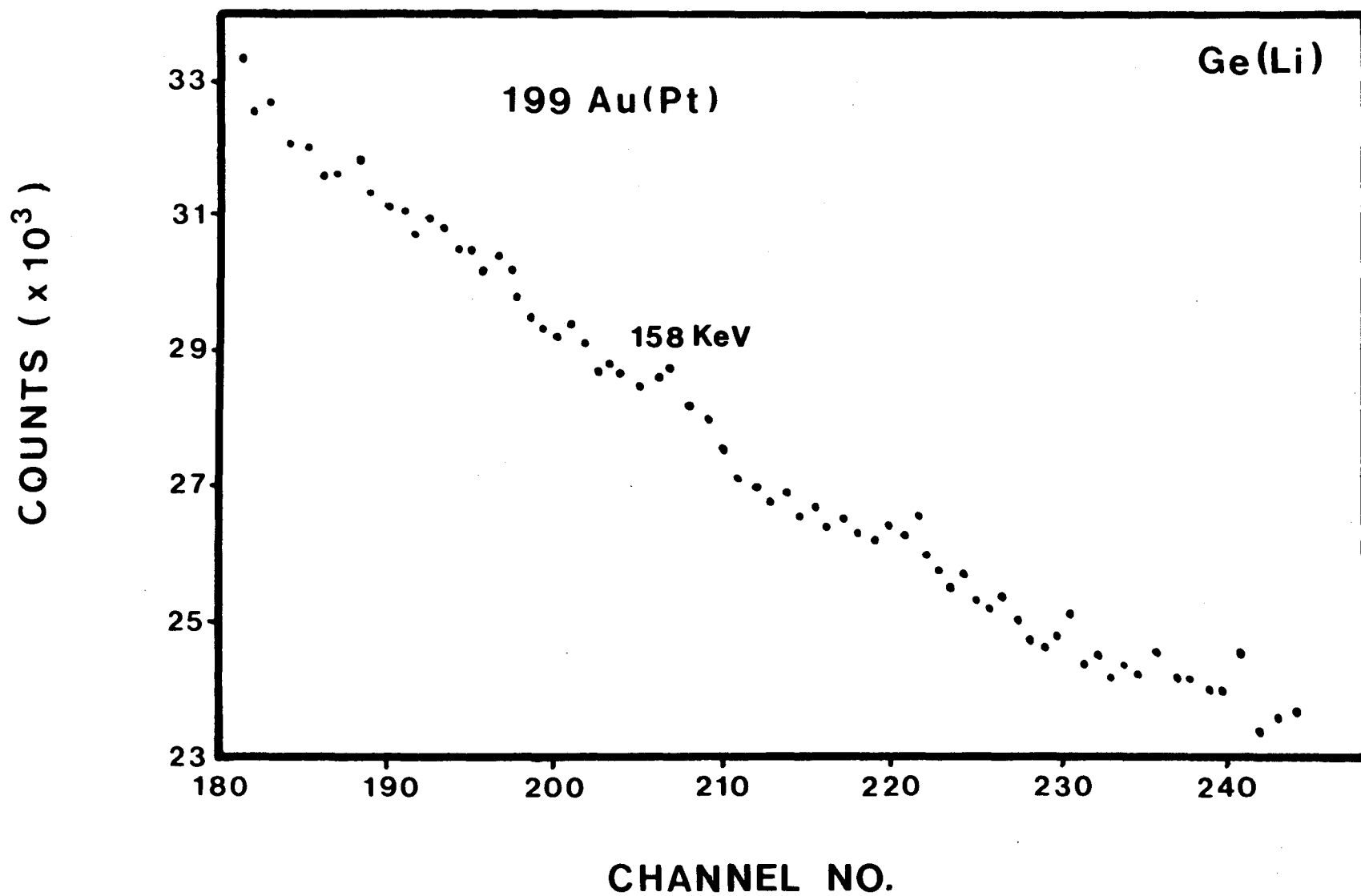
As PGE co-precipitation on Te is not quantitative for the procedure used here, the fraction recovered is quantitatively determined by irradiation of the recovered carrier; that is, of the Te precipitate from each sample.

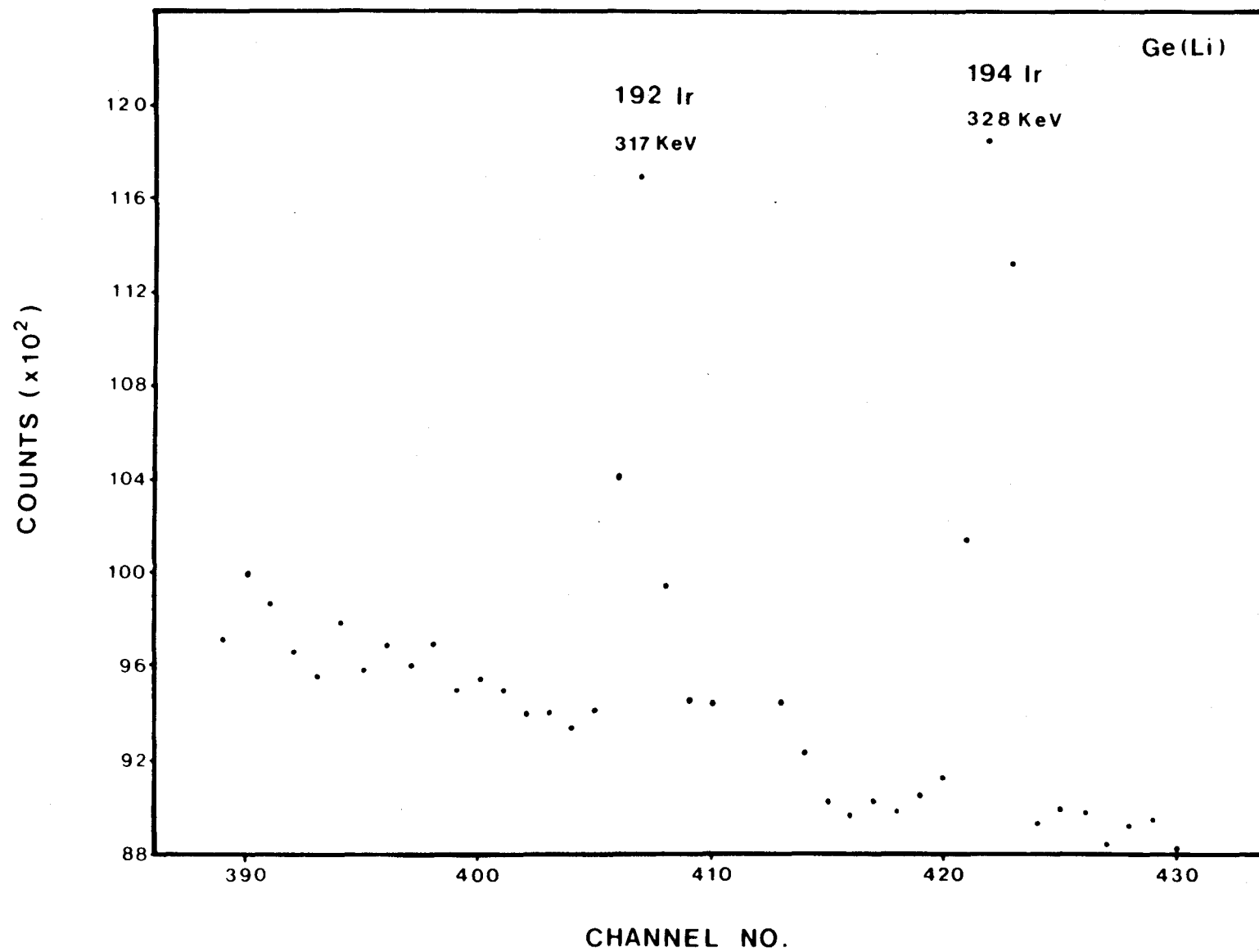
Packaging

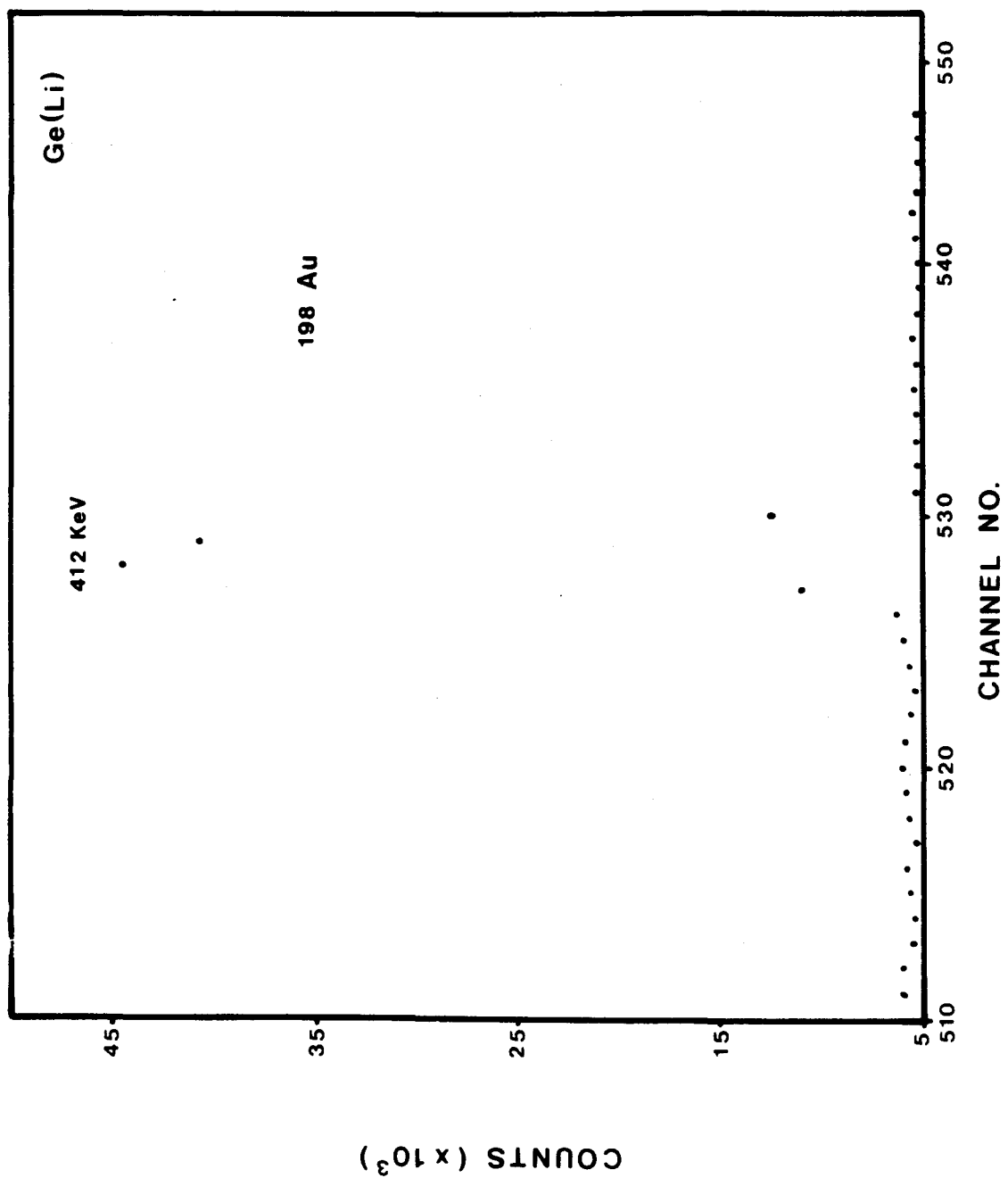
After about 18 days (or more), most of the activities in the sample have decayed, so samples may be packaged for re-irradiation and chemical yield determination. Stack the sealed, labelled envelopes so that the filter papers lie directly on top of one another, and tape the set with mylar tape. The stacks should be placed in a 5.5 cm diameter petri dish with a











lid. Up to 2 sample and standard sets (2 experiments) may be irradiated in the same package. (Each set may contain up to 5 samples and 4 standards).

Re-irradiation

Irradiate the package in a flux of 8×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 4 minutes. Immediately after the irradiation numerous short-lived nuclides (^{38}Cl , ^{131}Te , ^{192m}Ir , ^{109m}Pd), will be present. They must be allowed to decay for 12-18 hours. After cooling, the most active species will be ^{198}Au , with a $\gamma + \beta^-$ dose rate of 1.5 mR/hr at 1 meter away from one set of 5 unshielded samples and 4 unshielded standards.

Counting

Wrap each 2.5cm x 3.8cm sample envelope in a square of thin plastic wrap (Saran Wrap). Place each sample in a 3.18cm x 5cm counting envelope, and center the sample on the counting tray as in plate 2. Count the samples 10-15 cm from the coaxial Ge(Li) detector for ^{109}Pd at 88 KeV, ^{194}Ir , ^{198}Au and 2-5 cm from the planar Ge(Li) for ^{109}Pd from the 22 KeV x-ray. The Pt relative yields are determined by re-irradiation of samples and standards, from the 412 KeV peaks of ^{198}Au in the samples and Pt standards. Counts of 500 seconds

give adequate counting statistics ($\pm 5\%$) for all elements on the $>20\%$ efficient coaxial detector, whereas 1000 sec counts may be required on the 10% efficient coaxial and the low energy planar detector if the ^{109}Pd is determined via the 22 KeV peak. Dead times are ca. 3-5% and stable on the coaxial Ge(Li) detector and 1.5% and stable on the planar Ge(Li).

J. DATA REDUCTION

Calculation of noble metal concentrations were obtained from a Fortran program written by Mr Abdul Kabir, and a Lotus 1-2-3[®] spreadsheet prepared by the author.

Basic Equation

Calculate the concentration of noble metals in each sample from;

$$\text{ppb NM} = \frac{w}{W} \cdot \frac{N_{\text{samp}}}{N_{\text{std}}} \cdot \frac{\text{TCF}}{\text{TCF}'} \cdot \frac{N'_{\text{std}}}{N'_{\text{samp}}}$$

where w is the weight of noble metal in the standard in ng; W is the weight in g; N_{samp} and N_{std} are the net counts in the sample and standard respectively, after the first irradiation and radiochemistry. TCF is the time correction factor for N_{samp} and N_{std} , which corrects for

variable decay times between the counting of a given sample and the standards and the exponential decay of the isotopes during the count. TCF' is the time correction factor for N'_{samp} and N'_{std} , the net counts in the sample and standard peaks after re-irradiation for chemical yield.

Calculating Net Counts in Peaks

The net count is the difference between the total count over a selected number of channels and the background over the same channel suite. Net counts, N_{net} is usually calculated as:

$$N_{\text{net}} = N_{\text{gross}} - n/2b(N_h \text{ back} + N_l \text{ back})$$

where N_{gross} is the total number of counts in a peak of n channels, $N_h \text{ back}$ is the number of counts in b channels of background on the high energy side of the peak, and $N_l \text{ back}$ is the number of counts in b channels, symmetrically distributed on the low energy side of the peak. Because the γ -ray spectra obtained for radiochemically processed samples are relatively simple (see examples of typical spectra in fig. 4.2), the peak centrum is taken as the channel equivalent to the analytical γ -ray energy (e.g. 412 KeV for ^{198}Au) and the peak designated as an equal or nearly equal (± 1)

number of channels on either side of the centrum channel, laying above the best straight -line fit to the spectrum base for 15 to 20 channels either side of the centrum. A more mathematical definition of peak area, as frequently needed to define peaks in INAA spectra, was deemed unnecessary. For the low energy peaks (22 KeV and 88 KeV ^{109}Pd and the 158 KeV $^{199}\text{Au}(\text{Pt})$ a 4 channel peak (0.8 KeV per channel) contains 90% or more of the total number of counts on the full net peaks ($n = 4$). For the higher energy nuclides (^{192}Ir , ^{194}Ir , and ^{198}Au), 95% of the full peak is contained in 6-8 channels (ie, $n = 6-8$).

Counting Statistics Errors

Under the simplest conditions, the standard counting error is;

$$S_c = \sqrt{N}$$

where N is the total number of counts and other errors are not significant compared to the standard counting error under consideration (Leibhafsky et al., 1972). According to the law of combination of errors, the standard counting error will be larger if more than one count is needed to establish an analytical result. In this case, both the standard and sample counts for both a first and second irradiation are needed. If N_t is the total counts under the peak and N_b is the background count over the same number of channels, then the counting

error of the difference $N_t - N_b$ is;

$$S_c = \sqrt{(S_{ct})^2 + (S_{cb})^2} = \sqrt{N_t + N_b}$$

since the rule for the combination of independent errors when an error of a difference is sought calls for the addition of squares under the radical. For this work, the total counts under the peak (N_t) is given as N_{gross} , and the background (N_b) are calculated as $n/2b$ ($N_h \text{ back} + N_l \text{ back}$).

Where the counting error relative to the concentration of the element sought is required,

$$S_c = \frac{\sqrt{N_t + N_b}}{N_t - N_b}$$

In this technique, $N_t - N_b$ is represented as;

$$N_{net} = N_{gross} - n/2b (N_h \text{ back} + N_l \text{ back})$$

The individual counting errors for the standards and samples for both the initial irradiation and the yield determination must be calculated and summed ¹;

1. This formula overestimates S_c for $2b > n$ and underestimates S_c for $2b < n$, but the error is generally small.

Table 4.2.STANDARD COUNTING ERROR FOR HOUSE STANDARD, JHC-6

Element	Sample	N(ppb)	Standard Counting Error S_c total
Au	1	3.1	0.1
	2	2.9	0.18
	3	2.5	0.082
	4	2.0	0.09
Ir	1	2.0	0.58
	2	1.9	0.08
	3	1.8	0.99
	4	1.7	0.86
Pd	1	25	1.5
	2	23	1.5
	3	17	1.4
	4	11	1.4
Pt	1	15	10
	2	15	2.0
	3	13	13

$$S_c \text{ indiv.} = \frac{\sqrt{N_{\text{gross}} + n/2b (N_{\text{Hback}} + N_{\text{Iback}})}}{N_{\text{net}}}$$

and

$$S_c \text{ total} = \sqrt{(S_c \text{ samp})^2 + (S_c \text{ std})^2 + (S'_c \text{ samp})^2 + (S'_c \text{ std})^2}$$

S_c total gives the combined counting error for the estimation of the concentration, including contributions for N_{net} of the sample, standard and yield determination, where the primed errors are those calculated for yield determination counts. Ranges of S_c errors for the house standard are given in Table 4.2.

Time Correction Factors

The time correction factor is given by;

$$\text{TCF} = \frac{e^{-\lambda t_b} - e^{-\lambda t_a}}{e^{-\lambda t_2} - e^{-\lambda t_1}}$$

where t_a and t_b are the starting and ending times for the count of the standard, t_1 and t_2 are the starting and ending times for the count of the sample, and λ is the decay constant. When $t_b - t_a = t_2 - t_1$, then $\text{TCF} = e^{\lambda(t_1 - t_a)}$. TCF' is analogous to TCF , with re-irradiation count times substituted into the equation. An additional correction should be applied to long

counts in order to correct for decay before counting starts (ie brings all sample and standard counts back to an arbitrary "start" time);

$$Nnet_0 = Nnet \times e^{-\lambda(t_0 - t)}$$

where t_0 is the arbitrary start time and t is the time for the start of sample or standard count. The corrected $Nnet_0$ should be used in ppb calculations.

For additional information on the development of the Te co-precipitation technique, refer to Stockman (1982).

CHAPTER 5

APPLICATION OF TELLURIUM COPRECIPITATION METHOD TO ULTRAMAFIC ROCK STANDARDS

5.1 Data and Interpretation for PCC-1, DTS-1 and JHC-6

Abundances of Au, Ir, Pd and Pt in PCC-1, DTS-1 and JHC-6 (house standard) determined throughout the present work are given in Table 5.1 a-c. These data are compared with values for PCC-1 from Stockman (1983), Oshin (1981), (determined using the technique of Crocket et al., 1968), and other literature values for PCC-1 and DTS-1 determined via NAA techniques.

PCC-1 is a peridotite collected as stream boulders from Cazadero, Sonoma County, California (Flanagan, 1967). Petrographic studies (Flanagan, 1967) show that the rock is composed of primary granular olivine (58%) and orthopyroxene (9%), both partially replaced by mesh structure serpentine. Other minerals present include primary disseminated chromite, secondary magnetite, some talc associated with primary orthopyroxene, and a carbonate mineral.

DTS-1 is a dunite from the Twin Sister area, Hamilton, Washington. It is dominated mineralogically by

TABLE 5.1a. REPLICATE ANALYSIS OF U.S.G.S. STANDARD, PCC-1.

Element	This Work	Stockman, (1982)	Oshin, (1981)	Literature
Au	0.78, 0.88, 0.96, 1.07, 1.10, 1.20, 1.37, 1.46 $\bar{x} = 1.10 \pm 0.22$ CF = 20 ¹	0.67, 0.68, 0.88 0.92, 0.95, 1.07 $\bar{x} = 0.86 \pm (0.16, 0.15)^2$ CF = 19, 17	0.50, 0.50, 0.54, 0.59, 0.59, 0.60, 0.64, 0.83, 0.83, 0.85, 0.85, 0.89, 0.90, 1.14 $\bar{x} = 0.73 \pm 0.19$ CF = 26.2	0.63 ^a , 0.73 ^f , 0.73 ^g , 0.76 ^a , 0.79 ^k , 0.80 ^b , 0.80 \pm 0.5 ^h , 0.89 ^c , 0.95 ^k , 1.18 ^k , 1.3 ^g , 1.42 ⁱ , 2.2 ^e , 2.28 ^d , 3.14 ⁱ , 3.14 \pm 1.4 ^j , 3.2 ^e , 4.4 ^e $\bar{x} = 1.63 \pm 1.12$ CF = 69
Ir	4.4, 4.7, 5.5, 7.4, 7.4, 7.4, 8.7, 9.3 $\bar{x} = 6.9 \pm 1.7$ CF = 24	5.0, 5.6, 5.85, 6.08, 7.62, 8.1 $\bar{x} = 6.4 \pm (1.2, 1.1)$ CF = 19, 17	2.76, 2.85, 3.07, 3.32, 3.33, 3.60, 3.96, 5.21, 6.69, 6.73, 6.77, 6.79, 7.36, 7.38 $\bar{x} = 5.0 \pm 1.87$ CF = 37.5	2.5 ^l , 2.6-3.6 ^m , 2.94 ^k , 3.5 \pm 0.4 ^l , 4.45 ^k , 5.0 \pm 2 ⁿ , 5.1 \pm 2.2 ^o , 5.6 ^g , 5.7 ^p , 6.6 ^b , 6.6 ^q , 6.7 ^q , 6.7 ^t , 7.1 ^r $\bar{x} = 5.11 \pm 1.53$ CF = 30
Pd	3.2, 3.4, 5.4 $\bar{x} = 4.0 \pm 0.99$ CF = 25	3.6, 3.7, 3.8, 4.3 $\bar{x} = 4.2 \pm (0.8, 0.7)$ CF = 19, 17	3.05, 3.38, 3.52, 3.56, 3.61, 3.68, 3.72, 3.85, 3.86, 4.00, 4.22, 4.37, 4.71, 4.94, 5.37 $\bar{x} = 4.0 \pm 0.63$ CF = 15.7	3.0 \pm 0.1 ^j , 4.4 ^v , 4.7 ^w , 5.9 \pm 0.6 ^g , 6.0 \pm 0.3 ^g , 6.3 \pm 0.4 ^s , 7 ^t , 7.1 \pm 0.4 ^u $\bar{x} = 5.6 \pm 1.3$ CF = 24
Pt	7.6, 7.8, 12, 13, 15, 16 $\bar{x} = 12 \pm 3$ CF = 26	5, 6, 7, 10, 12 $\bar{x} = 8 \pm (2.7, 2.4)$ CF = 34, 30	2.24, 2.77, 3.28, 3.35, 3.73, 5.25, 6.16, 6.59, 7.12, 7.91, 7.94, 8.07, 9.91, 9.96, 10.41 $\bar{x} = 6.3 \pm 2.76$ CF = 43.8	3.15 \pm 1.7 ^g , 5.7 ^v , 5.8 ^v , 5.1 \pm 1.5 ^l , 13.5 \pm 2.9 ^u $\bar{x} = 6.7 \pm 3.6$ CF = 53

1. Coefficient of variance (CF in %) is given for a standard deviation of n-degrees of freedom.
2. First and second values in parentheses are standard deviations with n-1 and n-degrees of freedom respectively
All values are in ppb.

TABLE 5.1b. REPLICATE ANALYSIS OF U.S.G.S.
STANDARD, DTS-1.

Element	This Work	Literature
Au	0.72, 0.74, 0.81, 0.89 1.23, 1.37, 1.62 $\bar{x} = 1.04 \pm 0.30$ CF = 29	0.45-0.98 ^f , 0.6 ^h , 0.7 ^c , 0.7 ^e , 0.8 ^e , 0.8 ^b , 0.85 ^a , 0.85 ⁱ , 0.91 ^d , 0.97 ⁱ , 1.0 ^e 1.0 ^k , 1.08 ^k , 1.4 \pm 0.5 ^j $\bar{x} = 0.9 \pm 0.2$ CF = 22
Ir	0.77, 0.75, 1.14, 1.27 1.76, 1.79, 1.84, 1.95 2.03, 2.03 $\bar{x} = 1.53 \pm 0.48$ CF = 31	0.34-4.5 ^m , 0.4 ^l , 0.5 ^b , 0.5 \pm 0.1 ⁿ , 0.51 ^q , 0.55 ^k , 0.56 ^p , 0.58 ^k , 0.58 \pm 0.21 ^o , 0.6 \pm 0.09 ^j , 0.65 ^r , 1.51 ^q $\bar{x} = 0.61 \pm 0.28$ CF = 46

REFERENCES FOR LITERATURE VALUES IN TABLES 5.1a and b.

- a) Bartel, A.J., (1969).
- b) Ehmann, W.D. et al., (1970).
- c) Anoshin, G.N. and Perezhogin, G.A., (1969).
- d) Graber, F.M. et al., (1970).
- e) Laul, J.C. et al., (1970).
- f) Rowe, J.J. and Simon, F.O., (1968).
- g) Millard, H.T.Jr. and Bartel, A.J., (1970).
- h) Gillum, D.E. and Ehmann, W.D., (1971).
- i) Green, T.E. et al., (1976).
- j) Nadkarni, R.A. and Morrison, G.H., (1974).
- k) Shaw, D.M. et al., (1976).
- l) Belt, C.B., (1967).
- m) Greenland, L.P. et al., (1971).
- n) Das, H.A. et al., (1971).
- o) Baedeker, P.A. et al., (1972).
- p) Baedeker, P.A. et al., (1971).
- q) Gijbels, R. et al., (1971).
- r) Gijbels, R. and Govaerts, A., (1972).
- s) Ahmad, I. et al., (1977).
- t) Haffety, J. and Riley, L.B., (1968).
- u) Gilbert, E.N. et al., (1976).
- v) Page, N.J. et al., (1980).
- w) Rowe, J.J. and Simon, F.O., (1971).

TABLE 5.1c. REPLICATE ANALYSIS OF HOUSE STANDARD, JHC-1.

Element	This Work	Other ¹
Au	1.85, 1.93, 1.98, 2.43, 2.48, 2.53, 2.81, 2.88, 2.89, 2.90, 2.91, 2.97, 3.13, 3.14, 3.17 $\bar{x} = 2.67 \pm 0.43$ CF = 16	2.28 ^a , 2.25, 2.38, 2.51, 2.88, 2.99 $\bar{x} = 2.55 \pm 0.29$ CF = 11
Ir	1.72, 1.74, 1.75, 1.79, 1.80, 1.92, 2.0, 2.02, 2.04, 2.2, 2.3, 2.37, 2.67 $\bar{x} = 2.03 \pm 0.28$ CF = 13	0.88 ^a , 1.57, 1.90 $\bar{x} = 1.45 \pm 0.43$ CF = 29
Pd	9, 10, 10, 11, 11, 13, 17, 23, 25, 27, 28, 28 $\bar{x} = 18 \pm 8$ CF = 43	9.25, 9.37, 10.01, 10.52, 11 ^a , 11.05 $\bar{x} = 10.2 \pm 0.72$ CF = 7
Pt	13, 15, 15 $\bar{x} = 14 \pm 0.94$ CF = 7	7.64, 11.61, 12.16, 15.71, 18.24, 19 ^a $\bar{x} = 14.06 \pm 3.99$ CF = 28

1. All values obtained using the technique of Crockett et al., (1968).

a) MacRae (1982), remainder by Kabin.

All values given in ppb.

medium grained primary olivine (99%), with some orthopyroxene, clinopyroxene, disseminated chromite, traces of light green amphibole and spinel (Flanagan, 1967).

JHC-6 was taken (MacRae, 1982) from the fine grained olivine spinifex zone of a komatiitic peridotite (South Flow from MacRae, 1982) from Pyke's Hill (also known as Spinifex Hill), Munro Township, Ontario. It was chosen because the rock is thought to have crystallized rapidly from a crystal-free melt (Pyke et al, 1973; Arndt et al., 1977; MacRae, 1982). In addition, the lack of sulfide or chromite phases, low Na_2O content (0.58 weight percent), relatively high PGE content, and high Pt/Au ratio (ca. 8.6) in this rock are desirable features for PGE analysis. Spinifex texture develops in a clear liquid, after crystal settling, (Arndt et al., 1977) and therefore if any original chromite or sulphide were initially present in the magma when it erupted, the spinifex rock is the least likely to have incorporated it.

PCC-1 - In the case of PCC-1, a direct comparison between this work and that of Stockman (1983) is possible. Some of the values obtained in this work (Table 5.1a) fall within the range of literature values, although most are slightly higher. The average value of 1.10 ± 0.22 for Au in PCC-1 is at the high end of literature values and is higher than Oshin's average of

0.73 ± 0.19 ppb. While the variability of literature values (0.63 to 4.4 ppb) can be attributed in part to the difference in analytical techniques employed by various workers, the average value of 1.1 ± 0.22^1 ppb from this study is also higher than Stockman's average of $0.86 \pm 0.16, 0.15$, attained using the same technique. The most likely causes of this disparity are analytical error, or real differences in the distribution of noble metals between the aliquots of sample analysed. Duplicate Au standards from a single irradiation agree to within 5% for Au, suggesting that analytical variation is not responsible for the observed deviation. Au standards from different irradiations, corrected for differences in weight, flux (determined by the inclusion of flux wires in each irradiation package), and counting time, agree within 5 to 10%. This gives an indication of the potential agreement attainable with this method using highly homogeneous materials. A sample is a more heterogeneous matrix than a standard, and therefore, represents a higher potential for interfering activities under the 411.8 KeV ^{198}Au peak. If this were the case, however, the contaminating nuclide would have to emit γ -irradiation of exactly 411.8 KeV

1. Standard deviations of 1σ are given for this work.

energy but no assymetry in the Au γ -ray peak was ever seen. Even where very high values of Au were determined, which represents the most likely case for the presence of an interfering nuclide at 411.8 KeV, there was no evidence of peak distortion. The chances that problems arose from statistical counting errors is unlikely since sufficient counts (10^4) were taken to reduce statistical counting error to approximately 1%. Without minimizing the possibility of other kinds of analytical error, each of which would require specific and extensive analytical assessment, it seems the most logical explanation for the variability in Au values in PCC-1 is sample heterogeneity.

Fritze and Robertson (1968) investigated W-1 (U.S.G.S. diabase) in order to determine the degree of homogeneity of Au content, and concluded that there was a bimodal distribution of Au values among their analyses. The lower concentration samples were thought to contain a homogeneous distribution of minerals having low but relatively constant amounts of Au (silicate minerals), whereas the samples with higher concentrations were said to contain a larger proportion of one or more gold-rich minerals (possibly pyrite), which show a strong tendency towards segregation. It is not inconceivable that a similar situation exists within the aliquot of PCC-1 analysed here, and even between

the aliquots analysed by Stockman and this author.

The majority of the literature values for Ir in PCC-1 are in the 5-7 ppb range, in agreement with the 6.9 ± 1.7 average determined here, the 5.0 ± 1.9 ppb average determined by Oshin, and the $6.4 \pm 1.1, 1.2$ determined by Stockman. A potential problem with Ir is the presence of primary disseminated chromite in PCC-1. Chromite can concentrate 3-4 times the whole rock average of Ir, and any heterogeneity in chromite distribution throughout the aliquot of PCC-1 analysed could lead to anomalously high values. This does not appear to have been a problem in this case.

The majority of Pt data on PCC-1 from this work are on the high side of the literature values. The Pd average (4.0 ± 0.99) agrees within error with that of Stockman ($4.2 \pm 0.8, 0.7$). The essential problem encountered with the low energy end of the spectrum was the low signal to noise ratio. It was not possible to reduce the background to low enough levels to see the 88 KeV ^{109}Pd peak or the 158 KeV $^{199}\text{Au}(\text{Pt})$ peak in a statistically satisfactory way. This did not pose a serious problem for Pd determination as the 22 KeV AgK x-ray was available, but there were no other Pt peaks present. No adjustment of irradiation, counting or analytical parameters lowered the background levels

sufficiently in this region (ca. 70-170 KeV). The high background radiation did not emanate from the samples (analytical technique seems to have minimized sample background as much as can be expected), and it was therefore concluded that natural U-Th series radioactivity present in the counting room was the source of high background levels. This background will have to be reduced by development of an efficiently shielded counting environment. Ultra-pure Pb must be used so as not to generate as much U from the Pb shielding as is already present in the room. Further experiments concerning detector shielding are required. The Pt peak is located on the Compton backscatter peak at 160 KeV generated from the intense 411.8 KeV ^{198}Au γ -peak. The excessive background problem was therefore initially interpreted as a Pt/Au ratio control or detector efficiency problem.

DTS-1 - Values of Au determined for DTS-1 (Table 5.1b, 1.04 ± 0.33) are within the literature range (0.45-1.45), although 4 of the 7 determinations exceed the average literature value of 0.87 ± 0.22 . The possible explanations are analagous to those discussed for Au in PCC-1. The Ir values found in this work are higher than the literature values (1.55 ± 0.51 and 0.61 ± 0.29 respectively). The presence of disseminated chromite in the various aliquots of DTS-1 analysed could be a factor

here. (Cr values for the different aliquots analysed are not available. The average Cr content of DTS-1 by NAA is 4121 ± 343 ppm; Govindaraju, 1983). It was not possible to determine Pd or Pt in DTS-1 due to poor counting statistics and high background; that is, the concentrations of these elements are too low for satisfactory analytical determination by this method. Stockman does not determine Pt in W-1 for similar reasons.

JHC-6 - In the case of JHC-6, the house standard included in all irradiations, a direct comparison of the results from the Te coprecipitation technique and the procedure of Crocket et al. (1968), can be made. Determinations of Au, Ir, Pd and Pt in JHC-6 made by MacRae (1982) and Kabir (unpublished data), using the method of Crocket et al. (1968), are given in Table 5.1c. The value of gold determined in this study, 2.67 ± 0.43 ppb agrees within error with the 2.55 ± 0.29 ppb average obtained from MacRae and Kabir's results. Pt values from this work (14 ± 0.94) also compare well with those of MacRae and Kabir (14 ± 3.99).

Values of Ir and Pd are at least a factor of two higher in this work. Some Pd values are in the range of 11 ppb, similar to values obtained by MacRae and Kabir, although 6 of 12 determinations are about a factor of 2 higher. The differences in Pd values are most easily explained by the differences in the two techniques, as Pd

is determined by beta counting in Crocket et al.'s (1968) technique and was gamma counted in this work. Beta counting is more sensitive, but does not provide the discrimination inherent in differential gamma counting, and consequently requires extremely pure sources (Crocket, 1971). The purity of the Pd source counted in this technique, although extremely good for such a simple procedure, cannot compare to that of Crocket et al. (1968), and therefore, the Pd-values of MacRae and Kabir are probably more reliable than those determined in this work. Again, no distortion of the Pd peaks were seen, but much of the 88 KeV γ -ray peak was lost to Compton backscatter, so that counting statistics were poor. It should also be noted that the value given by MacRae is from one determination, and therefore Kabir's values are potentially more reliable.

5.2 Precision

Based on replicate analyses of PCC-1, DTS-1 and JHC-6, the average precision¹ of the Te co-precipitation technique is $\pm 23\%$ for Au and Ir, $\pm 27\%$ for Pd and $\pm 30-35\%$ for Pt. This precision is slightly poorer than that reported by Stockman (1983) for Au, Ir

1. The coefficient of variation, (ratio of standard deviation to the mean of replicate analyses) is used as the precision statistic.

and Pd ($\pm 16\%$) and comparable for Pt. The most precise noble metal values in the literature appear to be those of Ahmad et al., (1977), with an average precision of $\pm 6\%$ for Au, Pd, Pt and Ir in W-1 and PCC-1 and Crocket et al. (1968) with an average precision of $\pm 13\%$ for replicate analyses of Au, Ir and Pd in W-1. Many noble metal analytical techniques give precisions worse than $\pm 20\%$ (Stockman, 1982). Poor precision for Pt is fairly typical at the ppb level, and is due to the correction required for gold interference from the $(2n,\gamma)$ reaction.

5.3 Detection Limits

The detection limit is defined as the lowest concentration of an element that can be shown to be statistically different from an analytical blank, for a given method (IUPAC definition, 1975), or that amount of element that can reliably be detected (MacDougall and Crummett, 1980). Method sensitivity is defined as the ratio of change in the instrument response to the change in element concentration (slope of the calibration curve of instrument response; counts versus concentration. The two should not be confused. When determining detection limits for a given neutron activation technique, factors which are important include neutron flux, elemental nuclear

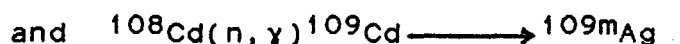
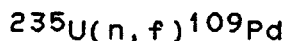
characteristics (neutron cross-section, half-life, decay constant), irradiation, cooling and counting times, detector efficiency and sample material (rock type). Since the analysed elements, rock type (PCC-1), neutron flux, irradiation parameters, and detector efficiency used in this work were all identical to those used in Stockman's (1982) study, the analytical detection limits¹ are assumed to be identical. Stockman (1982) analysed a 0.5 gram sample of peridotite and determined detection limits of 0.01-0.02 ppb Au, 0.1-0.4 ppb Pd, 1-2 ppb Pt and 0.02 ppb Ir. Due to the background interference on the $^{199}\text{Au(Pt)}$ peak at 158 KeV, this lower limit was not obtained in practice.

5.4 INTERFERENCES

Although the general purpose of RNAA is to produce a γ -ray spectrum free of interfering peaks, it is still possible that in a procedure where multi-element analysis of a single precipitate source is employed, some interferences will be present.

The 88 KeV ^{109}Pd and 22 KeV AgK x-ray may suffer the following potential interferences;

1. Detection limits defined as L_D of Curie (1968) by Stockman (1982).



According to Gijbels (1971), the first reaction may generate 0.025 ppb Pd per 100 ppb U. This reaction is therefore, completely negligible as the average U content of ultramafic rocks is 14 ppb U (Rogers et al., 1974). It is of more concern in mafic rocks in which the average U content is 0.43 ppm (basalt) to 0.84 ppm (gabbro) (Rogers et al., 1974). The second reaction is normally unimportant as Cd activates very poorly in comparison to Pd and is not precipitated by Te. Although no contaminating peaks were seen in the 22 KeV region (AgK x-ray peak), absorption of this soft radiation may become important if the counting medium (Te precipitate) is not always thin and uniform. Stockman (1982) calculated the absorption coefficient of the Te-noble metal precipitate at 22 KeV to be 140 cm^{-1} . A significant difference in absorption of the x-ray is seen between a totally uniform (2% absorption) and totally erratic (clumped, 20% absorption) distribution of precipitate. Since the standards and samples are counted in the same matrix, and precipitate distribution in this work was usually uniform in both, absorption effects were minimized. Fortuitously, the nature of the yield determination by re-irradiation effectively cancels absorption error. The concentration of Pd in the sample is related to measured activities and absorption factors

in the following way;

$$Pd_{smp} \propto \frac{N_{smp}(1-A_{std})}{N_{std}(1-A_{smp})} \cdot \frac{N_{std}'(1-A'_{smp})}{N_{smp}'(1-A'_{std})}$$

where N_{smp} and N_{std} are the net counts in the sample and standard x-ray peaks after the first irradiation; N'_{smp} and N'_{std} are the net counts after re-irradiation for chemical yield; A_{std} and A_{smp} are the fractions of x-rays absorbed in the standard and sample after the first irradiation, and A'_{std} and A'_{smp} are the fractions of x-rays absorbed after re-irradiation for chemical yield. Since the same precipitate used for initial counting is also used for the chemical yield determination, the counts before and after re-irradiation are made in the same geometry;

$$A_{smp} \approx A'_{smp}$$

and $A_{std} \approx A'_{std}$

and the absorption factor is eliminated.

As stated earlier, the signal/noise ratio at low energy is such that no significant 88 KeV ^{109}Pd γ -ray can be determined with satisfactory counting statistics. No interferences to the 88 KeV γ -ray were observed because of high background, but several potential interferences are listed in Table 5.2. If shielding the

Table 5.2.POSSIBLE INTERFERENCES TO 88.1 KeV ^{109}Pd PEAK

	<u>KeV</u>	<u>Comment</u>
<u>Shielded System</u>		
	85, 87	Pb x-rays from excitation of detector shielding.
<u>Unshielded System</u>		
	80-100	U-Th series background (internal conversion x-rays cause erratic background)
<u>General</u>		
	87.7	^{77}As
	88.1	^{161}Tb
	88.3	$^{176\text{m}}\text{Lu}$
	91.4	^{147}Nd

detector provides a viable solution for the high background problem, it should also be noted that potential secondary interference from the 87.3 KeV Pb K β 2 x-rays produced from the interaction of γ -rays with the shielding could become a problem. Lining the detector cave with Cd (0.23 cm) or Fe (1.24 cm) (calculated from x-ray absorption coefficients given in Liebhafsky et al., 1972, by Stockman, 1982) reduces the Pb x-rays by a factor of 100.

Since there is no Pb interference peak in the 22 KeV region, and the 22 KeV ^{109}Pd x-ray is the most intense peak for Pd determination, it is recommended for ^{109}Pd determination wherever possible. Where it has been possible to obtain analyses from both the 22 and 88 KeV radiations, Table 5.3, the results have agreed to within 4.7%. Again the 22 KeV ^{109}Pd x-ray peak is considered most reliable.

The interference on the 158 KeV $^{199}\text{Au(Pt)}$ γ -ray is primarily that of;



which was discussed in Chapter 3. Corrections were made by irradiating separate Au and Pt standards, and subsequently estimating the contribution of the (2n, γ) reaction to the Pt peak. Activated Te, obviously coprecipitated with the noble metals, produces a 158 KeV γ -ray via the reaction;

TABLE 5.3. A Comparison of Pd Analyses (ppb)
Obtained in Different Irradiations.

Sample	22 KeV x-ray on LEPS	88 KeV γ -ray on coaxial detector
JHC-6 (fine spinifex zone of peridotitic komatiite)	10.24 11.36 9.36 11.14	10.75 12.94 12.70 24.39
PCC-1 (peridotite)	3.19 3.36	5.65 5.95



Stockman (1982) determined, (both by calculations from nuclear data, and by irradiating Te and Pt and comparing peak heights) that 1 ppb of Pt produced more than 100 times as many 158 KeV γ -rays as 1 ppb of Te. Within the precision of Pt determinations, the interference can normally be ignored since Te is less abundant than Pt in sulphur-poor ultramafic and mafic rocks (0.01-0.001 ppm Te in igneous rocks; Leutwein (1974); 10 - 20 ppb Pt in ultramafic rocks, 5 - 10 ppb Pt in mafic rocks; Crocket, 1981). The broad backscatter peak at 160 KeV produced by the 411.8 KeV ^{198}Au peak also poses an interference to the 158 KeV $^{199}\text{Au}(\text{Pt})$ γ -ray, and raises background levels in this region.

Decay of ^{198}Au produces an intense 411.8 KeV γ -ray which suffers no significant interference in normal determinations.

Interferences on the 317 KeV ^{192}Ir and 328 KeV ^{194}Ir γ -rays are seldom seen, but Stockman (1982) notes small amounts of ^{51}Cr , precipitated with the Te, may cause 320 KeV γ -ray interference. Co-precipitated Cu may cause a broad backscatter under both the 317 and 328 KeV peaks due to the ^{64}Cu 511 KeV β^+ annihilation peaks. Since the half-life of ^{64}Cu is 13.5 hours, suitable decay is the best defence against this problem.

Important non-noble metal features of the spectrum, not necessarily interferences, are given in Table 5.4.

Table 5.4.

IMPORTANT NON-NOBLE METAL FEATURES OF THE SPECTRUM

ISOTOPE	T1/2	ENERGY (KeV)	COMMENTS
51 Cr	28d	320.1	Weak in mafics, stronger in ultramafics.
59 Fe	45d	1099.3 1291.6	Generally weak
64 Cu	13hr	511	Often 1 - 10 times Au peak immediately after processing.
76 As	27hr	596.0 599.2	Strong in sulphur-rich rocks
75 Se	120d	264.6 279.5	Only after long decays in sulphur - rich rocks.
110m and 110 Ag	253d	657.6 884.5	ditto
U-Th series background	80-100		Internal conversion x-rays contribute to background in poorly shielded systems.
Backscatter		160	Broad peak from 412KeV 198 Au.
		300	Broad shelf from 511 KeV 64 Cu.

CHAPTER 6

APPLICATION OF TELLURIUM COPRECIPITATION METHOD TO ARCHEAN GREENSTONES

6.1 PGE Content of Red Lake, Ontario, Greenstones

Ten metabasalt (greenstone) samples of varying composition were analysed for Au, Ir, Pd and Pt using the Te co-precipitation method. The samples, from the Red Lake area, Ontario, are briefly described by Cowan (1979). The data are given in Table 6.1 together with Au values obtained by Cowan, (1979) using the technique of Crocket et al. (1968).

Three or four determinations were made on each sample. In some samples, the replicate values are acceptable (sample 78-77, for example gives precisions of $\pm 21\%$ for Au, $\pm 34\%$ for Ir, $\pm 18\%$ for Pt and $\pm 16\%$ for Pd), but the average precisions ($\pm 35\%$ for Au, $\pm 31\%$ for Ir, $\pm 30\%$ for Pt and $\pm 27\%$ for Pd) are not as good as those obtained on the standard rocks PCC-1 ($\pm 20\%$ for Au, $\pm 24\%$ for Ir, $\pm 26\%$ for Pt and $\pm 25\%$ for Pd), DTS-1 ($\pm 29\%$ for Au, $\pm 31\%$ for Ir) and JHC-6 ($\pm 16\%$ for Au, $\pm 13\%$ for Ir, $\pm 7\%$ for Pt and $\pm 43\%$ for Pd). A probable explanation for the poorer precision on the greenstones is that the Red Lake

TABLE 6.1 PLATINUM GROUP ELEMENT CONCENTRATION OF RED LAKE GREENSTONES

Rock Type	Sample	Au values of Cowan (1979)	Au	Ir	Pt	Pd
pyroxene komatiite	78-28	5.3	2.7, 15, 57 $\bar{x} = 25 \pm 23.1$ CF = 93	0.95, 2.0, 2.0 $\bar{x} = 1.7 \pm 0.5$ CF = 30	61, 66 $\bar{x} = 64 \pm 3$ CF = 4	8.0, 13, 27 $\bar{x} = 16 \pm 8$ CF = 50
pyroxene komatiite	78-31	3.3	1.1, 1.3, 3.4 $\bar{x} = 1.9 \pm 1.0$ CF = 54	0.52, 1.2, 1.2 $\bar{x} = 1.2 \pm 0.42$ CF = 36	51, 89 $\bar{x} = 70 \pm 19$ CF = 27	107, 170 $\bar{x} = 143 \pm 36$ CF = 25
pyroxene komatiite	78-84	4.6	4.4, 4.6, 4.8 $\bar{x} = 4.6 \pm 0.2$ CF = 3.4	0.86, 1.1, 1.4 $\bar{x} = 1.1 \pm 0.21$ CF = 19	12, 41, 63 $\bar{x} = 39 \pm 21$ CF = 54	6.5, 18, 23 $\bar{x} = 18 \pm 7.3$ CF = 40
basaltic komatiite	78-22	4.0	1.7, 1.8, 3.2, 4.8 $\bar{x} = 2.0 \pm 1.3$ CF = 44	0.14, 0.4, 1.0 $\bar{x} = 0.52 \pm 0.37$ CF = 71	4.6	38, 47 $\bar{x} = 43 \pm 5$ CF = 11
basaltic komatiite	78-88	0.9	1.4, 1.6, 2.3 $\bar{x} = 1.8 \pm 0.4$ CF = 23	0.17, 0.37, 0.48 $\bar{x} = 0.43 \pm 0.6$ CF = 14	100, 167 $\bar{x} = 137 \pm 30$ CF = 22	42, 53 $\bar{x} = 47 \pm 5$ CF = 11
high Mg- tholeiite	78-95	6.3	4.2, 5.0, 8.9 $\bar{x} = 6.0 \pm 2.0$ CF = 34	0.95, 1.25, 1.6 1.7 $\bar{x} = 1.4 \pm 0.30$ CF = 22	21, 52 $\bar{x} = 36 \pm 15$ CF = 43	29, 37, 50 $\bar{x} = 41 \pm 12$ CF = 30
high Fe- tholeiite	78-34	300	150, 150, 220 250 $\bar{x} = 195 \pm 45$ CF = 23	/	/	/

TABLE 6.1 con't.

Rock Type	Sample	Au values of Cowan (1979)	Au	Ir	Pt	Pd
high Fe tholeiite	78-35	44	30, 72, 101	0.30, 0.39, 0.58 1.4	25, 30, 64	21, 47, 48
			$\bar{x} = 51 \pm 42$ CF = 42	$\bar{x} = 0.35 \pm 0.16$ CF = 45	$\bar{x} = 40 \pm 17$ CF = 43	$\bar{x} = 39 \pm 12$ CF = 32
high Fe-tholeiite	78-44	4.5	2.2, 3.1, 5.8	0.46, 0.70, 0.71 0.99	20, 55, 60	7.2, 7.4
			$\bar{x} = 3.7 \pm 1.5$ CF = 41	$\bar{x} = 0.72 \pm 0.19$ CF = 26	$\bar{x} = 40 \pm 14$ CF = 29	$\bar{x} = 7.3 \pm 0.12$ CF = 1.7
andesite	78-77	/	7.0, 10, 12	0.35, 0.74, 0.87	124, 181	23, 20, 31, 36
			$\bar{x} = 11 \pm 2.3$ CF = 21	$\bar{x} = 0.65 \pm 0.22$ CF = 34	$\bar{x} = 153 \pm 29$ CF = 18	$\bar{x} = 29 \pm 5$ CF = 16

1. Sample weight is 100 mg.
2. Concentrations are given in ppb.
3. CF is the coefficient of variance for a standard deviation with n-degrees of freedom.

samples were not subject to the rigorous homogenization and mixing procedures used in preparation of the international standards, and that a more heterogeneous distribution of PGE occurs in the greenstones, particularly if low grade metamorphism causes slight mobilization of the metals. Thus, real differences in noble metal concentrations between aliquots of the same sample may exist in the case of the Red Lake suite. Operator procedure error would lead to differences in chemical yield between samples, which would affect counting statistics. However, no large losses of precipitate were observed as might be expected if yields varied significantly from sample to sample. Pre-irradiation contamination was improbable as careful handling of powder (ie., no jewelry worn, clean work area and balance pan etc.) and simple preparation techniques were employed.¹ Post-irradiation contamination was also improbable as this could only occur if radioactive isotopes were added during the chemical procedure, an especially remote possibility where relatively short-lived nuclides are involved. All other radioactive substances were stored far from the fume hoods where radiochemistry was performed. Real compositional

1. As all available samples were pre-crushed, no comment can be made as to how carefully crushing procedures were done.

differences between sample aliquots is a possible explanation for variation in data, as sulphide phases were observed in some samples by Cowan (1979) and this author.

The Red Lake greenstone samples have been altered to greenschist facies, which may lead to the secondary introduction of Au and even Pd. Hamlyn et al. (1985) reported the mobilization of Au and perhaps Pd in greenschist facies, low-Ti magmas from Mt. Wellington, Heathcote (Victorian Greenstone belts, Australia) and King Island (Tasmania). The distribution of Ir in these lavas suggested no apparent losses during alteration, but the behavior of Pd was not so coherent. Within one low-Ti lava series studied by Hamlyn et al. (1985), Pd tended to be enriched in silicate liquids relative to fractionating silicates (incompatible), but the absence of such trends within the remaining series suggested a heterogeneous distribution of Pd, possibly induced by alteration. Hamlyn et al. (1985) note, that although secondary mobilization of Pd is a possible explanation for the erratic Pd behavior, the process has not been extensive in their samples. In contrast, Au has been shown to be easily mobilized during greenschist facies metamorphism (Keays and Davidson, 1976; Ross and Keays, 1979; Oshin and Crocket, 1982). The introduction of Au and perhaps Pd during the alteration of the Red Lake

volcanics cannot, therefore, be overlooked.

The majority of Au values compare favourably with those of Cowan (1979) where only one determination per sample was made. Where there are discrepancies (ie. samples 78-20 and 78-34), they are probably accounted for by heterogeneous distribution of PGE in some samples. For sample 78-20, the range of Au values is from 2.7 to 57 ppb. There is direct evidence (thin and polished section) of a heterogeneously distributed sulphide phase, possibly enriched in Au, in this sample. For sample 78-34, a large amount of Au is present in the rock as evidenced by the 380 ppb Au determined by Cowan (1979) and the 150 to 250 ppb found in this work. It is possible in this case that particulate gold is inhomogeneously distributed throughout the sample aliquot. Disseminated sulphide phases were also noted in this sample.

A comparison of average coefficients of variation shows that all elements are determined with about the same degree of precision, $\pm 25-30\%$, a range close to that obtained on the ultramafic rock standards ($\pm 23-35\%$).

6.2 GEOCHEMISTRY OF PGE IN GREENSTONES

The PGE are siderophile-chalcophile elements commonly associated with sulphides in ultramafic and mafic rocks, and are therefore present in low abundances in sulphur-poor silicate rocks. A review of the PGE content of sulphur-poor rocks is provided by Crocket (1981).

Compositionally, the greenstones studied represent a fractionation trend from ultramafic through intermediate rocks (pyroxene komatiite through andesite as listed in Tables 6.1 and 6.2). The rock classifications were determined by Cowan (1979) from a Jensen cation plot (Jensen, 1976) for the classification of subalkalic volcanic rocks; $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{TiO}_2 - \text{Al}_2\text{O}_3 - \text{MgO}$. Trends indicating the geochemical behavior of the PGE during fractional crystallization can be discerned in such sequences.

Ir behaves in a compatible manner, decreasing during fractional crystallization (Keays and Davison, 1976; Hamlyn et al., 1985). The concentration of Ir in mafic and ultramafic rocks from various tectonic settings is reasonably well known. Ir ranges from 1 to 10 ppb, in ultramafic rocks, and is usually present in concentrations of 0.01 to 0.5 ppb in mafic rocks (Crocket, 1981). Within the sequence analysed here, a weak trend of decreasing Ir content can be seen from pyroxene komatiite

through andesite, within the precision of analyses (Table 6.2). Within the komatiitic rocks, the more evolved basaltic komatiite has at least a factor of 2 less Ir, and a similar trend exists within the tholeiitic rocks. Crocket (1981) notes a thousand-fold decrease in average Ir content from ultramafic to felsic rocks.

The majority of ultramafic rocks contain 2-10 ppb Au, whereas most mafic rocks contain 0.5-5 ppb Au (Crocket, 1981). Kerrich (1983) reports average Au concentrations in primary igneous ultramafic rocks as 0.8 ppb and those in primary igneous mafic rocks as 1.7 ppb. Due to metamorphic alteration and subsequent mobilization of Au throughout the Red Lake samples, any trends within the series have been obscured.

Pd concentrations vary from 2 to 10 ppb in ultramafic rocks and 0.1 to 10 ppb in mafic rocks (Crocket, 1981; Hamlyn et al., 1985). Crocket (1981) suggests that although Pd data are less well constrained than Ir, Pd is also generally more concentrated in ultramafic rocks. Hamlyn et al. (1985) suggest Pd is incompatible in low-Ti lavas, tending to be enriched in the more evolved members.

Clearly Pd is geochemically incoherent. A simple trend of Pd enrichment/depletion is not present in the Red Lake greenstones, perhaps a result of analytical difficulties discussed earlier or due to remobilization

of Pd during metamorphism, or real differences in the sample analysed.

Pt concentrations generally vary from 10 to 20 ppb in ultramafic rocks and 5 to 10 ppb in mafic rocks and are thought to decrease with increasing silica content (Crocket, 1981). As with Pd, trends of Pt enrichment/depletion within the Red Lake samples are not apparent.

Whereas gabbroic rocks host some of the worlds richest PGE deposits, mafic volcanic rocks are not important hosts of PGE mineralization (Crocket, 1981). Excluding Au, Pd and Ir are the elements for which the most reliable and numerous data are available (Crocket, 1981). The Pd/Ir ratio is a useful index of magma evolution in that Ir contents decrease with fractional crystallization, and Pd contents increase. Therefore, as mafic magma becomes more evolved through fractional crystallization, successive crystallized products have increasing Pd/Ir ratios (Crocket, 1981; Mitchell and Keays, 1981; Barnes et al., 1985). The explanation of this phenomenon, as suggested by Keays (1981), is that in the crystallization of mafic magma, Pd partitions into the melt relative to olivine, whereas Ir is normally co-precipitated with olivine or the first crystallizing phase. PGE concentrations and Pd/Ir ratios of various Phanerozoic mafic rocks, including some magnesian

low-Ti lavas (LTL) are provided in Table 6.2, along with data obtained on the Archean greenstones analyzed in this work.

An attempt can be made to compare the PGE content, proposed nature of the source region and PGE geochemical characteristics (eg. Pd/Ir ratios) of the Archean metavolcanics to more recent mafic rocks. As the greenstones may be the primitive analogues of modern day rift system volcanics or mid-ocean ridge basalts (MORB) (Taylor and McLennan, 1985), these rock types will be the major focus of the comparison. Comparison to PGE-rich LTL will also be made.

The greenstones have higher PGE contents (ca. 11 to 100 times the Ir, 7 times the Pd and 10 times the Pt) than the vast majority of Phanerozoic mafic rocks according to surveys of Crocket (1981) and Hamlyn et al. (1985). The Archean Ir values are much higher than those of the average MORB where Ir is very low, typically 0.02 - 0.05 ppb (Hamlyn et al., 1985; Crocket, 1981) and are, in fact, much higher than the average for any Phanerozoic rocks, except the intraplate types. Intraplate mafic lavas probably tap more pristine mantle than MORB lavas (Basaltic Volcanism Study Project, 1981).

Gottfried and Greenland (1972) and Crocket (1979) have proposed that pronounced Pd and Ir deficiencies observed in MORB may be related to the incompatible

TABLE 6.2. PLATINUM GROUP ELEMENT CONTENT OF
MAFIC ROCKS.

Rock Type	Au	Ir	Pd	Pt	Pd/Ir	S
Intraplate basalt*	--	0.36	1.6	--	4.4	
Spinifex textured basalt (Archean)	--	1.47	9.2	14*	6.26	
Ocean floor basalt*	--	0.061	<0.7	--	<11.5	
Ophiolitic high Fe-tholeiite*	--	0.019	<0.3	6.2	<16.0	
MORB (average)	1.3	<0.02	<0.83	--	>42.0	800
Continental plateau basalt*	--	0.092	8.3	--	90.2	
Ophiolitic high Mg-tholeiites*	--	0.056	9.7	9.2	173	
Troodos (Mesozoic) Komatiitic basalts	1.3 2.6 2.1 3.1	<0.07 0.10 0.08 0.08	9.4 14 13 11	-- -- -- --	>134 140 162 138	80 50 20 210
Mariana Fore-arc arc tholeiites-DSDP 458	1.4 2.7	<0.02 <0.02	<5.0 2.0	-- --	>250 >100	40 60
Rambler area, Nfld. pillowed basaltic komatiite	0.51	0.07	38	--	543	60
This Work	Au	Ir	Pd	Pt	Pd/Ir	S
Pyroxene komatiite	25±23 4.6±0.2 1.9±1.0	1.7±0.5 1.1±0.2 1.2±0.4	16±8.0 18±7.3 143±36	64±2.5 46±17 70±19	9.4 16 119	128 464 121
Basaltic komatiite	2.8±1.3 1.8±0.4	0.52±0.4 0.43±0.1	43±4.5 47±5.3	4.6 137±30	83 109	132 278
High Mg-tholeiite	6±2.0	1.4±0.3	41±12	36±5	29	2699
High Fe-tholeiite	3.7±1.5 51±42	0.72±0.2 0.35±0.2	7.3±0.1 39±12	56±6.2 88±38	10 110	1073 1748
Andesite	11±2.3	0.65±0.2	29±5.0	164±30	45	3983

TABLE 6.2 con't.

All values are in ppb except S which is in ppm.
Red Lake sulphur data from Cowan (1979).
Values marked with * are taken from Crocket (1981).
Values of spinifex textured komatiite are from
Keays (1981) and references therein.
All remaining values, except those from this work,
are taken from Hamlyn et al. (1985).
All are of Phanerozoic age except the STK and those
analysed in this work.

element-depleted nature of the mantle source. The Pd-poor nature of MORB magmas can also be explained if the Pd separated out in an immiscible sulphide fraction during the initial stages of fractional crystallization (Hamlyn et al., 1985). MORB magmas are thought to be S-saturated at the time of eruption (Mathez, 1976; Czamanske and Moore, 1977; MacLean, 1977; McGoldrick et al., 1979), and it is suggested that sulphur saturation originates in the source region (Mitchell and Keays, 1981; Roedder, 1981; Wendlandt, 1981). The average Pd/Ir ratios of the greenstones is 59, with a range from 9 to 119. It can be postulated that the greenstones were derived from a source region with similar relative Pd and Ir values to the MORB tholeiites, even though the absolute abundances of those elements are much higher in the Archean rocks.

In a detailed study of LTL (found in ophiolites and modern island arc settings), Hamlyn et al. (1985) gave many lines of evidence in support of the theory that these lavas were derived from mantle sources that had experienced varying degrees of incompatible element enrichment and were moderately to severely depleted by earlier melting events. Compared with MORB, LTL contain 18 times as much Pd and only 27% of the Se (considered a geochemical analogue of S; Goldschmidt and Hefter, 1933). This is consistent with the proposal that LTL are generated from a mantle source previously depleted by a

MORB-like melting event. A subsequent melting event, producing the LTL, entirely dissolves the PGE-rich sulphide component (retained from the earlier anatexis) and LTL are consequently enriched in PGE, but deficient in sulphur. This model assumes that the amount of sulphur remaining after the first melting event is less than the S-capacity of the LTL. (Several lines of evidence in support of this assumption are presented in Hamlyn et al., 1985).

If sulphur undersaturated conditions extend into the fractional crystallization of the low-Ti lavas, a concentration of chalcophile metals in the melt would result. As noted earlier, Ir behaves in a compatible manner during fractional crystallization, regardless of the presence of an immiscible sulphide phase. This and the contrasting, exclusively chalcophile nature of Pd are shown on fig. 6.1. Under constant S-saturated conditions, Pd and Ir will decrease, as shown by the MORB trend. In a S-undersaturated, low-Ti magma, Ir will be rapidly depleted as it enters olivine, chromite or Ca-poor pyroxene, but Pd will remain in the liquid phase until S-saturation occurs and immiscible sulphides segregate. The dashed line in fig. 6.1 is the inferred fractionation trend for S-saturated MORB-type liquids. The inferred trend for low-Ti lavas during the initial stages of S-undersaturated fractionation would be

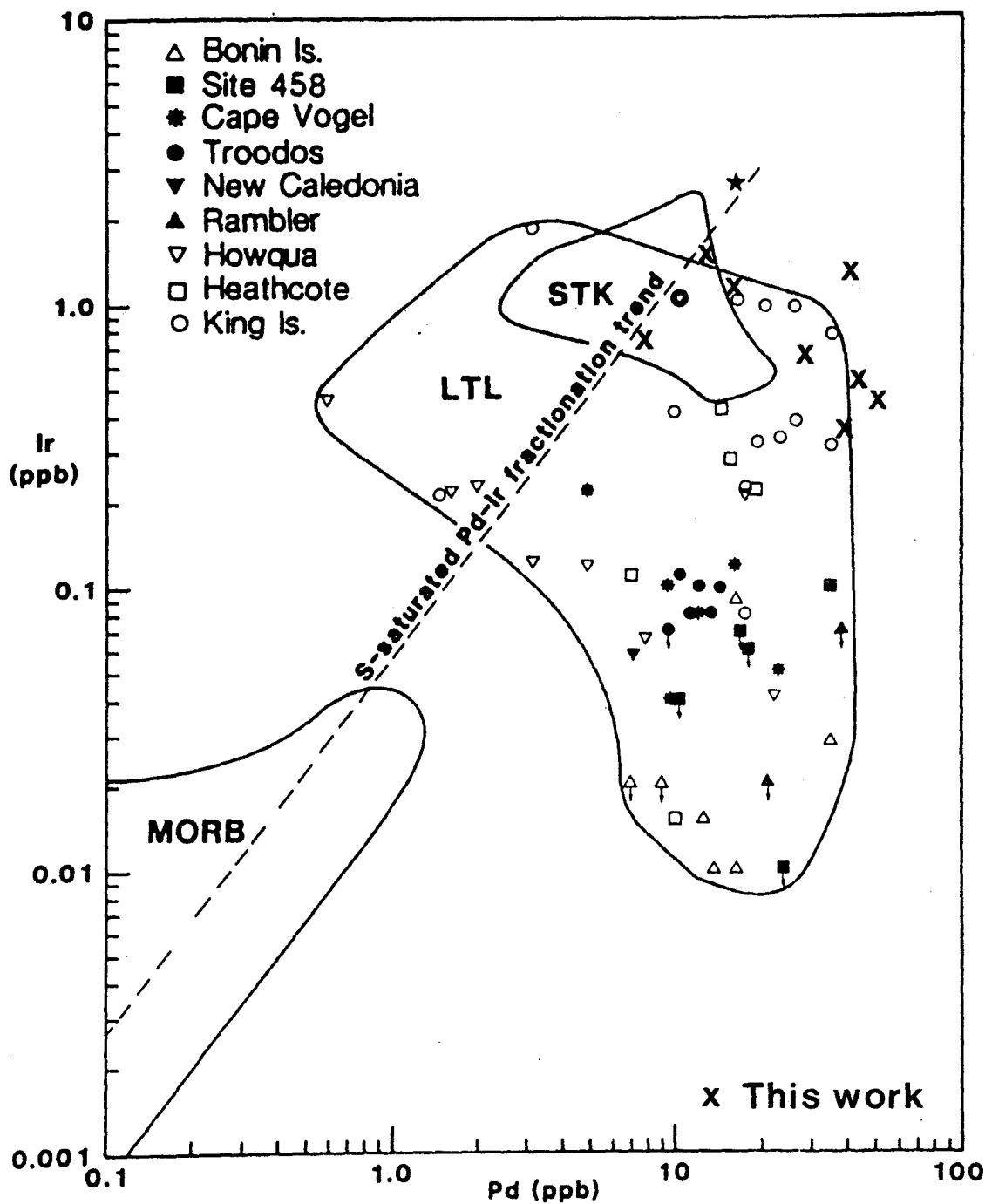


Figure 6.1

perpendicular to the saturated trend (Hamlyn et al., 1985).

The Archean greenstones also have high Pd concentrations, and high Pd/Ir ratios. A comparison of S contents of LTL and the greenstones is given in Table 6.2. Low values, similar to those of the LTL are seen in the pyroxene and basaltic komatiites. Hamlyn et al. (1985) note that the LTL have S concentrations below the determined solubility of sulphur in basaltic magmas (800 - 1500 ppm; Haughton et al., 1974; Katsura and Nagashima, 1974; Mathez, 1976). If the S-poor nature of these rocks was a reflection of low S solubility in the magma, then immiscible sulphide globules should be present in the glassy portion of the boninites, as they are in MORB glasses. As this is not the case, it is inferred, that the low S-content was not a result of low S solubility, but rather of the S-undersaturated nature of the magma. If this line of reasoning is applied to the Archean greenstones, the sulphide minerals noted in some of the Red Lake samples (very finely disseminated pyrrhotite and chalcopyrite, two members of the widely recognized magmatic assemblage pyrrhotite-pentlandite-chalcopyrite) may be immiscible late-stage phases which separated out when S-saturation finally occurred. It is therefore conceivable that these Archean rocks were derived during a similar second-stage melting event. A further

association between Archean greenstones and a rock series similar to the Phanerozoic boninites has been noted by Hamlyn et al. (1985). S-undersaturated second-stage melts inherit a higher PGE content from their mantle source, and retain it until the later onset of S-saturation. If the onset of S-saturation were to coincide with the eruption of a lava, the liquid would be laden with Au- and base metal-rich immiscible sulfides. As the role of S-saturation is most critical for metals strongly partitioned into molten sulphide, S-saturation may be particularly relevant to Au concentration due to its highly mobile nature. For instance, Redman and Keays (1985) recognized a "siliceous high-magnesian" series of magmas associated with Au deposits in the Archean of Western Australia. The bulk rock chemistry and incompatible-like behavior of siderophile metals in the differentiated lavas are similar to those of Phanerozoic boninites. Hamlyn et al. (1985) cite an overlap in the compositional fields (on a TiO_2 vs $100\text{Mg}/(\text{Mg} + \text{Fe})$ plot) of modern low-Ti lavas and spinifex textured komatiites as further evidence indicating the occurrence of similar lavas in the Archean (Hamlyn et al., 1985; figure 1). The Archean greenstones analysed in this work also fall within the low-Ti lava field on figure 6.1. It follows, then, that these older metavolcanics might also have a

similar origin to the low-Ti lavas. Hamlyn et al. (1985) concludes that it is conceivable that Au mineralization associated with volcanics in the Archean and modern terrains may be derived from disseminated Au-rich sulfides incorporated in evolved second stage (low-Ti) magmas.

Mitchell and Keays (1981) proposed that the proportion of Ir entering a partial melt is dependent on temperature, and the degree of melting. It is possible, therefore that where the Pd/Ir ratios are lowest (highest Ir values), the temperature in the source region was highest. There does not seem to be a coherent trend here between rock types (komatiite, tholeiite, andesite) either in terms of temperature of the source, or evolution of the magma. The Pd/Ir ratios on Table 6.2 confirm this as the komatiite, tholeiite and andesite ratios are all approximately 35 to 50.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

The tellurium coprecipitation technique, developed by Stockman (1982, 1983) provides a rapid and simple radiochemical neutron activation method which utilizes a group separation of Au, Ir, Pd and Pt. The method is applicable to PGE levels in sulphur-poor rocks and was evaluated by replicate analysis of U.S.G.S. standards (PCC-1 and DTS-1) and an ultramafic house standard, JHC-6. Values obtained in the present study fall within the range of literature values reported for these rock standards in most cases. Where serious discrepancies occur, they are accounted for by sample heterogeneity or by high Compton background, especially in the case of Pt.

The technique has been applied to the determination of PGE in ultramafic rocks, and chromite by Stockman (1982), and in this study to PGE analysis of mafic rocks. The method could perhaps be adapted to studies of more felsic rocks, on which PGE data are very scarce.

A serious limitation of the present procedure as applied to PGE analyses of mafic rocks is

that high levels of 15 hour ^{24}Na activity are generated by the 6 hour irradiation and 24 hour decay, which are optimum for the four PGE of interest. This problem does not arise for some Archean greenstones, such as many of the Red Lake suite, in which low Na levels (<0.5 wt. % Na_2O ; Cowan, 1979) are encountered, but would be a serious one for fresh basalts (eg. Hawaiian basalt with 2 wt. % Na_2O ; Basaltic Volcanism Study Project). This problem might be managed by employing a relatively long irradiation (ie. 3 days) and a sufficiently long decay time for substantial decay of ^{24}Na (ie. 10 to 20 days). This scheme would allow Pd determination by the 17-day ^{103}Pd isotope via the $^{102}\text{Pd}(n,\gamma)^{103}\text{Pd}$ reaction. A comparison of the nuclear characteristics of each isotope is given below.

Table 7.1.

Comparison of the nuclear characteristics of ^{103}Pd and ^{109}Pd .

Isotope	Target Isotope	Abundance of Isotope	Gamma Energy (KeV)	Thermal Neutron Cross-Section
^{103}Pd	^{102}Pd	1%	40,358	5
^{109}Pd	^{108}Pd	26.7%	22,88	0.19

A gamma peak is present at 40 KeV for ^{103}Pd , outside the range of low energy U-Th series radiation. This energy

could be detected on either a Ge(Li) or low energy planar detector. A large γ -peak is present at 357.6 KeV, an energy easily resolved on a coaxial Ge(Li) spectrum. Production factors, a convenient means of comparing relative sensitivities, are given in Table 7.2a for each Pd isotope along with ^{24}Na , ^{198}Au , $^{199}\text{Au}(\text{Pt})$, ^{192}Ir and ^{194}Ir . The production factors are calculated for the irradiation parameters utilized in the present work (6 hour irradiation and 24 hour decay period) as well as for a longer irradiation and decay time (3 days and 12 days respectively). Also included are $^{24}\text{Na}/\text{NM}$ production factor ratios in order that an estimation of ^{24}Na activity relative to each isotope, for each irradiation-decay scheme, can be made. Relative to the irradiation parameters used in this work, a 3 day irradiation and 12 day cooling reduces the sensitivity for ^{109}Pd determination by a factor of 10^5 , and increases the sensitivity for ^{103}Pd determination by a factor of 10. ^{24}Na sensitivity is reduced by a factor of $> 10^4$ with the longer irradiation and decay times. The lowest Na/Pd ratio of sensitivity is seen with the 3 day-12 day scheme and the ^{103}Pd isotope. In summary, a longer irradiation and decay time would dramatically reduce ^{24}Na activity, while still allowing Pd determination via the ^{103}Pd isotope. The sensitivity for ^{194}Ir is not improved with

TABLE 7.2a. A COMPARISON OF RELATIVE SENSITIVITIES OF NOBLE METALS (NM) AND SODIUM WITH VARYING IRRADIATION PARAMETERS.

Noble Metal	T(1/2)	Production Factor		Na/N.M (ratio of production factors)		% Max Saturation Activity Remaining	
		t(ir)=6h t(decay)=24h	t(ir)= 3d t(decay)=12d	t(ir)=6h t(decay)=24h	t(ir)=3d t(decay)=12d	t(ir)=6h t(decay)=24h	t(ir)=3d t(decay)=12d
¹⁰⁹ Pd	13.5h	7.9×10^{-1}	4.0×10^{-6}	10.2	41.2	7.7	3.7×10^{-5}
¹⁰³ Pd	17.5d	9.7×10^{-2}	7.1×10^{-1}	0.82	2.3×10^{-4}	0.9	7.0
¹⁹⁸ Au	2.65d	963	466	8.3×10^{-3}	1.7×10^{-2}	4.9	2.4
¹⁹⁹ Au(Pt)	3.15d	1.7×10^{-2}	1.3×10^{-2}	470	615	4.3	3.4
¹⁹⁴ Ir	19h	72	3.8×10^{-1}	1.1×10^{-1}	21	0.2	2.5×10^{-3}
¹⁹² Ir	74d	1.7×10^{-1}	1.9×10^{-1}	47	42	0.2	2.5
²⁴ Na	15h	8	1.6×10^{-4}	/	/	0.0	1.6×10^{-4}

TABLE 7.2b. COMPARISON OF RELATIVE SENSITIVITIES FOR ¹⁰⁹Pd AND ¹⁰³Pd WITH A SHORT IRRADIATION-DECAY SCHEME.

Noble Metal	% Saturation Activity		Production Factor	
	t(ir)=3h t(decay)=12h		t(ir)=3h t(decay)=12h	
¹⁰⁹ Pd	7.7		8.2×10^{-1}	
¹⁰³ Pd	0.5		5.0×10^{-2}	
²⁴ Na	7.4		7.4	

-0.5 gram samples.
-t(ir) = irradiation time.
t(decay) = decay time.

a longer irradiation and decay time, and those of ^{192}Ir and $^{199}\text{Au}(\text{Pt})$ remain essentially unchanged. ^{198}Au sensitivity is reduced by 52%, but the ^{197}Au parent isotope is so efficiently activated and abundant, that the reduction in sensitivity is acceptable. The production factor data are supported by the amount of saturation activity remaining at counting time for each isotope, using each irradiation-decay scheme.

If the technique were to be optimized for Pd alone, the ^{103}Pd isotope is recommended. A short irradiation (3 hours) and decay (12 hours) does little to improve the sensitivity of ^{109}Pd and generates as much ^{24}Na activity as the 6 hour 24 hour scheme (refer to Table 7.2b for percentage of saturation activity remaining and production factors using this scheme).

The technique could also be adapted for Pt, Au and Ir analysis alone using the 6 hour-24 hour irradiation scheme. The incorporation of Ru and Os (PGEs with half-lives on the order of days) into the package could be accomplished with the addition of the appropriate carriers. Although Ru, Os and Ir are assumed to be geochemically coherent (Crocket, 1981), this should be further investigated in various rock types. The 40 day ^{103}Ru and 15 day ^{191}Os isotopes might be analysed in the same irradiation, with the same irradiation parameters used in the present study. RNAA determination

of Ru is subject to interference from ^{103}Ru produced by fission of ^{235}U (Gijbels and Zels, 1977), and a determination of U must be made. Although RNAA is not recommended for Ru analysis in mafic rocks, the interference is often negligible in some silicate and oxide minerals from gabbros and ultramafic rocks, plus meteorites, ultramafic rocks and chromites. Applications of this method might, therefore, be extended to Ru studies in ultramafic rocks from ophiolites, peridotitic komatiites and layered ultramafic complexes. A potential source of error in Os analysis is the ease with which Os volatilizes as $\text{OsO}_4(\text{g})$ (osmium tetroxide) from dilute aqueous solutions (Morgan, 1965). The fusion step of any RNAA procedure adapted for Os analysis must be fast, in order to mix the Os with the carrier before it vaporizes. Complexing the Os with chlorides is one way to reduce this problem. In this procedure, the carriers, initially lining the crucible in solution with NaOH when fusion begins, are chloride based and will complex with the Os early in the fusion process. Morgan (1965) discussed OsO_4 loss and described a procedure involving reduction of the tetroxide prior to equilibration with the carrier which also eliminates this problem.

The Ir anomaly in the Cretaceous-Tertiary boundary clay has been the focus of attention in the

recent past, as the causal event for the many extinctions, and therefore the source of Ir, is still under debate. A method such as the present procedure would be of great advantage in this specific case since samples as small as 0.1 mg can be analyzed with sufficient sensitivity to accurately determine the Ir content. The 74 day ^{192}Ir isotope could be analyzed utilizing long irradiation and cooling times, thereby reducing radiation dose to the analyst.

As and Se are already coprecipitated with the PGEs in this technique. As and Se peaks were seen in the γ -ray spectra and are listed in tables 5.2 and 5.4. Adaptation of the method for these elements would simply involve the addition of those specific carriers. The INAA package of As, Au, Se and possibly W and Sb could probably be duplicated here with better sensitivity and the PGE determination as well.

From an industrial standpoint, in a large automated laboratory, this procedure could be adapted to large scale biogeochemical prospecting or stream/lake bottom sediment geochemical prospecting, where large numbers (ie. 10^2) of samples with low PGE concentrations have to be rapidly processed.

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APPENDIX I

SUPPLEMENT TO DETAILED ANALYTICAL PROCEDURE

This appendix is designed to supplement chapter 2. It is a detailed account of the analytical procedure which should be studied if the procedure is to be attempted. Information is also provided as to changes made from the original work on the procedure by Stockman (1982).

A. STOCK SOLUTIONS

1. Carriers

Stockman (1982) used ammonium hexachloroplatinate as a base for the platinum stock solution. Pure Pt sponge was used in the present work, and the preparation is therefore slightly different. Although ammonium chloroiridate was used in the present work instead of ammonium hexachloroiridate as Stockman (1982) used, the procedure was identical. A correction for the amount of Ir in the complex was made when the concentration of the stock solution was calculated. Pd and Au stock solutions were also prepared as in Stockman (1982).

II. Tellurium Solution

Correct preparation of this solution should take approximately 3-5 hours. It is critical that incipient dryness be reached or yields may be affected (lowered). Incipient dryness is interpreted as the presence of a white chloro-nitrate precipitate plus a small amount of yellowish liquid (ca. 2-3 ml) in the beaker. The precipitate should readily dissolve when conc. HCl is added.

III. Stannous Chloride Solution

If many experiments are carried out within the 2 month life expectancy of this solution, the amounts made at one time should be doubled (ie. weigh 45 grams of salt, and dilute in 32 ml of HCl; fill to 200 ml volume).

V. Dilute Acids

2 litres of 2:1 (v/v) HCl:H₂O = 1333ml HCl : 660 ml H₂O

2 litres of 1:11 (v/v) HCl:H₂O = 166ml HCl : 1833ml H₂O

B. PREPARATION OF STANDARDS

I. Preparation of poly vials

In order to include 2 Au-Ir and 2 Pd-Pt standards in each irradiation, it would be advantageous to prepare 80 standards initially (40 of each). To prepare the SiO₂

powder, glass rods were crushed to 100 mesh, washed in aqua regia, rinsed in water, and distilled water, and dried. It is not necessary to use flip-top poly vials, and in fact, poly vials with separate lids resist opening during irradiation better, and are easier to open once processing begins.

C. PREPARATION OF SAMPLE CRUCIBLES AND STANDARD BEAKERS

1. Sample Crucibles

An alternate method for crucible preparation was suggested by Stockman (1982), in order to prevent the plating of noble metals onto the crucible walls when the carrier is added as an acid solution. Stockman (1982) coated the inside walls of the Ni crucibles with an extremely thin coating of EPOXY-PATCH epoxy (the crucible should look as if it had been barely wetted with light oil, and then wiped dry). The coating should be applied twice. If the coating is too thick, an explosion will result when Na_2O_2 is later heated in the crucible. The procedure was not adopted in the present study after several unsuccessful attempts with inactive samples. Uncoated crucibles, put through the fusion process with radioactive samples were later counted, and no noble metals were detected. Stockman (pers. comm)

noted that the coating may not be necessary since the Na_2O_2 -NaOH usually etches the crucible surface anyway.

In the procedure described in section 4.2 C, the heat lamp should be at least 30 cm above the crucibles, and complete dryness is attained in 2.5 hours.

D. PREPARATION OF SAMPLES

Stockman (1982) used polyethylene tubing instead of poly vials for sample packaging.

E. RADIOCHEMISTRY- SAMPLES

Fusion

Due to the changes developed in the present work in the preparation of the sample crucibles, the start of the fusion procedure had to be correspondingly adjusted. For the original fusion technique used with epoxy coated crucibles, refer to Stockman (1982).

Sample crucibles should sit on the bunsen flame during initial heating. After ca. 5 minutes, the fusion cake will be nearly melted, and the flame can be turned up to envelop about one-half of the crucible, occasionally touching the lid. When the contents of the crucible have a dull red glow (best seen with the lights

off in the fume-hood, and if possible a semi-darkened room), dull red heat is reached. It is possible that an electric heater would provide much more even heating and a more controlled fusion, temperature-wise.

Leaching Fusion Cake

After cracking has occurred, the crucible is set on its side in the beaker with 60 ml of H_2O . The hot plate is set on low. The amounts of acid used to leach the fusion cake should be measured exactly, as total acidity of the solution is critical to the precipitation step. Immediately after 15 ml of HCl is added, the solution should turn clear. If it does not, the temperature of the the fusion was too high (sides of the crucible will be coated with black oxides, and an ashy substance will remain in the solution after all acid has been added), too low (the sample was not fused completely and fine rock powder remains in the bottom of the beaker), or the acidity of the solution has not been controlled properly.

F. RADIOCHEMISTRY-STANDARDS

The standards may be processed within 3-4 hours. The lengthy portion of the procedure is bringing the solution repeatedly to incipient dryness. For incipient

dryness, 3-4 ml of solution should remain in the beaker.

APPENDIX II: Sample spectra taken directly off coaxial
and LEPS detectors during a chemical yield
determination.

TIME(L)= 789
PSET(L)= 1000

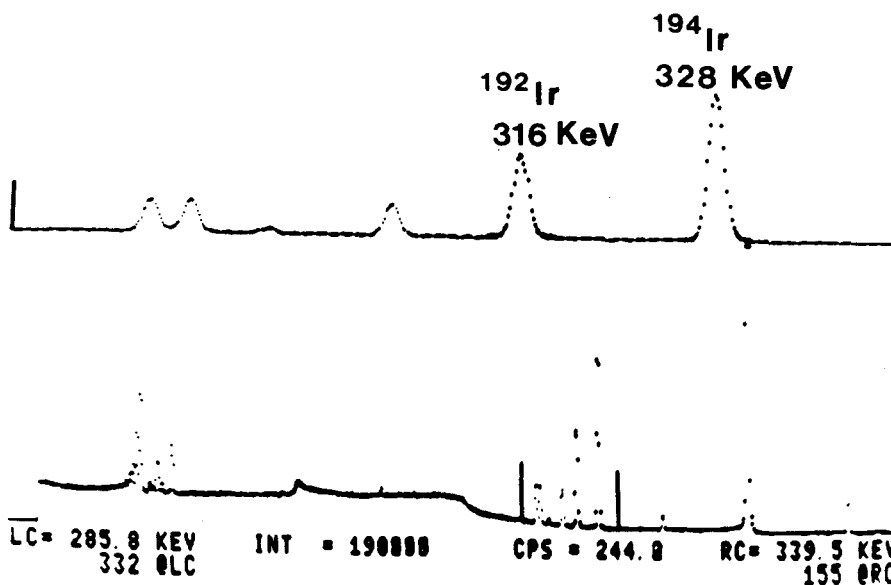
STD 10N 1034 311006

10:49 30 OCT 86
UNIT 2 DT= 92
TASK 12 157
339.5 KEV

285.8 KEV VFS= 8192

CRT=(17-32)

129



A

Au-Ir STANDARD

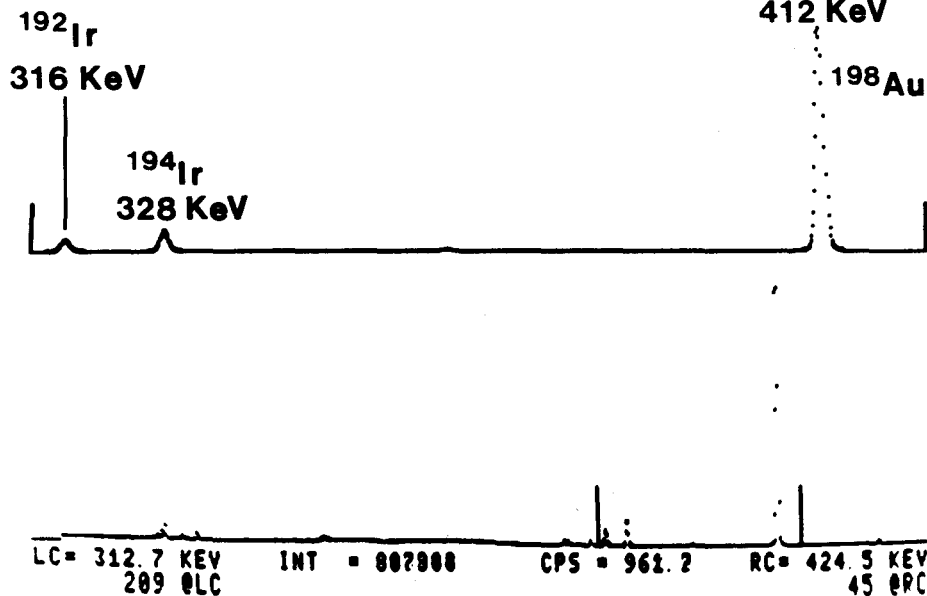
TIME(L)= 889
PSET(L)= 1000

STD 10N 1034 311006

10:50 30 OCT 86
UNIT 2 DT= 92
TASK 12 157
424.5 KEV

312.7 KEV VFS= 65536

CRT=(17-32)



B

Au-Ir STANDARD

Coaxial Ge(Li) spectrum (A) of a sample showing 88 KeV ^{109}Pd and 158 KeV $^{199}\text{Au}(\text{Pt})$ gamma-ray peaks. LEPS spectrum (B) of the same sample showing the 22 and 25 KeV ^{109}Pd peaks.

TIME(L)= 918
PSET(L)= 1000

SAMP 1 1225 301006

12:42 30 OCT 86 130
UNIT 2 DT= 132
TASK 12:57
199.5 KEV

85.1 KEV VFS= 2040

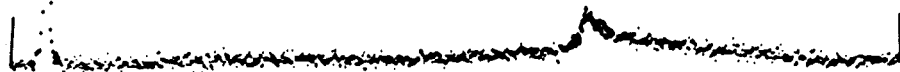
CRT=(17-32)

88 KeV

¹⁹⁹Au(Pt)

¹⁰⁹Pd

158 KeV



LC= 85.1 KEV
918 OLC

INT = 908809

CPS = 1111

RC= 199.5 KEV
890 OLC

A

Ge(Li) detector

SAMPLE

TIME(L)= 948
PSET(L)= 1000

SAMP 1 1814 301006

18:31 30 OCT 86
UNIT 2 DT= 52
TASK 12:57
1117 CH0

831 CH0 VFS= 512

CRT=(17-32)

¹⁰⁹Pd

22 KeV

25 KeV



LC= 831 CH0
97 OLC

INT = 35200

CPS = 37.2

RC= 1117 CH0
112 OLC

B

LEPS detector

SAMPLE

Total sample spectrum from the coaxial Ge(Li) detector
(A) (0-495 KeV) and the total sample spectrum from the
LEPS detector (B) (0-120 KeV). Pd and Pt peaks are
displayed at top.

TIME(L)= 968
PSET(L)= 1000

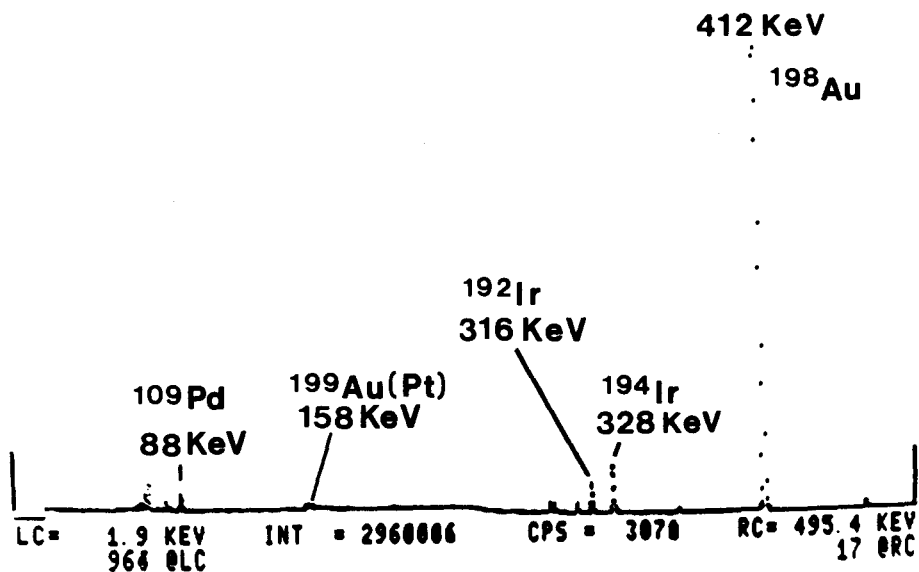
SAMP 2 1253 301006

13:11 30 OCT 86
UNIT 2 DT= 82
TASK 12 12:57
495.4 KEV

131

1.9 KEV VFS= 65536

CRT=(17-32)



A

Ge(Li) detector

SAMPLE

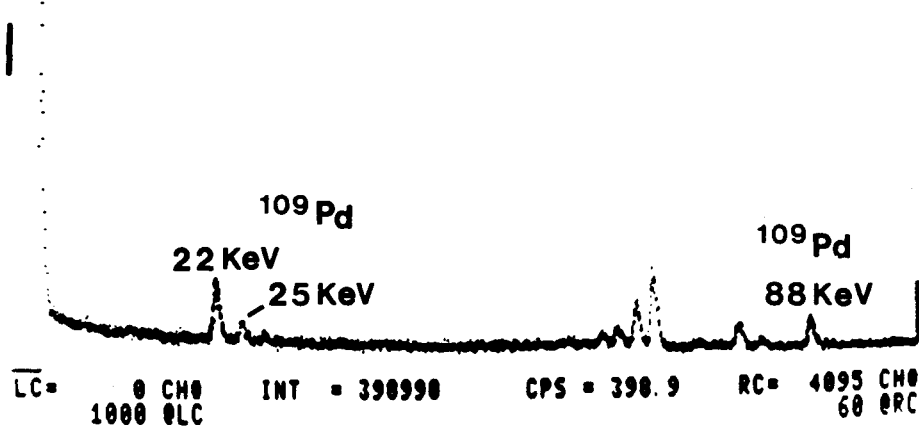
TIME(L)= 1000
PSET(L)= 1000

SAMP 1 1514 301006

19:34 30 OCT 86
UNIT 2 DT= 52
TASK 12 12:57
4095 CH0

0 CH0 VFS= 2040

CRT=(17-32)



B

LEPS detector

SAMPLE