PALLADIUM, IRIDIUM AND GOLD IN DEEP-SEA CORES

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SCOPE AND CONTENTS: Neutron activation procedures have been applied to the determination of palladium, iridium and gold in three Antarctic and one Caribbean deep-sea cores. Manganese content in these cores has also been determined, using a non-destructive, direct gamma-counting technique.

Analytical results for Pd, Ir, Au and Mn in a total of 49 samples are presented. Precious metal content in different components of deep-sea sediments, their variation within each core and the possibility of an extraterrestrial origin of these precious metals is discussed. An estimation of the accretion rate of extraterrestrial material on the earth is derived from the iridium value in deep-sea manganese nodules.

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ABSTRACT

Wet chemical neutron activation analysis procedures for Au, Pd and Ir together with a non-destructive gamma-counting procedure for Mn are described and applied to the determination of these metals in three Antarctic (E21-17, E13-3 and E17-10) and one Caribbean (P6304-9) deep-sea cores.

A total of 49 samples were analyzed. The average values of Au, Pd, Ir in ppb and Mn in Wt. % (together with standard deviations of the mean) are:

	Au	Pd	Ir	Mn
core P6304-9 (calcareous ooze)	2.17±0.92	1.78±0.43	0.34±0.13	0.1924±0.1018
core E21-17 (Globigerina ooze)	1.16±0.56	1.55±0.50	0.29±0.18	0.0096±0.0044
core E13-3 (siliceous ooze)	0.87±0.30	7.47±2.16	0.26±0.15	0.4599±0.0704
core E17-10 (pelagic clay)	1.63±0.54	5.42±1.34	0.34±0.10	0.3866±0.0440

No significant correlations were observed between these elements in the cores.

No large differences exist between Au, Pd and Ir concentrations in different types of deep-sea sediments nor in cores from different areas and their values are within the general concentration range found in most crustal rocks.

A general discussion of the sources of precious metals in deep-sea sediments is given. The most important precious metal source in the cores studied in this work is detrital material from land. The contribution of extraterrestrial material to the Au and Pd content of deep-sea sediments is not important but in cores with depositional rates as low as a few tenths of a mm per thousand years, extraterrestrial material may account for more than half of the total Ir content.

From the non-detrital Ir content of deep-sea manganese nodules the accretion rate of extraterrestrial material over the entire surface of the earth is calculated to be about 200 tons per day with an upper limit of 310 tons per day. The constancy of Ir content in deep-sea cores as a function of depth suggests that the influx of extraterrestrial material during the past 3 to 4 million years was probably fairly constant.

CHAPTER ONE

INTRODUCTION

Previous studies on the geochemistry of the precious metals in the natural environment were largely restricted to meteorites and ore deposits in which they are concentrated to the part per million level. Recent development of the neutron activation technique has made it possible to measure precious metal contents at the part per billion level in silicate rocks thus widening our knowledge concerning their behaviour in ordinary crustal materials. A significant amount of precious metal abundance data for igneous rocks is now available in the literature, but the precious metal geochemistry in sedimentary rocks and sediments has received much less attention and the existing data are very limited.

Because the precious metals, particularly Ir and Os, are strongly depleted in the earth's crust relative to meteorites, the main interest in their study in sediments is concerned with the possibility of using the precious metal content of slowly accumulated deep-sea sediments as a sensitive tool for estimation of the mass accretion rate of extraterrestrial material to the earth's surface. Pettersson and Rotschi (1952) and Goldschmidt (1954) first pointed out that in ocean basins, far from continents, the deposition rate of terrestrial material is very slow, and that under this condition one may be able to measure the accretion rate of cosmic matter on the surface of Earth by measuring the addition rate of platinum group metals of extraterrestrial origin to the deep-sea sediments. Barker and Anders (1968) measured the Ir and Os content of five Pacific deep-sea sediments and obtained an estimate of 330 tons per day as the upper limit of the influx rate of extraterrestrial material over the entire surface of the earth. Harriss et al. (1968) analyzed deep-sea manganese nodules from different localities for Au, Pd, and Ir. Average Ir concentration in the nodules was found to be 50 times higher than in deep-sea sediments. They concluded that the slow growth rate and the enrichment of Ir in these nodules were strongly suggestive of a significant extraterrestrial component of Ir in deep-sea manganese nodules.

Four long, deep-sea, piston cores consisting of different types of sediments collected from the Caribbean and Antarctic areas were available for this study. Absolute dating in these cores by either C^{14} or Th^{230}/Pa^{231} methods (core P6304-9; Rona and Emiliani, 1969) or paleomagnetic stratigraphy (core E13-3; Hays and Opdyke, 1967 and core E17-10; Goodell and Watkins, 1968) has been carried out.

Contents of three precious metals (Au, Pd and Ir) in 37 bulk samples and in 12 samples of different size fractions separated from bulk core material have been determined using a wet chemical neutron activation method. Mn concentrations in the same samples were also obtained by non-destructive neutron activation analysis in order to determine if any correlation exists between precious metals and manganese in these cores.

It was expected that the precious metal values in different components of deep-sea sediments and their variations within single cores would have an important bearing on problems related to importance of cosmic contribution of precious metals to deep-sea sediments. These considerations should lead to a better understanding of the behaviours of precious metals in the marine environment.

CHAPTER TWO

SAMPLE DESCRIPTION

Precious metal contents were determined in a total of 37 bulk samples from four deep-sea cores including two calcareous ooze cores (Caribbean core P6304-9 and U.S.N.S. ELTANIN core 21-17), one siliceous ooze core (U.S.N.S. ELTANIN core 13-3) and one clay core (U.S.N.S. ELTANIN core 17-10).

P6304-9 is a Caribbean core collected by the Institute of Marine Science, University of Miami, Florida. The three Antarctic cores were raised by U.S.N.S. ELTANIN cruises from the Southern Ocean. Cores were collected using piston corers with inner plastic liner.

Fig. 2-1 and Fig. 2-2 show the geographic localities of the cores.

All the samples were donated by Dr. R. C. Harriss, Department of Oceanography, The Florida State University, U.S.A.

2-1. Caribbean Core P6304-9

Caribbean core P6304-9 was collected from the east of Beata Ridge (Latitude 14°57' N, Longitude 68°55' W) at a depth of 4126 meters.

This core has been analyzed in considerable detail both isotopically (Emiliani, 1966) and micropaleontologically (Lidz, 1966). These studies demonstrated that the core contains continuous and undistrubed sections of globigerina ooze sediment, ranging in an age from the present to an estimated 425,000 years ago. Absolute dating by C^{14} and Th^{230}/Pa^{231}

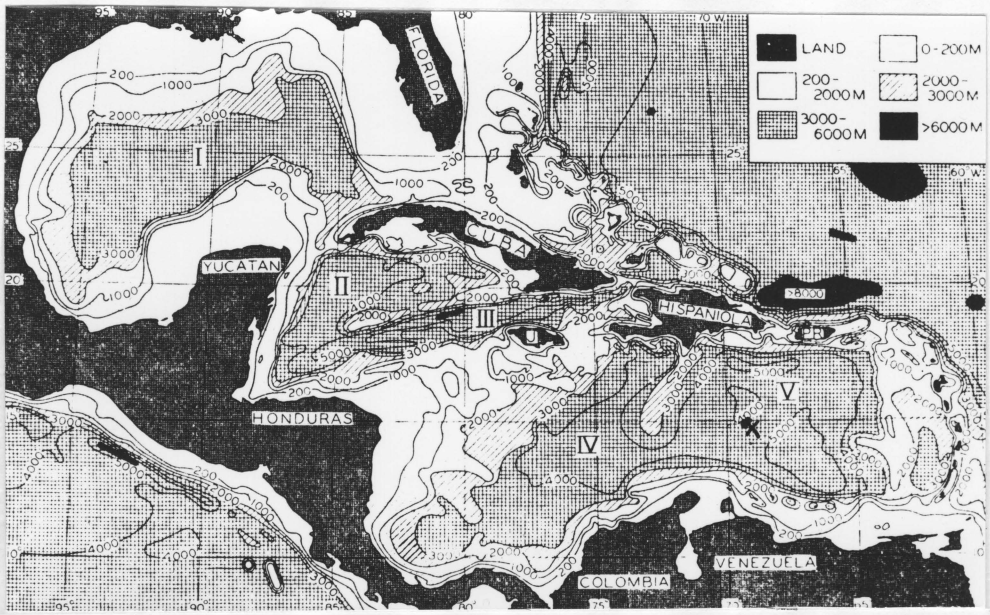

Figure 2-1. Geographic locality of Caribbean core P6304-9(X)

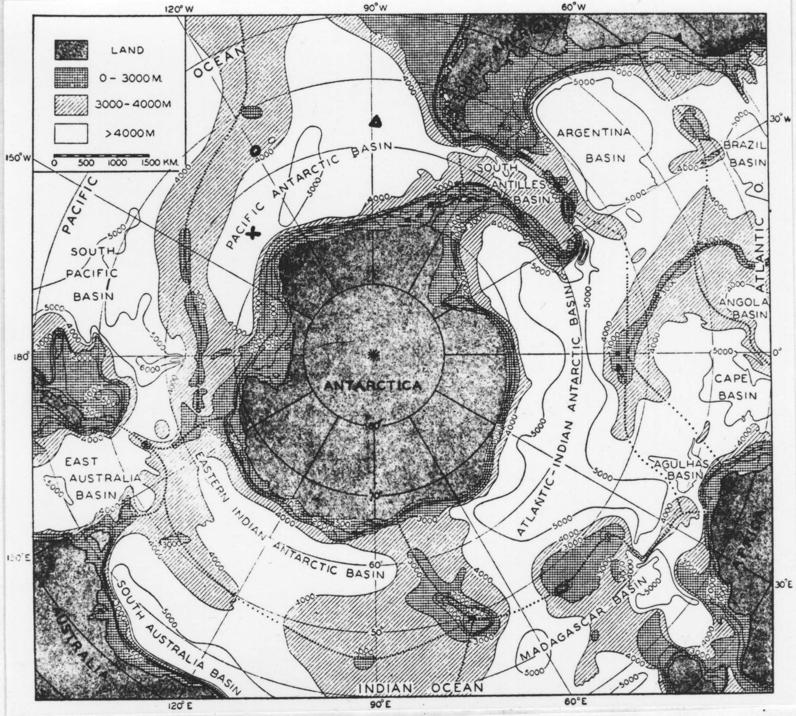

Figure 2-2. Geographic localities of U.S.N.S. ELTANIN cores E21-17(0), E13-3(Δ), and E17-10(X).

method has been reported by Rona and Emiliani (1969). The Th^{230}/Pa^{231} data gave a deposition rate at 3.64 cm/1000 yr. for the uppermost 539 cms of the core during the past 147, 200 years.

15 samples were taken at different depths from this 1429 cms core.

Fig. 2-3 gives the sample position in the core, the carbonate content, the δO^{18} ($^{o}/oo$) variation curve (after Emiliani, 1966) and the relative absolute age.

2-2. U.S.N.S. ELTANIN Core 21-17

Core E21-17 with a length of 1006 cm. was raised from 2816 meters at Latitude 55° 28.5' S., Longitude 119° 56' W.

This core is a nearly pure calcareous ooze which contains predominantly Globigerina shells. No direct measurement concerning the depositional rate of the sediment is available.

Nine samples were obtained from this core. Fig. 2-4 gives the depth in the core and the carbonate content of each sample.

Carbonate content of samples from P6304-9 and E21-17 were determined in this work by an EDTA-titration method modified from Turekian (1956).

2-3. U.S.N.S. ELTANIN Core 13-3

The 1603 cm. long core E13-3 was collected from the Bellingshausen Basin (Latitude 57°0.3' S., Longitude 89°29' W.) at a water depth of 5090 meters.

This siliceous core contains an upper layer (0 to 1000 cm.) of Radiolarian clay (also diatoms), which overlies a tan clay (1000 to 1603 cm.) (Hays and Opdyke, 1967). This is a common phenomenon in many Antarctic siliceous cores (Goodell and Watkins, 1968). Hays (1965) suggested that the change from highly diatomaceous sediments in the tops of these Antarctic cores to sediments containing few siliceous fossils below was caused by recently increased productivity in Antarctic waters due to intensification of vertical oceanic circulation associated with ice formation around the continent.

The sedimentation rate of this core has been determined with reference to paleomagnetic-polarity records in the core (Hays and Opdyke, 1967) The data demonstrate a very constant depositional rate of 3.34 mm./1000 yr. for the upper 1120 cm. of the core using 3.35 m.y. as the boundary of Gauss-Gilbert paleomagnetic epochs.

Nine samples were taken from this core at depth intervals according to different magnetic-event records in the core. (Fig. 2-5).

2-4. U.S.N.S. ELTANIN Core 17-10

Four samples are available for the 1585 cm. core E17-10 raised from 4658 meters at Latitude 65° 1' S., Longitude 134° 52' W. (Fig. 2-6).

The upper part of the core (0 to 800 cm.) contains silty clay while the remainder (800 to 1585 cm.) contains clayey silt.

The average sedimentation rate for E17-10 above 1370 cm. is 5.82 mm./1000 yr. and was determined paleomagnetically using 2.35 m.y. as the boundary of the Matuyama-Gauss paleomagnetic epochs (Goodell and Watkins, 1968).

Appendix A lists the information on samples from the three Antarctic cores: E13-3, E21-17 and E17-10, described by the original collectors.

Sample number	Interval (cm.)	$CaCO_3$ (wt. %)
C-01	19- 20	69.3
C-02	86- 87	61.5
C-03	318- 319	58.3
C-04	398- 399	64.6
C-05	528- 529	45.4
C-06	608- 609	60.7
C-07	762- 763	59.0
C-08	822- 823	44.9
C-09	948- 949	15.4
C-10	975- 976	68.6
C-11	1034-1035	47.5
C-12	1128-1129	29.4
C-13	1198-1199	52.8
C-14	1302-1303	41.0
C-15	1368-1369	43.7

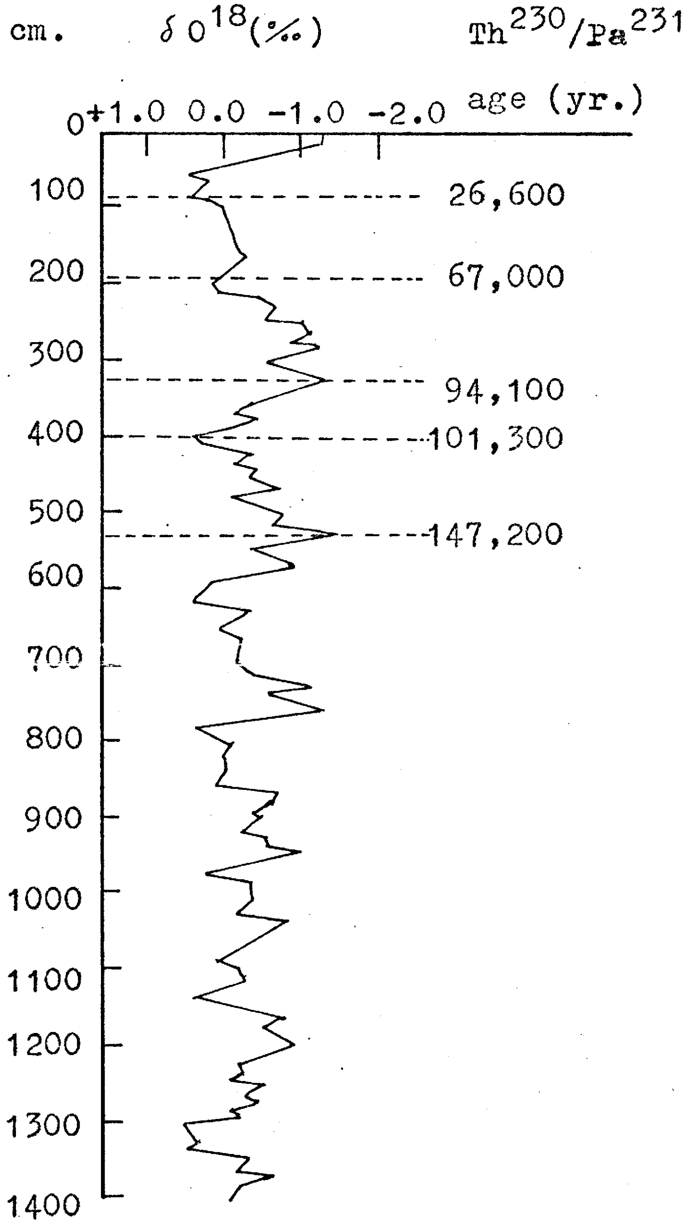

Figure 2-3. Number, position, carbonate content, δ 0^{18} (‰) variation curve in pelagic Globigerinoides sacculifera and dating information of P6304-9 samples

Sample Number	Interval (cm)	$CaCO_3$%
21-17-1	0- 125	86.8
21-17-2	125- 200	82.0
21-17-3	200- 275	94.9
21-17-4	275- 325	85.1
21-17-5	325- 400	86.5
21-17-6	500- 600	86.3
21-17-7	600- 750	85.6
21-17-8	750- 950	83.0
21-17-9	950-1006	80.9

Fig. 2-4. Number, position and calcium carbonate content of E21-17 samples.

Sample number	Interval (cm.)
13-3-1	0- 225
13-3-2	225- 605
13-3-3	605- 655
13-3-4	655- 865
13-3-5	865-1115
13-3-6	1025-1125
13-3-7	1125-1280
13-3-8	1280-1440
13-3-9	1440-1600

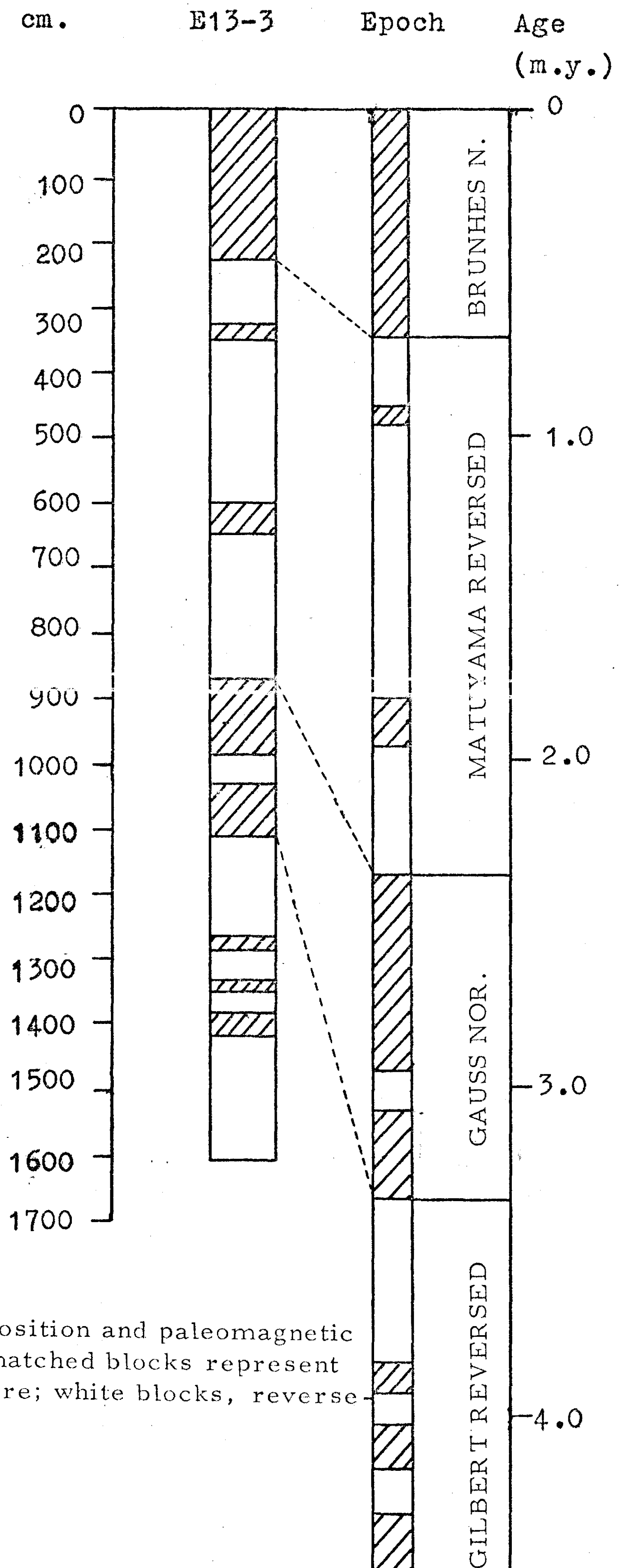

Figure 2-5. Sample number, position and paleomagnetic stratigraphy of E13-3 (hatched blocks represent normally magnetized core; white blocks, reversely magnetized).

Sample number	Interval (cm.)
17-10-1	0- 400
17-10-2	400- 800
17-10-3	800-1400
17-10-4	1400-1585

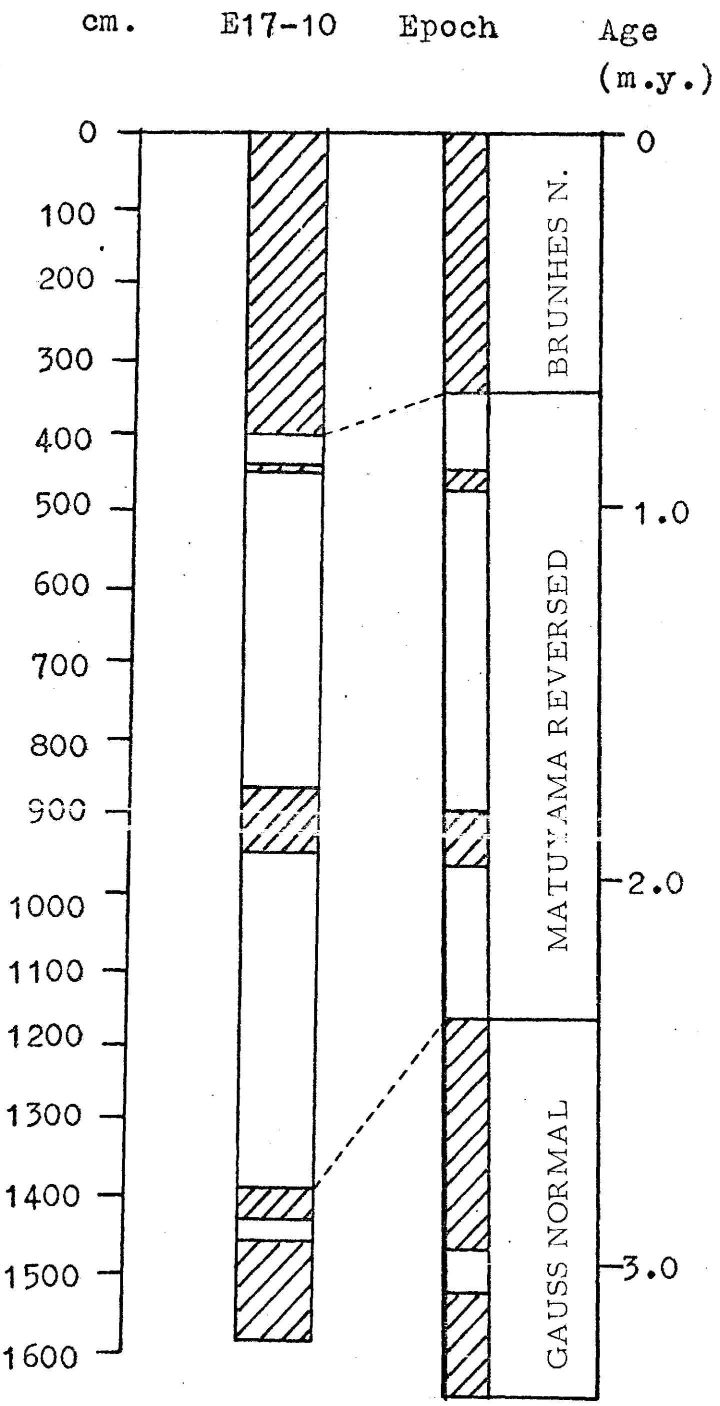

Figure 2-6. Sample number, position and paleomagnetic stratigraphy of E17-10 (hatched blocks represent normally magnetized core; white blocks, reversely magnetized).

CHAPTER THREE

EXPERIMENTAL METHOD

3-1. Sample Preparation

About twenty grams of dried material were available for each sample taken from the three Antarctic cores (E21-17, E13-3 and E17-10). For Caribbean core P6304-9, two grams of material were available for each sample. The sample was divided into two parts of approximately equal amount. One portion was used for bulk sample chemical analysis and the other retained for future reference.

3-1-1. Bulk Sample

Water-soluble salts from sea water were first removed by repeated washing of the sediments with distilled water. Samples were then dried under an infrared lamp, broken up in an agate mortar until all the material passed through 200 mesh silk bolting cloth. After crushing, the sample was transferred into a glass bottle, mixed for 20 minutes on a Spex mixer and dried in an oven at 105°C. for five hours. The sample was stored in a glass bottle for analysis.

3-1-2. Mechanical Separation of the Bulk Sample

In order to investigate the partition of precious metals between different sedimentary phases, some of the samples were mechanically sized by either wet sieving or a settling method.

I) Wet Sieving -----

Particles with diameter greater than 150 microns were obtained from a number of calcareous ooze samples (core P6304-9) by wet sieving the original sample material through 100 mesh silk bolting cloth. Prior to sieving, samples were washed and shaken for 20 minutes on a Spex mixer with distilled water to effect dispersion. Materials retained on the sieve were dried, crushed and bottled.

II) Separation by Settling Velocity -----

The sediment was washed and disaggregated with distilled water and transferred to a one liter graduated cylinder. It was then diluted with distilled water to a sufficient volume so that the suspension filled the cylinder to a depth of greater than ten centimeters. The suspension was stirred and mixed throughly and allowed to settle for a sufficient length of time (4.5 minutes at room temperature) to permit particles greater than 20 microns to decend ten centimeters. At the end of the time period allowed for free settling, the top ten centimeters of the supernatant liquid containing particles of diameter smaller than 20 microns is siphoned off and evaporated to dryness. This gives a size fraction of less than 20 microns from the original bulk sample. Size fractions consisting of particles less than 2 microns were obtained in a similar manner from four clay rich samples (core E17-10). At room temperature, it required eight hours for particles greater than 2 microns to sink from the top ten centimeters of the settling column.

No deflocculating agent was added during the process.

3-2. Analytical Procedure

For irradiation, 100 mg. of sample powder was weighed into a labelled 3 mm. O. D. x 2 mm. I. D. fused quartz ampoule and sealed with a polyethylene plug. The quartz tube was previously cleaned by immersing in acetone.

Analytical procedures for the determination of Au, Pd and Ir used in this study are mainly based on the procedures for simultaneous determination of Ru, Pd, Os, Ir, Pt and Au by neutron activation analysis given by Crocket _et_ _al._ (1968).

Samples and standards are irradiated together in the reactor. After cooling, the ampoules are opened and the powder transferred to a ziranium crucible containing non-radioactive carriers. Carriers and sample are taken into solution by high temperature peroxide fusion. Separaration and radiochemical purification of the elements of interest was achieved by ion exchange, precipitation and solvent extraction processed. The purified radiation was measured by either differential gamma spectroscopy or gross beta counting and compared with that of a standard to give the elemental concentration.

Owing to the low concentration of Ir in deep-sea sediments and its long half-life (74 days for Ir^{192}) compared to Pd (13. 6 hours for Pd^{109}) and Au (2. 7 days for Au^{198}), Ir was determined in separate irradiations whereas

Pd and Au were determined simultaneously. Mn was also determined in this study by non-destructive activation analysis using a Li-drifted germanium diode detector.

3-2-1. Standard and Carrier Preparation

I) Standards -----

Dilute acidic precious metal solutions prepared from "Specpure" palladium sponge, gold sponge and ammonium chloroiridate (Johnson and Matthey Company) were used as standard solutions. The metallic Pd and Au were taken into solution with small amounts of aqua regia at low heat on a hot plate, followed by two digestions with conc. HCl. The chlorosalts of Pd and Au were then dissolved and diluted in volumetric flasks with 1M HCl. The $(NH_4)_2IrCl_6$ salt was dissolved and diluted with 3M HCl.

Densities of standard solutions were determined with a calibrated 1 ml. pipette by pipetting several 1 ml. aliquots of the solution into weighing bottles.

The final flux monitor standard solution of Au and Pd contain 0.0320μg Au/ml. and 0.2734μg Pd/ml.; that of Ir contains 0.00555μg Ir/ml.

Standards for Au+Pd and Ir were prepared by weighing about 30 mg. of the standard solution into pre-weighed fused quartz ampoules. An adequate amount of coarse-grained quartz powder (prepared by grinding pure quartz tubes in an agate mortal to produce a powder which was cleaned by boiling in aqua regia) was added into the ampoules to just absorb all of the solution. Ampoules were then put in a drying oven set at 65°C. for

12 hours and sealed with a polyethylene plug.

In case of Ir determination, a high gas pressure is usually produced inside the ampoule after long (1 week) irradiations and considerable care is necessary on opening. Ampoules for samples and standards were sealed by pulling out the tube in an oxygen flame.

Since no carrier is used in the Mn determination, quantitative recovering of the standard after irradiation is critical. For this reason, a solid standard, a thin, homogeneous aluminum foil (Aluminum Company of Canada, alloy No. 3003), was used. A certain amount of Mn and Cu has been added into the foil during the manufacturing process: The average Mn content of this foil is (1.247±0.040)% as determined by neutron activation against a dilute liquid standard (average value of 36 determinations of defferent parts of the aluminum foil)*

Strips of aluminum foil of a few tens mg.weight were sealed into quartz ampoules for irradiation.

II) Carriers -----

Carrier solutions of each metal were prepared in the same manner as in standard solution preparations. 4 mg Au/ml., 1 mg Pd/ml. and 2 mg Ir/ml. were the approximate concentration of each carrier solution

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*Determinations by Dr. K. Fritze, Department of Chemistry, McMaster University.

For each irradiated sample five ml. carrier solution of each element was added.

No carrier was used in the analysis of Mn.

3-2-2. Irradiation

Eight samples together with three standard ampoules packed side by side in an aluminum can were irradiated in a high flux position in the McMaster Reactor. The average neutron flux was 10^{13} neutrons/cm.^{2}/sec. For Au and Pd, samples and standards were irradiated for 24 hours and cooled for 12 hours before chemical processing. Counting on Pd started approximately 40 hours after the end of irradiation.

One week's irradiation followed by one week's cooling is needed to produce enough Ir activity.

In Mn determination, irradiation were performed via the pneumatic "rabbit" system. Samples and standards were loaded in the "rabbit", a plastic cylindrical container, which is propelled by air pressure through a tube system from the loading station to a position close to or within the reactor. They remain there for the desired time period, and are then rapidly removed from the reactor through a similar tube.

Ten seconds irradiation usually produced enough Mn activity for counting (for Mn-poor samples, such as calcareous ooze, 20 seconds irradiation was required). A few hours' cooling period is necessary before counting.

Table 3-1 gives information on isotopic abundance of stable isotopes, neutron capture cross-sections and neutron induced radionuclides of Au, Pd, Ir and Mn used in this study.

3-2-3. Analytical Procedures for Samples

Fig. 3-1 is a flow sheet of the chemical treatment for Au, Pd and Ir used in this work.

I) Au and Pd -----

i) Carrier:

Add 5 ml each of Au and Pd carrier solution to clean 25 ml zirconium crucibles (cleaned by Na_20_2 + Na0H fusion prior to each experiment). Carefully evaporate to dryness under an infra-red lamp.

ii) Fusion:

a) Transfer the irradiated sample powder quantitatively into the crucible. Add about 1 gm Na_20_2/100 mg sample and 0.5 gm Na0H/100 mg sample.

b) Put the crucibles over Meeker burners and heat with a low flame for 2-3 minutes. Then fuse in full blast for another 5 minutes. Swirl the crucibles twice to ensure that sample powder and carriers are completely dissolved and well mixed.

iii) Dissolution:

a) After cooling, dissolve the fusion cake in conc. $HN0_3$ carefully (first, slowly add small amount of distilled water to minimize the strong initial effervescence which results from sample reaction with acid).

Naturally occurring isotope	Isotopic abundance (%)	Thermal neutron cross section (barn)	Nuclide produced by (n, γ) reaction	Half - life	Radiation (MeV) measured in this work
Mn^{55}	100	13.3	Mn^{56}	2.58 hr.	γ :0.85, 1.81, 2.12
Pd^{108}	26.71	10.4	Pd^{109}	13.6 hr.	β :1.03
Ir^{191}	37.3	700	Ir^{192}	74.0day	γ :0.316, 0.47 0.30
Au^{197}	100	98.8	Au^{198}	2.7day	γ :0.412, 0.674

Table 3-1. Nuclear data for Mn, Au, Pd and Ir used in this work

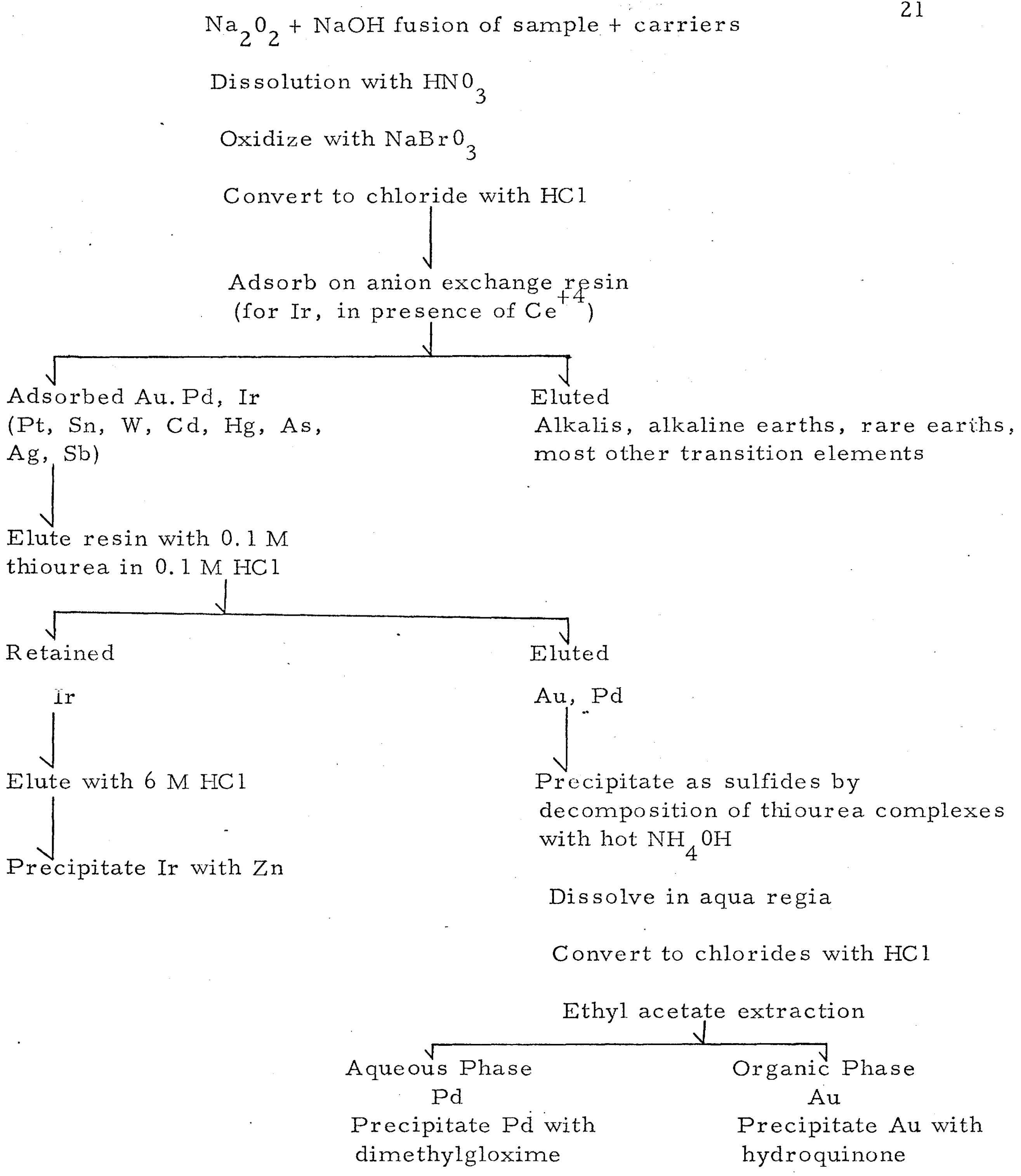

Figure 3-1. Generalized flow chart for Au, Pd and Ir analysis procedure

b) Transfer the solution to a 400 ml beaker, add 10 ml of 10 wt. % $NaBrO_3$ and evaporate to about 20 ml in volume (Ru which would otherwise contaminate the Ir sources is removed through distillation). Add 10 ml conc. HCl and evaporate to incipient dryness.

iv) Ion Exchange:

a) Filter the sample solutions through a Whatman No. 41 filter paper onto ion exchange columns which are made up with 1.75 x 0.8 cm of chromatographic grade Rexyn 201(Cl) resin and are pretreated with 120 ml of 0.5 M HCl before loading. Allow sample solutions to pass through columns at a rate of 1/2 ml per minute.

b) Wash through the column with 120 ml of 0.5 M HCl. Discard all the effluent to radioactive waste*

v) Elution of Au and Pd:

Au and Pd are eluted from the column with 120 ml of 0.1 M thiourea in 0.1 M HCl. Collect with elutate into a 400 ml beaker.

vi) Precipitation of Au and Pd Sulfides:

a) Warm the thiourea elutate on a hot plate, add 30 ml of conc. NH_4OH to decompose the thiourea and release $S^{=}$ ion precipitating Au and Pd sulfides.

b) Evaporate to a volume of 80 to 90 ml (excess evaporation of the thiourea will cause partial resolution of the sulfides). Centrifuge and wash the

---

*All procedures prior to this step were performed in the fume hood behind 2 inch thick lead brick shielding.

sulfide precipitates once with hot distilled water (use hot water only, otherwise precipitate becomes colloidal).

vii) Separation of Au and Pd:

a) Dissolve the sulfides in 5 ml aqua regia and convert to chlorides by two digestions with conc. HCl.

b) Take Au and Pd chlorides up in 15 ml of 6 M HCl and transfer into a 125 ml separatory funnel. Add 15 ml of ethyl acetate and shake for 2 minutes to extract Au into the acetate phase, leaving Pd in the HCl phase.

c) Drain the HCl phase into a fresh 125 ml separatory funnel, add another 15 ml of 6 M HCl to the Au-ethyl acetate fraction and shake for 2 minutes to remove traces of Pd. Add this Pd-HCl fraction to the original Pd solution.

d) Add 15 ml of ethyl acetate to the Pd solution and shake for another 2 minutes. Drain the Pd-HCl phase into a 25- ml beaker. Add the acetate to the original Au-acetate phase.

viii) Purification of Au:

a) Transfer the Au-acetate phase to a 100 ml beaker, add an equal volume of 2 M HCl and warm gently on a hot plate until the Au chlorides transfer to the aqueous phase and the acetate has been evaporated. Finally boil the solution for an additional 5 minutes to remove traces of acetate.

b) While the solution is still warm add about 1 gm of hydroquinone to reduce Au to the metal.

c) Transfer to a 50 ml centrifuge tube, centrifuge and discard the supernatant. Wash twice with H_20, slurry with alcohol, and transfer to a pre-weighed 1 dram pyrex vial. Place in a drying oven set at 80°C, dry and cool.

ix) Purification of Pd:

a) Evaporate the Pd-HCl phase from step (vii-d) to a volume of 3 to 4 ml. Dilute to 20 ml with distilled water and transfer to a 50 ml centrifuge tube.

b) Add 10 ml of 1.5 wt.% dimethylglyoxime in alcohol to precipitate Pd-dimethylgloximate. Centrifuge, decant the supernatant, wash twich with 25% ethanol.

c) Destroy the precipitate by heating with 1 ml of aqua regia on an electrical bunsen. Convert to chlorides by two digestions in conc. HCl, finally take up in 10 ml of 2 M HCl, add 10 ml of H_20.

d) Repeat the dimethylgloxime precipitation and ethanol washing.

e) Slurry the Pd precipitate with alcohol and plate out evenly on a pre-weighed aluminum planchet, dry under an infra-red lamp.

II) Ir -----

Step (i) to (iv) are essentially the same as for Au and Pd. The only difference is that after fusion and dissolution, the 0.5 M HCl used to take sample salts into solution (step iii-c) contains 0.004 moles of ceric ion per ml (prepared by dissolving 3.288 gm of $(NH_4)_2Ce(N0_3)_6$ in 1500 ml of 0.5 M HCl); also, the ion exchange column was treated with 50 ml of 0.5 M HCl containing

0.004 moles ceric ion per ml immediately prior to the introduction of the sample solution.

v) Elution of Ir:

a) Put 50 ml of 0.1 M thiourea in 0.1 M HCl through the column to remove Au and Pd and to reduce Ir^{+4} to Ir^{+3} (Ir^{+3} is only weakly adsorbed in strong HCl medium and can subsequently be eluted with 6 M HCl).

b) Wash the column with 20 ml of 0.1 M HCl. Elute Ir with 120 ml of 6 M HCl into a 400 ml beaker.

vi) Precipitation of Ir:

a) Evaporate the elutant to incipient dryness, add 5 ml aqua regia, again evaporate to incipient dryness. Treat twice with conc. HCl. Finally take up in 50 ml of 2 M HCl.

b) Place on a hot plate, heat to near boiling, and precipitate Ir by adding Zn powder to the solution slowly. Dissolve excess Zn with conc. HCl.

c) Transfer to 50 ml centrifuge tube, centrifuge, decant the supernatant and boil the precipitate with two ml of aqua regia for a few minutes. (In some clay samples where contamination at 0.6 MeV appeared in the Ir spectrum, probably due to 60-day Sb^{124}, samples were retreated with boiling aqua regia for a longer time.)

d) Wash twice with distilled water, slurry with alcohol and transfer to a pre-weighed 1 dram pyrex vial. Place in a drying oven set at 80°C, dry and cool.

III) Mn -----

i) After 10 seconds irradiation and 3 hours cooling, samples were transferred into pre-weighed 1 dram pyrex vials from the quartz ampoules. (actual sample weight can be obtained by weighing the vial+sample after counting).

ii) Put on the screw cap and seal with masking tape. The samples are then ready for counting.

3-2-4. Analytical Procedures for Standards

I) Au, Pd and Ir -----

i) Equilibration with Carriers:

a) Carefully clean the outside of the standard ampoules with boiling aqua regia. Pour the quartz powder from the ampoule into a 100 ml. beaker containing 5 ml each of Au, Pd and Ir carrier solution. Crack the ampoule open and add it to the beaker.

b) Add 10 ml of aqua regia, cover with a watch glass, digest gently on a hot plate for 20 minutes. Using a capillary pipette, ensure complete removal of precious metals from the inside of the ampoule by repeated washing with hot carrier solution.

c) Evaporate to incipient dryness, add another 10 ml of aqua regia and again evaporate to incipient dryness. Convert to chlorides by two treatment with conc. HCl, finally take up in 15 ml of 6 M HCl.

ii) Separation of Au from Pd and Ir:

a) Filter the standard solution into a 125 ml separatory funnel.

b) Add an equal amount of ethyl and shake for 2 minutes to extract Au into the acetate phase leaving Pd and Ir in the aqueous phase as described in the sample procedure (I-vii).

iii) Purification of Au:

Precipitate Au from ethyl acetate in the same manner as in sample procedure (I-viii).

iv) Separation of Pd and Ir:

a) Precipitate Pd from the 6 M HCl aqueous phase with dimethylglyoxime as in sample procedure (I-ix) and filter the supernatnat containing Ir into a 125 ml beaker.

v) Purification of Pd:

Same as described in procedure (I-ix) for samples.

vi) Precipitation of Ir:

Ir is precipitated from 2 M HCl solution by Zn powder as in sample procedure (II-vi).

II) Mn-----

i) After irradiation, transfer the standard aluminum foil strips into a one dram pyrex vial.

ii) Add a few drops of 6 M HCl to dissolve the foil slowly, make the final volume of the standard solution about the same as those of samples to provide similiar counting geometry.

iii) Put on the screw cap and seal with masking tape.

3-3. Counting and Calculations

3-3-1. Counting Equipment

I) Beta Counting -----

A low background Nuclear Chicago planchet counting system which includes a scaler-timer, an automatic sample changer, a gas flow geiger-Müller counting tube with anti-coincidence shielding (utilizing a gas mixture of 98.7 % helium and 1.3% butane), and a paper-tape printing lister, was used for beta counting. The whole system had an average background of 2 counts per minute.

Samples were loaded on aluminum planchets for counting. Machine drift was monitored by three uranyl acetate standards.

II) Gamma Counting -----

The Nuclear Chicago gamma counting system used in this work consists of i) solid state scintillation crystal; ii) high-voltage supply unit; iii) pre-amplifier; iv) amplifier; v) 1600 channel pulse hight analyzer; vi) display oscilloscope; and vii) teletype print out.

Au and Ir sources were counted on a 3" x 3" well-type NaI(Tl) crystal. For non-destructive gamma-counting of Mn, a 130 gm Ge(Li) crystal with 8 cm^2 active area facing the window was used.

3-3-2. Counting

I) Palladium -----

Palladium dimethylglyoximate was plated out and dried on an aluminum planchet as an even thin film. The activity of 13.6 hr. Pd^{109} was followed for at least three half-lives.

Errors due to self-absorption from differences in size of sources were not considered in this study because the chemical yield (mostly between 50 to 80%) of samples and standards were usually quite uniform within one experiment (slightly higher for standards).

II) Gold -----

The activity of γ-photons emitted by 2.7 day Au^{198} was measured on the NaI(Tl) crystal. Counts under the 0.412 MeV photopeak area were used to calculate the activity of Au^{198}.

III) Iridium -----

Using the NaI(Tl) crystal, gamma activity of 74.0 day Ir^{192} was counted. The area under 0.32 MeV photopeak was integrated to give the Ir^{192} activity.

IV) Manganese -----

The Ge(Li) crystal was used for non-destructive determination of Mn. Photopeaks of Cr^{51} (0.320 MeV), Cs^{137} (o.662 MeV), Zn^{65} (1.115 MeV) and Co^{60} (1.173 and 1.333 MeV) were used as the energy standards to determine the energy of the unknown peaks in the sample spectrum. Decay curves of unknown peaks were followed for several half-lives to ensure that the proper isotopic species were measured. The Mn photopeak at 0.847 MeV was used to calculate the activity of Mn^{56}.

The FWHM (Full Width at Half Maximum) of the .662 MeV photopeak of Cs^{137} is 6 KeV at the setting of the system used in sample counting.

3-3-3. Calculations

I) Activity Calculation -----

Gross beta activities of samples and standards can be read directly from the counter as counts per minute. A decay curve over at least 3 half-lives was established and sample and standard counting rates extrapolated to zero (or a common time) for the purpose of calculation. In a few cases, small amounts of long-lived impurity were recognized and a graphical correction was applied to the initial counting rates.

The half-peak area method was used to represent the γ-ray activities. The spectrum over a "window" of several channels was integrated over the full width at half maximum of a particular peak in the background subtracted to obtain the half-peak area. In calculating the half-peak area of the Mn^{56} photopeak in the spectrum of the whole sample, "background" was determined from the average activity of several channels on both sides of the peak in that particular spectrum. Here the "background" is largely due to the Compton plateaus from higher energy γ-photons.

II) Element Concentration Calculation -----

Element concentrations were obtained by comparing the specific activity of the element in the sample with that in the standards.

The following relation was used in the calculation:

$$C = \frac{M}{W} \cdot \frac{a_o}{A_o} \cdot 10^9$$

where

M = weight of the element in the standard.

W = weight of the sample irradiated.

a_o = specific activity of the sample at t_o.

A_o = specific activity of the standard at t_o.

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

CHAPTER FOUR

RESULTS

4-1. Precision and Accuracy

General factors such as variation in neutron flux, differential self-shielding between standards and samples, difference in conditions of counting sources, failure to equilibrate carrier and sample during chemical processing and other potential sources of error in determination of Au, Pd and Ir have been discussed by Skippen (1963), Chyi (1968) and Keays (1968).

Discussed below are some factors that should be considered in the present work:

4-1-1. Competing Reactions in Pd Determination

Nuclear reactions producing 13. 6 hr. Pd^{109} or 21. 0 hr. Pd^{112} from a nuclide other than Pd would affect the accurary of Pd determination. Crocket and Skippen (1966) investigated experimentally the possible interference from reactions Ag^{109} (n, p) Pd^{109}, Cd^{112} (n, α) Pd^{109} and U^{235} (n, f) Pd^{112}, Pd^{109}. Ag/Pd and Cd/Pd ratios required for one percent interference were found to be at least 10, 000/1 (much greater for Cd). From Pd values found in this study (average 6 ppb) and data for Ag (0. 11 ppm) and Cd (0. 42 ppm) in deep-sea clays (Turekian and Wedepohl, 1961), the Ag/Pd and Cd/Pd ratios in deep-sea clays are about 20 and 70 respectively. No significant interference from Pd produced by Ag or Cd is expected. On the other hand, they found that after 16 hours irradiation and 20 hours cooling, a U/Pd ratio of 180 in the sample would cause a one percent interference due to production of Pd isotopes by U^{235} fission. The average U content in deep-sea clays is around 3 ppm (Ku, 1965; Bertine et al., 1970). This gives a U/Pd ratio of 500 in deep-sea clay samples, which in turn would give rise to a two to three percent interference. Thus the Pd values reported in this work may suffer an average U fission interference of 2 to 3 percent.

4-1-2. Non-destructive Determination of Mn

In the present work, Mn^{56} activities were measured directly from the gamma spectrum of the neutron activated samples. The main difficulty in non-destructive counting techniques is the interference caused by the presence of other gamma-emitting nuclides. The recent development of high-resolution lithium-drifted germanium Ge(Li) crystals (Tavendale and Ewan, 1963) makes a large improvement in instrumental activation analysis. The principal advantage of Ge(Li) detectors is their much higher resolution as compared to the NaI(Tl) scintillation detectors commonly used for gamma ray spectrometry. The FWHM of the peak produced by the 0.662 MeV γ-ray from Cs^{137} is less than 2 KeV under very favourable conditions with Ge(Li) detectors whereas it is typically about 50 KeV for NaI(Tl) (Hollander, 1966).

Typical spectra for a clay sample and an aluminum foil standard recorded with the Ge(Li) detector at different time intervals (30 minutes, 3 hours and 24 hours) after the end of 10 seconds of irradiation are shown in Fig. 4-1 and Fig. 4-2.

Photopeak produced by the 0.847 MeV γ-photon from Mn^{56} was used to calculate the neutron induced activity of Mn^{56} in each sample. Possible interference from gamma rays with similiar energy emitted by other nuclides after short periods of irradiation (10 seconds) are 0.834 MeV γ-photon of 9.5 minute Mg^{27} and 0.842 MeV γ-photon of 9.3 hr. Eu^{152m}. From Mn values found in this study (average 0.5%) and data for Mg (2.1%, Turekian and Wedepohl, 1961) and Eu (2ppm, Haskin and Gehl, 1962) in deep-sea clays, the activity ratios of Mg^{27}/Mn^{56} and Eu^{152m}/Mn^{56} at 0.85 MeV peak area after 10 seconds irradiation and 3 hours cooling period were calculated to be 2×10^{-7} and 2×10^{-3} respectively. Hence, at the time of counting (3 hours after the end of 10 seconds irradiation) activity due to Mg^{27} will have essentially died out and activity from Eu^{152m} may contribute a maximum of 0.2% to the Mn^{56} activity. At the time of counting the only important photopeaks other than Mn^{56} are those produced by the γ-photons from 15.0 hr. Na^{24} which will not interfer in the Mn determination. The 0.847 MeV photopeak of Mn^{56} is therefore relatively free from interference from other nuclides and is thus used to calculate the activity of Mn^{56} in the sample. Mn produced by the reaction $Fe^{56}(n,p)\,Mn^{56}$ is considered negligible (Brunfelt and Steinnes, 1966).

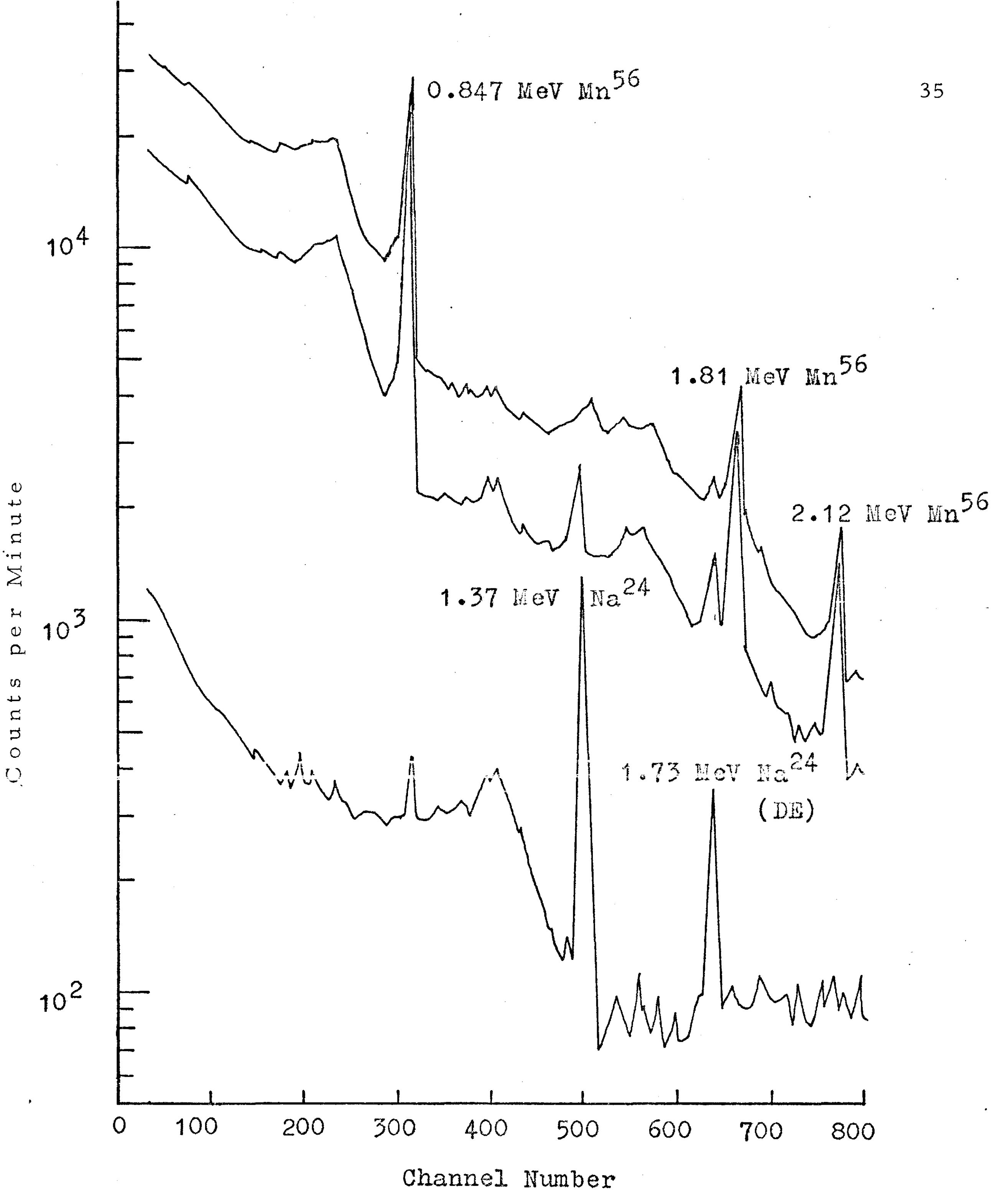

Figure 4-1. Typical gamma-ray spectrum from a clay sample recorded by Ge(Li) detector at 3 minutes, 3 hours and 24 hours after the end of 10 seconds irradiation.

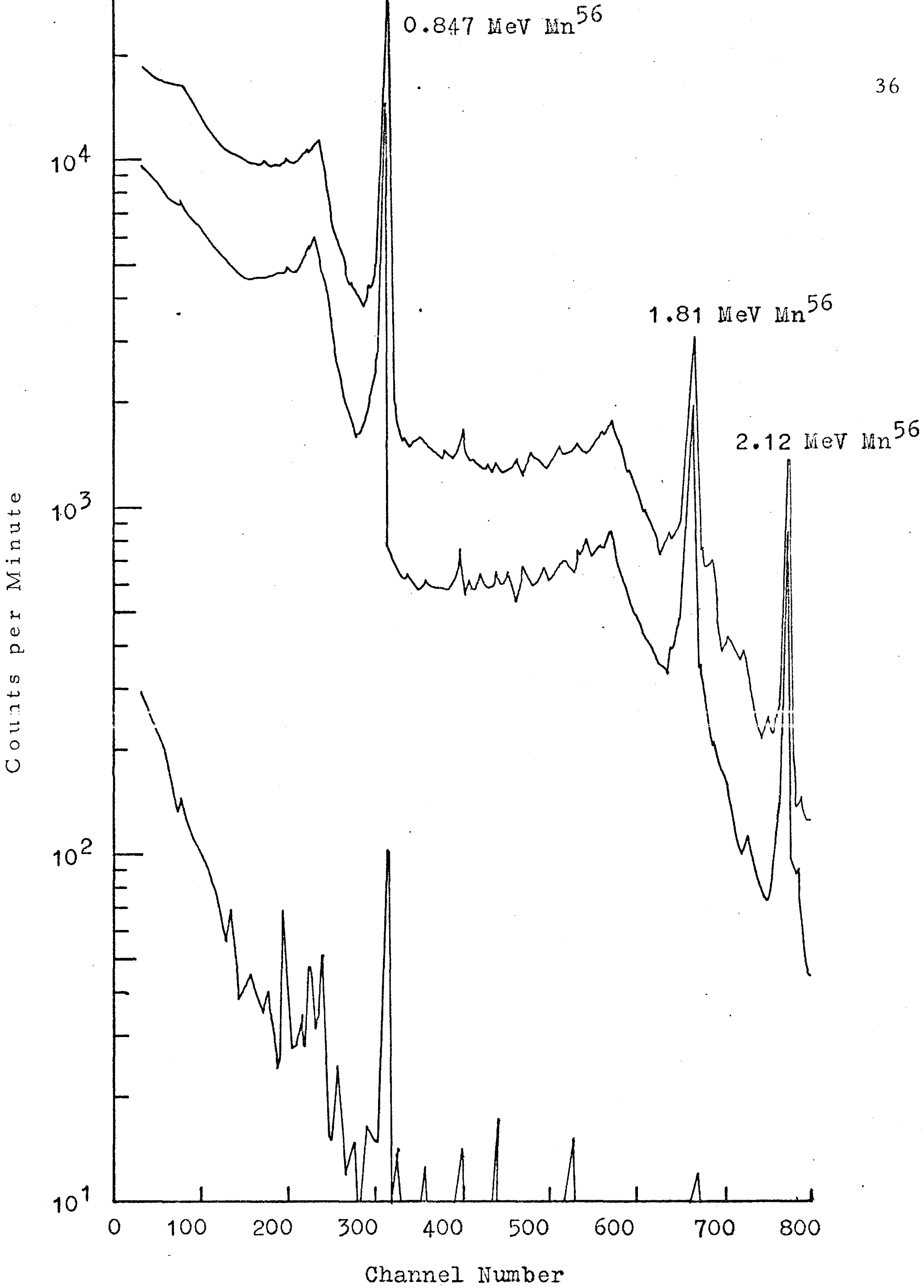

Figure 4-2. Typical gamma-ray spectrum from an aluminum foil standard recorded by Ge(Li) detector at 3 minutes, 3 hours and 24 hours after the end of 10 seconds irradiation

4-1-3. Sample Inhomogeneity

Relatively low precision in replicates for activation analysis of precious metals in rock samples are generally encountered. Sample inhomogeneity is often considered responsible. Fritze and Robertson (1968) gave evidence that the trace quantities of Au in G-1 and W-1 standard rocks are not homogeneously distributed by analyzing eight equal aliquots of samples split from one irradiated powder sample. They suggested that there is evidence for one mineral in the rock samples that contains a relatively constant amount of Au and is homogenously distributed. In addition, there exists one or more Au containing minerals which show a strong tendency towards segregation. This would lead to a relatively constant "base level" Au abundance with sporadically occurring higher abundances in those aliquots of the powder sample which contain the Au-rich aggregates.

Ehmann et al. (1970) performed a similar precision study on the Ir distribution in a powdered meteoritic sample using a non-destructive coincidence counting technique and found the situation is the same for Ir in meteorite as that of Au in standard rocks. They concluded that sample inhomogeneity may be responsible for the low precision of their analytical results.

For Au, Ir and other strongly siderophilic elements "true value" of elemental content of samples may not be identical for different irradiation where only a small aliquot of the whole sample is taken for analysis. Under this condition the precision of replicates on an inhomogeneous sample reveals not only the reproducibility of the analytical method but also the degree of inhomogeneity of the sample with regard to the distribution of the element. Au, Pd and Ir concentrations in standard rocks G-1 and W-1 have been reported by many authors (Crocket and Skippen, 1966; Baedecker and Ehmann, 1965; Shcherbakov and Perezhogin, 1964 etc.). Yet, the variation of the analytical results do not qualify G-1 and W-1 as absolute standards for precious metals. This is presumably due to the difficulty of the analysis of these elements at such low concentration levels and the inhomogeneity of the samples.

No attempt to analyse standard rock for Au, Pd and Ir was made in this work. Duplicate analyses of more than half of the analysed samples were performed to check the reproducibility of the present work. All replicates were run in separate irradiations except for C-14 and C-15 from core P6304-9. Average coefficients of variation (coefficient of variation is calculated as the percentage standard deviation with respect to the average value for each sample) for samples analysed in replicate are: 22% for Au; 13% for Pd; 28% for Ir.

Precision and accuracy for the determination of Mn by non-destructive gamma-counting method was checked by analyses of the standard rock W-1. The results obtained were 1362, 1344 and 1242 ppm (average 1316 ± 65 ppm) which agree well with the accepted value of W-1, 1320 ppm (Fleisher, 1969).

4-2. Analytical Results

The analytical results for samples from each core are shown in Table 4-1 to 4-4 and Fig. 4-3 to 4-6.

4-3. Elemental Correlations

The correlation matrices between Au, Pd, Ir and Mn in each core were calculated using the Control Data 6400 computer. The correlation coefficients for various pairs of elements at the 95% confidence level are presented in Table 4-5 to 4-8.

No strong positive inter-element correlation is apparent. Moderate correlation is observed between Pd-Mn in core 13-3. This is probably caused by a unique condition in this core (see description in paragraph 2-3), where, as pointed out by Chave and Mackenzie (1961) fluctuation in the concentration of one major constituent (biogeneous silica in this case) results in positive correlation coefficients between mineralogically unrelated elements because they are both negatively correlated with this major constituent.

No inter-element association between Ir-Mn exists in any of the cores.

Table 4-1 Analytical results of Caribbean core P6304-9 (calcareous ooze)

Bulk sample:

Sample Number	Interval (cm)	Au (ppb)		Pd (ppb)		Ir (ppb)		Mn (%)
		Result	Average	Result	Average	Result	Average	
C-01	19-20		3.48		1.86	0.31,0.76,0.82	0.63	0.0915
C-02	86-87		3.30		1.59	0.39,0.20,0.19	0.26	0.1419
C-03	318-319	2.38,1.43,1.53	1.78		1.25	0.24,0.45	0.33	0.1268
C-04	398-399		3.03		1.93	0.47,0.18,0.22	0.29	0.2935
C-05	528-529		1.38	1.35,2.34	1.85	0.16,0.16	0.16	0.1379
C-06	608-609	1.91,2.00	1.96	1.94,1.98	1.96	0.48,0.20	0.33	0.2569
C-07	762-763	3.32,1.52	2.42	1.46,1.89	1.68	0.34,0.15	0.25	0.1061
C-08	822-823		1.13		1.38	0.42,0.35	0.39	0.3516
C-09	948-949		3.96		2.77	0.18,0.33	0.26	0.1274
C-10	975-976		3.08		1.74	0.44,0.23	0.32	0.3189
C-11	1034-1035	0.69,1.08,1.46	1.53	1.51,1.04	1.28	0.27,0.34	0.31	0.1091
C-12	1128-1129		0.94	1.35,1.37	1.36	0.44,0.19	0.32	0.2167
C-13	1198-1199	1.15,1.43	1.29		2.54		0.17	0.1237
C-14	1302-1303	1.39,1.39	1.39	1.62,1.76	1.69		0.55	0.3843
C-15	1368-1369	1.81,1.94	1.88	2.03,1.69	1.86		0.49	0.1002
Average		2.17±0.92		1.78±0.43		0.34±0.13		0.1924± 0.1018

Table 4-1 continued/

Less than 20 micron fraction (core P6304-9):

C-12	1128-1129	3.96	1.78	0.28	-
C-13	1198-1199	2.21,4.38 3.30	3.51,4.78 4.15	0.20	-
C-14	1302-1303	5.26	4.04	0.79	-
C-15	1368-1369	2.49	1.97	0.55	-
Average		3.75	2.99	0.46	-

Greater than 150 micron fraction (P6304-9):

C-09	948-949	5.64*	3.13*	0.16	-
C-10	975-976	1.17	0.72	0.10	-
C-11	1034-1035	0.29	0.55	0.07	-
C-12	1128-1129	0.83	0.52	-	-
Average		0.76	0.60	0.11	-

*These two values were excluded when calculating the average

-not determined

Figure 4-3. Elemental concentrations in core P6304-9

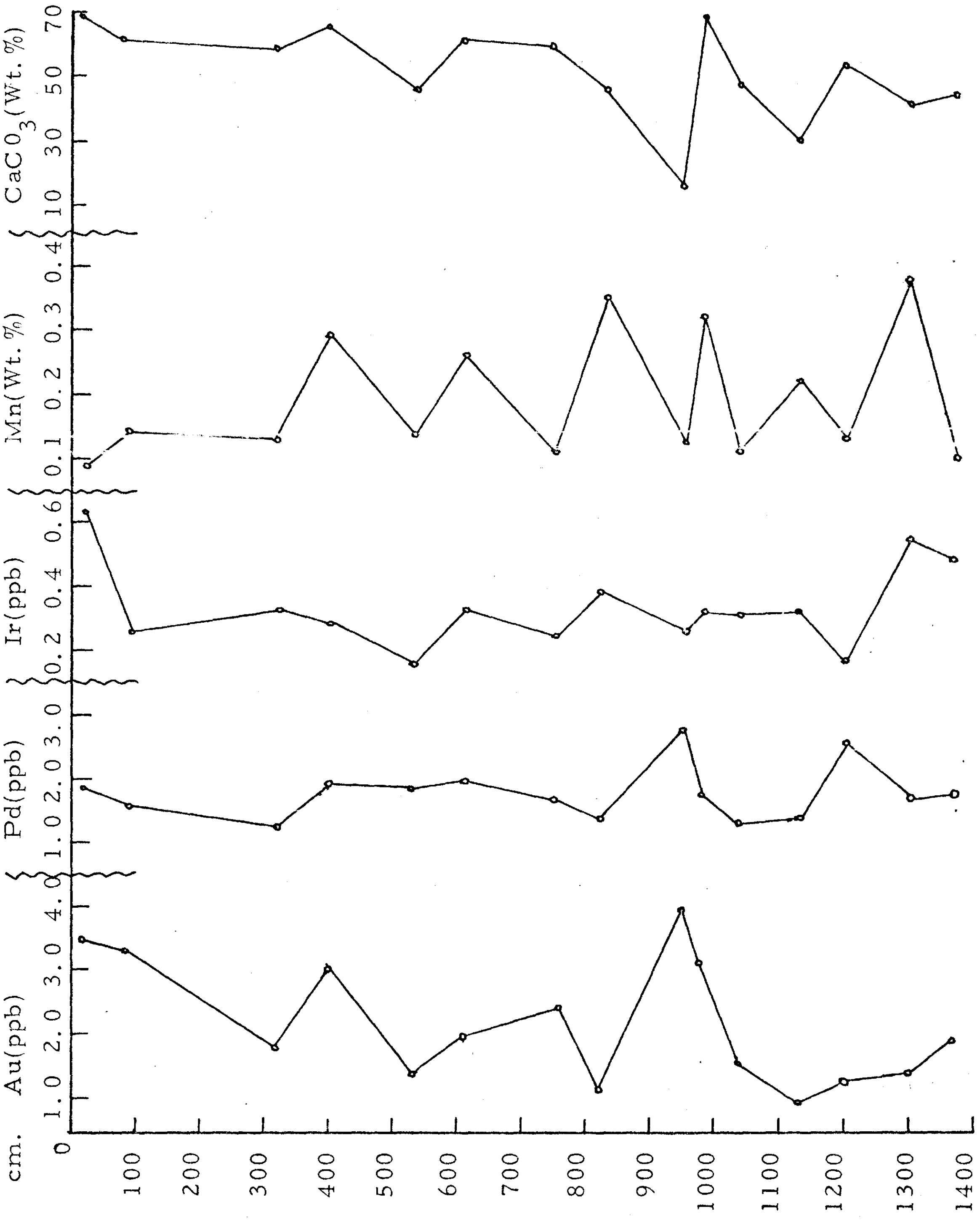

Table 4-2. Analytical results of U.S.N.S. ELTANIN core 21-17
(Globigerina ooze)

Bulk Sample

Sample Number	Interval (cm)	Au (ppb)		Pd (ppb)		Ir (ppb)		Mn(ppm)
		Result	Average	Result	Average	Result	Average	
21-17-1	0-125		1.04		1.34	0.09,0.13	0.11	212
21-17-2	125-200		0.63		1.56	0.25, 0.15	0.20	94
21-17-3	200-275		1.09		2.53	0.51,0.27	0.39	85
21-71-4	275-325		1.19		1.83	0.11,0.31	0.21	88
21-17-5	325-400		2.29		1.10	0.20,0.25	0.23	70
21-17-6	500-600		0.87		1.76	0.16,0.16	0.16	77
21-17-7	600-750		0.98		1.35	0.27,0.34	0.31	68
21-17-8	750-950		1.85		1.72	0.68,0.74	0.71	78
21-17-9	950-1006		0.57		0.76	0.35,0.30	0.33	93
Average		1.16 ± 0.56		1.55 ± 0.50		0.29 ± 0.18		96 ± 44

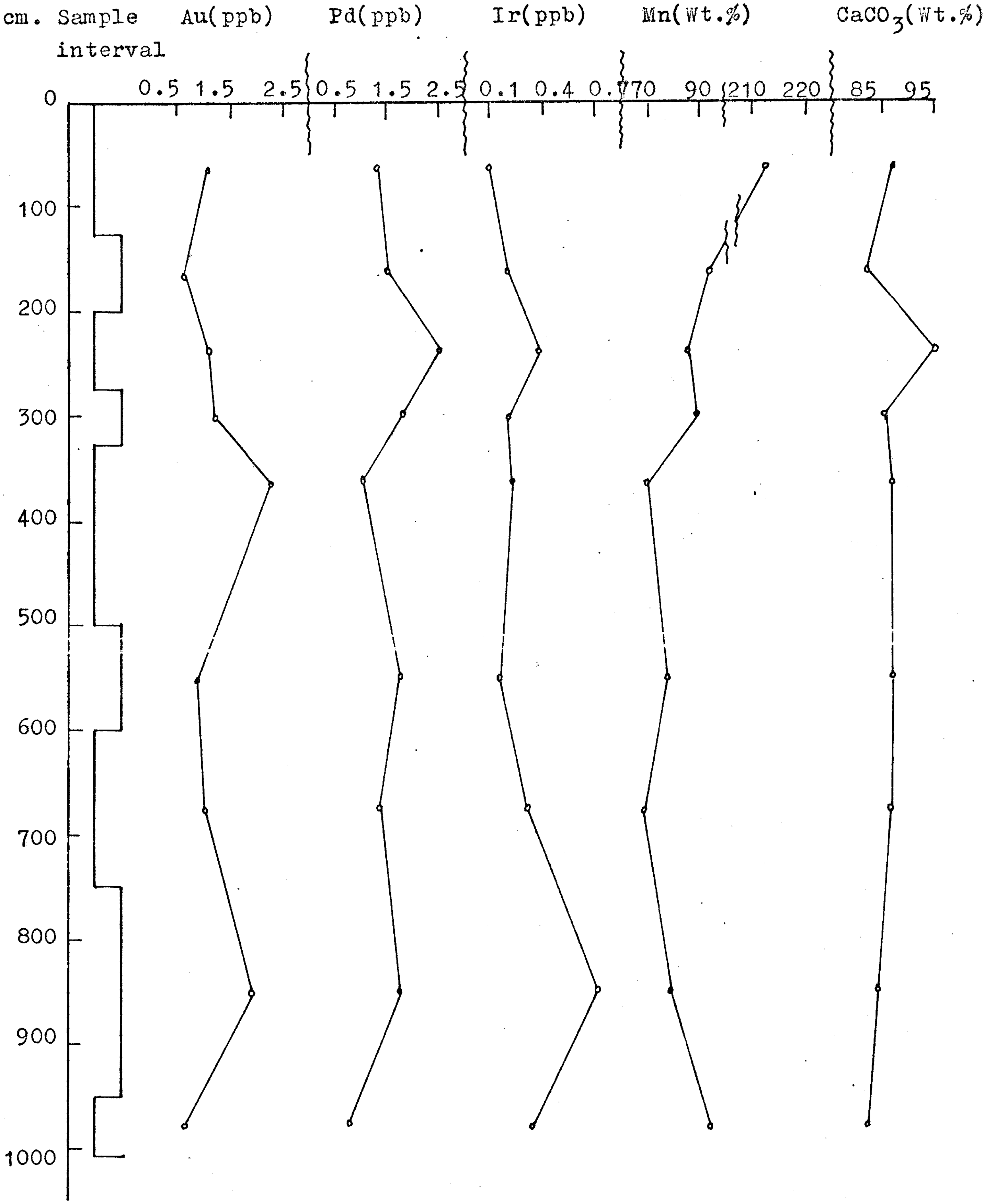

Figure 4-4. Elemental concentrations in core E21-17

Table 4-3 Analytical results of U.S.N.S. ELTANIN core 13-3 (siliceous ooze)

Bulk Sample

Sample number	Interval (cm)	Au (ppb)		Pd (ppb)		Ir (ppb)		Mn (%)
		Result	Average	Result	Average	Result	Average	
13-3-1	0-225	1.42, 1.59	1.51	4.35, 4.18	4.27	0.18, 0.13	0.16	0.3839
13-3-2	225-605	0.74, 0.79	0.77	5.95, 4.69	5.32	0.24, 0.14	0.19	0.3985
13-3-3	605-655	0.66, 1.24	0.95	5.45, 6.16	5.18	0.20, 0.23	0.22	0.4248
13-3-4	655-865		1.01		6.91	0.59, 0.67	0.64	0.3974
13-3-5	865-1115	0.48, 0.59	0.54		7.72	0.20, 0.16	0.18	0.4421
13-3-6	1025-1125	0.57, 0.69	0.63		8.96	0.24, 0.21	0.22	0.5257
13-3-7	1125-1280	0.57, 1.05	0.81		8.72	0.18, 0.25	0.22	0.4693
13-3-8	1280-1440	0.45, 0.71	0.58	8.42, 8.10	8.26	0.26, 0.30	0.28	0.5767
13-3-9	1440-1600	0.84, 0.80	0.82		11.27	0.23, 0.26	0.25	0.5211
Average		0.87 ± 0.30		7.47 ± 2.16		0.26 ± 0.15		0.4599 ± 0.0704

Figure 4-5. Elemental concentrations in core E13-3

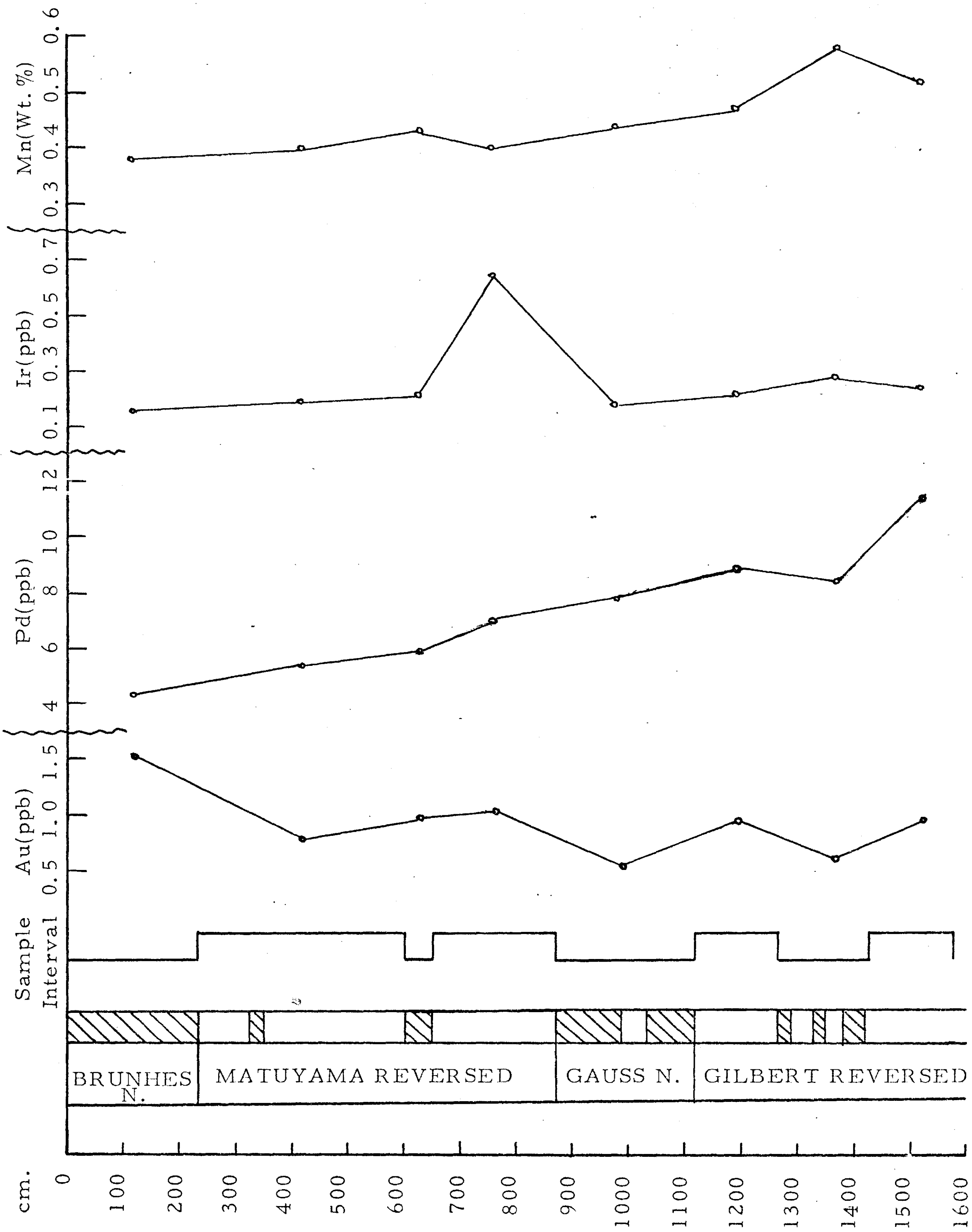

Table 4-4 Analytical results of U.S.N.S. ELTANIN core 17-10 (pelagic clay)

Bulk Sample

Sample Number	Interval (c m)	Au (ppb)		Pd (ppb)		Ir (ppb)		Mn (%)
		Result	Average	Result	Average	Result	Average	
17-10-1	0-400		1.48		3.64		0.42	0.4196
17-10-2	400-800		2.30		6.88		0.31	0.4266
17-10-3	800-1400		1.75		5.70		0.22	0.3596
17-10-4	1400-1585		1.00		5.44		0.42	0.3406
Average		1.63 ± 0.54		5.42 ± 1.34		0.34 ± 0.10		0.3866 ± 0.0440

Less than 2 micron fraction (E17-10):

17-10-1	0-400		1.85		4.08		0.33	0.4345
17-10-2	400-800		1.42		2.02		0.30	0.3748
17-10-3	800-1400		1.15		3.07		0.34	0.1979
17-10-4	1400-1585		0.98		2.85		0.35	0.1232
Average		1.35 ± 0.38		3.01 ± 0.85		0.33 ± 0.02		0.2826 ± 0.1462

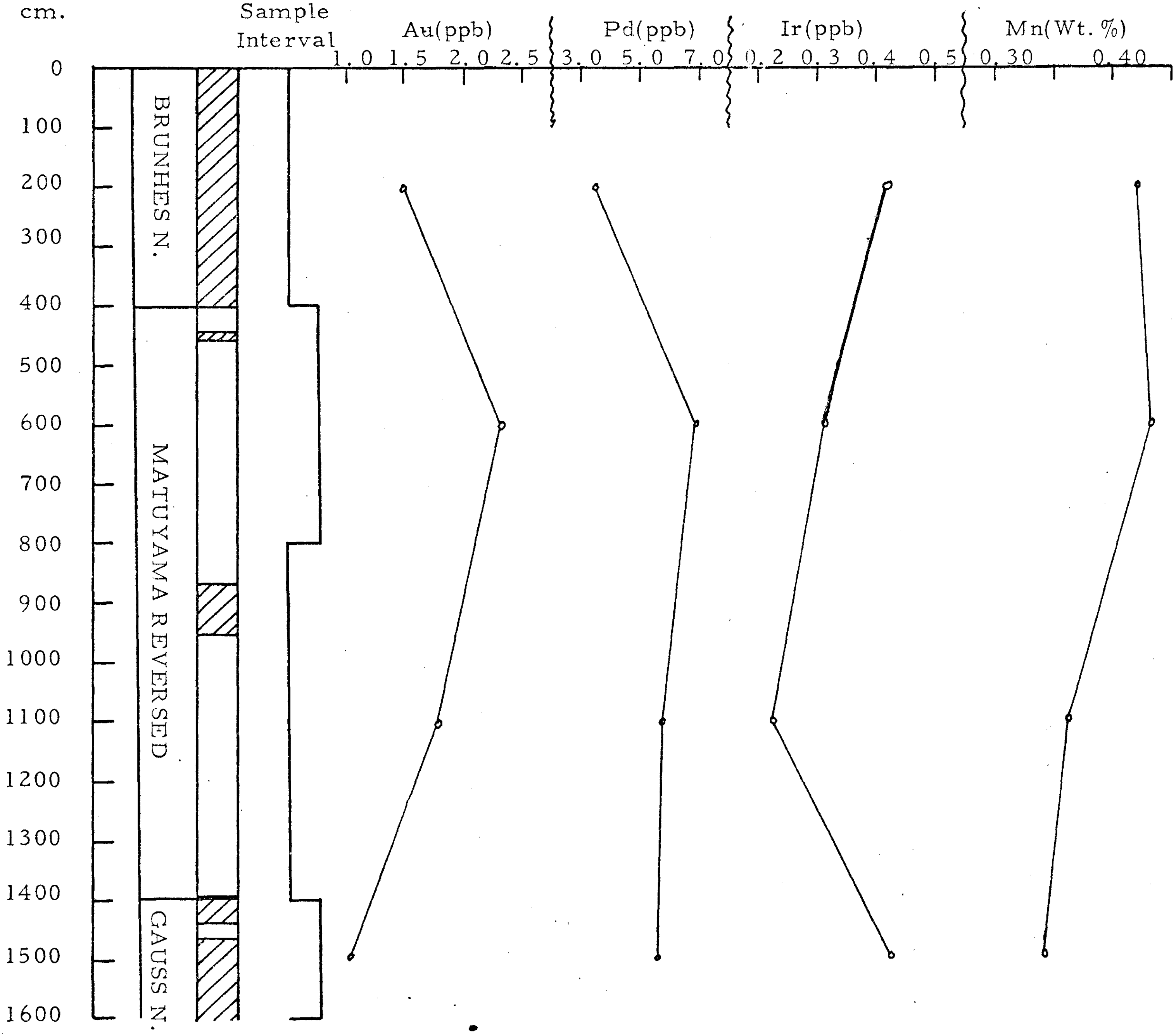

Figure 4-6. Elemental concentrations in core E17-10

	Au	Pd	Ir	Mn
Au	1.000			
Pd	0.428	1.000		
Ir	0.082	-0.230	1.000	
Mn	-0.199	-0.182	0.204	1.000

Table 4-5. Correlation coefficient for Au, Pd, Ir and Mn in core P6304-9 (calcareous ooze)

	Au	Pd	Ir	Mn
Au	1.000			
Pd	0.004	1.000		
Ir	0.364	0.206	1.000	
Mn	-0.210	-0.139	-0.399	1.000

Table 4-6. Correlation coefficient for Au, Pd, Ir and Mn in core E21-17 (Globigerina ooze)

	Au	Pd	Ir	Mn
Au	1.000			
Pd	-0.588	1.000		
Ir	0.077	0.069	1.000	
Mn	-0.633	0.772	-0.130	1.000

Table 4-7. Correlation coefficient for Au, Pd, Ir and Mn in core E13-3 (siliceous ooze)

	Au	Pd	Ir	Mn
Au	1.000			
Pd	0.581	1.000		
Ir	-0.616	-0.561	1.000	
Mn	0.681	-0.051	0.080	1.000

Table 4-8. Correlation coefficient for Au, Pd, Ir and Mn in core E17-10 (pelagic clay)

CHAPTER FIVE

DISCUSSION

5-1. Previous Work

Platinum metals belong to group VIII in the periodic table. They are strongly siderophile in character, often occur in nature as pure metals and alloys, but may also exhibit chalcophilic tendency and combine with sulfur, tellurium, bismuth and arsenic. In the presence of coexisting metal and sulfide phases, they enter the former preferentially (Ehmann, 1970). In the case of coexisting sulfides and silicates, they tend to be concentrated in the sulfide phase (Crocket, 1969) indicating their weak lithophilic character. Owing to these characteristics, the platinum metals are found relatively enriched in meteorites. In the earth they are probably enriched in the Ni-Fe core and hence depleted in the lithosphere.

Gold is a member of group IB in the periodic table. Since Au forms ions with a partly filled d electron shell, its chemical behavior is, on the whole, quite similar to that of other transition elements. Au is treated as the third transition series element with some members of the platinum metals. With reference to its manner of occurrence in nature, Au resembles the siderophilic platinum metals and is found predominantly as the pure metal and alloys, or often as selenides and tellurides.

Because of the low abundances of these metals in natural materials, most of the classical analytical methods are plagued with problems of reagent and laboratory contamination at low concentration level. Brown and Goldberg (1949) and Goldberg and Brown (1950) were the first to use the neutron activation technique to determine Au and Pd contents in meteorites. Since then, activation analysis has been widely applied to the direct determination of many noble metals in geological materials with higher sensitivity and better reliability.

By now, considerable information on the distribution of precious metals in meteorites and terrestrial igneous rocks is available. Summaries of some recent determinations of Au, Pd and Ir in meteorites (Table 5-1) and silicate rocks (Table 5-2) are presented below:

Au, Pd and Ir abundances in meteoritic material, except achondrites, are mostly in the range of 0.1 to 10 ppm and are 3 to 4 orders of magnitude higher than in terrestrial rocks. Various studies on meteorites have shown that virtually the entire noble metal content of the ordinary chondrites is in their free metal phase (Fouche andSmales, 1967; Ehmann et al,. 1970) and that strong positive correlation exists between Ir and Os in the Irons (Herpers et al., 1969; Crocket, personal communication).

Au and Ir are enriched in lunar surface fragmental material (Apollo 11, types C and D lunar material, breccia and soil respectively) relative to lunar rocks (Apollo 11, types A and B). Keays et al. (1970) attribute this enrichment to meteoritic and cometary matter. They

Table 5-1. Average Au, Pd and Ir concentrations (ppm) in meteorites

	Class	Au[1]	Pd[2]	Ir[2]
Irons	Octahedrites	1.3(92)[3]	3.8(85)	3.4(65)
		0.43-8.7[4]	1.6-9.3	0.01-18.6
	Hexahedrites	0.67(17)	2.1(22)	12.5(17)
		0.43-1.2	1.4-3.7	0.03-59
Chondrites	Ce	0.33(8)	0.88(6)	0.62(7)
		0.13-0.41	0.67-1.9	0.54-0.70
	Ch	0.21(9)	1.04(15)	0.82(15)
		0.14-0.29	0.72-1.5	0.39-1.5
	Cl	0.15(8)	0.72(16)	0.47(34)
		0.10-0.19	0.44-1.65	0.13-0.63
	Cc	0.16(8)	0.60(7)	0.55(8)
		0.10-0.23	0.33-0.79	0.38-0.69

1. Data from Jones (1969) and Ehmann *et al.* (1970).
2. Data from complication by Crocket (1969) together with that of Ehmann *et al.* (1970), Herpers *et al.* (1968), Rider and Wänke (1968), Kimberlin *et al.* (1968), Tander and Wasson (1968).
3. Figure in parentheses is the number of meteorites analysed.
4. Range of Values.

Table 5-2. Average Au. Pd and Ir concentrations (ppb) in terrestrial and lunar samples*

Sample		Au	Pd	Ir
Basic rocks including basalt, diabase, gabbro and andesite		4.5(26)[1]	6 (26) [2,3,4,5]	2 (10)[5,6]
Ultrabasic rocks including garnet peridotite and eclogite inclusions		6.2(13)[1,7]	13 (3) [2,7]	3 (5) [6,7]
Granite		7.1 (20)[1]	1.6 (G-1)[5]	0.044 (G-1)[5]
Deep-sea sediments including pelagic clay, calcareous and siliceous ooze		2.7(28)[4,8,9,10,11]	4.4(28)[4,8,9,10,11]	0.32(15)[8,9,10,11,12]
Lunar rock (Apollo 11)	A, B types	0.041[14]	3.8[13,14]	0.066[14]
	C, D types	2.95[14]	9.50[14]	7.59[14]

* Figure in parentheses is the number of samples analysed. For deep-sea sediments it is the number of cores analysed.

References for Table 5-2:

1. Jones, R. (1969) U.S.G.S. Cir. 610, 28p.
2. Crocket, J. and Skippen, G. (1966) Geochim. Cosmochim. Acta., v. 30, p. 129.
3. Grimaldi, F. and Schnepfe, M. (1967) U.S.G.S. Prof. Paper 575-C, p. C141.
4. Vincent, E. and Smales, A. (1956) Geochim. Cosmochim. Acta, v. 9, p. 761.
5. Crocket, J., Keays, R. and Hsieh, S. (1968) J. Radioanal. Chem., v. 1, p. 487.
6. Ehmann, W., Baedecker, P. and McKown, D. (1970) Geochim. Cosmochim. Acta, v. 34, p. 493.
7. Chyi, L. (1968) M.Sc. Thesis, McMaster University.
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9. Morgan, J. (1965) Anal. Chim. Acta, v. 32, p. 8.
10. Macdougall, J. (1968) M.Sc. Thesis, McMaster University.
11. This work.
12. Bate, G. and Huizenga, J. (1963) Geochim. Cosmochim. Acta, v. 27, p. 345.
13. Smales, A. et al. (1970) Science, v. 167, p. 509.
14. Keays, R. et al. (1970) Science, v. 167, p. 490.

estimated an influx rate of 0.0029 mg/cm^2/1000 yr on the lunar surface.

Work of DeGrazia and Haskin (1964), Shcherbakov and Perezhogin (1964), Vincent and Crocket (1960) all show that Au in a wide variety of rock types exhibits only small concentration ranges. DeGrazia and Haskin suggested that finely divided gold remains chemically inert during most geochemical processes and the tiny particles tend to remain suspended in melts or solutions.

Crocket and Skippen's work (1966) on basalts demonstrated that oceanic basalts are quite uniform and relatively low in Pd content (average 1.9 ± 1.2 ppb) while continental plateau basalts are characterized by distinctive and different Pd contents (range from 0.45 to 29 ppb with an average of 8.5 ppb).

Keays and Crocket (1970) analysed sulfide mineral samples from Sudbury Nickel Irruptive, Canada for Ru, Pd, Os, Ir and Au. They found a marked geochemical coherence of Ru-Os-Ir in this deposit and showed that the fractionation and mineral partition trends of these metals were in marked contrast with those of Au and Pd.

In general, not enough samples have been analysed to evaluate the extent of fractionation of precious metals between major rock types. However, the considerably lower Ir content in granite G-1 relative to either basic or ultrabasic rocks suggests a significant fractionation between the earth's crust and mantle. Pd is not greatly different in G-1 than in basic rocks and Au, for which adequate data are available, is not strongly fractionated between acidic, basic and ultrabasic rocks. The very tentative picture to emerge suggests that Au and Pd are relatively unfractionated between acidic and basic-ultrabasic rocks in contrast to Ir which is markedly depleted in granitic rocks.

Reliable precious metal data for sedimentary rocks and recent sediments are limited to a very few analyses. Table 5-3 lists some recent determinations of Au, Pd and Ir in marine deposits. The very limited data suggests that the spread of Au and Pd concentrations in different types of sediments from widely separated localities are fairly narrow and are within the general concentration range found in most crustal rocks. Ir is most depleted in sediments relative to meteoritic materials. Au and Pd in marine manganese nodules are similar to those in pelagic sediments, while the sediments are depleted in Ir by a factor of 50 relative to the marine nodules.

5-2. Sources of Precious Metals in Deep-sea Sediments

Arrhenius (1963) defines pelagic sediments as those marine sediments in which the fraction derived from the continents indicates deposition from a dilute mineral suspension with a relatively slow rate of deposition. The composition of sediment at any given place is the resultant of a group of relatively independent processes. The components of pelagic sediments can be classified, according to their sources, as biogenous, cosmogenous,

Material		Au	Pd	Ir	Reference
Argentine Basin core (depth in core)	100 cm	2.6	-	≤ 1.4	Baedecker and Ehmann (1965)
	355 cm	-	-	≤ 0.012	
	675 cm	2.1	-	≤ 0.033	
	1024 cm	3.0	-	≤ 0.14	
Mid. Pacific core (depth in core)	12-16 cm	-	-	≤ 0.030	
	56-60 cm	9.0	-	≤ 0.073	
	214-218 cm	-	-	not detected	
	369-373 cm	-	-	not detected	
Central Pacific pelagic sediments (5)*		-	-	0.16	Barker and Anders (1968)
Antarctic pelagic sediments (3)		3.2	2.1	< 0.1	Crocket *et al.* (1968)
Arctic nearshore sediments (9)		2.1	2.7	< 0.1	
East Pacific Rise sediments (14)		5.2	3.1	< 0.1	
Pacific calcareous ooze (1)		1.7	1.8	-	
Oceanic manganese nodules		2.91(19)	5.29(19)	8.52(16)	Harriss *et al.* (1968)
Freshwater manganese concretions (2)		0.38	0.05	< 0.1	

* Figure in parentheses is the number of samples analysed.

Table 5-3. Summary of recent determinations of Au, Pd and Ir in marine deposits (ppb) hydrogenous and lithogenous (Goldberg, 1954). Biogenous components are remnants of organisms; cosmogenous components are materials of extraterrestrial origin; authigenic minerals precipitated from sea water are classified as hydrogenous and the lithogenous contribution to sediments is defined as rock debris derived from terrestrial erosion, submarine volcanism and underwater weathering. The relative importance of these sources in regard to the precious metal content of deep-sea sediments is discussed below:

5-2-1. Biogenous Components

The most important components of the biogenous fraction of deep-sea sediments are calcium carbonate (mainly from shell remnants of Foraminifera, coccolithophorids and petropods) and silicon dioxide (mainly from diatoms and radiolaria). The extraction of certain trace metals by living plankton in surface waters, may with subsequent sinking after death, lead to an increase of the metal content of bottom sediments.

Comparison of the precious metal content of the greater than 150 micron fraction (mainly tests of Globigerina) of three calcareous ooze samples from core P6304-9 with that of the bulk sample (Table 4-1) suggests that carbonate shells are depleted in precious metals. The carbonate content of samples collected from calcareous oozes P6304-9 and E21-17 were determined in this work. Plots of $CaCO_3$ versus precious metal content (Fig. 5-3) also suggest negative correlations.

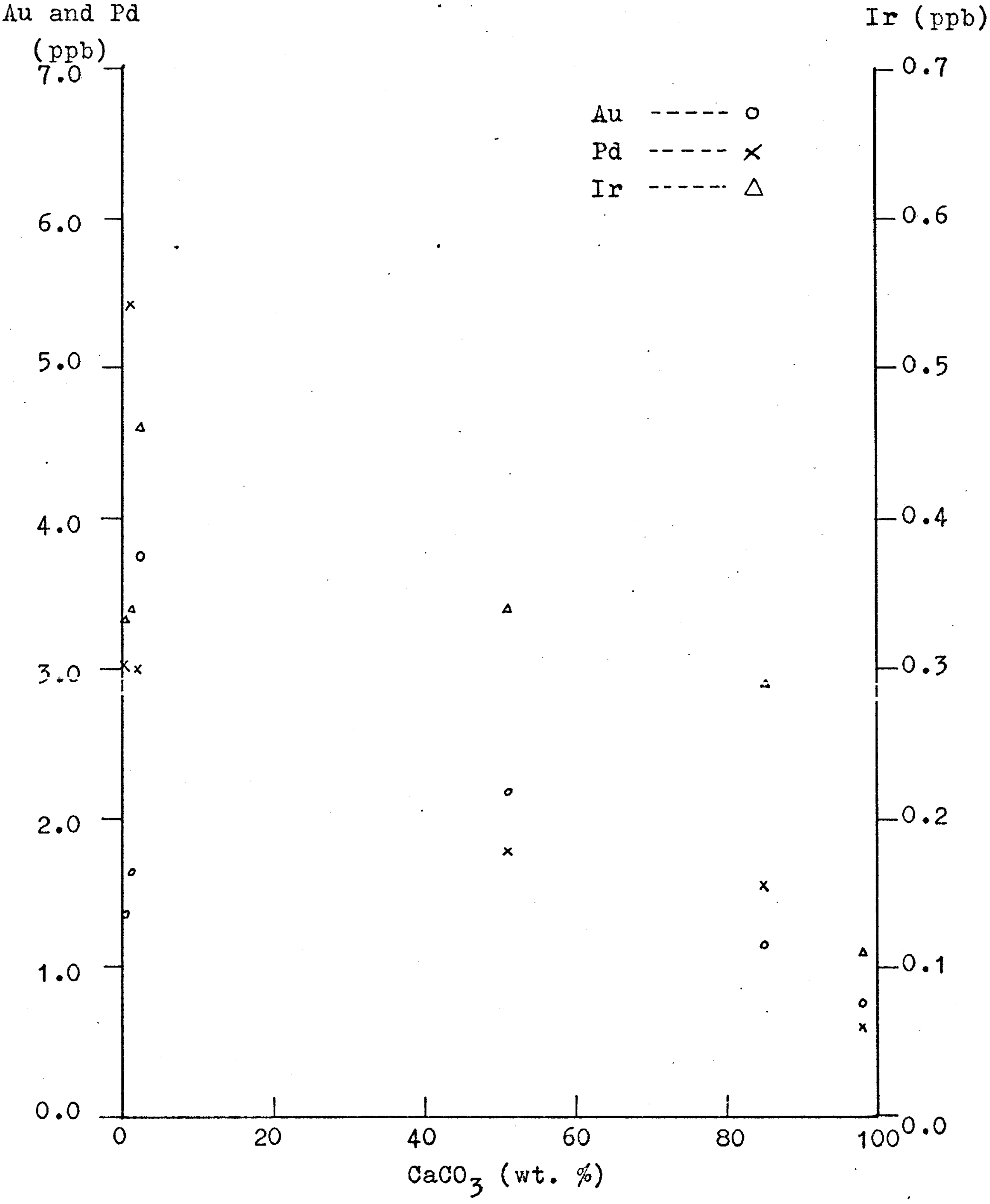

Figure 5-3. Relations of Au, Pd and Ir with carbonate content for core samples

Some diatom species are found to have concentrate iron and cobalt in their body tissues (Vinogradov, 1953).

No information concerning the precious metal contens of the biogenic siliceous phase is available. The precious metal concentrations in samples from the siliceous ooze core E13-3 do not show any significant enrichment compared to other types of sediments. In core E13-3, samples collected from the upper 1000 cm. of the core contain a large proportion of radiolaria and diatoms while samples below 1000 cm contain essentially no biogenic siliceous material (see paragraph 2-3) Analytical results indicate that Pd and Mn contents of the samples from the lower part of the core are higher than those of the samples from the upper part of the core. This tentatively suggests that both Pd and Mn are relatively depleted in the biogenic siliceous phase compared to the non-biogenic phase of the samples.

5-2-2. Cosmogenous Components

It is well known that the earth is continously bombarded by meteoritic material ranging in size from dust to bodies of hundreds of tons or more in weight. Spherules of extraterrestrial origin in deep-sea sediments have been recognized by many investigators beginning with Murray and Renard (1891). The flux of meteoritic material to the earth has been studied by many researchers using different techniques. Their results vary from approximately 10 to 10^6 tons per day for the whole surface of the earth (Parkin and Tilles, 1968). In general, in bulk marine sediments meteoritic material occupies only a minute part. However, when dealing with some trace elements which are strongly depleted in the earth's crust relative to the meteorites, as for example the precious metals, extraterrestrial material may be recognized in deep-sea sediments with extremely slow depositional rates.

The relative importance of the extraterrestrial contribution of precious metals to the deep-sea sediments will be further discussed in paragraph 5-3 and 5-4.

5-2-3. Hydrogenous Components

The most common and important chemical precipitation on the deep-sea floor is the formation of authigenic ferromanganese minerals which may form either minute mineral grains or large nodules. Many trace elements including copper, nickel, cobalt, lead and the rare earths etc. are strongly enriched in these ferromanganese minerals relative to the sediments. Cu, Ni and Co etc. in deep-sea sediments are shown to be highly correlated with the manganese content of the sample (Goldberg and Arrhenius, 1958; Cronan, 1969) It is believed that these minor metals are largely associated with the authigenic ferromanganese grains which may account for more that 80% of the manganese in pelagic clays (Chester and Hughes, 1966, 1967).

Au and Pd concentrations in many marine manganese nodules are similar to those in deep-sea sediments (Harriss *et al.*, 1968). It is safe to assume, therefore, that Au and Pd are not strongly enriched in the authigenic ferromanganese minerals. However, the Ir content of the marine manganese nodules is found to be 50 times higher than in the sediments. Yet, the Ir value in fresh water manganese concretions is lower by a factor of 100 than in marine manganese nodules. Harriss et al. relate the high Ir content of marine manganese nodules to the slow growth rate of the nodules and a significant extraterrestrial Ir component.

The calculated correlation matrixes in this work (Table 4-5 to 4-8) also strongly suggest that no inter-element association between Ir-Mn exists in any of the cores.

5-2-4. Lithogenous Components

Materials derived from rock weathering and carried into the ocean by either rivers or wind are the most immediate source of the non-biogenous sedimentary material in the ocean. Non-biogenous, detrital material in sediments of the Caribbean Sea and the Pacific-Antarctic Basin are considered to be derived primarily from the nearby continents (Koster, 1966). The concentration levels of Au, Pd and Ir in the Caribbean and Antarctic samples are within the general range found in most crustal rocks which is approximately from 0.1 to 10 ppb (Table 5-2). They are neither strongly enriched nor depleted in deep-sea sediments as compared with igneous rocks.

The state and behaviour of precious metals during weathering and sedimentation are essentially unknown at the present time. However, no significant differences in precious metal contents were found between soils, near-shore sediments and deep-sea sediments in a study of Artic sediments by Macdougall (1968). Also, no pronounced fractionation of precious metals between weathered and fresh basalts from Tahiti was observed by Crocket (unpublished data).

Clays are known for their absorption of certain elements. The less that 2 microns fraction of samples from the Antractic core E17-10, which consists of 60% clay and 40% silt size particles, were separated for precious metal analysis. The Au, Pd and Ir contents of the less tha~~t~~n 2 microns fraction are similar to those of bulk samples (Table 4-4). Precious metals are apparently not strongly enriched in the aluminosilicates of the less than 2 microns fraction.

These facts tentatively suggest that because of the chemical inertness of Au, Pd and Ir (high lattice energies, high oxidation states and low oxidation potentials etc.) and their possible occurrence in igneous rocks as neutral, uncharged atoms included in crystal defects or as discrete minerals, as suggested by Vincent and Crocket, 1960; De Grazia and Haskin, 1963; Keays, 1968 etc. they do not tend to be highly mobile during weathering processes, and perhaps are carried into the sea in suspension still bound in detrital minerals. A large proportion of the Au, Pd and Ir in marine sediments is contributed by weathering detritus either from land or from ocean floor.

Debris and/or solutions from submarine volcanic activity may add certain elements (for example Co) to deep-sea sediments. Boström (1966,

1970) found high transition metal contents in sediments collected on the ridge of the East Pacific Rise. He explained this enrichment by contributions from local volcanic activity. Precipitates that originated from hydrothermal solutions may accumulate in sediments near the source of the emanations. Although Boström did not find any gold enrichment across the crest of the Rise, Macdougall (1968) analysed the same East Pacific Rise samples for Au, Pd and Ir found higher value for Pd (9.5 ppb) and Au (7.6 ppb) in one sediment sample collected on top of the Rise crest. The Pacific-Antarctic Ridge is a zone of active tectonism and submarine volcanism (Zhivago, 1962) and fragments of volcanic glass often occur in the three Antarctic cores (Koster, 1966; Mather, 1966). However, no exceptionally high precious metal values were found in these cores except for the Pd content which is slightly higher than the average value for marine sediments. It seems that if submarine volcanic processes do contribute additional precious metals to deep-sea sediments the process is only significant in sediments deposited very close to the source of the emanations. Further work is necessary before conclusions can be drawn on the importance of volcanic precious metal contributions to deep-sea sediments.

5-3. Accretion Rate of Extraterrestrial Material

Studies of precious metals in deep-sea sediments have been primarily concerned with the question of the mass accretion rate of extraterrestrial material to the earth's surface. The precious metal abundances in meteoritic materials are generally 3 to 4 orders of magnitude higher than values characteristic of terrestrial rocks. Because the earth is continuously bombarded by meteoritic material, deep-sea sediments and polar ice with their low deposition rate should have a maximum extraterrestrial component.

The particle sizes of extraterrestrial material range from dust particles of 10^{-14} g to pieces heavier than 10^{12} g. Yet, the nature and flux of this extraterrestrial material is still highly uncertain. Total accretion rates obtained by various methods (spherule counts, penetration satellites, mesh collections, particle impacts on space probe, meteorites, crater counts and chemical methods etc.) scatter widely, with recent measurements converging on 10^2 to 10^3 tons/day. Chemical methods (measurements of radioactivities of cosmic origin, rare gases or trace elements) cover the entire size range of incoming objects and seem to be among the most promising. Table 5-4 lists some recent estimates of the extraterrestrial accretion rate by various chemical methods.

Pettersson and Rotschi (1952) and Goldschmidt (1954) first pointed out that because depositional rates of terrestrial material are very low in deep-sea ocean basins one might be able to measure the accretion rate of cosmic material by measuring the addition rate of platinum metals of extraterrestrial origin to deep-sea sediments. Pettersson and Rotschi made some attempt to determine Pd in deep-sea sediments to evaluate the possibility of a cosmic origin, but found negative results.

Technique	Accretion rate (tons/day, entire earth's surface)	References
Cl^{36} in deep-sea sediments	$<5 \times 10^3$	Schaeffer *et al.* (1964)
Ni in deep-sea sediments	$< 10^4$	Bonner and Lourenco (1965)
Ni in Antarctic ice	10^4 to 3×10^4	Brocas and Picciotto (1967)
Al^{26} in Greenland ice	880	McCorkell (1967)
Ir and Os in deep-sea sediments	< 330	Barker and Anders (1968)
Ir in marine manganese nodules	< 310	Harriss *et al.* (1968) and this work

Table 5-4. Some recent accretion rate estimates for extraterrestrial material by chemical methods

Barker and Anders (1968) using neutron activation techniques measured the Ir and Os contents of sediments from five Pacific deep-sea cores. They noted that Ir and Os were strongly correlated and that their concentrations varied inversely with the sedimentation rate. The extraterrestrial fraction of Ir and Os was estimated by subtracting an appropriate terrestrial component obtained from a plot of Ir and Os abundance versus the inverse of the sedimentation rate. They obtained an estimate for the mass accretion rate of extraterrestrial material(carbonaceous chondritic composition) to the entire earth's surface of 160 tons per day (0.012 $mg/cm^2/1000$ yr.) with an upper limit set at 330 tons/day (0.024 $mg/cm^2/1000$ yr.).

Harriss et al. (1968) analysed deep-sea manganese nodules from different localities for Au, Pd and Ir. Au and Pd concentrations are similar to those in deep-sea sediments, while Ir is enriched by a factor of 50 in the nodules. No correlation of Au, Pd and Ir was found with other trace or major elements nor with geographic location, water depth, or type of associated sediment. Individual nodules showed an internally homogenous distribution of metals. Further, fresh water manganese concretions were lower by a factor of 100 with respect to Pd and Ir. They concluded that the slow growth rates and the enrichment of Ir in the deep-sea nodules were strongly suggestive of a significant extraterrestrial component.

Manganese nodules, with their very low accumulation rates relative to detrital silicate sediments, should be particularly useful for determining the sedimentation rates of individual elements on the deep-sea floor. The accretion rates of precious metals and manganese in deep-sea manganese nodules can be obtained by:

$$A = C \cdot R \cdot D$$

where A = accretion rate of element in the sample

C = element concentration in the sample

R = accumulation rate of the bulk sample

D = bulk density of the sample

Using the following values for C, R and D; C= 2.91 ppb for Au, 5.27 ppb for Pd and 8.52 ppb for Ir (Harriss et al., 1968); R = 4 mm/10^6 yr. (Bender et al., 1966; Barnes and Dymond, 1967); D = 2.5 g/cm^3 for a nodule with 20 wt. % Mn (Mero, 1965), the accretion rates for precious metals and manganese in deep-sea nodules as listed in Table 5-5 are obtained. Precious metal and Mn accretion rates in cores P6304-9, E13-3 and E17-10 can be calculated in the same manner and are also included in Table 5-5. Values for C and D for each core used in the calculations are: Au = 2.17 ppb, Pd = 1.78 ppb, Ir = 0.34 ppb, Mn = 0.1924% and R = 36 mm/1000 yr for P6304-9; Au = o.87 ppb, Pd = 7.47 ppb, Ir = 0.26 ppb, Mn = 0.4599% and R = 3.3 mm/1000 yr for E13-3; Au = 1.63 ppb, Pd = 5.42 ppb Ir = 0.34 ppb, Mn = 0.3866% and R = 5.8 mm/1000 yr for E17-10; (from chapter 2 and Tables 4-1, 4-3 and 4-4). 0.7 g/cm^3 is used as the in situ density of the deep-sea cores.

Table 5-5. Au, Pd, Ir and Mn accretion rates in deep-sea cores and manganese nodules.

Sample	Element	Accumulation rate of bulk sample (mg/cm^2/1000yr)	Accretion rate of element (mg/cm^2/1000yr)
Core P6304-9	Au	2500	55×10^{-7}
	Pd		45×10^{-7}
	Ir		8.5×10^{-7}
	Mn		4.9
Core E13-3	Au	230	2.0×10^{-7}
	Pd		17×10^{-7}
	Ir		0.60×10^{-7}
	Mn		1.1
Core E17-10	Au	390	6.6×10^{-7}
	Pd		22×10^{-7}
	Ir		1.4×10^{-7}
	Mn		0.90
Manganese nodules	Au	1.0	2.9×10^{-9}
	Pd		5.3×10^{-9}
	Ir		8.5×10^{-9}
	Mn		0.20

Manganese nodules on the average contain 27 wt. % detrital component (insoluble in HCl; Metro, 1965). If it is assumed that the precious metal content of deep-sea sediments as tabulated in Table 5-2 (Au = 2.7 ppb, Pd = 4.4 ppb, Ir = 0.32 ppb) is due entirely to a detrital component, then these data can be used to give the maximum detrital contribution of precious metals to the nodules. The accretion of detrital material in manganese nodules can be calculated to be 0.27 mg/cm^2/1000 yr. (using the same method as for elemental rate calculations in Table 5-5) which results in accretions of 0.73 x 10^{-9} mg/cm^2/1000 yr. Au, 1.2 mg/cm^2/1000 yr. Pd and 0.086 mg/cm^2/1000 yr. Ir. Thus, the maximum precious metal contribution from detrital components in the manganese nodules is about 25% for Au, 23% for Pd and only 1.0% for Ir. The remainder must be contributed by authigenic precipitates and/or extraterrestrial material.

Sea water is undersaturated with respect to Au and has a concentration of 0.004 ppb Au in solution, principally as $AuCl_4^-$. The complex chloride of gold is quite stable and thus gives gold a rather long residence time (5.6 x 10^5 years) in sea water (Goldberg, 1963).

The concentration and residence time of Pd and Ir in sea water are unknown. Possibly they also exist in solution as anionic halogen complexes. Pd may have a similar or lower concentration in sea water and Ir probably has the lowest concentration of the three metals. Since in general, the precious metals exhibit low valence states in nature as exemplified by their common occurrence as native metals and alloys. The tendency of Ir to form complexes is probably less than Au and Pd, because of its higher stable oxidation states, smaller numbers of d-electrons and lower polarization properties so that higher oxygen potential is required to oxidize Ir to its higher oxidation state than that necessary for Au and Pd. For this reason, incorporation of precious metals into the manganese nodules by coprecipitation or chemical adsorption will probably not be large. This is also suggested by the fact that low precious metal contents (Au $\simeq$ 0.38 ppb, Pd = 0.05 ppb and Ir $<$0.1 ppb; Harriss *et al.*, 1968) were observed in fast growing freshwater manganese concretions.

Local submarine volcanism may add additional precious metals to the marine environment. However, no enrichment of precious metals in nodules from active volcanic areas relative to those from non-volcanic provinces was observed by Harriss *et al.* (1968). The fact that Ir enrichment was found in all the marine manganese nodules collected from widely scattered areas is not compatible with the idea that volcanic activity is essential for the Ir enrichment.

These factors lead to the conclusion that most of the Ir in marine manganese nodules is of extraterrestrial origin. Cosmogenic Au and Pd may also contribute a significant proportion of these elements to the nodules.

Precious metal ratios are about the same in most meteorite classes (Keays, 1968) and quite different from crustal rocks. Table 5-6 lists the

Table 5-6. Precious metal ratios in terrestrial and meteoritic materials

Ratio	Ultrabasic rocks	Basic rocks	Granitic rocks	Deep-sea sediments	Manganese nodules	Meteorites	
						Irons	Chondrites
$\frac{Au}{Ir}$	2.1	2.3	161	8.4	0.34	0.12	0.34
$\frac{Pd}{Ir}$	4.3	3.0	36	14	0.62	1.4	1.3

calculated precious metal ratios in different terrestrial and meteoritic materials (data used are from Tables 5-1 and 5-2). The ratios are quite different in deep-sea sediments and manganese nodules suggesting different sources of precious metals in these materials. The remarkable similarity between the precious metal ratios in manganese nodules and in meteorites add support to the conclusion that precious metals in marine manganese nodules are mainly of extraterrestrial origin.

Bender _et al_. (1966, 1970) found that deep-sea sediments and manganese nodules accumulate "excess" Mn, Ni, Co and Cu at similar rates and suggested that nodules and the surrounding sediments accumulate these "excess" elements by the same mechanism. Owing to the lack of data, "excess" precious metal accretion rates in the cores can not be obtained but from the above considerations and the element accretion rates in Table 5-5, it is apparent that "excess" precious metals are more important in the nodules whereas detrital precious metals are more important in the cores.

Two inter-related factors are important in governing precious metal concentrations in sediments and manganese nodules. One is the precious metal content of the bulk material, that is, detrital material in the case of sediments and authigenic ferromanganese oxides in the case of nodules. For sediments detrital material is expected to be considerably higher in precious metals than the authigenic ferromanganese oxides. This factor causes an increase in precious metal concentrations in sediments relative to nodules. The second is the growth rate of sediment or nodule. If a precious metal contributor independent of the bulk constituents (detrital clays, biogenic constituents, ferromanganese oxides etc.) is important, then the accumulation or growth rate will control the degree of dilution experience by this constituent. In the case of a possible significant extraterrestrial component whose precious metal concentration would greatly exceed that of the bulk sample, precious metal concentration in the bulk sample should vary inversely as the growth rate. The precious metal concentration of deep-sea deposits depends upon both these factors.

It is possible to derive the accretion rate of extraterrestrial material to the Earth from the accretion rates of non-detrital precious metals in deep-sea manganese nodules if the following assumptions are made: the influx of extraterrestrial material is constant and homogenous over the surface of the ocean floor, the rate of manganese nodule growth is constant, the abundance data on precious metals obtained from studies on large meteorites is representative of the average composition of extraterrestrial material falling on earth and the amount of precious metals incorporated into the authigenic ferromanganese minerals from sea water is negligible. The accretion rate is then given by:

$$A = \frac{P}{a}$$

where

A = accretion rate of extraterrestrial material.

P = accretion rate of non-detrital precious metal in deep-sea manganese nodules, which is obtained by subtracting the precious metal accretion rate in the detrital component from the total precious metal accretion rate of the nodules.

a = the abundance of precious metal in extraterrestrial material.

If we choose precious metal contents of average chondrite (0.21 ppm for Au, 0.81 ppm for Pd and 0.62 ppm for Ir; Table 5-1) as the representative composition of extraterrestrial material and use 2.18×10^{-9} $mg/cm^2/1000$ yr., 4.10×10^{-9} $mg/cm^2 1000$ yr and $8.43 \times 10^{-9} mg/cm^2/1000$ yr. as the accretion rate of non-detrital Au, Pd and Ir in deep-sea manganese nodules respectively (total elemental accretion rate from Table 5-5; assumed detrital component 27 wt. %), the accretion rate of extraterrestrial material to the ocean floor required to supply all the non-detrital Au, Pd and Ir in manganese nodules is approximately 0.010 $mg/cm^2/1000$ yr. (140 tons/day over the entire surface of the earth), 0.0051 $mg/cm^2/1000$ yr. (71 tons/day) and 0.014 $mg/cm^2/1000$ yr. (200 tons/day) respectively. In order to obtain an upper limit for the accretion rate and to compare with upper limits obtained by other authors, minimum precious metal values in carbonaceous chondrites (0.10 ppm for Au, 0.33 ppm for Pd and 0.38 ppm for Ir; Table 5-1) are used in the calculation. This gives an upper limit for the accretion rate of extraterrestrial material of 0.022 $mg/cm^2/1000$ yr. (310 tons/day) from Au, 0.012 $mg/cm^2/1000$ yr. (160 tons/day) from Pd and 0.022 $mg/cm^2/1000$ yr. (310 tons/day) from Ir.

Regardless of the fact that significant proportions of Au and Pd in deep-sea manganese nodules is of detrital origin and, given the uncertainties involved, the accretion rate of extraterrestrial material calculated from the individual accretion rate of non-detrital Au, Pd and Ir agrees quite well. The excellent agreement between the estimated upper limit of extraterrestrial material derived from the accretion rate of non-detrital Ir in deep-sea manganese nodules (310 tons/day over the entire surface of the earth) and excess-Ir in deep-sea clays (330 tons/day; Barker and Anders, 1968) can hardly be explained by simple coincidence. Further work on precious metal content, particularly Ir, in manganese nodules with known and variable growth rates could provide better knowledge of precious metal behaviour in the oceanic environment and give more accurate estimates of the accretion rate of extraterrestrial material to the earth.

5-4. Variation between and within the Cores

No great differences exist between Au, Pd and Ir concentrations in different types of sediments nor in cores from different areas. This confirms the previous findings of Crocket *et al*. (1968). Turekian (1965) pointed out that if a trace element is transported to sediments in detrital material a correlation between trace elements accumulation rate and "clay" accumulation rate should be observed. The calculated precious metal accretion rates in each core are listed in Table 5-5. While sediment accumulation rates as well as precious metal and Mn accretion rates are similar in the Antarctic core E13-3 and E17-10, sediment accumulation rate in the Caribbean core P6304-9 is higher than the Antarctic cores by a factor of 10 as is the precious metal and Mn accretion rate. This supports the previous discussions that detrital material is the major precious metal supplier in the cores studied in the present work.

Considering the analytical precision at this low concentration level, the Au, Pd and Ir contents of individual cores are very constant (Fig. 4-3 to 4-6) regardless of the fact that cores E17-10 and E13-3 represent a time span of 3 to 4 million years and core P6309-9 bears records of Pleistocene climatic changes. In most cases precious metal variation between samples from the same core is less than 50% at one standard deviation (Table 4-1 to 4-4). Reversal of the earth's magnetic field (Fig. 2-5 and 2-6) and the different weathering conditions in the Caribbean area during glacial and interglacial epoches (Boström, 1969) do not seem to have affected the precious metal content of the cores to any great extent.

If we accept 0.022 $mg/cm^2/1000$ yr. (310 tons/day over the entire surface of the earth) calculated from the non-detrital Ir accretion rate in deep-sea manganese nodules as the upper limit of the accretion rate of extraterrestrial material, the contribution from cosmic dust to the precious metal content in core E13-3 (sediment accumulation rate = 3.3 mm/1000 yr., average Au content = 0.87 ppb, Pd content = 7.47 ppb and Ir content = 0.26 ppb; Table 4-3) will be around 1.3% for Au, 0.30% for Pd and 16% for Ir. Because of the high background of detrital material, the contribution from extraterrestrial material to the Au and Pd content of deep-sea sediments will not be significant. However, due to the strong depletion of Ir in crustal material compared to meteoritic matter, Ir of extraterrestrial origin palys an important factor in slowly accumulated deep-sea deposits and may account for more than half of the total Ir content of sediment in cores with depositional rates of a few tenths of a mm. per thousand years. Millard and Finkelman (1970) measured the Ir content in magnetic spherules of meteoritic origin recovered from deep-sea clays also concluded that Ir content in these spherules may be responsible for 10 to 50% of the total Ir in deep-sea sediments.

The constancy of Ir content in deep-sea cores as a function of depth also suggests that the influx of extraterrestrial material during the past 3 to 4 million years was probably fairly constant and not much different from the present influx rate. An increase in the influx rate by a factor of 100 would increase the Ir content by a factor of 10 in cores with depositional rates at several mm/1000 yr. as in cores E17-10 and E13-3. More detailed studies of Ir variation in cores with extremely low depositional rates from different localities would have to be carried out before a definite conclusion on this topic can be established.

5-5 Conclusions

Neutron activation analysis is capable of determination of Au, Pd and Ir in deep-sea sediments although irradiations of one week are needed to give a better sensitivity for Ir. Interference in non-destructive determination of Mn and fission product interference in Pd determination are not considered significant.

Au, Pd, Ir and Mn in all of the cores studied are quite constant as a function of depth in the core and no significant correlations are observed between them. No great differences exist between Au, Pd and Ir concentrations in different types of deep-sea sediments nor in cores from different areas and their values are within the general concentration ranges found in most crustal rocks.

Biogenous carbonate and silicon dioxide are relatively depleted in precious metals. Authigenic ferromanganese minerals and clay size particles do not adsorb or otherwise concentrate metals to any large degree. Contributions from submarine volcanism are uncertain and further work is necessary on this aspect of the marine geochemistry of these metals. Precious metals carried by detrital material to a depositional site at the ocean bottom can account for most of the precious metals in the sediments. The total precious metal content, particularly Ir, of deep-sea manganese nodules however can not be explained by detrital supply alone. The different precious metal accretion rates and the precious metal ratios suggest that different conditions prevail in the accretion of precious metals in deep-sea sediments and manganese nodules. It is believed that accumulation of some high-precious metal material of extraterrestrial origin must be invoked to account for the excess precious metal in slowly accumulated deep-sea deposits.

From the non-detrital Ir content of deep-sea manganese nodules, the accretion rate of extraterrestrial material is calculated to be about 200 tons per day with an upper limit of 310 tons per day over the entire surface of the earth. This will not affect the Au and Pd concentration of deep-sea sediments to any significant extent but may account for more than half of the total Ir content in cores with depositional rates as low as a few tenths of a mm per thousand years.

Changes in climatic condition and earth's magnetic field do not affect the precious metal content of the cores greatly. The constancy of Ir content in these cores as a function of depth suggests that the influx of extraterrestrial material during the past 3 to 4 million years was probably fairly constant.

Further study on precious metal content, particularly Ir, in manganese nodules with known and variable growth rates could provide a more accurate estimate of the accretion rate of extraterrestrial material and would certainly give a better knowledge of precious metal behaviour in the oceanic environment.

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APPENDIX A

DETAILED DESCRIPTION OF ANTARCTIC CORE SAMPLES

A-1. U.S.N.S. ELTANIN Core 21-17

Latitude 55°28.5' S. Longitude 119°56' W. Water Depth 1540 F.

No ultra-violet raction

Sample No.	Interval (cm)	Texture	Remarks
21-17-1	0-125	Ooze, foraminiferal	Black sand grains scattered throughout.
21-17-2	125-200	Ooze, foraminiferal	Black granules and sand grains scattered throughout.
21-17-3	200-275	Calcilutite	Very cohesive. Grades into upper and lower units.
21-17-4	275-325	Ooze, foraminiferal	Granules and black sand grain scattered throughout.
21-17-5	325-400	Calcilutite, foraminiferal	Scattered black sand grains.
21-17-6	500-600	Ooze, foraminiferal	Small percentage of black micronodules throughout.
21-17-7	600-750	Ooze, foraminiferal	Small percentage of black micronodules. Two cm. subround igneous pebble at 615-617 cm.

21-17-8	750-950	Ooze, foraminiferal	Continued scattered micronodules.
21-17-9	950-1006	Ooze, foraminiferal	Scattered micronodules. Altered volcanic glass at 975-985 cm.

A-2. U.S.N.S. ELTANIN Core 13-3

Latitude 57°0.3' S.   Longitude 89°29' W.   Water Depth 2785 F.

Sample No.	Interval (cm)	Texture	Remarks
13-3-1	0- 225	Ooze, diatomaceous, silty	Matrix of diatom ooze with pure ooze blebs associated with silty clay
13-3-2	225- 605	Ooze, diatomaceous, clayey	Massive with minor blebs of pure ooze
13-3-3	605- 655	Ooze, diatomaceous, clayey	Massive with minor blebs of pure ooze
13-3-4	655- 865	Ooze, diatomaceous	More than 70% diatoms
13-3-5	865-1115	Ooze, diatomaceous, with silty clay	
13-3-6	1025-1125	Ooze, diatomaceous	Very moist and very cohesive
13-3-7	1125-1280	Clay, silty	Ooze begins to grade into silty clay
13-3-8	1280-1440	Ooze, diatomaceous	Mixture of diatom ooze and silty clay
13-3-9	1440-1600	Ooze, diatomaceous	Mixture of silty clay and diatom ooze

A-3. U.S.N.S. ELTANIN Core 17-10

Latitude 65°1' S. Longitude 134°52' W. Water Depth 2457 F.

Sample No.	Interval (cm)	Texture	Remarks
17-10-1	0- 400	Clay	Few sand grains and granules scattered throughout
17-10-2	400- 800	Clay, silty	Quite homogeneous
17-10-3	800-1400	Silt, clayey	
17-10-4	1400-1585	Silt, clayey	