The Platinum Group Metals in Iron Meteorites

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ABSTRACT

Solvent extraction methods have been developed for the determination of Ru, Pd and Pt in iron meteorites. The method for Ru is based on the oxidation of this element in HCl solutions with sodium periodate followed by extraction of the tetroxide into $CHCl_3$. The $CHCl_3$ phase is then removed to a HNO_3-$NaIO_4$ "keeper" solution for storage up to 17 hours prior to analysis. The method for Pd and Pt entails simultaneous extraction of their stable iodocomplexes into methylisobutyl ketone after removal of Fe(III) as the chlorocomplex. The digestion of the samples with reference to these elements has also been investigated.

All three elements were determined by the graphite furnace atomic absorption spectrometry technique. The limit of detection was lowered by increasing the volume of organic phase placed in the graphite furnace. The lowest absolute detection limits achieved in this study were 0.5 ng for Ru, 0.5 ng for Pd and 5 ng for Pt.

The platinum group metal values for 108 authentic iron meteorites were subjected to Principal Components Analysis and Discriminant Analysis. These procedures confirmed the validity of the classification of iron meteorites developed over the past 25 years, but highlighted poor fits for some individual iron meteorites within a group. Possible reclassification of these members was evaluated after consideration of the meteorite's morphological features.

The cases for the merging of some groups were investigated and discussed with reference to the chemical features of those groups.

The data obtained also revealed several cases of meteorite pairings (related members of a single meteorite shower catalogued as separate meteorites), instances of the mislabelling of museum fragments and two putative meteorites which proved to consist of man-made materials.

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Chapter One

General Introduction

I.1.Introduction

A primary purpose of meteorite research is to learn more about the origin and evolution of the solar system and the bodies within it. Meteorites are the oldest rocks available to us for study, relics of a dim past when a plasma of interstellar dust and nebular gas gave birth to our Sun. The great majority of meteorites formed before the Earth (Dodd, 1986). The ones that are of the same age as the Earth contribute to our understanding of this planet and its evolution.

Until the Apollo-11 lunar mission in 1969, meteorites were the only extraterrestrial samples of the solar system available for laboratory study. Lunar and planetary missions have so far sampled only the surface of those bodies, and thus the representation of the body is very incomplete compared to the many types of meteorites that have fallen to Earth and been recovered (McCall, 1973). Meteors are fragments of destroyed planetesimals. Through a series of complex perturbations, they leave their orbits in the asteroid belt between Mars and Jupiter and fall towards the Sun. If the Earth is in the flight path of the meteor and if the meteor passes through the atmosphere and lands on the Earth, it is then a meteorite. These samples come to us continuously and at no cost and have been referred to as "the poor man's space probe" (Dodd, 1986). To the geologist, they represent the only samples known to represent material from the interior of a planet, and are useful for understanding the probable structure and conditions in the interior of the Earth.

A more recent and spectacular reason for scientific interest in meteorites is in the considerable and still contested evidence that they have played a role in the history of Earth's inhabitants. The impact of a large (>10 km diameter) chondritic meteorite is held responsible for the extinction of 70% of all life forms at the terminal Cretaceous (Alvarez *et al.*, 1980). A periodic pattern of extinctions throughout the history of the Earth has been demonstrated and summarized in popular articles (Angier *et al.*, 1985), resulting in great public interest in meteorites and comets.

A working hypothesis to account for the diversity of samples breaks the meteorites down into three broad, general categories (Mason, 1962; Wasson, 1985):

1) Aerolites, or stony meteorites (≤1% reduced metal)
2) Siderolites, or stony irons (≈50% reduced metal)
3) Siderites, or irons (≥99% reduced metal)

These different meteorite types have been compared to rocks thought to compose the Earth's upper mantle, lower mantle and mantle-core interface, and core, respectively. Though it is apparent that meteoritic material was formed under confining pressure regimes that are low compared to that of the deduced internal shells of the Earth, no better analogy can be drawn (McCall, 1973).

Of these categories, the irons are the most readily preserved once they land on the Earth due to their resistance to physical and chemical weathering processes. These samples are thought to be the fragments of the cores of small planets and therefore represent the product of igneous processes similar to those that produced the Earth. It is doubtful that we shall ever be able to directly study the interior of the larger, terrestrial planets, for only smaller meteorite parent bodies appear to have suffered disintegration.

The iron cores differ from each other due to the size of the original planet and of the planetary heat sources that provided the energy to melt the primitive starting material into the differentiated phases. To understand the nature of these samples, classification schemes are necessary to separate the different types of iron core fragments that fall as meteorites.

I.2. Classification of Iron Meteorites

The usefulness of any classification scheme is two-fold (Sears, 1978). Firstly, it should be possible to determine how many different types of meteorite there are, and it should provide a descriptive label for each type so that once a scheme has been drawn up and accepted, much of what is known about that class may be assumed to apply to any individual in it. Secondly, the establishment of classes may ultimately prove to have some genetic relevance. If a number of meteorites can be put together in one class, it seems very probable that they will have shared a similar origin or a common history. Ideally, the classes should have distinctly different compositions, although the members of a class should be reasonably similar to each other.

It is much easier to distinguish different types of meteorite than to demonstrate relationships between them. An important reason for this difficulty is that meteorite researchers cannot yet visit the meteorite parent bodies, if they still exist. Field observations help to identify associations of related rocks. An established relationship is easier to understand than a random assortment of samples (Dodd, 1986).

There are two entirely different classification schemes for iron meteorites now in use (McSween, 1987).

I.2.a. Structural

In 1808, Alois von Widmanstätten acid-etched a polished surface of an iron meteorite and observed the beautiful and striking structures now called Widmanstätten patterns. The appearance of the intergrown plates of kamacite (α-Ni/Fe alloy) and taenite (γ-Ni/Fe alloy) varies depending on the orientation of the cut face of the meteorite. Sketches of how the Widmanstätten pattern would appear in various sections through a parent taenite crystal are shown in Figure I.1. The bandwidths of the kamacite crystals are used to group meteorites. Earlier structural classes of iron

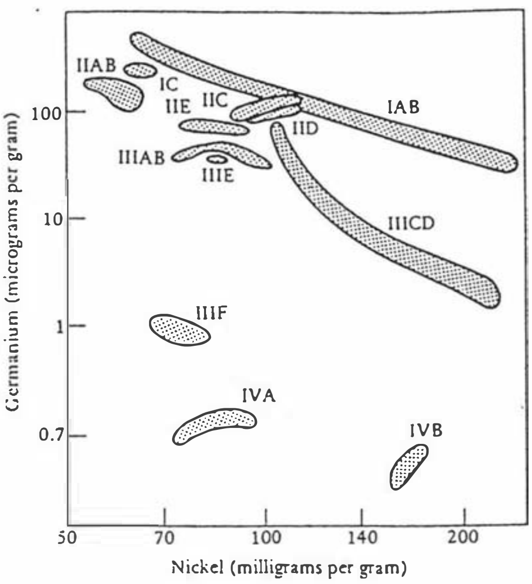


Figure I.2. Logarhithmic plot of Ni vs. Ge in iron meteorite groups (McSween, 1987)

meteorite were defined somewhat arbitrarily due to an inability to distinguish groups of genetically related irons (Wasson, 1974). Buchwald (1975) proposed bandwidth divisions with limits increasing as a geometric series of a nearly constant factor of 2.5 (Table I.1). These divisions minimize the number of structural classes within a given chemical group.

I.2.b. Chemical

The most successful chemical classification scheme is one based on the Ga, Ge, Ir and Ni content of an iron meteorite (Wasson, 1974). In different groupings of meteorite, Ga and Ge show quantized abundances rather than being present over a continuous range of concentrations (Figure I.2). To a lesser extent, Ni and Ir also show quantization (Table I.2). The choice of these chemical parameters is arbitrary and studies of other elements can be shown to yield the same classification of irons into groups, with differing degrees of resolution and success (Scott, 1972). The chemical scheme poses more constraints than the structural one, though the two are related to each other and should be used together in the classification of any specimen.

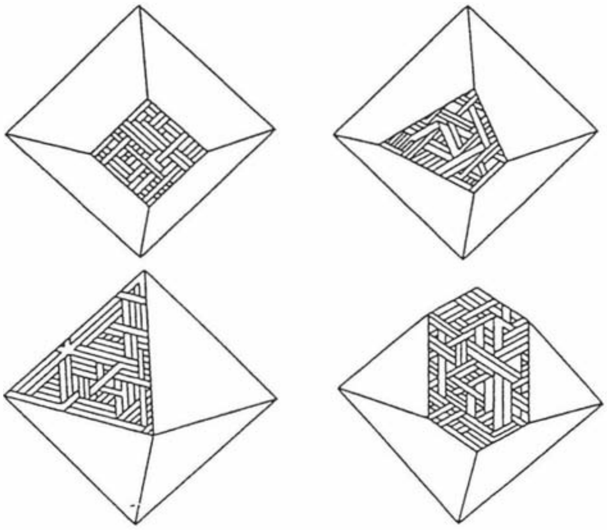


Figure I.1. The appearance of the Widmanstätten structure as controlled by the crystallographic orientation of the section (Mason, 1971)

Table I.1. Structural classification according to Buchwald (1975)

Class	Symbol	Kamacite Bandwidth(mm)	Remarks
Hexahedrites	H	--	No octahedral orientation even in large sections.
Coarsest Octahedrite	Ogg	>3.3	Taenite may or may not be present.
Coarse Octahedrites	Og	1.3-3.3	
Medium Octahedrites	Om	0.5-1.3	
Fine Octahedrites	Of	0.2-0.5	
Finest Octahedrite	Off	<0.2	Distinct bands of kamacite.
Plessitic Octahedrites	Opl	<0.2	Kamacite sparks and spindles.
Ataxites	D	--	Well-developed, slowly annealed plessite; kamacite spindles very rare.
Anomalous	AN	--	Includes all irons which demand individual descriptions.

Table I.2. Chemical parameters for the classification of iron meteorites according to Wasson (1974)

Group	%Frequency	% Ni	μg/g Ga	μg/g Ge	μg/g Ir
IA	17.1	6.4-8.7	55-100	190-520	0.6-5.5
IB	1.7	8.7-25	11-55	25-190	0.3-2.0
IIA	8.3	5.3-5.7	57-62	170-185	2.0-60
IIB	2.6	5.7-6.4	46-59	107-183	0.01-0.5
IIC	1.5	9.3-11.5	37-39	88-114	4-11
IID	2.6	9.8-11.3	70-83	82-98	3.5-18
IIE	2.3	7.5-9.7	21-28	60-75	1-8
IIIA	24.9	7.1-9.3	17-23	32-47	0.17-19
IIIB	7.0	8.4-10.5	16-21	27-46	0.01-0.17
IIICD	2.6	10-23	1.5-27	1.4-70	0.02-0.07
IIIE	1.7	8.2-9	17-19	34-37	0.05-6
IIIF	1.1	6.8-7.8	6.3-7.2	0.7-1.1	1.3-7.9
IVA	8.3	7.4-9.4	1.6-2.4	0.09-0.14	0.4-4
IVB	2.3	16-26	0.17-0.27	0.03-0.07	13-38

Aims of Research

One of the aims of this project is to assess the usefulness of some other elements in the classification of iron meteorites. Many irons cannot be classified neatly by the chosen parameters and are lumped into an "anomalous" or "ungrouped" category. Occasionally, there are a sufficient number of meteorites showing similar elemental concentration ratios and structural characteristics to warrant the formation of a new group. Wasson (1974) proposed that the proven existence of five like irons would be sufficient to confer those irons with separate group status. This was the case most recently with the establishment of the IIF group (Kracher *et al.*, 1980). The classification constraints are also sometimes relaxed to admit meteorites into groups that fulfill *most* of the requirements for that group, but do not fit in completely. An example of this is Mundrabilla, a IIICD-AN (Scott and Wasson, 1976). The "AN" tag calls attention to the point that all of the requirements, chemical or structural, are not satisfied so that such a meteorites is to some degree anomalous.

The Ir content of irons, though not as diagnostic as Ga, Ge and Ni, is still considered to be a valuable parameter for classification. All of the platinum group metals (PGMs) are strongly siderophilic. Goldschmidt's (1958) idea that individual elements have distinct geochemical behaviors led to the description of elements as siderophile, chalcophile and lithophile for elements with tendencies to concentrate in metal, sulfide and silicates, respectively. Planetary core formation has the effect of scavenging the PGMs, but their affinities with the metal phase can vary with temperature, pressure or chemical environment (McSween, 1987). This would explain the non-linear relationship Ir displays when plotted against Ni content. In Figure (I.3), it is apparent that Ni is controlling the degree of separation between groups, and Ir is not well quantized for some

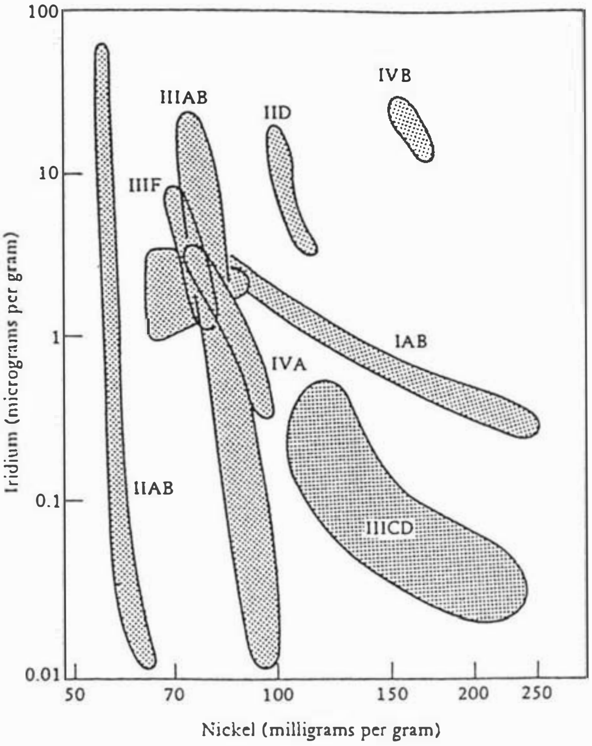


Figure I.3. Logarithmic plot of Ni vs. Ir in iron meteorite groups(McSween, 1987) groups (IAB, IIAB, etc.). The other five PGMs (Ru, Os, Rh, Pd, Pt) might show more limited ranges of abundance within groups, and it was decided for this project that these elements should be determined in iron meteorites.

Iridium and osmium are best detected by neutron activation analysis (NAA). In fact, Ir was first determined in iron meteorites because of its sensitivity and relative ease of quantification by radiochemical-NAA (RNAA) (Wasson, 1974). In order to determine Ir and Os for this project, a partnership was formed with the Trace Analysis Research Centre (TARC) of Dalhousie University, Halifax, Canada. The TARC group uses instrumental-NAA (INAA), which is nearly as sensitive and precise as RNAA for Ir and Os. Ryan and Holzbecher have recently developed a new method for the determination of Rh using INAA (Ryan *et al.*, 1990). This leaves me the task of developing methodology for the determinations of Ru, Pd and Pt. These three PGMs can be quantified by RNAA (Pernicka and Wasson, 1987; Smales et al., 1967), but with great difficulty, expense and large relative errors (up to 18% between replicates). Graphite furnace atomic absorption spectrometry (GFAAS) instrumentation was available in the Analytical Laboratory of this university, and proved to be a very sensitive and precise means for the detection of these three remaining PGMs. The Brian Mason Meteorite Research Unit (BMMRU) has been established in this laboratory to honor a native New Zealander who has been prominent in the field of meteoritics.

The usefulness of Ga and Ge as taxonomic parameters is due to their volatility under different conditions. Germanium is easily determined at the BMMRU by hydride generation-AAS (Guo and Brooks, 1990). Gallium has been measured in the past spectrophotometrically (Onishi and Sandell, 1955) and by RNAA (Brown and Goldberg, 1949; Wasson and Kimberlin, 1966). Because we do not have RNAA capacity readily accessible to us, a GFAAS method to determine Ga will be sought. In addition, the Tl content of the Toluca (IAB) iron meteorite was to be determined by a GFAAS method (Hoashi, 1988) to assess the possibility of using Tl as a taxonomic parameter.

The methodology developed for the determination of Ru, Pd and Pt by GFAAS and the studies performed for Ga, Tl and Ni are presented in the first part of this thesis.

The second part of this work will include the application of the procedures developed in part one to the determination of Ru, Pd and Pt in iron meteorites, and discussions on the PGM abundances (including the data collected by TARC) for these samples.

It was hoped that this work would provide rapid, inexpensive, sensitive and precise methods for the determination of Ru, Pd, Pt and Ga in iron meteorites and that a contribution could be made towards a better understanding of the relationships the meteorites have with each other and with the solar system.

Part One

Development of Methods

Chapter Two

Ruthenium

II.1. Introduction

In 1826, Osann examined a sample of the residue remaining from the treatment of crude Pt from the Urals with aqua regia. He announced the discovery of three new elements, which he named Pluranium, Ruthenium and Polonium. This work was later taken up by Klaus, who showed that Osann's determinations were done on impure oxides of only one metal, which he named Ruthenium, both in honor of his native Russia and of the pioneering work of Osann (Griffith, 1967). In 1844 Klaus isolated the last PGM, and determined its physical properties: a melting point of 2310 ^{o} C and a density of 12.41 g/cm^3 (Livingstone, 1973). Ruthenium and osmium are the only elements in the entire periodic table that exhibit octavalency (Griffith, 1975).

Much work has been accomplished on the chemistry of Ru since World War II. The first stimulus for this came from the observation that Ru is one of the main products of nuclear fission of heavy atoms. The more recent reason has been the realization that many Ru complexes have unusual structures and reactivities, and that some have potentially valuable catalytic properties (Griffith, 1975).

Industrially, Ru is used as an alloy with other PGMs as a hardener. Platinum or palladium alloys with Ru are used for electrical contacts for high wear resistance and a Ru-Ir alloy is used for surgical blades. The corrosion resistance of Ti is improved a hundred-fold by the addition of 0.1 % Ru (Hammond, 1990), and Ru is a versatile catalyst used in the oxidation of organic compounds in synthesis (Griffith, 1975).

Ruthenium metal does not tarnish at room temperature but oxidizes to form a thin film of RuO_2 at greater than 400 ^{o}C (Chaston, 1975).

Ruthenium is not soluble in hot or cold acids, aqua regia or alcohols, but is attacked by alkali fusion (Hammond, 1990). It is similar in reactivity to Os and both metals are homologs of Fe. Like Fe, Ru is rich in color reactions and colorimetry and spectrophotometry were the methods preferred for the determination of Ru (Sandell, 1959). Other methods for the detection of Ru include gravimetry where it is determined as the metal (Gilchrist, 1935); catalysis and induction where the acceleration of a slow oxidation-reduction reaction which is dependent on the quantity of oxidant present is measured (Sandell, 1959); atomic absorption spectrometry (AAS) where the Ru in solution is loaded onto a graphite tube that heats electrically and generates a population of atoms which are detected as in flame AAS (Guerin, 1972); radiochemical neutron activation analysis (RNAA) where ^{102}Ru (31.3% isotopic abundance) is transformed by (n,γ) reaction into 40-day ^{103}Ru and counted after radiochemical separation (Crocket *et al.*, 1968).

Despite the number of instrumental methods available for the determination of Ru, it is not an easy element to detect in geological samples because of its low crustal abundance (0.01 µg/g, Mason and Moore, 1982). Pretreatment of the samples is often necessary to remove interferences and to concentrate Ru sufficiently to exceed instrumental detection limits.

In a series of articles published in the 1920's, Gilchrist confirmed the accuracy of a Pb assay method originally employed by Deville and Stas in 1877 for the determination of PGMs in a Ir-Pt alloy (Kauffman, 1977). Sandell (1959) describes the similar collection of Ru by a Pb button, which is the method preferred by Beamish and Van Loon (1977), who also describe a fire assay method in which Ag scavenges Ru and other PGMs in prills.

Other methods used to purify and concentrate Ru include chromatography (including ion exchange), liquid-liquid (or solvent) extraction, co-precipitation and distillation methods (Korkisch, 1969).

II.2. Selection of Instrumentation

Of the instrumental methods available for the determination of Ru, graphite furnace atomic absorption spectrometry (GFAAS) was chosen for this project for several reasons. Radiochemical-NAA requires use of a nuclear reactor which is unavailable for research purposes in New Zealand. In addition, it is costly, varying from NZ$200-$400 per sample for the analysis (Ryan, 1990). Flame atomic absorption spectrometry (flame-AAS) is too insensitive (LOD ≈ 2 μg/g) for the amount of Ru present in iron meteorites. Catalysis is rejected, despite its reported sensitivity (1 ng) as it is an indirect method and heavily dependent on the purity of reagents as well as the temperature of reaction (Sandell, 1959). Fire assay methods require a high degree of operator expertise and experience to avoid chemical and mechanical losses of sample (Beamish and Van Loon, 1977). Gravimetry requires expertise and is more appropriate for macro-analyses of Ru rather than for the small amount present in iron meteorites.

Despite the multitude of color reactions for Ru, colorimetry and spectrophotometry are rejected because of the documented interference of Os, which also reacts with the same colorimetric reagents. Osmium and ruthenium have many similar reactions (Cotton and Wilkinson, 1980). Separation of Ru and Os would be necessary, or at least Ru determination would be possible only if Os/Ru ratios were "favorable" for the chosen reagent. This is especially important for the more sensitive determinations (Sandell, 1959). In addition, the requirement of time and heat for some of the color-developing reactions can result in losses of Ru.

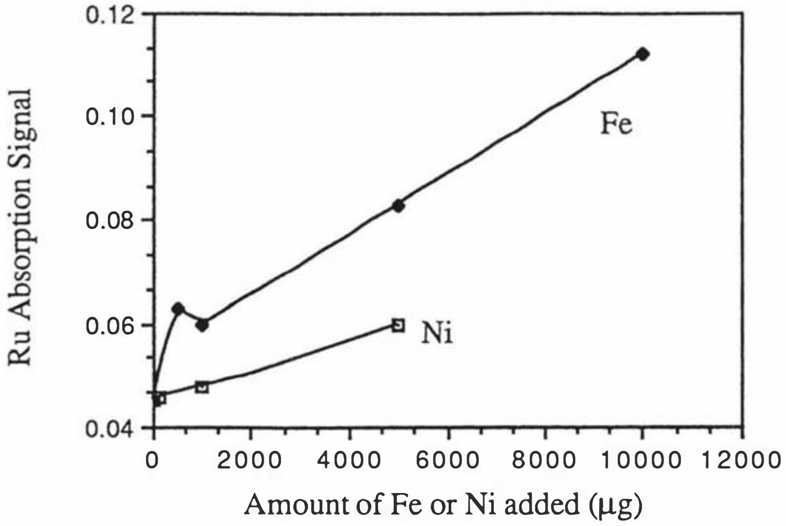
A method for Ru determination utilizing inductively coupled plasma (ICP) emission spectrometry has been investigated by Wilson *et al.* (1985). In this procedure, an alternative spectral line of slightly less sensitivity than the most sensitive line for Ru was used, this alternative line falling within one of the existing windows of the ICP instrument. Preliminary results were promising for concentrated Ru samples, but were abandoned because of poor reproducibility and inadequate sensitivity for

Cretaceous-Tertiary boundary samples first reported by Alvarez *et al.* (1980) to be enriched in Ir. Wilson *et al.* (1985) had hoped to find an enrichment of Ru in the same samples.

GFAAS is very sensitive for the determination of Ru with no interference from Os (indeed, Os cannot be detected using GF-AAS) if the furnace program is manipulated to take advantage of the multiple loading of sample into the furnace. Because the sample is heated in three stages (dry, char and atomization) a sample may be loaded onto the graphite furnace and dried repeatedly prior to charring. In this way, even very dilute solutions (<1 ng/mL) can be analyzed for Ru. The method is fairly inexpensive at less than NZ$2 per sample for three replicate analyses and is conducive to automation, thus eliminating the need for a very highly skilled operator. However, despite the automation, complete familiarity with the GFAAS instrument is necessary to achieve the lowest possible limit of detection (LOD).

A major difficulty with GFAAS is that interelement interferences are very pronounced and precision can be quite poor (Christian, 1978). By introducing digested or liquid samples directly into the furnace, the problem lies in the accumulation of unvolatilized material, which decreases sensitivity, precision and furnace life. Methods for separating analyte from the interfering sample matrix must be utilized to overcome these disadvantages. This holds true for all but the simplest of water samples.

Figure II.1. Effect of Fe and Ni on the absorption signal of 1 μg/mL Ru



III.3. Purification of Ruthenium

Chemical analyses almost always involve two steps: separation of the desired constituents and the measurement of these constituents (Morrison and Freiser, 1966). Purification of the constituents allows better sensitivity and reproducibility as fewer interferences are likely to be encountered.

Separation of Ru from its matrix is necessary as GFAAS is prone to a larger number of interferences than flame-AAS. In iron meteorites, the Fe content averages 88% and the Ni concentration averages 8%. The effect of these two elements on the behavior of Ru absorption on GFAAS is shown in Figure II.1. To overcome these interferences, matrix modifiers can be used instead of separating the analyte. This causes the matrix to be bound so it does not present itself as an interference. Unfortunately, many elements are so well stabilized by matrix modifiers that increased atomization temperatures are necessary with the concomitant reduction of furnace and electrode life. In addition, the modifying components must not include any analyte elements, as enhancement may result in later determinations (Voth-Beach and Shrader, 1987; Hoashi, 1988). Palladium is a well-studied chemical modifier for GFAAS work, but is not applicable to PGM determinations.

II.3.i. Fire Assay

Fire assay requires a high degree of expertise to avoid chemical and mechanical losses. This procedure involves the addition of alkalic flux materials and metal to separate and collect the PGMs from their matrix. In classical (Pb) fire assay, the resultant Pb bead containing the PGMs and Ag undergoes cupellation, which oxidizes and melts the Pb. The liquid then wets the vessel (cupel) and is absorbed into it along with other base metals, leaving the PGMs and the Ag in the cupel. This resultant PGM-enriched Ag prill is then analyzed. Beamish and Van Loon (1977) note that no data are available on the optimum Pb button size for concentrations of noble metals in a sample, though Ag prill weights appear to be independent of the amount of noble metals taken up. The nature of the Pb or Ag/Ru mixture is not elucidated, though it appears to be mechanically mixed. This is evidenced by the inhomogeneity of the beads with respect to Ir and Ru, though homogeneity was achieved for Au, Ag, Pt, Pd and Rh (Lewis, 1977). Hoffman *et al.* (1978) noted a similar inhomogeneity for NiS fire assay beads. This indicates that careful handling and digestion of the whole bead is necessary. Lewis (1977) also points out that the beads were prepared from ores or metallurgic concentrates where high concentrations of Ru were present and that a satisfactory degree of reproducibility was still unattainable. A comparison of Pb vs. NiS collection of Ru was presented by Beamish and Van Loon (1977) for several Ru-enriched samples (Table II.1) and Ru determined by flame-AAS. The NiS bead appears to collect Ru more efficiently than Pb does. The amount of sample to be taken and the content of total PGMs must be considered in order to produce a button weighing 25-30 g (Table II.2).

Hoffman *et al.* (1978) used large sample weights (50 g) of PTC-1, a standard flotation sulfide ore distributed by the Geological Survey of Canada (McAdam *et al.*, 1973), to determine Ru by INAA. In view of the better sensitivity of GFAAS for the determination of Ru, a fire assay

Table II.1. Collection of Ru in various materials using fire assay (from Beamish and Van Loon, 1977)

Sample Description	Method of Concentration	Number of Results	Average Results (ppm)
Chromite	Pb Collection	8	0.52 ± 0.05
	NiS Collection	4	1.16 ± 0.02
Merensky Reef Ore	Pb Collection	6	0.35 ± 0.04
	NiS Collection	12	0.86 ± 0.06
Flotation Concentrate	Pb Collection	14	10 ± 0.8
	NiS Collection	12	14 ± 0.4
Matte	Pb Collection	4	23 ± 1
	NiS Collection	4	34 ± 1

Table II.2. Weights of sample to be taken for determination of all PGM by fire assay procedures (from Beamish and Van Loon, 1977)

Estimate of total PGM (µg/g)	Weight of Sample (g)
>1000	5.0
500-1000	10.0
250-500	15.0
100-250	25.0
50-100	35.0
<50	50.0

concentration was attempted here using a NiS bead on a smaller (0.5 g) sample of PTC-1, but no Ru could be detected. The Ru content has not been standardized in PTC-1, but its concentration was determined by Hoffman *et al.* (1978) as 0.59 µg/g. This is well within the GFAAS detection capabilities, but either the NiS bead failed to collect the Ru, or losses must have occurred.

Table II.3a. The effect of precipitating Ni as hydroxide on concentration of PGMs in solution

PGM 10 µg/mL	Absorbance Before	 After	≈% PGM adsorbed from solution
Ru	0.016	0.003	81.2
Pt	0.006	0.006	0.0
Pd	0.031	0.015	55.0
Rh	0.033	0.005	84.8

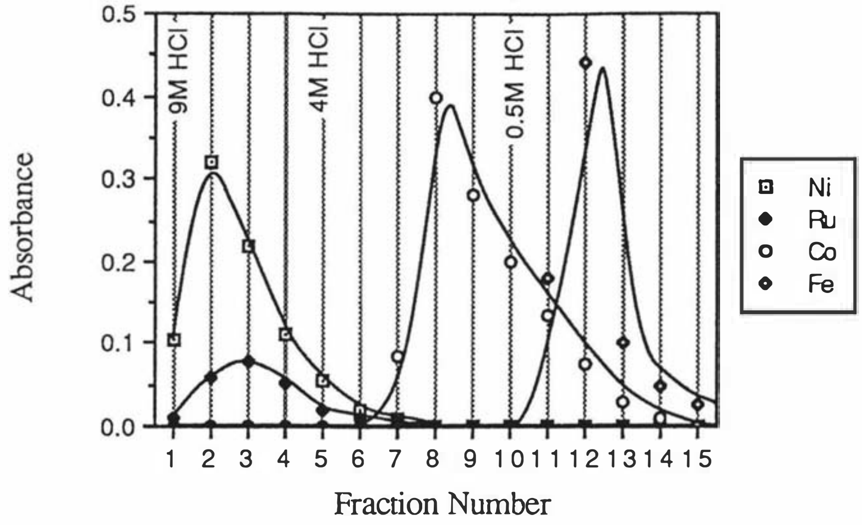
Table II.3b. The effect of precipitating Ni as the DMG complex on the concentration of PGMs in an acidic solution

PGM 100 µg/mL	Absorbance Before	 After	≈% PGM adsorbed from solution
Ru	0.070	0.054	23.0
Pt	0.043	0.044	0.0
Pd	0.121	0.002	100
Rh	0.159	0.092	40.0

II.3.ii. Coprecipitation

Coprecipitation of the Ru is accomplished by $Fe(OH)_3$ at pH 4.8 to 10.5, or in acidic, reducing conditions by CuS or PbS (Korkisch, 1969). Iron meteorites are digested in oxidizing acids and the analytes require separation from the major components, especially Fe, making these methods of coprecipitation inappropriate. The final stages that produce the individual PGMs are carried out industrially by selective precipitation, but this is inefficient as far as the degree of separation is concerned as most methods of coprecipitation are incomplete with regards to Ru (Charlesworth, 1981). Precipitation of Fe and Ni were attempted, with the hope that the Ru would remain in solution, but all trials resulted in the coprecipitation of Ru to varying degrees (Table II.3).

Figure II.2. Elution of metals from Dowex-1x8 anion exchange resin



II.3.iii. Ion Exchange Chromatography

Since the PGMs form stable anionic chlorocomplexes of the general type $[MCl_n]^{2-}$ where n = 4 or 6, these elements are not retained by strong acid cation exchange resins from HCl solutions. The distribution coefficients for Ru(III) and Ru(IV) in 0.2 to 9M HCl are less than 1.0 (Korkisch, 1969). In weak (<0.5M) HCl solutions, many cations including Fe, Ni and Co, are strongly absorbed onto a cation exchange resin, while all of the PGMs pass through as effluent. On anion exchange columns, the reverse is true and Ru(IV) is apparently adsorbed onto Dowex-1 with distribution coefficients ranging from 1600 (0.1M HCl) to 40 (11.6M HCl).

For the isolation of Ru from Fe, Ni and Co, it is more desirable to bind the Ru onto the anion exchange resin rather than collecting it with the eluent using a cation exchange resin. The anion exchange resin with its loading of PGMs can be ashed in a muffle furnace and redissolved in a small volume of acid. If cation exchange resins were used instead, the PGMs would be present in several collected fractions. These fractions would require evaporation, resulting in possible contamination and mechanical losses, to concentrate the solution so that the determination of Ru is practical.

Anion exchange was performed on a synthetic mixture of the PGMs plus Fe, Ni and Co, the main macro-constituents of iron meteorites. From the graph (Figure II.2) 100 μg of Ru is not retained on the column and it elutes with Ni in 9M HCl. It was thought that the large amount of Fe and Co (5000 μg) in the synthetic solution could have taken up all sites on the resin. Because it was hoped to retain Ru on the resin for subsequent ashing and dissolution for over 100 iron meteorites, it was not practical to increase the amount of resin used. Alternatively, Fe and Co could be removed by solvent extraction prior to the separation of Ru from Ni using the Dowex-1x8 resin.

II.3.iv. Solvent Extraction

Solvent extraction is a separation process relying on the desired metal being selectively extracted from an aqueous phase by an immiscible organic solvent. It was also considered equally important that the metal must be capable of being back extracted, or stripped, into another suitable aqueous medium (Sandell, 1959; Charlesworth, 1981). Alterations to standard analytical procedures would then not be required (Morrison, 1950). For GFAAS this is only necessary if the solvent is not compatible with the technique due to its viscosity or high boiling point (Brooks and Lee, 1988; Frankenberger *et al.*, 1990). The greater drying efficiency of many organic solvents is a desirable trait in GFAAS. However, this indicates that standard solutions and samples should be presented to the instrument in the same matrix. Thus it is advisable that standards undergo the same extraction processes that the samples are subjected to, in order to achieve matrix matching.

Solvent extraction enjoys a favored position among analytical separation techniques because of its ease, simplicity, speed, versatility and selectivity (Morrison and Freiser, 1966). In addition, the equipment necessary for small scale analyses using this technique are available in any analytical laboratory. It was this method that was ultimately selected in the development of a procedure for the simplified determination of Ru in iron meteorites.

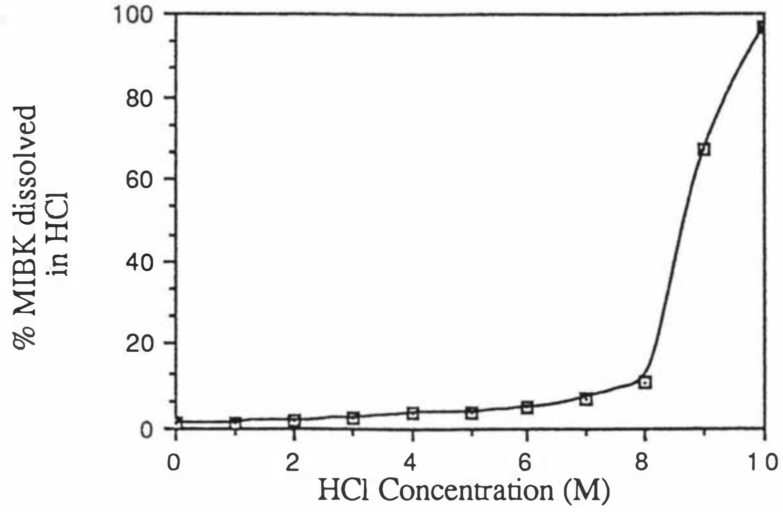
The usefulness of a solvent extraction system depends on the distribution ratio D, which is defined as (Morrison 1950):

$$D = \frac{\text{Total Concentration of Analyte in Organic Phase}}{\text{Total Concentration of Analyte in Aqueous Phase}}$$

Goto and Kakita (1958) examined the extraction of several metals and noted that 99.9% Fe(III) could be extracted into methylisobutyl ketone (MIBK) from >6M HCl. However, Co and Ni were not extracted under any conditions. To determine if Ru or any of the other PGMs were extracted into MIBK, the experiments of Goto and Kakita (1958) were repeated for the PGMs using varying concentrations of HCl as the aqueous matrix. It was noted by those workers that MIBK dissolved appreciably in acid solutions. The solubility of MIBK increases steadily up to 66% at 9M HCl (Figure II.3). For this reason, solvent extraction tests were carried out only from 0-6M HCl and the MIBK was pre-equilibrated by shaking it with acid prepared at the appropriate concentration prior to extraction with the aqueous sample. To carry out solvent tests up to 10M HCl, methylamyl ketone (MAK) was considered as an alternative organic extractant phase. In <6M HCl solutions, there is no significant extraction of the PGMs into either MAK or MIBK. However, MAK extracts Fe(III) less efficiently than MIBK, and the latter is preferred for removal of Fe.

Combining solvent extraction with the previously described anion exchange procedure was not promising as no Ru could be detected in the ashed, redissolved solution. Ruthenium metal tarnishes at about 400°C to form RuO_2. At higher temperatures, up to 720°C, the RuO_2 combines with available oxygen to form volatile RuO_4 (bp ≈101°C) (Chaston, 1975). Dowex resin was ashed at 450°C overnight, but perhaps this was sufficiently hot for the Ru bound to the resin as Ru(III) or Ru(IV) to oxidize to RuO_4.

Figure II.3. The solubility of MIBK as a function of HCl concentration



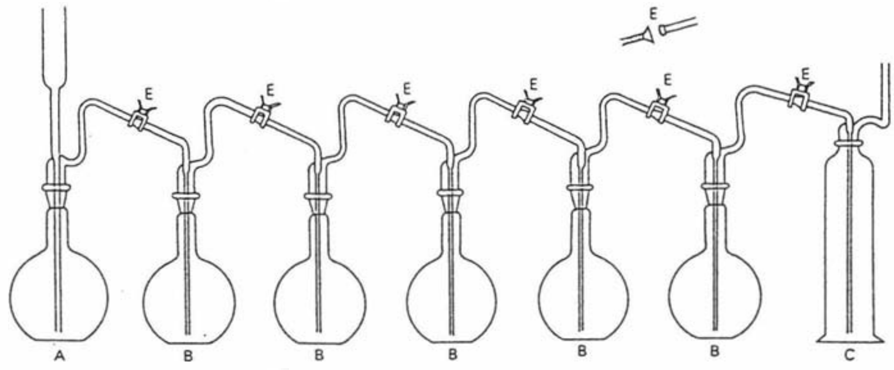


Figure II.4. Distillation train used for the separation of Ru and Os from iron meteorite matrices (Beamish and Van Loon, 1977)

Ruthenium can also be isolated by oxidizing to RuO_4 in acid solutions and distilling, which effects a separation from most other elements except Os. A strong oxidizing agent is needed to convert Ru(III) or Ru(IV) to RuO_4. Sandell (1959) recommends boiling the sample in hot $HClO_4$ and distilling the vapor into a cold solution of hydroxylammonium chloride, NaOH or 3% H_2O_2 to absorb and reduce the volatile tetroxide. Beamish and Van Loon (1977) used the hot $HClO_4$ digestion and 3% H_2O_2 as a receiving liquid in a distillation train containing four traps (Figure II.4.) to avoid possible losses of RuO_4 in their analyses of iron meteorites. Cotton and Wolf (1962) used a $H_2SO_4/NaBiO_4$ flux and distilled RuO_4 into $\approx$5M Na_2CO_3 at 0°C. Using the same oxidizing mixture, Kesser *et al.* (1966) distilled RuO_4 into CCl_4 at 0°C.

This method is extremely cumbersome, and Sandell (1959) suggests that the isolation of Ru could be simplified by extracting RuO_4 with an immiscible organic solvent, bypassing the distillation. The tetroxide is very soluble in non-oxygenated organic solvents with which it does not react, such as cyclohexane or CCl_4 ($D = 58$ between CCl_4 and water--Martin, 1954). In organic chemistry, RuO_4 is extracted into CCl_4 and used as a catalyst for oxidation in synthesis reactions (Griffith, 1989). Matlack and Meadows (1962) refer to unpublished work of Herrington and Powell as the first to utilize extraction of Ru with CCl_4, and they describe their Ru separation into CCl_4 from aqueous solutions at pH4 with an equilibration time of one hour. The RuO_4 was back-extracted into 3M NaOH for subsequent radiochemical determination. This extraction method, though simple, appeared at first to be inappropriate for iron meteorite solutions, which should be dissolved in acid to avoid precipitation of major and trace constituents (Mottana *et al.*, 1977). Bringing the solution to the appropriate

Table II.4. Reagents used to oxidize aqueous Ru to RuO_4 and their references

Oxidant	Reference
ClO^-/OH^-	Howe & Mercer, 1925
$NaBrO_3$	Thiers et al., 1948
$Cr_2O_7^{2-}$	Kambara, 1956 (in Korkisch, 1966)
$Ce(SO_4)^{2-}$	Kambara, 1957 (in Korkisch, 1966)
PbO_2	Kambara, 1958 (in Korkisch, 1966)
$HClO_4$	Sandell, 1959
$NaBiO_3/H_2SO_4$	Larsen & Ross, 1959
$KMnO_4/NaBiO_3$	Hara & Sandell, 1960
$NaBiO_3/O_2$	Menis & Powell, 1962
$NaClO_4$	Lee & van der Engh, 1973
$NaIO_4$	Lee & van der Engh, 1973

pH would result in the co-precipitation of Ru with $Fe(OH)_3$, $Ni(OH)_2$, $Co(OH)_2$, etc., as well as unnecessarily and excessively diluting the sample solution. Pre-extraction of the Fe with MIBK was considered, but the concentrations of Ni (≈10%) and Co (≈0.5%) are also high in the remaining solutions, as they are not extracted detectably into MIBK (Goto and Kakita, 1958; Brooks *et al.*, 1985).

Ruthenium tetroxide is easily generated in an aqueous solution from $RuCl_3{\cdot}nH_2O$ or $RuO_2{\cdot}H_2O$ by a variety of oxidants, singly or in combination as shown on Table II.4. From this list, it should be possible to find an oxidant to convert Ru (III) or Ru(IV) to RuO_4 in acidic media for extraction into an appropriate solvent, although Larsen and Ross (1959) describe the behavior of Ru as "complex and contrary" in acidic solutions. Goldstein *et al.* (1961) determined Os by oxidizing it with $KMnO_4$ in 3M H_2SO_4 and extracting it into CCl_4 from a 3M H_2SO_4 + 9M HNO_3 mixture. The OsO_4 in the CCl_4 phase was determined directly by spectrophotometry.

Table II.5. The use of various oxidants for the extraction of Ru into $CHCl_3$ and CCl_4

Oxidizing Agent	% Ru extracted CHCl3	CCl4	Background Interferences
$NaBiO_3$	12.0	10.0	---
$Na_2S_2O_8$	89.0	72.8	44% of signal height
$Ce(NO_3)_4 \cdot 2NH_4NO_3$	97.0	91.0	25% of signal height
$NaIO_4$	101	95.0	---

Oxidation of Ruthenium to the Tetroxide

Ruthenium tetroxide is a more powerful oxidant than OsO_4 because Ru, being a second-row transition element, will hold its outer d-electrons more tightly than Os does (Griffith, 1989). Ruthenium is more easily reduced than Os, as $FeSO_4$ in slight excess reduces RuO_4 completely and rapidly (<5 minutes) and OsO_4 slowly (≈99% Os recovered after 5 minutes) (Sandell, 1959). A stronger oxidizing agent than $KMnO_4$ is probably needed to keep Ru in the octavalent state in acid. This was confirmed here in a test where $KMnO_4$ was added to 1 µg/mL Ru in 3M H_2SO_4, extracted into CCl_4 and determined by GFAAS. Only 40% of the Ru was recovered in the organic phase.

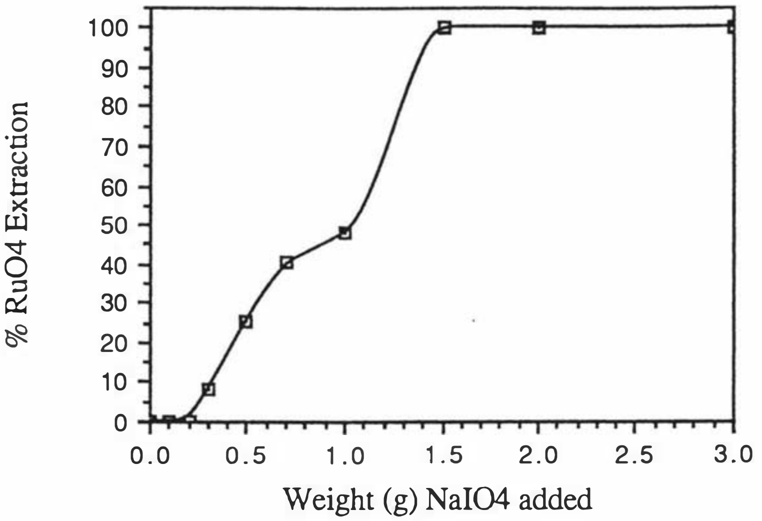
A variety of oxidizing agents was used in the attempt to oxidize Ru for quantitative extraction and a comparison was made using CCl_4 and $CHCl_3$ as the organic phase with a HNO_3 aqueous phase. The procedure involved 5 mL of a 0.2 µg/mL Ru solution in 2M HNO_3 placed in a 10 mL Quick-Fit centrifuge tube to which 1g of oxidizing agent and 1 mL of organic solvent were added and shaken for 3 minutes to equilibrate the phases, followed by centrifuging. The organic phase was analysed by GFAAS. The results are presented in Table II.5.

Sodium bismuthate required heating to dissolve it in HNO_3, and it is likely that RuO_4 volatilized and so was not available for extraction into the organic phase upon cooling of the solution. Cooling of the solution was necessary prior to addition of the organic phase as the vapor pressures of both $CHCl_3$ and CCl_4 are very high. In unheated solutions, no extraction of Ru was effected because either Ru adsorbed onto the solid phase in the $NaBiO_3/HNO_3$ suspension, or because Ru was not sufficiently oxidized. Sodium peroxodisulfate did not sufficiently extract the Ru from HNO_3 in either $CHCl_3$ or CCl_4. Sandell (1959) states that in any case, peroxodisulfate is not a satisfactory oxidant for Ru in the presence of Fe(III). When $Ce(SO_4)_2$ is used as oxidant, it was possible to extract nearly 100% Ru into $CHCl_3$ and ≈90% into CCl_4, but the orange reagent color was also efficiently extracted into both solvents. This caused a substantial background interference signal, which was not desirable.

Sodium periodate did not extract into the organic phase, so did not cause any reagent interference. Ruthenium was completely extracted into $CHCl_3$ though less so in CCl_4. This is probably due to the relative solubilities of each solvent in acid. A longer equilibration (shaking) time might have improved the amount of Ru extracted into CCl_4.

On the basis of these results, a series of optimization experiments were done using $NaIO_4$ as the oxidant prior to extraction of Ru into $CHCl_3$ as RuO_4.

Figure II.5. Extraction of RuO4 in HNO3 into CHCl3 phase as a function of weight NaIO4 added to the mixture



Optimum Amount of Sodium Periodate

Figure II.5 indicates that the extraction of Ru increased with an increasing amount of NaIO4 until a limiting value was reached at 1.5 g $NaIO_4$ for a 200 μg loading of Ru, ie.--7.5 mg $NaIO_4$ per 1 μg Ru. Apparently, there must be an excess of periodate over Ru for the extraction to be complete, possibly because of the presence of other oxidizable species in the solution. Amounts of periodate in excess of the minimum ratio for $NaIO_4$/Ru do not appear to affect the efficiency of the extraction. However, $NaIO_4$ has to be dissolved completely into the solution to extract all of the Ru. Apparently, RuO_4 will adsorb onto any solid $NaIO_4$ and will not extract into $CHCl_3$. For this reason, the sodium salt is preferred to the potassium salt as the former is more soluble in acid and in water, whereas KIO_4 is slightly soluble only in KOH and in hot water.

Shaking Time

The shaking time is critical, as seen in Figure II.6. For an aqueous to organic phase volume ratio of 5, a minimum period of 2.5 minutes is required for the extraction of RuO_4 into $CHCl_3$ from 2M nitric acid.

Figure II.6. Extraction of RuO4 into CHCl3 as a function of shaking time

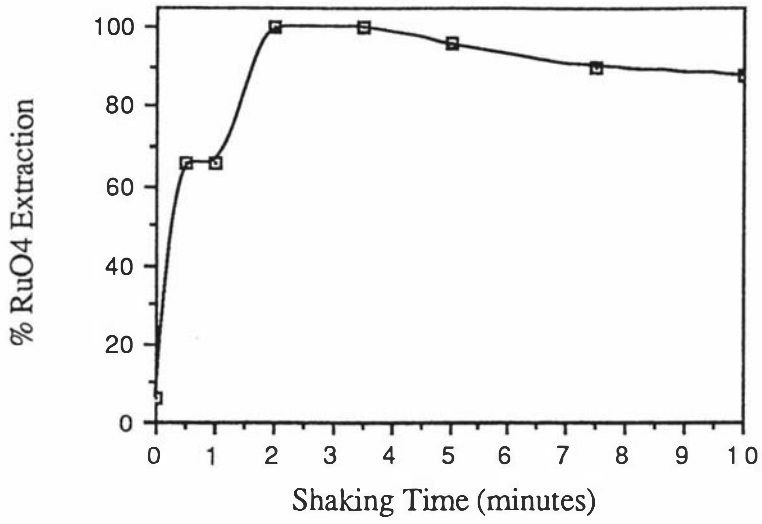
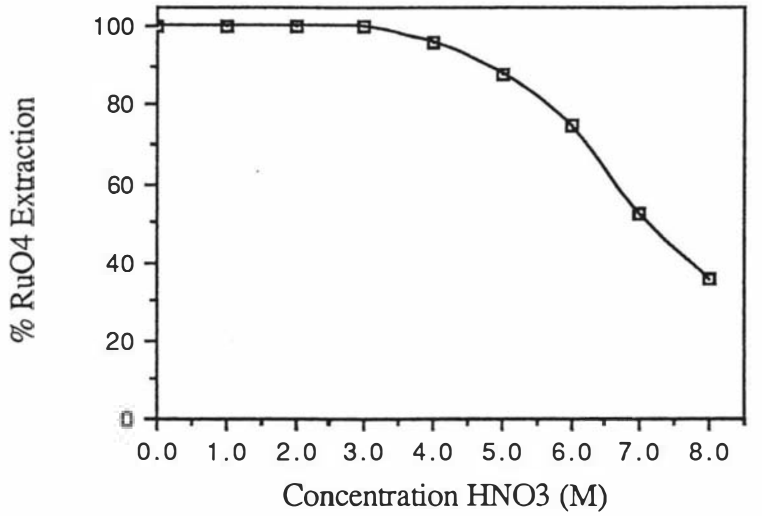


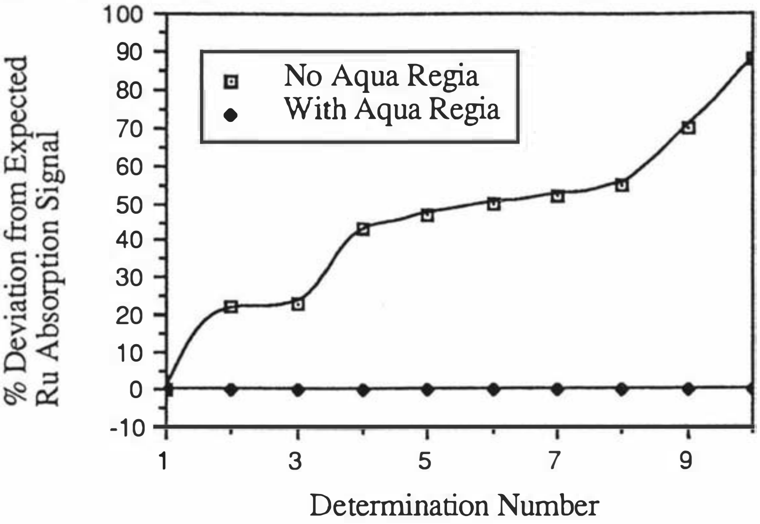
Figure II.7. Extraction of RuO4 into CHCl3 phase as a function of HNO3 concentration



Acidity

Ruthenium tetroxide is extracted completely from HNO_3 solution with concentrations up to 3M (Figure II.7). Sodium periodate became less soluble in more concentrated solutions of HNO_3. An acid concentration of 2M is desirable to keep the constituents of iron meteorites in a stable solution. All samples and standards were ultimately prepared in solutions with a final HNO_3 concentration of 2M.

Figure II.10. Successive Ru determination in the same glassware with and without aqua regia-soaking between procedures



Cleaning of Glassware

When the same glassware was used for successive Ru determinations, an enhancement could be seen in the Ru absorbance signal in spite of the glassware having been cleaned in detergent between determinations (Figure II.8). After nine analyses, there was ≈100% enhancement in the Ru signal. Ruthenium tetroxide is readily reduced and deposited on the walls of glass stills as RuO_2 (Larsen and Ross, 1959). Particular care must be taken to ensure the cleanliness of the apparatus. Ruthenium dioxide is soluble in hypochlorite solutions which Howe and Mercer (1925) used to clean apparatus in which Ru was precipitated. Kesser *et al.* (1966) used hot perchloric acid to clean Ru-contaminated glassware and went so far as to use only distilled water for rinsing, scrupulously avoiding contact of the apparatus with soap, detergents, grease or deionised water.

Ruthenium is apparently not soluble in aqua regia since it was first discovered in the residues of platinum samples dissolved in this acid mixture (Griffiths, 1963). However, aqua regia had previously been used successfully as a soaking liquid in this laboratory's cleaning procedures for Pt and Pd. When Ru-contaminated glassware was soaked in aqua regia, no subsequent enhancement of Ru was observed (Figure II.8). Commercial (drum) grade HCl and HNO_3 were used for this procedure and the mixture saved and reused for up to 30 soakings. No excess traces of Ru were detected at any point. The reason for this was discovered later and will be discussed in Section II.4.iii.

II.3.vi. Summary of the Proposed Methodology

Five mL of the sample solution is placed in a 10-mL Quick-Fit stoppered centrifuge tube. One mL of $CHCl_3$ and 1 g $NaIO_4$ is added and this mixture is shaken for 3 minutes. The mixture is centrifuged and the $CHCl_3$ phase is analyzed with the GFAAS instrument using the program outlined in Section VII.4. Standards are treated in the same manner in order to match matrices. All glassware in contact with any Ru solution is soaked at room temperature in an aqua regia solution for >2 hours in a fume cupboard and thoroughly rinsed with deionised and distilled water afterwards to remove all traces of the acid mixture.

II.4. Study of the Digestion of Iron Meteorites

II.4.i. Sample Preparation

The iron meteorite samples were cut with a hacksaw to yield a 0.5-1g piece free of fusion crust and inclusions and the sawings were retained. Any protective lacquer coating was removed with acetone or scraped off manually with a small file, as was any paint transferred to the sample from the commercial hacksaw blade. The sample was weighed in a Quick-Fit 50 mL conical flask and refluxed with constant-boiling nitric acid until dissolution was complete (generally after 15 minutes). The reflux apparatus was rinsed with 5-10 mL 2M nitric acid and the contents were quantitatively transferred to a 50 or a 100 mL volumetric flask, noting the amount of water and constant boiling nitric acid used in the transfer so that the final solution had a concentration of 2M HNO_3. It was later discovered that the sawings could be used for the determination of Ru, as any foreign metal acquired from the sawing procedure was not present in sufficient amounts to dilute the Ru content of the meteorite. In addition, the hacksaw blade does not contain detectable quantities of the PGMs, and no resultant enhancement by contamination is observed.

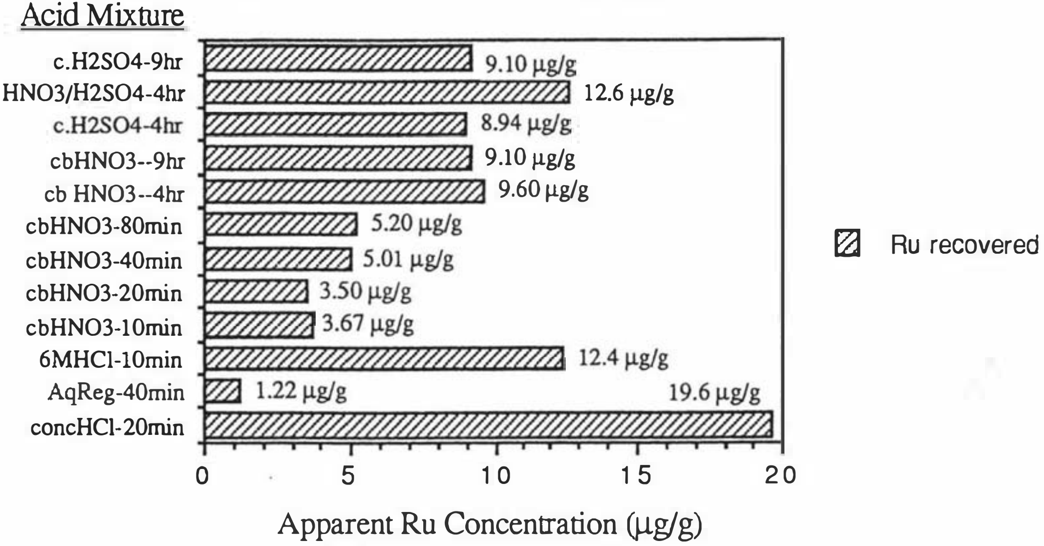
II.4.ii. Selection of a Reference Material

A study of the distribution behavior of pure substances is a preliminary step towards the solution of problems in analytical extractions. One should bear in mind the effects produced by the presence of components in a complex mixture (Morrison, 1950). Much of the information obtained on analytical extractions has been derived from empirical studies of synthetic, nonideal solutions. To check the practical application of any proposed method, a reference standard should be tested. Unfortunately, there are no standards with matrices similar to iron meteorites with a detectable amount of Ru for checking the proposed methodology (eg.--PGM-doped high-Ni steels or other iron meteorites). It was necessary to rely on the accuracy of values for an iron meteorite analysed by RNAA. North Chile (IIA) was used to test the methodology, as IIA irons are hexahedrites, which are thought to have cooled slowly enough to become large kamacite crystals to the exclusion of taenite, with unresolved bandwidths. Hexahedrites, because of their lack of crystal structure, are more likely to be homogeneous than other types of iron meteorites (Wasson, 1974). In addition, the sample was donated to this laboratory in the form of turnings. The advantage is that the material may be subsampled to ensure homgeneity at least within this vial of turnings, and the tedious hacksawing and cleaning steps outlined in Section II.4.i. are unnecessary. Pernicka and Wasson (1987) report a Ru value of 19.3 μg/g for North Chile. The high concentration of Ru means that small (0.05 g) samples of the hexahedrite can be taken without sacrificing precision and accuracy.

Table II.6. The effect of time on the apparent Ru content for the HNO_3 digestion of North Chile (IIAB) iron meteorite

Time (minutes)	Apparent Ru content (µg/g)
10	12.4
20	11.9
40	12.3
80	12.1

Figure II.9. Effect of different acid and acid mixtures on the dissolution of Ru from the North Chile (IIAB) iron meteorite



II.4.iii. Selection of Acid for Digestion

The results of refluxing the sample in nitric acid were disappointing, as only 3.67 µg/g Ru was detected in North Chile (IIA). Refluxing for longer periods of time showed a slight increase in this value (Table II.6). This appeared to indicate that Ru was present in the meteorite as Ru metal, which is insoluble in acids (Hammond, 1990). Iron meteorites had been digested in 70% perchloric acid by Sen Gupta and Beamish (1963) but this was rejected as their data were in poor agreement with those of other workers. They had experienced difficulties with control of their procedure, and it frequently led to explosions. In addition, their method required distillation as a separation scheme for Ru.

A variety of other acids and acid mixtures were attempted here in the hope that µg amounts of Ru would digest completely when refluxed in acid.

Table II.7. Results for six complete replicates for the determination of Ru in the North Chile (IIAB) iron meteorite

Replicate Number	Ru Abundance (μg/g)
1	21.3
2	19.0
3	19.6
4	19.3
5	19.5
6	21.3
Mean	20.0
RSD	5.2%

The results are shown in Figure (II.9). Oxidative attack appears to cause Ru to dissolve, then to volatilize from most of the acid mixtures; this is the probable reason for the losses, rather than an incomplete dissolution. This is also the probable reason behind the success of aqua regia as a cleaning reagent for Ru-contaminated glassware. The acid mixture caused oxidation of precipitated and adsorbed RuO_2 to a more soluble and perhaps volatile species, removing the contamination from the walls of the glass- and plasticware (Section II.3.v.).

Although Ru in high concentrations does not apparently dissolve in mineral acids (Livingstone, 1973) it appears to digest fairly well in concentrated HCl at the μg level. Indeed, HCl was used to digest iron meteorites prior to the radiochemical separation procedures in the RNAA determination of Ru by Crocket (1972) and by Pernicka and Wasson (1987).

Precision and accuracy were tested by performing six full replicate analyses involving six separate dissolutions in HCl. The results are presented in Table II.7. This gave a mean value of 20.0 μg/g Ru in North Chile with a relative standard deviation of 5.2%. The precision is highly sastisfactory, and is comparable to literature value of 19.3 μg/g Ru (Pernicka and Wasson, 1987).

Table II.8. Results for 12 complete replicates for the determination of Ru in the flotation sulfide PTC-1

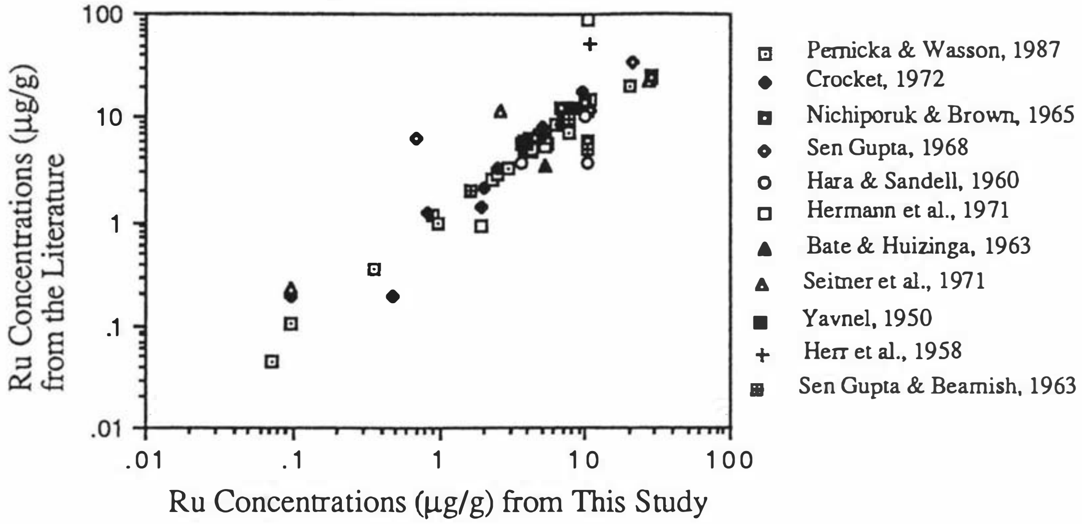
Replicate Number	Ru Abundance (µg/g)
1	0.48
2	0.50
3	0.48
4	0.50
5	0.50
6	0.49
7	0.46
8	0.46
9	0.51
10	0.45
11	0.45
12	0.49
Mean	0.48
RSD	4.21%

II.4.iv. Determination of Ru in PTC-1 Ore

As an additional check on precision and accuracy, replicate analyses were done using the standard ore PTC-1, a finely ground flotation sulfide distributed by the Canadian Geological Survey, though it does not have a standard value for Ru. However, McAdam *et al.* (1973) report an average value of 0.65 µg/g Ru in three determinations by two different methods, and Hoffman *et al.* (1978) found 0.59 µg/g Ru in three replicates determined by INAA using 30-50g of the PTC-1 ore.

Twelve replicates of PTC-1 refluxed in HCl yielded the results in Table II.54, with a mean value of 0.48 ± 4.21%. This value is 18.6% lower than that of Hoffman *et al.* (1978) and 26.2% lower than that of McAdam *et al.* (1973). However, the latter value is an estimated average and has a large 95% confidence interval (0.34-0.93 µg/g). It is possible that the 1 g subsamples used in this study were not as representative as those of Hoffman *et al.* (1978), though the standard deviation for the replicates performed here is quite low. Perhaps, too, the HCl digestion did not bring all of the Ru into solution, especially if any Ru was bound to the silicate phase of the ore. In addition, sulphur was present in the digested solution

Figure II.10. Comparison of Ru values for iron meteorites analyzed in this study with literature values



and could not be removed with boiling HCl. Normally, oxidizing acids are used to digest sulphur, but this could not be done in the presence of Ru for fear it would oxidize and volatilize the analyte. Nonetheless, the precision is good and confirms the reliability of the proposed methodology.

II.4.v. Comparison of Iron Meteorite Values with Available Literature Values

As a final check, Ru was determined in all of the meteorites listed in Appendix 2 and compared to values in the literature (Figure II.12). The agreement is very satisfactory.

II.5. Stability of the Extract

The RuO_4 is unstable if left in the HCl-$CHCl_3$ equilibrium mixture (Figure II.11). After ≈2 hours, there is a steady decrease in absorbance signal owing to reduction of RuO_4 in the presence of chloride and consequent back-extraction of the Ru. Hydrochloric acid reacts with RuO_4 and reduces it to the quadrivalent $RuOCl_2$ or the trivalent $RuCl_3$ (Livingstone, 1973). Excess IO_4^- is not available to re-oxidize Ru, as it has oxidized chloride to chlorine, allowing the reduced ruthenium to remain

Figure II.11. Stability of RuO4 in CHCl3 remaining in contact with HCl phase

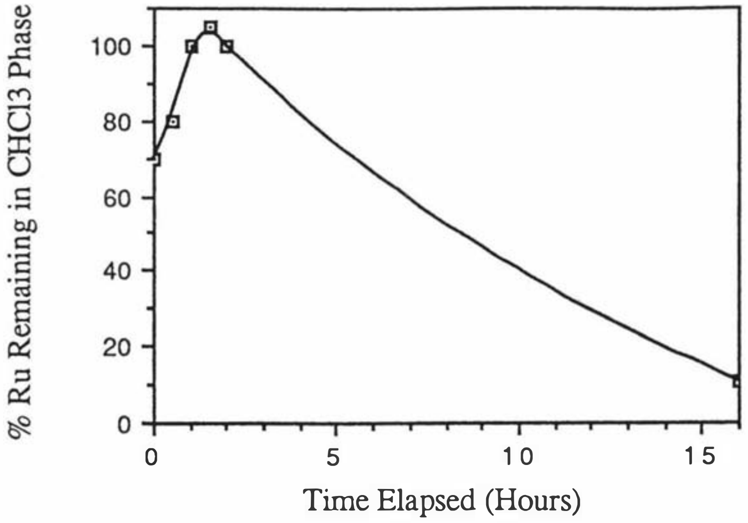
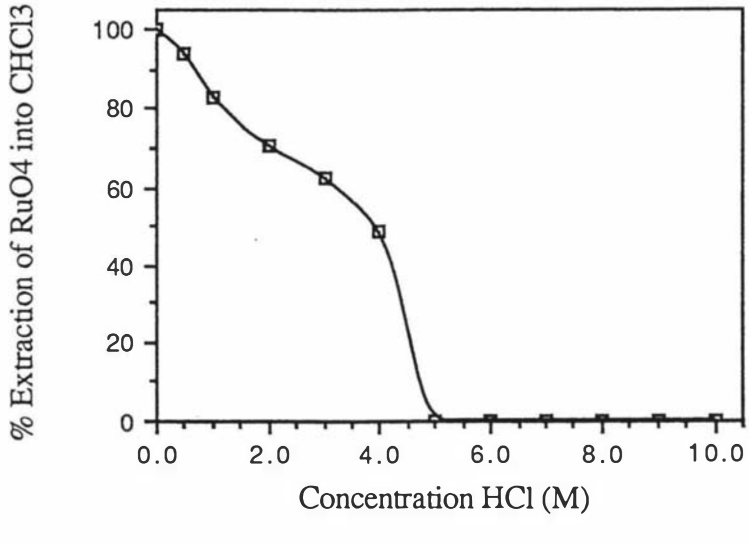


Figure II.12. Effect of HCl concentration on the extraction of RuO4 into CHCl3



back-extracted in the aqueous HCl solution. To illustrate this, Ru was extracted and left to stand in a range of HCl concentrations. The best extraction was realised in the total absence of HCl. At >4M, the Cl_2 generation was so great that nearly all of the sample was lost because of the violent frothing and overflow upon addition of the $NaIO_4$ to oxidize Ru(III) to RuO_4 (Figure II.12).

II.5.i. Use of a "Keeper" Solution

A modification to the procedure summarized in Section II.3.vi. was necessary. A "keeper" solution was prepared in which 1g of $NaIO_4$ was dissolved in 5 mL of 2M HNO_3. The $CHCl_3$ phase was transferred from the original HCl solution to the "keeper" solution immediately after shaking and centrifuging had been completed. This transfer need not be quantitative, and no detectable loss in signal occured in up to 16 hours. This is probably due to the ability of the RuO_4 to be regenerated in the presence of co-oxidants. The tetroxide can form again after reaction and reduction, which is how Ru functions as a catalytic oxidant for organic oxidations (Griffith, 1989).

II.6. Determination of the Distribution Coefficient

The value of the distribution ratio (D) is ≈670 (99.3% extraction, $V_a/V_o = 5$) for RuO_4 between $CHCl_3$ and 2M HCl. This value was obtained by comparing the absorbances for two successive extractions of Ru from the aqueous phase. When D is large, this procedure gives a good approximation to the value of D.

II.7. Calibration Curve

A calibration curve was prepared for absorbance as a function of Ru concentration in the $CHCl_3$ phase (Figure II.13). Initially, all of the calibration standards were refluxed in the same way as the samples, but it was later found that the standards need only be prepared in 2M HCl. No loss of the standard Ru solutions occurred during refluxing. Very dilute standards of Ru should preferably be prepared daily, although Sandell (1959) notes that 0.01 μg/mL solutions of Ru(IV) in 2M H_2SO_4 did not undergo a change in concentration in one year. Ruthenium trichloride

Figure II.13. Ru calibration curve

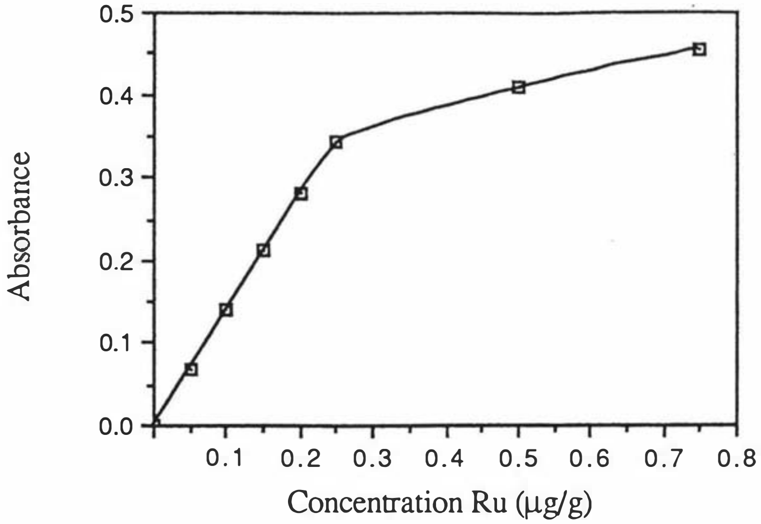
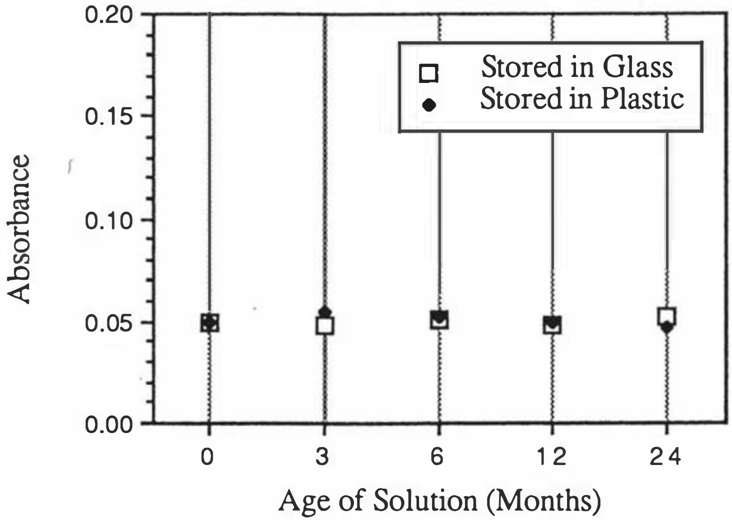


Figure II.14. Effects of storage of 1μg/mL Ru solutions in glass and plastic over time



solutions likewise did not undergo degradation after 6 months in either plastic or glass containers (Figure II.14). However, as a precaution, all solutions were made fresh as required from a 100 μg/mL stock solution of $[Ru_3O_2(NH_3)_{14}]Cl_6$ in 2M HCl, which suffered no losses for up to two years.

II.8. Final Analytical Procedure

The analytical procedure for the determination of Ru in iron meteorites that was finally adopted is as follows.

Weigh accurately 0.05-1.0 g of meteorite millings or clean metal (depending on the expected Ru concentration) and accurately transfer into a 50 mL Quick-Fit conical flask fitted with a reflux system. Add 10 mL of concentrated HCl and reflux for 15 minutes or until final sample dissolution is achieved.

Transfer the solution quantitatively to a 50 mL volumetric flask, rinsing with 6.7 mL of constant boiling (6M) HCl. Adjust the volume to mark with distilled water, giving a final concentration of 2M HCl. Place 5 mL of the solution in a 10 mL Quick-Fit centrifuge tube, and 1 mL of $CHCl_3$ and 1g of $NaIO_4$. Stopper the tube, shake for 3 minutes and centrifuge to separate the phases.

By use of a Pasteur pipette, immediately transfer the organic layer into a previously prepared tube containing 5 mL of a solution of 1g NaIO4 in 2M HNO_3. This transfer need not be quantitative.

Treat the standards prepared in 2M HCl in exactly the same way as the samples. A useful range of standards would contain 0, 0.002, 0.010, 0.020, 0.050, 0.100 and 0.150 µg Ru/mL in the aqueous phase, giving 0-0.75 µg Ru in 1 ml of the organic phase after extraction.

Determine Ru in the organic phase by GFAAS using the conditions in Section VII.4, Table VII.2a. Adjust the number of multiple injections to suit the expected Ru content in order to ensure that the absorbance values fall within the linear portion of the response curve (Section II.7).

Chapter Three

Palladium and Platinum

III.1. Introduction

Native Pt was used by the Indians of Ecuador before the arrival of the Conquistadores and probably before the Inca conquest 50 years earlier (Livingstone, 1973). The first definite reference to Pt was made in 1748 by de Ulloa of the Spanish navy (Hunt, 1980). He described the occurrence of an unworkable metal called "platina" in the gold mines of the Chocó district of present-day Colombia. The platina and gold occurred together as small grains in alluvial deposits and the separation of the two metals was tedious and costly, often rendering the Au-bearing ore worthless.

The first large samples of Pt to be investigated scientifically were brought to Europe in 1741 by a Mr. Wood, who was Assay Master in Jamaica (Hunt, 1980). Difficulty was experienced in working the metal because of its high melting point (1769°C) and specific gravity (21.45 g/cm^3). By 1805, Wollaston was producing malleable Pt by a process involving hot forging of the purified metal (Livingstone, 1973). During his researches on the purification of Pt, Wollaston isolated Pd in 1803 from the mother liquor following the precipitation of Pt as the chloroplatinate in aqua regia.

The principal uses of Pt are in chemical engineering, especially for its catalytic properties; electrical engineering as contacts; medical and dental applications; temperature measurements; and in jewellery (Livingstone, 1973). Palladium is used as a substitute for the more expensive Pt in many of the same applications.

III.2. Survey of Methods of Separation

III.2.i. Fire Assay

Because of their value to industry, many methods have been developed for the separation of Pd and Pt from each other and from other elements. Deville and Stas (1877) utilized Pb fire assay to determine the composition of Pt-Ir alloys used in the manufacture of the International Prototype meter and kilogram. Of the assay methods reviewed by Gilchrist

(1923), only this method of fire assay was found to be quantitative for 0.1-20% PGMs. For smaller concentrations, Hoffman *et al.* (1956) recognized an appreciable lack of precision in PGM values obtained by various laboratories using different methods of fire assay, with values varying by up to a factor of 10 for the same sample. The discrepancies could be due to procedural variations, or in the experience and skill of the operator. Beamish and his coworkers published a long list of research articles (see references) in which many aspects of fire assay were investigated to better understand and control extraction of the PGMs from ores into an assay button. Despite these efforts, Beamish and Van Loon (1977) were prompted to state that the "mixture of chemicals and ore used in the pot fusion provides a complex system, and the chemistry of the fusion process is still practically unknown. Thus, the technique of fire assay collection of the noble metals is largely an empirical process."

Despite its problems, fire assay procedures have been used to isolate minute amounts of the PGMs in sulfide minerals and silicate rocks (Sandell, 1959). Mingaye (1910) used Pb assay to produce a Ag prill on cupellation to collect 0.06 μg/g Pt in sands.

Early analyses indicate the necessity of careful sampling because of the non-homogeneous nature of many materials (Gilchrist, 1923). Hoffman *et al.* (1956) noted that scattered results are characteristic of samples in which the constituent sought is not intimately dispersed throughout the sample, but rather as "concentrated grains" (Kratochvil and Taylor, 1981), where the analyte is present entirely in a particular mineral within the ore sample. Ideally, a few μg of PGM mineral must be distributed evenly in the sample taken for analysis (the standard weight taken has often been "one assay ton," ie.-- ≈30 g). This situation frequently does not occur, so larger samples of ore are often necessary (Hoffman *et al.*, 1978--50g; Plummer and Beamish, 1959--100g). With other sample types, such large amounts are not usually available.

III.2.ii. Precipitation

To overcome the objections of the traditional fire assay, other methods of analyte separation have been explored in the present study. Gilchrist and Wichers (1935) and Gilchrist (1953) determined the PGM content of materials gravimetrically after separations of the PGMs as hydrated oxide precipitates. Berman and McBryde (1958) showed this method to be quantitative for 500 μg each of Rh, Ir, Pd and Pt using a $Ce(SO_4)_2$ carrier to aid in the precipitation of these metals. Currah *et al.* (1946) excluded the interfering sulfides of Cu, Ni and Fe from samples by precipitating Au, Pd, Rh and Ir with organic monosulfides.

Separation schemes utilizing precipitation are rejected because the procedures are time-consuming and cumbersome as well as often not quantitative. In their review of precipitation and crystallization as a separation technique, Hermann and Suttle (1961) hint at the difficulties of obtaining a pure and quantitative precipitate of an element. Incomplete precipitation and coprecipitation of other (interfering) elements are common errors associated with this technique (Charlesworth, 1981).

III.2.iii. Chromatography

Lederer (1948) separated several base and noble metals by inorganic paper chromatography. Burstall *et al.* (1950) achieved qualitative separation of elements by paper chromatography, which was later refined by Kember and Wells (1955) and Rees-Evans *et al.* (1958) to be quantitative on macro and micro scales, respectively. The limit of detection (LOD) using cellulose paper chromatography was 0.1 μg Pd and 2.0 μg Pt. Many authors used paper electrochromatography or ionophoresis to separate the PGMs from each other. Anderson and Lederer (1952) noted the movement of Au, Pt and Pd away from Cu. MacNevin and Dunton (1957) and Sherma *et al.* (1963) could not successfully separate noble metals from each other in simple solutions. The work of Majumdar and

Table III.1. Distribution coefficients (D) for Pd(II) and Pt(IV) using anion exchange

HCl Conc.	Pd(II)		Pt(IV)	
(M)	A	B	A	B
0.10	1600	45 000	>10 000	44 000
0.50	---	15 000	---	27 000
1.0	870	4 300	5 560	20 000
4.0	300	300	2 480	2 100
7.9	79	75	914	780
11.6	40	35	440	400

A--Kraus *et al.*, 1954
B--Berman and McBryde, 1958
NB: The difference in the values of D at lower concentrations is a function of the degree of loading.

Chakrabartty (1957, 1958a, 1958b) showed that complexing PGMs using thiourea effected their separation in ≈20 μg quantitites. However, the majority of the literature indicates that these separations are not very effective in removing PGMs from base metals.

Ross *et al.* (1965) used gas chromatography to determine 2.2 ng Rh as Rh(III) tri-fluoroacetyleacetonate and stated that this type of determination for PGMs offered excellent promise.

III.2.iv. Ion Exchange

Kraus *et al.* (1954) determined the extraction coefficients (D) of Pd(II) and Pt(IV) between an anion exchange resin (Dowex-1) and HCl. The value of D decreased with increasing HCl concentration, and this is characteristic of elements for which the concentration of adsorbable species does not increase with molar concentration of HCl (Table III.1). This results from a "displacement" effect of the Cl^- ions and the effect of the acid on the adsorption equilibrium. Berman and McBryde (1958) repeated these experiments using Amberlite IRA-400. They found that as long as the resin was not excessively loaded (≤2% of total calculated capacity), Pt(IV) was adsorbed strongly fron 0-12M HCl and Pd(II) from 0-2M HCl. Difficulty was experienced by Kraus *et al.* (1954) in subsequently removing the two metals fron the anion exchange column because of their very high affinity for the resin.

The separation of analyte from Fe, Co and Ni is necessary as iron meteorites possess large concentrations of these interfering elements. Iron(III) is strongly absorbed by Dowex-1 from 3-9M HCl (Moore and Kraus, 1950), which affords a method to separate Pd and Pt from Fe. Brooks and Ahrens (1960) separated noble metals from Fe by adsorbing Pd and Pt onto the resin and eluting Fe in 2M HCl. Nickel(II) shows no adsorption under any conditions using this resin (Kraus and Nelson, 1958). Cobalt adsorbs onto Dowex-1 at >5M HCl, and can be eluted from the column at lower acid concentrations. However, it must be noted that Fe(III) still adsorbs onto the anion exchange resin at low HCl concentrations (D = 100, 1M HCl--Kraus and Nelson, 1958).

Payne (1960) attempted to separate base metals from the PGMs by cation exchange, in which the base metals were adsorbed and the PGMs eluted. Some of the PGMs, particularly Pd, were retained on the column. On complexing the PGMs with nitrite, complete recovery was possible. Stevenson *et al.* (1953) accomplished separation of the PGMs from each other using Dowex-5 cation exchange resin. This was accomplished in the total absence of halides; to this end, PGM solutions were fumed in a mixture of HNO_3 and $HClO_4$.

III.2.v. Solvent Extraction

Kraus *et al.* (1954) noted an extremely close parallel between anion exchange adsorption and solvent extraction. In developing a spectrophotometric method for the determination of Pd, Yoe and Overholser (1939) noted that a Pd complex with p-nitrosodiphenylamine could be readily extracted with ether or ethyl acetate. Ryan (1951) extracted the same complex into chloroform from up to 0.1M HCl. This system possesses important advantages of eliminating the usual spectrophotometric masking interferences of Co, Ir and Rh. The Pd could also be concentrated in the organic phase with a resultant gain in sensitivity.

Young (1951) used solvent extraction to isolate the Pd-dimethylglyoxime (Pd-DMG) complex reported by Wunder and Thüringer (1912--referenced in Sandell, 1959) and conventionally used for the gravimetric determination of Pd. Young managed to effect a clean separation of Pd into chloroform, which was then evaporated and the residue dissolved with HCl for a subsequent volumetric determination with diphenyldithiocarbazone. Nielsch (1954) reported that this red chloroform phase could be analysed directly by spectrophotometry, eliminating the need to further process the sample using back-extraction or evaporation and redissolution.

As Ni is an interferent in the Pd-DMG system, other extraction systems were sought. West and Carlton (1952) extracted Pd into methylisopropyl ketone with thiocyanate. Forsyth *et al.* (1960) studied the structure of the Pd-pyridine-thiocyanate complex which was extracted into chloroform. Both publications ignore the strong complex which thiocyanate forms with Fe(III) (Vogel, 1989), making these extraction systems ineffective for separation of Pd from Fe. Yoe and Kirkland (1954) extracted both Pd and Pt into chloroform with diethyl dithiocarbamate. Brooks *et al.* (1989) used ammonium pyrrolidine dithiocarbamate to extract several elements, including Pd, into methylisobutyl ketone (MIBK). Khopkar (1966) used a combination of anion exchange and solvent extraction to effect the separation of Pd(II) and Pt(IV) from other metals in HCl/$AlCl_3$ aqueous phases into mesityl oxide. This shows the possibility of utilizing the difference between the ion exchange and solvent extraction methods for the separation of analyte.

Pantani and Piccardi (1960) noted that Au could be separated from other noble metals by extracting Au into isoamyl alcohol from HBr solutions, as the PGMs do not form extractable bromocomplexes into this solvent. Platinum will form a bromocomplex extractable into diethyl ether or ethyl acetate in a $HCl/SnCl_2$ mixture (Morrison, 1950). Extractable chlorocomplexes were not formed for extraction into ether (Linke, 1965) or into MIBK (Brooks and Lee, 1989). Iodocomplexes of Pd extract into methylisopropyl ketone (West and Carlton, 1952) and into MIBK (Duke and Stawpert, 1960). Faye and Inman (1963) accomplished a combined Pt and Pd iodocomplex extraction into 15% tri-n-butyl phosphate in hexane; Diamantatos (1981) and Brooks and Lee (1989) achieved the same extraction into MIBK.

III.3. Survey of Methods of Determination

III.3.i. Gravimetry

Gilchrist and Wichers (1935) outlined procedures for the gravimetric determination of Pt as metal and Pd as either the Pd-DMG complex or as metal. Though reliable, the gravimetric method is not suited to the determination of trace amounts of Pd or Pt. Besides this, gravimetry utilizes precipitation for the separation of elements, which is time-consuming and subject to the errors associated with precipitation (Section III.2).

III.3.ii. Spectrophotometry

Ayres and Tuffly (1952) showed that use of a spectrophotometer for the determination of Pd (40-200 μg) with bromide was faster than gravimetric methods, with comparable accuracy. Sandell (1959) outlined several methods for analysis by this method, and favors the red p-nitrosophenylamine complex with Pd, with a sensitivity of 1 μg/mL. For Pt determination, he cites complexes of $SnCl_2$, p-nitrosophenylamine and iodide, all with sensitivities of 0.5 μg/mL. Each of the spectrophotometric procedures stressed the need to separate the PGMs from each other as many of the color reactions are not specific for the desired element.

III.3.iii. X-Ray Fluorescence

MacNevin and Hakkila (1957) considered X-ray fluorescence to be a more rapid technique than gravimetry or colorimetry. They applied the sample solution to heavy absorbent paper and after drying, placed the paper on the holder of the X-ray instrument. Limits of detection for Pt and Pd were rather high: 100 μg/mL for Pt and twice that value for Pd.

III.3.iv. Atomic Absorption Spectrometry

Flame AAS was used by Lockyer and Hames (1959) as a convenient way to analyse materials containing PGMs, as no interferences were produced in the flame between the PGMs. Using this technique, the limit of detection (LOD) of Pt is 10 μg/mL and Pd is 2 μg/mL. Beamish and Van Loon (1977) predicted that the use of flameless cells would decrease the LOD of the PGMs by greater than one order of magnitude using the AAS instrumentation.

III.3.v. Neutron Activation Analysis

For the determination of Pd and Pt, GFAAS is superior to NAA in terms of sensitivity, though not in rate of sample throughput (Hall and Bonham-Carter, 1988). This efficiency is due to the multielement capacity of the NAA technique. However, Pd and Pt are as difficult to determine by this method as Ru. The multielement capacity is often not utilized when dealing with elements that are difficult to determine. Gijbels (1971) discussed the scope and limitations of NAA for PGMs, including interferences for which radiochemical separation is not possible (Table III.2). The technique requires processing of irradiated samples within a day after irradiation because of the relatively short half-lives of the radionuclides produced by Pd and Pt.

Smales *et al.* (1967) determined Pd by RNAA using 7.5-day ^{111}Ag, which decays from 22-minute ^{111}Pd. The longer-lived ^{111}Ag isotope is more easily measured that the 13.5 hour ^{109}Pd isotope. The Ag is

Table III.2. Isotopes of Pd and Pt produced by RNAA irradiation (from Gijbels, 1971 and Crocket *et al.*, 1968)

	Sensitivity	Decay Products
Pd	4 ng/g	^{108}Pd -(β^-)->^{109}Pd (13.5 hour) ^{110}Pd -(n,γ)->^{111}Pd -(β^-)->^{111}Ag(7.5 day)
Pt	10 ng/g	^{196}Pt -(β^-)-> ^{197}Pt (18 hour) ^{198}Pt -(n,γ)-> ^{199}Pt -(β^-)->199Au (3.15 day) ^{198}Pt -(β^-)->^{198}Au (2.6 day)

precipitated as a chloride in a separate sample, thus making this determination a single-element one.

Crocket (1972) determined Pt as the sum of 4.1-day ^{195}Pt, produced from ^{194}Pt, plus 3.0-day ^{199}Au from ^{198} Pt (Baedecker and Ehmann, 1965). To simplify the radiochemical separation involved, Pernicka and Wasson (1987) determined Pt by measuring ^{199}Au activity only, though a correction had to be made for the production of this isotope directly from ^{198}Au. This procedure also required that Pt be determined in a separate sample, and not as part of a multielement suite.

III.3.vi. Inductively Coupled Plasma

Hall and Bonham-Carter (1988) mention the use of ICP atomic emission spectrometry (ICP-AES) as a popular technique for the detection of Pt and Pd. A disadvantage of ICP-AES is that in order to achieve low LOD, a high sample to volume ratio (typically 20 g in 3 mL) must be used with no sample remaining for replicate analyses. These authors favor ICP-mass spectrometry as its sensitivity rivals that of GFAAS. Interferences are minimized with the calibration strategy of isotope dilutions, with the exception of the interferences caused by spectral overlap.

Table III.3. Range of values for Pd and Pt found in iron meteorites

Range	Reference
Pt: 0.07 - 38.3 µg/g	Pernicka & Wasson, 1987
Pd: 1.6 - 19.7 µg/g	Smales *et al.*, 1967

Figure III.1a. Effect of Fe and Ni on the absorption signal of 1 µg/mL Pd

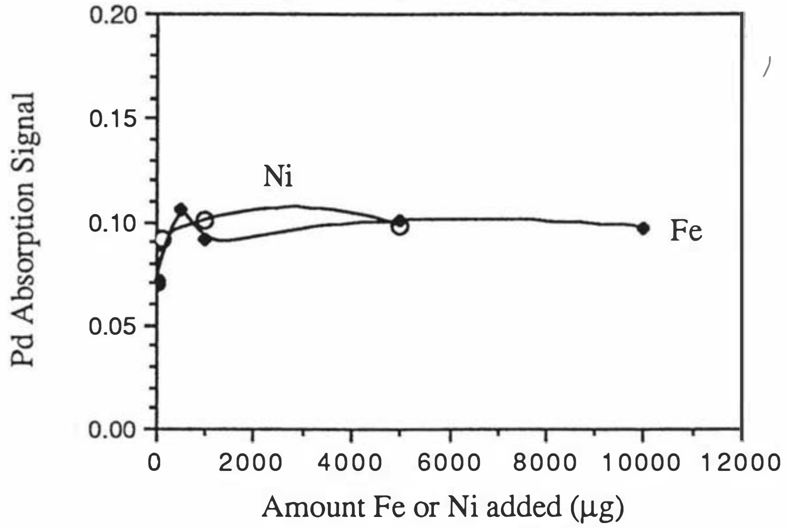
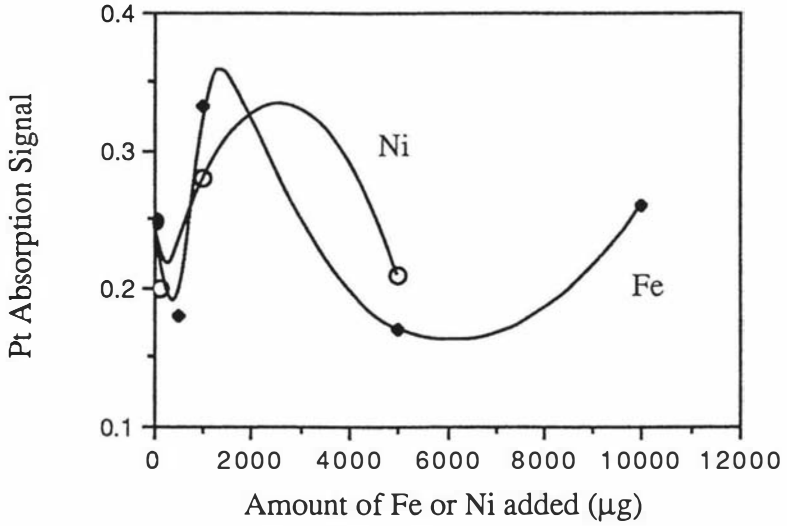


Figure III.1b. Effect of Fe and Ni on the absorption signal of 1 µg/mL Pt



III.3.vii. Selection of Technique

Graphite furnace AAS is the only method available to us with good enough sensitivites for Pd and Pt determinations in iron meteorites (Table III.3) without the need to use large sample weights. Though the other instruments are capable of simultaneously determining many elements (and effectively decreasing the weight of sample required per element), the detection of Pt and Pd is sufficiently difficult as to warrant a separate sample for the sole determination of either Pt or Pd. In this respect, GFAAS is superior as smaller sample weights are sufficient.

As outlined in the Ru chapter, a scheme is necessary to separate Pd and Pt from the sample matrix, as Fe, Ni and Co all have adverse effects on the absorbance signals for both Pd and Pt (Figure III.1). The Pd and Pt do not, however, interfere with each other when determined by GFAAS, so that separation of these two metals from each other is not necessary.

III.4. Studies on the Separation of Palladium and Platinum from Iron Meteorites

III.4.i. Ion Exchange

Both Pd and Pt are adsorbed onto anion exchange resins to the exclusion of Fe, Ni and Co at <2M HCl. Difficulties were experienced in subsequently eluting Pd from the resin (Kraus *et al.*, 1954), so in the present work the resin was ashed in a muffle furnace overnight at 450°C and the residue redissolved in a small volume of aqua regia for determination of both Pd and Pt by GFAAS.

Good agreement was obtained when a sample of Toluca (IAB) was put through this procedure (Table III.4). However, when testing the precision of this method, five replicate analyses of a sample solution prepared from Toluca indicated a relative standard deviation of approximately ±13%.

As in the case of Ru, losses of Pd and Pt may occur during ashing. Chaston (1975) notes that above 400°C, the PGMs form gaseous oxides

Table III:4. Pd and Pt content of Toluca (IAB)

Element	Mean ($\mu g/g$) This Work	Nichiporuk & Brown, 1965 ($\mu g/g$)	Accuracy (%)
Pd	3.74	4.0	6.48
Pt	6.56	6.5	0.91

(PdO, PtO_2) when heated in the metallic form. The ashing occurs at 450°C, and it is likely that some Pd and Pt are lost as oxide vapor.

Cation exchange of the sample where Pt and Pd could be eluted and thus separated from the adsorbed Fe and Co was rejected as Ni would also elute with the analytes. In addition, Pd tends to adsorb slightly onto the resin (Payne, 1960).

III.4.ii. Solvent Extraction

Solvent extraction initially did not appear promising, as Fe would usually coextract with Pd and Pt, or if Fe extracted to the exclusion of Pd and Pt, Ni would remain with the analytes in the aqueous phase. For the latter case, Diamantatos (1981) noted that an iodocomplex of Pd and Pt would extract into MIBK, though the bromocomplexes (Pantani and Piccardi, 1960) and the chlorocomplexes (Linke, 1965) did not. Brooks and Lee (1989) used this idea for the determination of Pd and Pt in Arctic plant material used for biogeochemical prospecting studies. They extracted Fe as a chlorocomplex from 6M HCl solutions into MIBK to remove the Fe, and then added KI to form the iodocomplexes of Pd and Pt. These were extracted into a fresh portion of MIBK. This effected separation from many elements that form extractable chlorocomplexes (Ga, Tl, Au--Morrison, 1950; Fe, Sb, As, Sn, Se, Te, Ge, Cr, V, Mo--Goto and Kakita, 1958).

Discussion

Platinum and palladium form a number of compounds and complexes in which the metals are tetravalent. However, there are many more Pt(IV)

Table III.5. Energy differences between analogous bonds (Pöe & Vaidya, 1959)

Bond 1	Bond 2	Difference in Energy (Bond 2 - Bond 1)
Pt--I	Pt--Cl	12 kcal
Pt--I	Pt--Br	4.5 kcal

Table III.6. Concentrations of Y^- necessary to displace X^- in the halocomplex $[PtX_6]^{2-}$ (from Schlesinger and Palmateer, 1963)

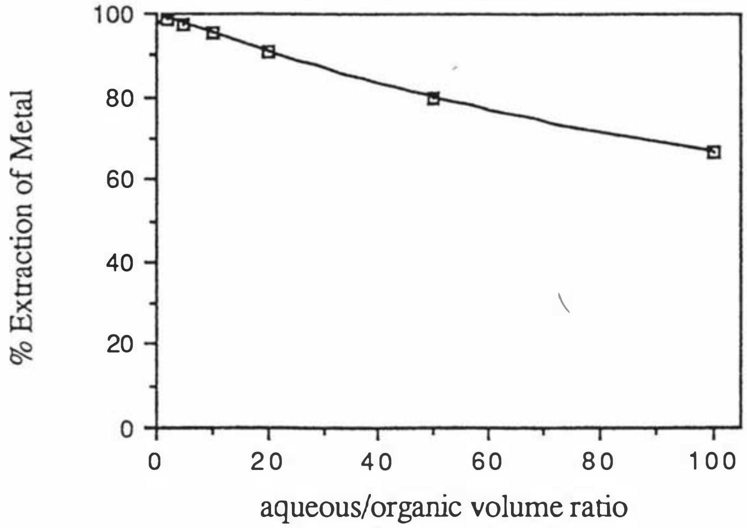
X	Y	Concentrations of Y needed relative to concentration of $[PtX_6]^{2-}$
Br	Cl	600
I	Br	25 000
I	Cl	16 000 000

compounds than of Pd(IV) because of the much higher ionization energies needed to produce the latter. In solution, Pd(II) and Pt(IV) predominate, with a smaller amount of Pt(II) (Hartley, 1973). In HCl solutions, these metals form the species $[PdCl_4]^{2-}$ and $[PtCl_6]^{2-}$. These species when protonated do not extract into MIBK, and a separation from Fe can be accomplished, as Fe(III) forms the extractable complex $[FeCl_4]^-$.

Pöe and Vaidya (1959) used ^{131}I to trace the formation of bonds with Pt(IV) at the expense of the bonds Pt--Cl or Pt--Br. Their findings are summarized in Table III.5. When the Pt--I bond is less than10-15 kcal weaker that the metal-chloride bond, the order of stability of the complex is I>Br>Cl, even though the bond strength order is the reverse of this. They concluded that solvation is an important effect, with an order of lability being I>Br>Cl in aqueous solutions.

The concentration of the lighter halide needed to displace a heavier halide from its $[PtX_6]^{2-}$ anion indicates that Pt(IV) have strong "soft acid" characteristics (Pearson, 1963). These soft acids exhibit a much greater preference for the heavier halides (Table III.6).

Figure III.2. Extraction of metal as a function of the ratio of volumes of phases if D=200



Among the simple anions (eg. F^-, Cl^-, Br^-, I^-, NO_3^-, PO_4^{3-}, SCN^-) the least electronegative is I^-. Steric hindrance also plays a part, and the formation of complexes with progressively greater atomic weight of the halogen corresponds to better extractions into ketones (Irving and Williams, 1961).

III.4.iii. Optimization of Extraction Parameters

In this work the scheme outlined by Brooks and Lee (1989) for the separation of Pd and Pt from the interfering matrix in iron meteorites was used. The method required modification to suit the samples and alterations required are presented below.

Optimum Amount of Iodide

Brooks and Lee (1989) noted better reproducibility if KI was added as an aqueous solution (100% w/v) prior to the extraction of Pd and Pt. They also noted that it was crucial to keep the ratio $V_a/V_o < 10$ (Figure III.2) as the recovery of the metals decreased with an increase in this ratio according to the relationship:

$$E = \frac{D}{D + (V_a/V_o)}$$

Figure III.3. Extraction of Pd and Pt iodocomplexes as a function of addition of KI as a solid

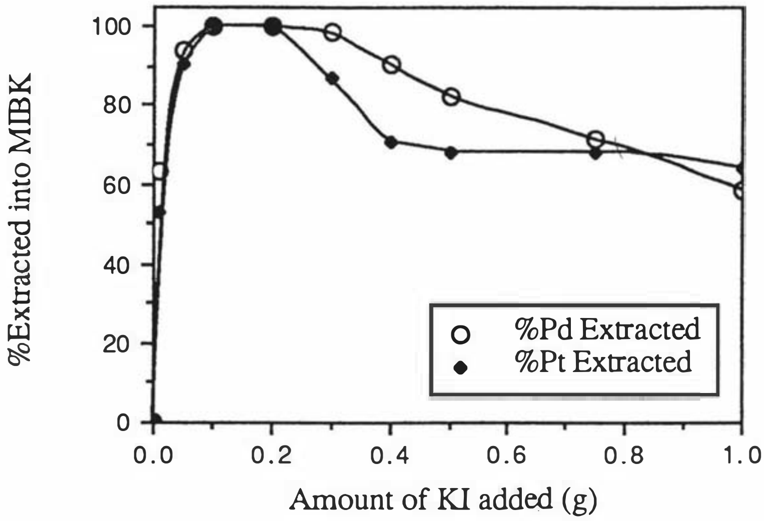


Table III.7. Proportion of KI needed to complex Pt and Pd completely

Amount of Element in solution	Amount of KI required
0.50 μg Pd	10 mg
5.00 μg Pt	100 mg
1 μg Pd or Pt	1 mg KI

where E = total fraction extracted

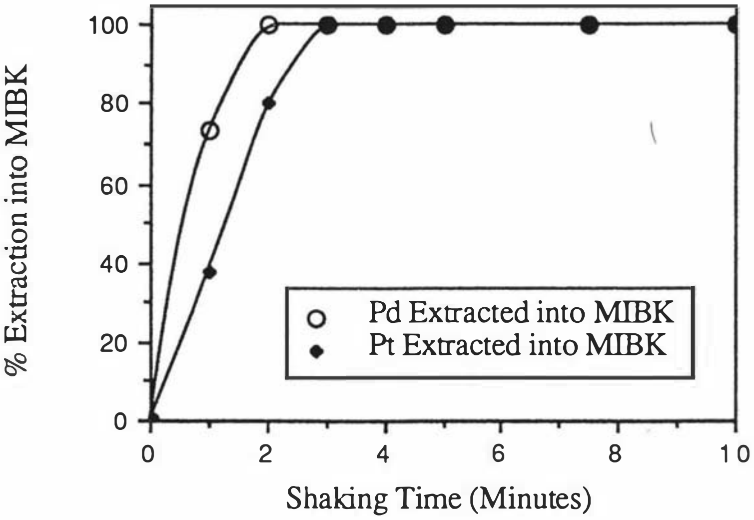
D = distribution coefficient

V_a = volume of the aqueous phase

V_o = volume of the organic phase

As the separation of Pd and Pt is also being used to concentrate the metals in the organic phase for enhanced sensitivity using GFAAS, it is desirable to use small volumes of MIBK (0.25-0.50 mL). Adding KI as a solid would not add significantly to the aqueous volume, and tests were carried out to determine the optimum amount of KI needed for 5-10 mL of 6M HCl

Figure III.4. Per cent extraction of Pd and Pt as a function of shaking time



solution to extract a known amount of Pd and Pt into MIBK (Figure III.3).

A large excess of KI seemed to lead to a decrease in the apparent extraction of Pd and Pt. The amount of KI added to the solution should reflect the expected amount of Pd and Pt to be extracted, following the ratios shown in Table III.7.

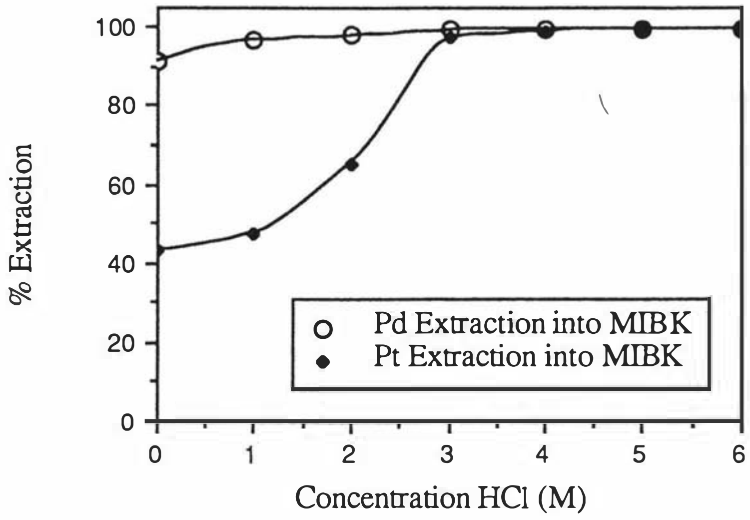
Shaking Time

The controlling step in the KI extraction is the formation of the complex (Irving and Williams, 1961). Known amounts of Pt and Pd were shaken for different amounts of time and the results are presented in Figure III.4. For optimum extraction, the solutions need to be shaken for 3-4 minutes.

Acid Concentration of the Aqueous Phase

The percentage extraction into MIBK by both Pt and Pd increased with increasing concetrations of HCl (Figure III.5). Greater than 99.9% Pd was extracted from 4-6M HCl, and the same amount of Pt was extracted from 3-6M HCl. The iodocomplexes were extracted here from 6M HCl solutions, as this is the concentration of constant-boiling HCl.

Figure III.5. Per cent extraction of Pd and Pt into MIBK as a function of HCl concentration



In order to avoid losses of MIBK due to dissolution in the acid solution, both the organic and aqueous phases required pre-equilibration for the reasons discussed in Section III.4.v.

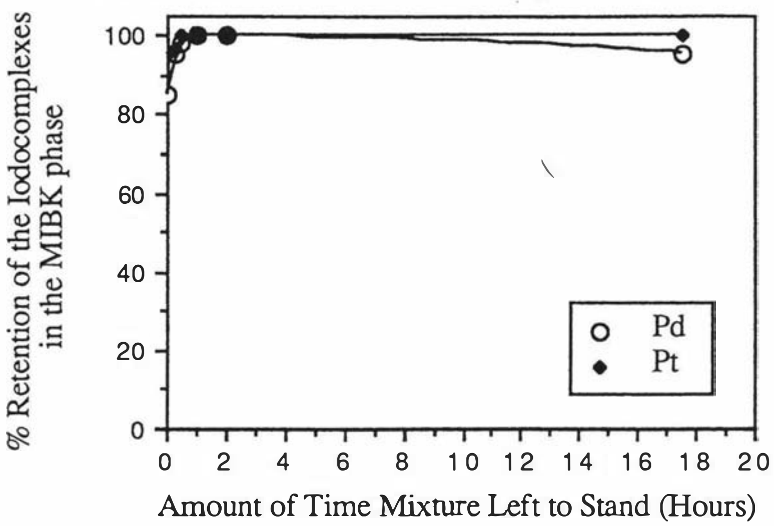
Stability of the Complexes

The equilibrated aqueous and organic phases were left to stand together for set amounts of time prior to analysis (Figure III.6). The $[PtI_6]^{2-}$ complex was stable from 0.5-17.5 hours. The $[PdI_4]^{2-}$ complex required ≈1 hour development time to reach ≈100% extraction, though this could be due to incomplete separation of the phases. Centrifuging the mixtures for 30 seconds allowed for complete phase separation, and no further difficulties were observed concerning "development time". The $[PdI_4]^{2-}$ complex is stable up to 5 hours. In general, the samples should be analyzed on the same day that they were processed.

III.4.iv. Cleaning of Glassware

In light of the cross-contamination problems encountered in the determination of Ru for successive analyses performed in the same test tube (Section II.3.v), all glassware and Teflon in contact with any sample or

Figure III.6. Stability of the iodocomplexes of Pd and Pt in MIBK with respect to time



standard solution was discarded (Pasteur pipettes) or soaked for over two hours in aqua regia made from a 3:1 mixture of commercial-grade HCl and HNO_3 mixed with one part water. Wollaston had dissolved Pt and Pd in aqua regia and isolated them via precipitation from this mother liquor (Livingstone, 1973), thus it is not surprising that aqua regia should remove all traces of these metals from the surfaces of the glassware. No difficulties were experienced regarding signal enhancement due to contamination when the glassware and Teflon beakers were treated in this manner.

As in the case for Ru, the aqua regia was poured back into a bottle and loosely capped after the soaking time was over. This acid mixture could be used up to 30 times (≈2 weeks) before discarding.

III.4.v. Pre-equilibration and the Removal of Iron

A study was done to test the feasibility of removing Fe from the sample solution by pre-extraction. Fe(III) forms a chlorocomplex that is readily extracted into MIBK (D = 330, Brooks *et al.*, 1989). Less than 0.1% of the Pt and Pd chlorocomplexes extract into MIBK, which affords a means to remove Fe. Iron meteorites contain ≈88% Fe, which gives the ratio $^{Fe}/_{(Pd + Pt)} = 10^5$ in the sample. For 10 mL of a 0.002% meteorite solution, a 98.5% extraction is achieved into 2 mL of MIBK, leaving ≈260 μg

Figure III.7a. Effect of storage and time on a 1μg/mL Pd solution in 6M HCl

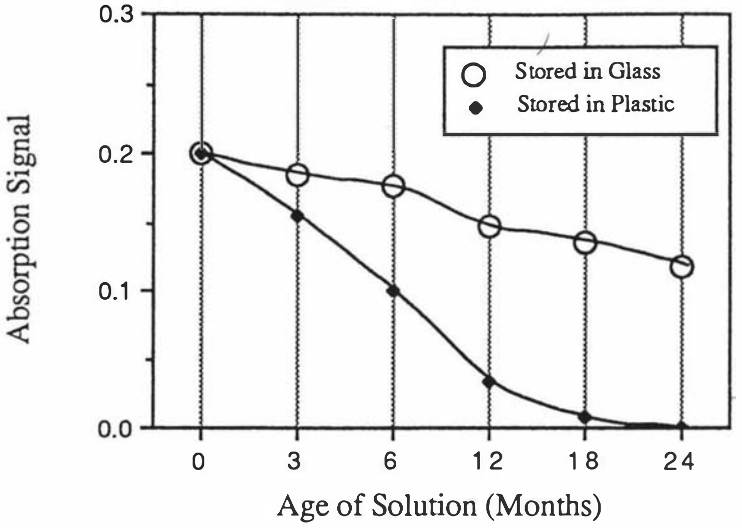
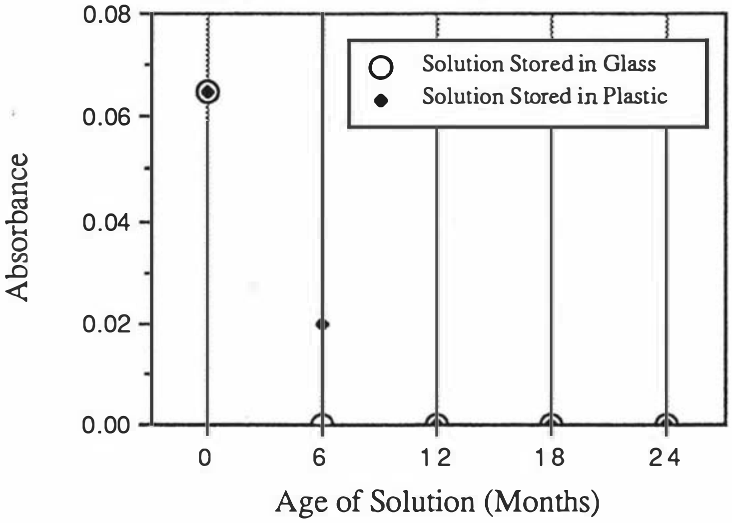


Figure III.7b. Effect of storage and time on a 1μg/mL Pt solution in 6M HCl



Fe in the aqueous phase. A second extraction with a fresh portion of MIBK on this solution would remove all but ≈4 μg Fe in the 10 mL solution (0.4 μg/mL). This small amount of Fe has no interfering effect on similar concentrations of Pd or Pt.

To remove Fe in the manner described, 2 mL of MIBK was added to 10 mL of sample solution in 6M HCl and capped the test tube was shaken for 30 seconds. A longer shaking time was not necessary; the time needed for extraction of the iodocomplexes of Pd and Pt into the organic phase is limited by time needed for the formation of the complex (Hartley, 1973). Since the chlorocomplex of Fe was already formed, a longer shaking time was not required to remove Fe to the organic phase. The mixture was centrifuged and the MIBK phase removed and discarded.

This pre-extraction step has the added advantage that it equilibrates the 6M HCl solution with MIBK. This pre-equilibration was necessary to avoid loss of the organic phase by dissolution into 6M HCl (Irving and Williams, 1961). In addition, the MIBK used for the extraction of the Pd and Pt iodocomplexes was also equilibrated with 6M HCl to prevent erroneous observations. However, the MIBK used to pre-extract the Fe should not be pre-equilibrated with acid, so that the sample solution may dissolve a maximum amount of MIBK into it prior to the Pd and Pt extraction.

III.4.vi. Standards

The Pt standard used was a 1000 μg/mL $[PtCl_4]^-$ solution in 1M HCl distributed by BDH as a spectroscopic standard. This was diluted to a stock solution of 100 μg/mL Pt in 6M HCl.

The Pd standard was prepared by dissolving $(NH_4)_2PdCl_4$ in 6M HCl to make a stock solution with a final concentration of 100 μg/mL Pd.

Very dilute solutions should be prepared daily as required. Over time, Pd and Pt solutions with concentrations of the order of 1 μg/mL degraded in both polyethylene and in glass containers (Figure III.7). Some loss of analyte was also seen in 10 μg/mL solutions, but not in 100 μg/mL solutions. It is assumed that both of these elements adsorb onto the walls of the container, which further emphasizes the need to clean all glass and plasticware in contact with Pd and Pt solutions carefully and thoroughly.

III.4.vii. Summary of the Extraction Procedure for Pd and Pt

To 10 mL of a sample solution in 6M HCl solution in a 20 mL test or centrifuge tube, add 2 mL of MIBK (not pre-equilibrated with acid) and shake for 30 seconds. Centrifuge the mixture and draw off the less dense organic phase with a Pasteur pipette and discard. Repeat the procedure, thereby removing 99.8% of the Fe in solution, plus virtually all of the other elements listed in Section III.4.ii., while retaining Pt and Pd in the aqueous phase.

To the now equilibrated aqueous solution, add 0.25-0.50 mL MIBK (previously equilibrated with 6M HCl) and solid KI in the proportion ≈1 mg KI to 1 μg Pd + Pt. Cap the test tube with a rubber bung and shake for 3.5 minutes. Centrifuge the mixture to separate the phases and analyse the organic phase for Pt and Pd within 5 hours using the GFAAS program presented in Table VII.2, Section VII.4.

Soak all glassware that has contacted the Pd and Pt samples and standard solutions in aqua regia for over two hours and wash and rinse thoroughly to remove all traces of aqua regia.

III.5. Studies on the Digestion of Iron Meteorites

Familiarity with processes for dissolution of a sample is a necessary first step in the determination of any element. The general method of dissolving Pd and Pt is treatment with aqua regia (Beamish and McBryde, 1958). This is the best solvent for Pt, though this element is also acted upon by alkali fusion (Hickman, 1968). Palladium is readily soluble in aqua regia though not in HCl alone. Nichiporuk and Brown (1965) used aqua regia for the digestion of iron meteorites prior to their determination using the emission spectrography technique. The presence of NO_3^- will interfere with many methods of analysis. For the method summarized in the previous section, NO_3^- will oxidize iodide to iodine in acidic media which generates heat, causing rapid evaporation of the MIBK from the sample mixture. Fuming the aqua regia with HCl removes the excess NO_3^- and encourages the formation of chlorocomplexes (Lincoln and Koller, 1962).

III.5.i. Selection of Apparatus

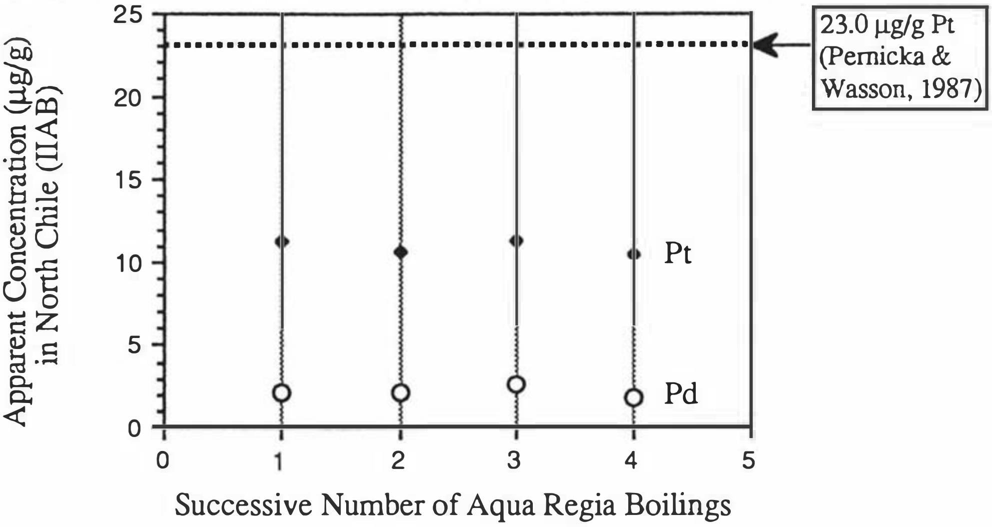
Because removal of NO_3^- by fuming is necessary, it was decided that a reflux apparatus was inappropriate for the digestion of samples for Pd and Pt determinations. Beakers allow the most rapid evaporation of solvent, but the use of glass is undesirable as etching of the glass can occur with oxidizing mixtures with resultant contamination from the vessel, and removal of residues can be difficult. Plastics seem to afford better possibilities, as their coefficients of friction are generally lower than for glass, reducing the difficulties in removal of sample residues as well as in cleaning.

For rocks and plants, Brooks and Lee (1989) used a mixture of 1:1:1 $HCl:HF:HNO_3$ in polypropylene containers over a water bath. The HF is necessary to destroy the silicates associated with their samples. Brooks (1960) originally used a similar mixture in Teflon beakers suspended in a waterbath. For greater heating efficiency, Sighinolfi (1973) placed a Teflon beaker in an Al vessel on a heating plate, and Simon *et al.* (1977) put a covered Teflon beaker directly onto the heating plate.

Work performed by Wilson (1991) showed that the latter two heating procedures softened, thinned and charred the Teflon containers, eventually burning a hole through the bottom of the container. Although Brooks (1960) reports that Teflon beakers can withstand temperatures up to 300°C without softening, in practice the Teflon fails at ≈200°C. This was observed in this work when a Teflon bomb was placed in a muffle furnace at 200°C with an aqua regia-rock mixture. The Teflon flowed and finally punctured at this temperature after 9 hours.

As a result of these experiences, it was decided to place the Teflon beakers in an Al vessel filled with sand. The sandbath temperature did not exceed 140°C at a point closest to the Al vessel, and the Teflon softened and warped slightly at this temperature, but did not char or puncture.

Figure III.8. Result of successive additions of aqua regia to one sample of North Chile (IIAB) in an attempt to dissolve Pt and Pd



III.5.ii. Selection of Reference Materials

As for Ru, no standards exist for Pd and Pt with a matrix matching that of iron meteorites. This is required in order to test the digestion and proposed methodology (Section II.4.ii). It was necessary, once again, to rely on the accuracy of values for an iron meteorite analyzed by other methods.

North Chile (IIAB)

North Chile, a meteorite of group IIAB, was used for the reasons mentioned in Section II.4.ii. No values for Pd exist in the literature for this sample, but Pernicka and Wasson (1987) have published a RNAA value of 23.0 µg/g Pt for this meteorite. As Pd is more soluble in aqua regia than Pt (Hickman, 1968), it may be assumed that if the Pt value obtained in this study is ≈23 µg/g, then all of the Pd will have been recovered as well.

Approximately 0.1 g of the North Chile meteorite turnings were weighed accurately into tared 50 mL Teflon beakers, and these were placed in a sandbath over a heating plate. Ten mL of freshly prepared aqua regia was added to the contents of the beaker. Dissolution of the Fe-rich sample resulted in an orange solution, which was taken to low bulk (≈2 mL). Ten mL of concentrated HCl was added to the mixture to remove NO_3^- as NO_2 gas. This solution was heated and evaporated to 5 mL and the

Table III.8. Attempts to completely dissolve Pd and Pt in North Chile (IIAB)

Procedure	Apparent Concentration Pd	Apparent Concentration Pt	Recovery* (%) Pt
Na_2O_2 fusion	0.417	1.90	8.2
Digestion with aqua regia and $Na_2S_2O_8$	1.10	5.11	22.2
Digestion with aqua regia and Br_2	1.77	15.0	65.2
Digestion with aqua regia and put through a 0.45µ filter; ash and redigest filter and in aqua regia	1.04	17.1	74.3
Increase volume of aqua regia to improve solubility	1.80	17.2	75.0
Add H_2O_2 to the hot aqua regia-iron meteorite solution	2.63	23.1	100

*Pernicka & Wasson, 1987 value for Pt in North Chile (IIAB) 23.0 µg/g

contents quantitatively transferred to a 50 mL volumetric flask with constant boiling (6M) HCl, and made up to volume with this same HCl solution.

The results were disappointing, as only 11.2 µg/g Pt was recovered, half the value of the RNAA result of 23.0 µg/g (Pernicka and Wasson, 1987). Assuming the possibility that some of the Pt was not dissolving in the 10 mL of aqua regia, successive amounts of aqua regia were added to the low bulk (2 mL) solution after the initial digestion. Four cycles of aqua regia addition did not improve the Pt or Pd recovery (Figure III.8).

In Vogel (1989) it is suggested that a ribbed watchglass be used over solutions digesting in beakers to avoid mechanical losses due to boiling action. Observable physical losses were halted and the recovery of an extra 3.0 µg/g Pt (total 14.2 µg/g) was effected. Unfortunately, this is still short of the reference value of 23.0 µg/g Pt. Use of larger (250 mL) Teflon beakers resulted in no loss of material from vigorous boiling of solution even without the use of a ribbed watchglass, and the larger surface area cut down the evaporation time of the acid from six hours to two hours. All further tests were performed in the 250 mL Teflon beakers without

Table III.9. Pd and Pt abundances for Henbury(IIIAB) and references

Concentration (µg/g) Pd	 Pt	Reference
2.1	--	Smales *et al.*, 1967
3.4/4.4	5.6	Nichiporuk & Brown, 1965
2.02	--	Goldberg *et al.*, 1951
--	16.1	Pernicka & Wasson, 1987

watchglasses.

Apparently, the action of aqua regia is not sufficient to oxidize all of the Pd and Pt in iron meteorites into soluble species. Several other digestion procedures were considered and attempted. The results are summarized in Table III.8. It was eventually discovered that Pt could be dissolved completely using the aqua regia digestion in which H_2O_2 (40% v/v) is added after the meteorite sample has apparently dissolved. It is likely that finely divided Pt and Pd-containing material remained undissolved in the absence of a more strongly oxidizing solution. To avoid mechanical losses due to violent frothing action, 10 mL of H_2O_2 was added slowly and carefully in 2 mL portions. When the frothing ceased after the addition of one 2 mL portion, the next portion was added and the cycle continued until all 10 mL was used.

Henbury (IIIAB)

To further test the apparent success of the aqua regia/H_2O_2 digestion procedure, the Henbury (a meteorite of group IIIAB) was used to check the methodology. Like the North Chile sample, Henbury was donated to this laboratory in the form of turnings, allowing easy subsampling of the contents of the vial. Unlike North Chile (IIAB), the IIIAB group of meteorites consists of relatively small (compared to the IIAB group) kamacite crystals. It is probable that the meteorite is not homogeneous

Table III.10. Result of 4 complete replicate analyses of Henbury (IIIAB)

Element	Concentration	Mean		RSD
	(µg/g)	(µg/g)	(µg/g)	(%)
Pd	4.52			
	4.51			
	4.35			
	4.39	4.44	0.08	1.93
Pt	16.99			
	16.98			
	16.62			
	17.38	16.99	0.31	1.83

with respect to Pd and Pt. However, values for Pd do not exist for North Chile. Several values for Pd are available in the literature for Henbury to use as general reference, and Pt values are also abundant for this meteorite (Table III.9). Larger sample weights (0.1 g) were taken to try to ensure that a representative sample would be used for the checking of the methods of digestion and extraction.

The results are presented in Table III.10 and show good agreement with the data of Pernicka and Wasson (1987) for Pt. Nichiporuk and Brown (1965) used emission spectrography to determine Pt in iron meteorites, and this method is considered to be only semi-quantitative for Pt as well as for other elements (Pernicka and Wasson, 1987). On the other hand, the Pd values here agree well with those of Nichiporuk and Brown (1965). Both of the values generated by RNAA (Smales *et al.*, 1967; Goldberg *et al.*, 1951) agree with each other, but are less than half of the value found here. No reason could be found for spurious enhancement of the Pd signal in this study. To eliminate the possibility of enhancement by memory effects (Sighinolfi, 1973), new furnaces were used, but gave the same results as previously used ones. It is possible that the digestions used by the RNAA workers did not dissolve Pd completely from the sample, or that losses of Pd occurred during their radiochemical separation procedures. In any case, the NAA technique is probably not well suited for the determination of Pd. Emission spectrography may actually produce better quality data for Pd in

Table III.11. Results of 4 replicate analyses of Gibeon (IV A) for Pd and Pt

Element	Concentration (μg/g)	Mean (μg/g)	σ (μg/g)	RSD (%)	Reference Value(μg/g)	Reference
Pd	3.41					
	3.39					
	3.22					
	3.25	3.32	0.06	1.70	3.5	Smales *et al.*, 1967
Pt	6.80					
	6.49					
	6.77					
	6.83	6.72	0.16	2.34	8.0	Crocket, 1972

iron meteorite samples.

Gibeon (IV A)

To further check that the large Pd value for Henbury was not due to some untraced error, the Gibeon (IV A) iron meteorite, also available as turnings, was analysed in four complete replicate analyses. The IV A group has a narrow kamacite bandwidth of 0.2-0.5mm (Mason, 1962). Although a small bandwidth does not guarantee homogeneity, a sub-sample taken from this meteorite is likely to be more representative than one from a coarser-grained group. However, to ensure once again a representative sample, 0.1g of material was used in the replicates. The results are presented in Table III.11. This time, the Pd values agreed with the RNAA data of Smales *et al.* (1967), but the Pt values did not agree with those of Crocket (1972). However, the relative standard deviation (RSD) values in RNAA are usually quite high: 18% for Pt (Pernicka and Wasson, 1987) and 13% for Pd (Anders *et al.*, 1988). Both of the values obtained here for Pt and Pd are within this large RSD value for the RNAA procedures.

Figure III.9a. Comparison of Pd values for iron meteorites analyzed in this study with avalable literature values

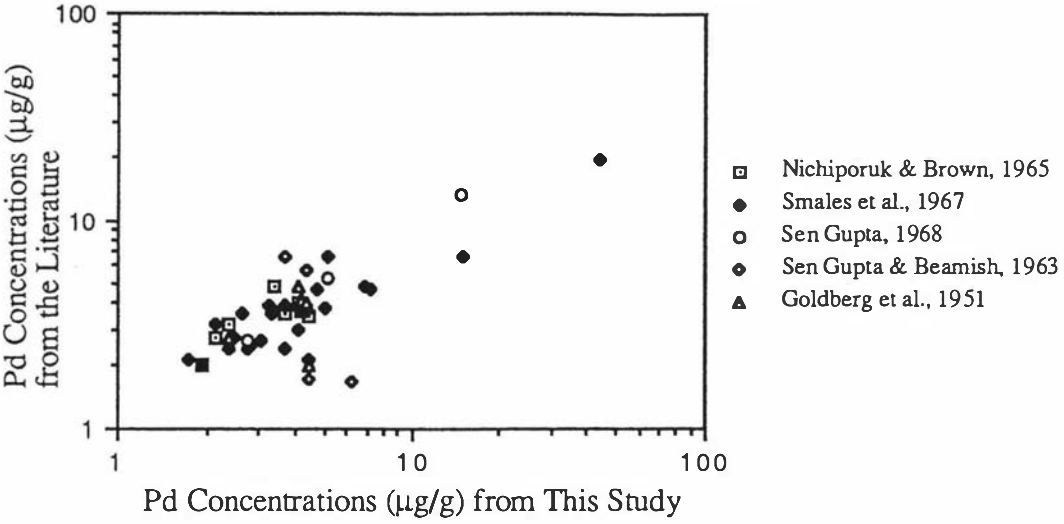
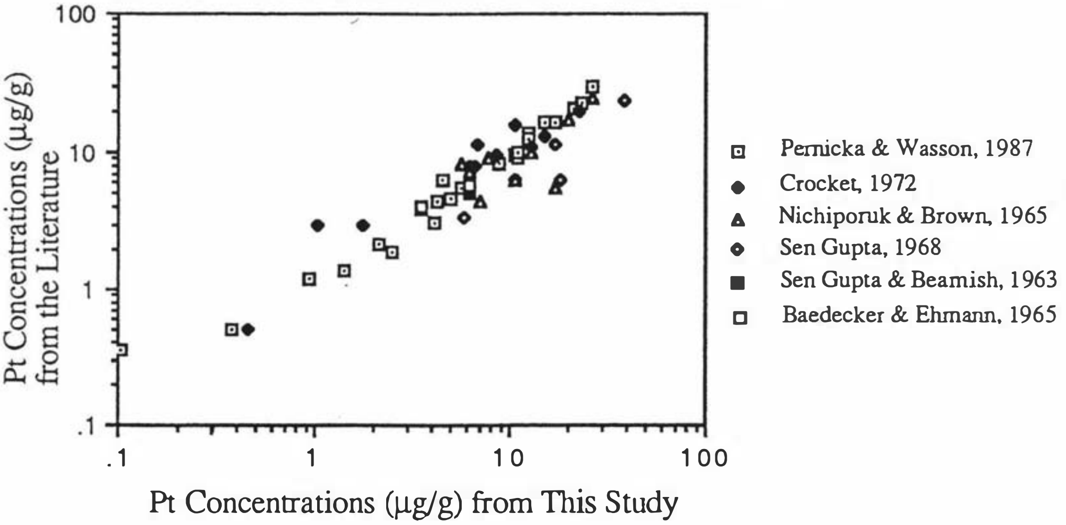


Figure III.9b. Comparison of Pt values for iron meteorites analyzed in this study with available literature values



Comparison of Iron Meteorite Values With Available Literature Values

Palladium and platinum were determined in all of the meteorites listed in Appendix 2 and compared to values in the literature (Figure III.9). The comparison of Pt values is highly satisfactory. The agreement for Pd is less satisfactory, though these values span only one order of magnitude, which is responsible for the clustering of points in the diagram. In addition, not many reliable data for Pd exist in the literature for iron meteorites. However, most of the Pd values fall along the 1:1 line, and there appears to be no serious reason to doubt the quality of the data

Table III.12. Result of 6 replicate analyses of PTC-1 for Pd and Pt

Element	Concentration (μg/g)	Mean (μg/g)	σ (μg/g)	RSD (%)	Reference Value (μg/g) McAdam *et al.*, 1973	Deviation
Pd	12.2					
	12.2					
	12.7					
	12.5					
	12.1					
	12.6	12.4	0.08	0.64	12.7	2.36%
Pt	2.97					
	2.98					
	3.01					
	2.99					
	2.98					
	3.01	2.99	0.05	1.77	3.0	0.33%

produced here.

PTC-1

As a final check, the standard ore PTC-1, available as a finely ground powder, was analysed for Pd and Pt to assess the extraction procedures. To destroy silicates and sulphur, the digestion mixture of Brooks and Lee (1989) for this same standard rock was used of 1:1:1 HF:HNO_3:$HClO_4$. Palladium and platinum did not display volatility at the temperatures observed in this mixture when heated to dryness in a Teflon beaker over a sandbath. The oxidation states of these elements are probably Pd(II) and Pt(IV), both of which are stable in solution at 140°C (Hartley, 1973), the temperature of the hottest part of the sandbath. Because Pd and Pt resist further oxidation, it is safe to use $HClO_4$ to destroy the colloidal sulphur in this sample, which could not be used when determining Ru (Section II.4.iv).

Ten mL of the 1:1:1 HF:HNO_3:$HClO_4$ mixture was added to 1 g of PTC-1 in a Teflon beaker and heated to dryness over a sandbath to remove all traces of HF and $HClO_4$. The resulting salts were redissolved in 10 mL of aqua regia. From this point, the same digestion and extraction procedures were used as for the iron meteorites. The results of six full replicate analyses are presented in Table III.12. The results are highly satisfactory for both Pd and Pt.

III.6. Separate Determinations of Palladium and Platinum

Although Pd and Pt were extracted simultaneously into MIBK as iodocomplexes, they could not actually be determined with optimum precision in the same extract. For example, IIICD iron meteorites have very low Pt abundances (0.07-0.63 μg/g) and rather high abundances of Pd (12.0-16.4 μg/g). To a 13.5 mL aliquot of sample, Pt was extracted into 0.25 mL of MIBK. Another 10 mL aliquot of the same sample solution was used to extract Pd into 1.0 mL of MIBK. Of course, Pd and Pt will extract together from both aliquots, but it was best to consider only one element per aliquot, as Pd and Pt concentrations are usually not comparable to each other in iron meteorites (Appendix 1). This was especially important because the two elements have rather different sensitivities when determined by the GFAAS technique. Palladium is four times more sensitive than Pt (see calibration curves, Figure III.10).

Each determination was duplicated after the dissolution stage in order to use the sample as efficiently as possible from the total 50 mL solution. As the Pd and Pt are not stable in the solution over time (Section III.4.vi), the determinations were all completed in one day, and any remaining solution was discarded.

It was not necessary to separate Pd and Pt from each other, as no cross interference was found using GFAAS. This is further confirmed by the good general agreement for all values of Pd and Pt with the literature (Section III.5.ii).

III.7. Calibration Curves

Calibration curves were prepared for absorbance as a function of Pd and Pt concentrations in the MIBK phase (Figures III.10). Initially, all of the calibration standards were subjected to the same digestion, fuming and

Figure III.10a. Calibration curve for Pd

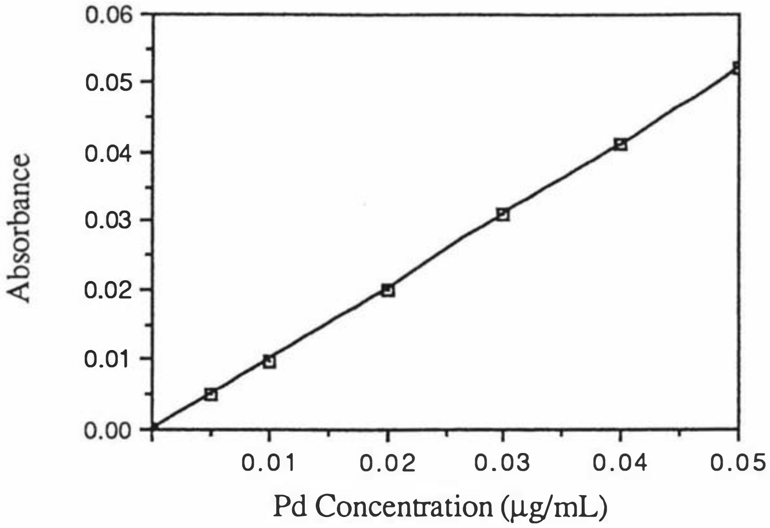


Figure III.10b. Calibration curve for Pd to 0.75 µg/mL

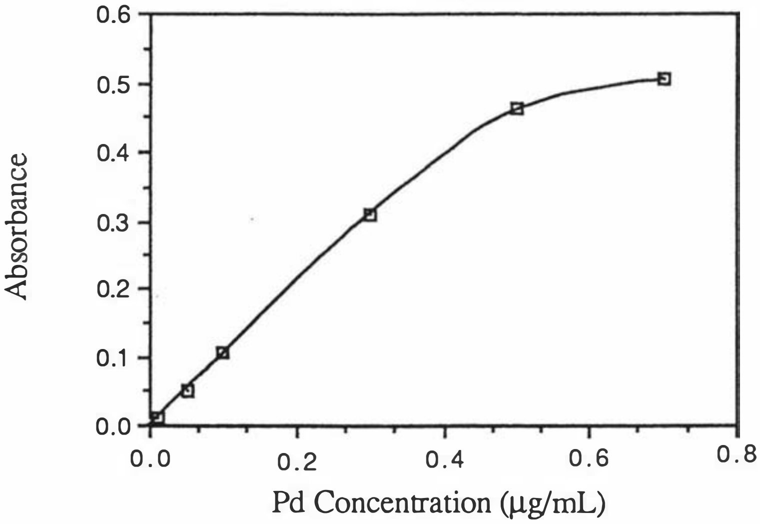
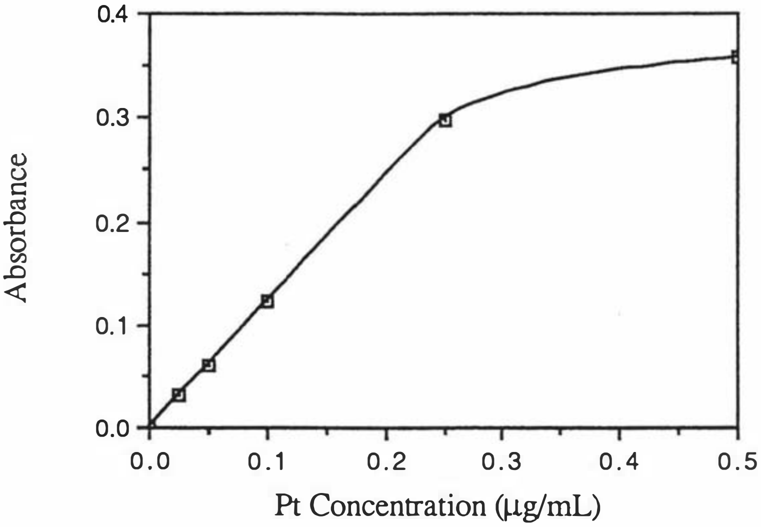


Figure III.10c. Calibration curve for Pt



dilution procedures as the samples. This was later found to be unnecessary, as no loss of the standard Pd and Pt occurred during these steps. However, it was necessary to go through the pre-extraction steps for the removal of Fe. Though no Fe was present in the standard solutions, pre-equilibration of the acid with MIBK was necessary to avoid dissolving the MIBK used for the final separation and concentration of the Pd and Pt iodocomplexes.

III.8. Final Analytical Procedure

The analytical procedure for the determination of Pd and Pt in iron meteorites that was finally adopted was as follows.

Weigh accurately 0.1-1.0 g of meteorite material (sawings, turnings or clean pieces--the weight is dependent on the expected concentration of Pd and Pt in the sample) into a tared 250 mL Teflon beaker. Place in a sandbath over a heating plate. Add 10 mL of freshly prepared aqua regia and heat until all material appears to have dissolved. Slowly and carefully add 10 mL of 40% H_2O_2, 2 mL at a time to avoid overflow and loss of sample due to violent frothing. Evaporate this solution down to low bulk (≈2 mL) and add 10 mL of concentrated HCl to fume off NO_3^- as NO_2. Heat once again to low bulk and add another 10 mL portion of concentrated HCl. When the volume is reduced to about one-half, quantitatively transfer the contents of the beaker to a 50 mL volumetric flask using 6M (constant boiling) HCl to rinse the beaker.

Take 10-15 mL aliquots of this solution and place in 20 mL test tubes. Add 2 mL of unequilibrated MIBK and shake for 30 seconds to remove Fe. Centrifuge to separate the phases, remove and discard the organic phase with a Pasteur pipette and repeat the procedure with another 2 mL portion of MIBK.

Add 0.25-1.0 mL of MIBK which has been previously equilibrated with 6M HCl. The amount of MIBK used depends on the expected concentrations of Pd and Pt in the sample. In general, 10 mL aliquots of a sample solution were taken for Pd and extracted into 0.5 mL MIBK. For Pt, 13.5 mL aliquots of the same solution were usually taken and the Pt extracted into 0.25 mL MIBK.

Solid KI is added to the mixture in the proportion of approximately 1 mg KI to 1μg total Pd + Pt. In general, the addition of 1 g of KI was sufficient to completely form the extractable iodocomplexes of these elements. The test tube is capped and shaken for 3.5 minutes, then the mixture is centrifuged for a short time to aid in the separation of phases.

Prepare the standards daily as they are required in 6M HCl. Process them in exactly the same way as the samples. A useful range of standards would contain 0, 0.005, 0.010, 0.050 μg/mL for Pd and 0, 0.050, 0.10, 0.25, 0.50 μg/mL Pt.

Determine Pd and Pt in the organic phases by GFAAS using the optimized conditions set out in Section VII.4, Table VII.2. Adjust the number of multiple injections to suit the expected Pd or Pt content to ensure that the absorbance values fall within the straight portion of the calibration curve.

Chapter Four

Gallium

IV.1. Introduction

The Ga content is one of the crucial parameters in the chemical classification of iron meteorites because of its quantized abundances for different groups (Table IV.1). This element has been determined in the iron samples predominantly by RNAA. This method of determination has several advantages. Radiochemical neutron activation analysis is very sensitive for Ga (0.1 ng/g--Wasson and Kimberlin, 1966) and offers freedom from reagent contamination problems.

Because of the expense and unavailability of RNAA facilities, it was hoped in this work to determine Ga in iron meteorites using GFAAS.

In iron meteorites various methods of analysis suffer interference from Fe on Ga. For example, in GFAAS the Ga absorbance is affected as shown in Figure IV.1. In their RNAA method, Wasson and Kimberlin (1966) precipitated Fe in ammonium hydroxide, noting that Ga is amphoteric and thus soluble in this solution. Their method is based on that of Brown and Goldberg (1949), who precipitated Fe(III) in 1-2M NaOH.

As the usefulness of precipitation-type separation procedures is often limited by incomplete precipitation and adsorption phenomena (Hope et al., 1936), several other methods have been used for the separation of Ga from Fe. Nachtrieb and Fryxell (1949) showed that Fe(III) and Ga(III) have similar distribution coefficients between HCl and ethers, and cannot be separated this way. Of the methods of separation of Ga from other metals, Korkisch (1966) lists only solvent extraction in the presence of a reducing agent to avoid co-extraction of Fe with Ga, and states that it is impossible to separate Ga from Fe using cation or anion exchange, or by precipitation, as Ga is collected by $Fe(OH)_3$. Kraus *et al.* (1954) reported the similar adsorptions of Fe and Ga onto Dowex-1 anion exchange resin, though Sandell (1959) reported a separation of Ga from Fe(III) in thiocyanate solutions using Amberlite IRA400. However, Onishi and Sandell (1955) preferred the extraction of Ga from HCl solutions into ether in the presence

Table IV.1. Range of Ga concentration in different groups of iron meteorites according to Wasson and Coworkers

Group	Range of Ga abundance (µg/g)
IAB	11-100
IC	42-54
IIAB	46-62
IIC	37-39
IID	70-83
IIE	21-28
IIF	8.9-11.6
IIIAB	16-23
IIICD	1.5-27
IIIE	17-19
IIIF	6.3-7.2
IVA	1.6-2.4
IVB	0.17-0.27

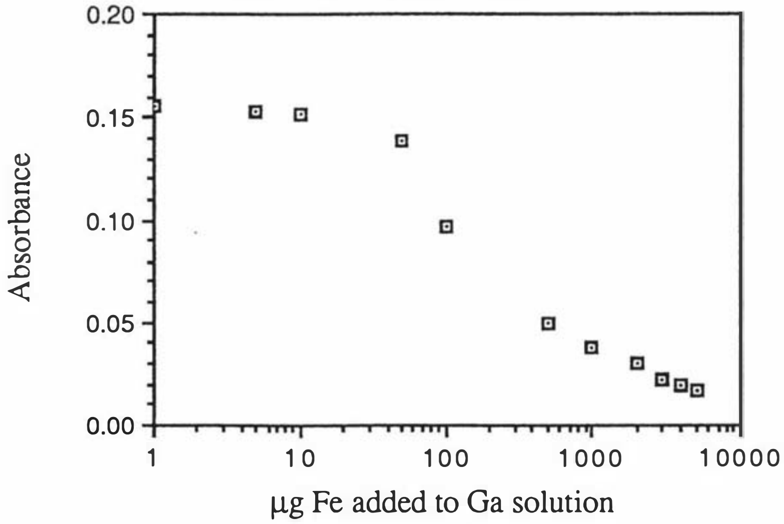


Figure IV.1. Effect of Fe on the absorption signal of 0.5 µg/mL Ga

of $TiCl_3$ as a reducing agent, as Fe(II) is not extracted into ethers (Irving and Rossotti, 1952).

IV.2. Development of an Extraction Procedure

An attempt was made to extract Ga(III) into MIBK, as Korkisch (1966) noted that extraction of Ga will occur into oxygen-containing organic solvents from acid solutions. Nachtrieb and Fryxell (1949) and Horrocks and Voigt (1957) observed the development of a third intermediate phase between acid and ether phases ("heavy ether phase") which contained >90%

Table IV.2. Effect of $TiCl_3$ on Ga absorption signal in the presence of Fe

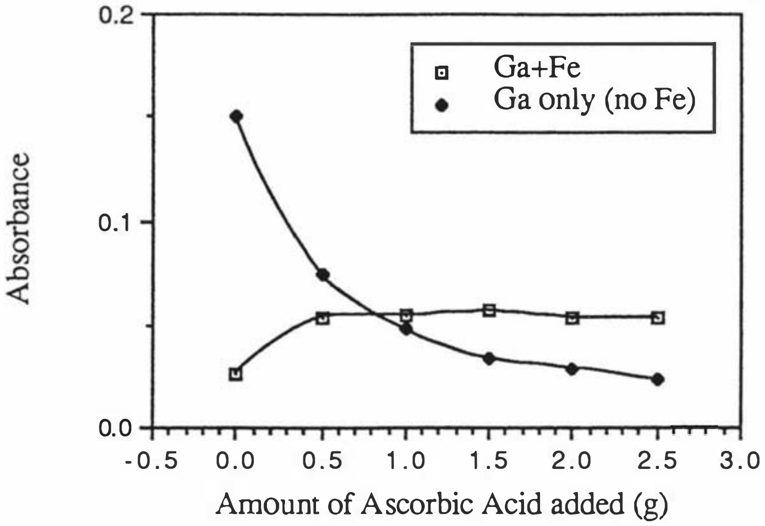
	Ga Absorption			
	in MIBK phase		in Aqueous Phase	
μg of Fe added to 1μg/mL Ga solution	with $TiCl_3$	without $TiCl_3$ (effect of Fe)	with $TiCl_3$	without $TiCl_3$ (effect of Fe)
0	0.160	0.160	0.000	0.000
500	0.160	0.140	0.110	0.080
1 000	0.160	0.139	0.080	0.100
2 500	0.180	0.137	0.060	0.070
5 000	0.080	0.120	0.000	0.000
10 000	0.002	0.185	0.000	0.000

of the Ga. Nachtrieb and Fryxell (1949) attributed this to the polymerization of the ether by multiple hydrogen bonds, causing difficulties when trying to obtain a clean separation between phases. To avoid the formation of the polymerized layer, MIBK was chosen as the organic phase instead of ether.

In a synthetic mixture of Fe and Ga, $TiCl_3$ was added dropwise till the purple color of the reducing agent persisted in the solution. This was shaken with an equal volume of MIBK, and the results are presented in Table IV.2. The purple color extracted into the organic phase and the Ti suppressed the Ga signal. Although $TiCl_3$ did reduce Fe(III) to Fe(II), Ti apparently presents a negative interference on Ga when determined by GFAAS.

As $TiCl_3$ was not suitable for use with MIBK, other reducing agents were sought. Korkisch (1966) lists $SnCl_2$ and finely divided metallic Cd or Ag. Tin is extracted appreciably into MIBK at the same range of concentrations as Ga (Brooks *et al.*, 1989). Cadmium is also extracted, though not as well as Sn. Silver, when oxidized, forms a precipitate with Cl^-, which could potentially adsorb Ga, removing it from solution as a co-precipitant. Sukhoveeva *et al.* (1979) reduced Fe(III) with ascorbic acid prior to extraction of Ga into MIBK. Hall *et al.* (1987) used this procedure to determine Ga in standard reference rocks.

Figure IV.2. Effect of ascorbic acid on the Ga absorption signal, with and without Fe in the solution



Ascorbic acid was used here to reduce Fe in a synthetic solution containing Fe and Ga. The amount of ascorbic acid that was necessary to remove the negative interference of Fe on extraction of Ga into MIBK as the chlorocomplex was determined (Figure IV.2). A minimum amount of 50 mg of ascorbic acid was needed to reduce 2 mg of Fe and give a reproducible Ga signal. However, this signal is only ≈50% of the absorbance for Ga extracted into MIBK from HCl in the absence of Fe or ascorbic acid. When the reducing agent was added to a solution containing only Ga and the analyte extracted, ascorbic acid was found to also interfere with the Ga signal (Figure IV.2).

Another problem was the equilibration of the aqueous HCl phase with MIBK prior to extraction of Ga. This pre-equilibration is necessary to avoid loss of organic phase volume (Section III.4.v). In the Pd and Pt separation, pre-equilibration was accomplished by way of the pre-extraction step that was necessary to remove a variety of metal ions, including Fe(III) and Ga(III). Unfortunately, such a pre-extraction step is not possible here.

The 6M HCl used had to be equilibrated with MIBK and used when preparing the synthetic solution. This, however, reduced the solubility of the ascorbic acid in HCl, so that a larger volume of sample had to be used to dissolve the reducing agent. The ratio V_a/V_o was increased as a result,

Table IV.3. Results of replicate Ga determinations for Toluca (IAB)

Ga Abundance (μg/g)	33.6, 43.0, 45.6, 47.5, 48.3, 49.3, 49.7, 53.8, 57.6, 59.8, 69.6, 70.7, 70.7, 80.0, 83.5, 84.9, 85.3, 90.0, 113.0, 114.5
Mean	67.5 μg/g
σ	22.1 μg/g
RSD	32.8 %
Reference Value (Wasson, 1974)	70.6 μg/g

which in turn affected the proportion of Ga extracted into the organic phase. However, at 6M HCl, D_{Ga} is very high ($\approx 10^5$--approximated from Kraus and Moore, 1958) so that even a $^{V}a/V_o$ ratio of 50 would still result in 99.95% extraction of Ga.

Because of the apparent decrease in absorbance peak height of the Ga signal in the presence of ascorbic acid, careful matrix matching for blanks and standards was necessary. However, it was not enough to merely add the reducing agent to a standard Ga solution prior to extraction into MIBK. The large amount of Fe(III) in solution did not reduce completely to Fe(II). This resulted in any unreduced Fe extracting with the Ga. A large excess of ascorbic acid is necessary to ensure the reduction of other reducible element species (eg.--Mo(VI), Cr(VI), etc.) as well as Fe(III), but an excess would also adversely affect the Ga signal.

This arrangement is clearly unsatisfactory. When this method was attempted on a sample of Toluca (an iron meteorite of group IAB), which has a well-documented Ga value of 70.6 μg/g (Wasson, 1974), a diverse range of values resulted (Table IV.3). The average value of 67.5 μg/g is close to the published Ga concentration for Toluca, but a large number of determinations is necessary to approach this value. Ga might suffer volatility from the furnace in the pre-atomization stages in the presence of Cl^- as does Tl (Hoashi, 1988). The addition of Ag^+ to remove the Cl^- by precipitation led to no difference in the quality or reproducibility of the Ga signal. The relative standard deviation of ±32.8% is unacceptably large, and the RNAA technique appears superior to GFAAS in the determination of Ga. Morris and Chambers (1960) point out that the carriers employed in the radiochemical separations eliminate the need for quantitative separations, as corrections are made for losses by measurement of the chemical yield of the carrier. Allen *et al.* (1970) calculated a consistent 60% chemical yield for Ga to be determined by RNAA using the precipitation procedure to remove Fe. However, quantitative separations are desirable over non-quantitative procedures.

IV.3. Conclusion

It was not possible to discover how to separate Ga effectively from Fe and to determine Ga reproducibly by GFAAS. It must be conceded that at this time, the Ga content of iron meteorites is best determined by RNAA.

Chapter Five

Thallium

V.1. Introduction

Gallium is a diagnostic parameter for the classification of iron meteorites and as Tl is in the same group in the periodic table, the Tl content of these samples was investigated to see if it could be detected. Reed *et al.* (1960) determined Tl by RNAA in some chondritic meteorites and troilite (FeS) phases of Canon Diablo and Toluca irons, though no studies were done on the metal phases surrounding the troilites. Because of its chalcophilic nature, Tl is relatively abundant in this FeS phase (Table V.1) and is expected to have lower concentrations in the metal phase. Graphite furnace AAS has a sensitivity of <1ng/g for Tl (Hoashi and Brooks, 1991), and is the method that was to be utilized for the quantification of this element in a Toluca iron meteorite sample.

V.2. Methodology

The method detailed by Hoashi (1988) was used to separate Tl from the Fe matrix. Briefly, the sample is digested in HNO_3, heated to low bulk (≈2 mL) and diluted to an appropriate volume with 2M HCl. An aliquot of this solution is oxidized with Br_2 vapor to ensure that all of the Tl is in the trivalent form. The Tl is extracted into MIBK as protonated $TlCl_4^-$, along with Fe(III). The organic phase is then washed with a solution of 0.5M HCl to back-extract Fe; Fe(III) extracts significantly into MIBK at >3M HCl, but D = 0.10 at 0.5M HCl (Brooks *et al.*, 1989). Thallium (III) has a value of $D \approx 10^3$ from 0.5-6M HCl, and remains in the organic phase during the back-washing step.

This organic phase is next evaporated over a 1M $AgNO_3$ solution in 2M HNO_3, as Tl(III) is volatile in the presence of Cl^-. The boiling point of $HTlCl_4$ is ≈140°C, making determination by GFAAS impractical unless the

Table V.1. Tl abundance of troilite nodules in iron meteorites (Reed *et al.*, 1960)

Meteorite	Abundance Tl (μg/g)
Cañon Diablo (IAB)	0.013
Toluca (IAB)	0.198

Cl$^-$ is removed. By evaporating the MIBK over a solution of $AgNO_3$, the Cl$^-$ is precipitated by Ag^+. The presence of the precipitate does not appear to affect the Tl(III) in solution.

V.3. Conclusion

Toluca was analysed using this method and was found to contain ≈0.6 ng/g Tl. No further analyses were performed on other meteorites. The small amount of Tl detected may indicate that this element is not useful in the classification of iron meteorites. However, the method developed by Hoashi (1988) may be used to determine Tl in the sulfide phase of iron meteorites, and a study of the inhomogeneity of the meteorite with regards to Tl can be carried out with determination of Tl partition coefficients. The presence of detectable amounts of Tl in this sample warrants further study of the Tl content of iron meteorite phases and minerals.

Chapter Six

Nickel

VI.1. Introduction

Nickel, after Fe, is the second most abundant element found in the iron meteorites. Iron is too abundant to measure without large and careful dilution of the samples, so it is Ni which is determined and used instead as a major taxonomic parameter in the classification of iron meteorites (Wasson, 1974). Traditionally in meteorite work, abundances of other elements are plotted as a function of Ni content, and it is crucial that the determination of this element is carried out carefully and accurately.

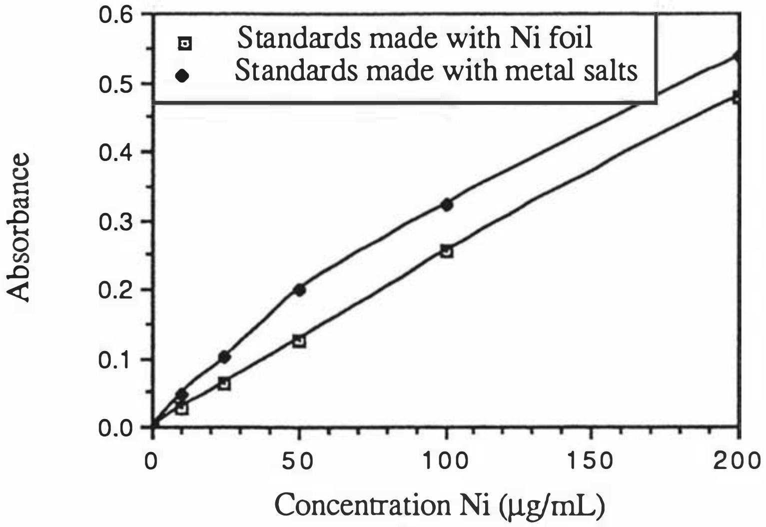
The most rapid method used to determine Ni is by flame AAS, which has a LOD of 0.01 µg/mL Ni (Robinson, 1966). Because Ni abundances in meteorites are so high, less sensitive lines are required to ensure that the calibration curve is linear for the absorption signal recorded. This is a better alternative to dilution of the sample solution, as excessive sample manipulation is limited.

Nickel determinations are performed routinely in this laboratory. The multielement standards are produced using soluble salts of the metals desired, dissolved in 2M HCl.

VI.2. Preparation of Sample Solution

Meteorite samples (1.0 g) were cut with a hacksaw and a piece free of fusion crust was cleaned with acetone to remove all traces of paint that may have come from the hacksaw. The piece of clean metal was weighed and refluxed in 10 ml of constant boiling HNO_3 or HCl until dissolution was complete (usually after 15 minutes). The contents of the conical flask were quantitatively transferred to a 100 mL volumetric flask with distilled water and the solution was analyzed by flame-AAS.

Figure VI.1. Calibration curves for Ni using two standard stock solutions



Vi.3. Results

The results (presented in Appendix 3) were high compared to the literature values (Wasson, 1974 ; Grahame *et al.*, 1985). This could potentially be caused by interferences from atoms or molecules of other elements, or by a low absorbance value from the standard, which would yield an apparently higher sample absorbance and concentration value. A new 1000 µg/mL stock solution was made from Ni foil digested in constant boiling HNO_3. The result of the calibration curves from the multielement standard and the Ni foil standard is shown in Figure VI.1. The Ni foil standards actually give a lower absorbances, causing an even larger deviation of the meteorite Ni values from the literature values.

A solution was prepared consisting of 1000 µg/mL Fe and 100 µg/mL Ni to simulate the ratio of $^{Fe}/_{Ni}$ found on average in the iron meteorite solutions. No interference from Fe was found when this solution was compared to the Ni solution on its own.

A dimethylglyoxime (DMG) gravimetric determination was performed on several samples, including National Bureau of Standards Steels #361 and #809B and the North Chile hexahedrite. These results were compared to a flame-AAS determination made on the same sample solutions. The results are tabulated (Table VI.1).

Table VI.1. Dimethyl glyoxime determination of standard steels and the North Chile (IIAB) iron meteorite

Sample	Digestion Acid	DMG Determination	Flame-AAS Determination	Reference Values
NBS #361	HNO_3	1.79%	1.89%	2.00% [*]
NBS #361	aqua regia	1.79%	2.11%	2.00% [*]
NBS #809B	aqua regia	3.34%	3.16%	3.29% [*]
North Chile	aqua regia	4.80%	5.36%	5.57% [†]
Synthetic Solution (Fe/Ni = ≈ 9/1)	HNO_3	8.82%	7.97%	8.94%

[*] US National Bureau of Standards Report
[†] Wasson, 1974

Table VI.2. Abundances of Ni in iron meteorites as determined by ICP-AES and flame-AAS

Sample	Ni Abundance (%)		Reference Value
	ICP-AES	flame-AAS	
Buenaventura	10.4	10.7	9.92[*]
Lonaconing	9.17	8.52	9.7 [†]
Denver City	8.86	7.71	8.40[*]
Red Rock	7.84	7.32	7.71[*]
Toluca	7.42	7.35	8.10[†]
Hoba	16.6	15.4	16.6 [†]
Bilibino (IIAB)	4.96	5.00	5.8 [*]
Ni standard	9.97	10.02	10.0

[*] Graham *et al.*, 1985
[†] Wasson, 1974

The agreement for both the DMG and flame-AAS values is less than satisfactory in comparison to the reference values. An additional study was done using ICP-AES and flame-AAS on the same solutions for various meteorites (Table VI.2).

These values are also unsatisfactory, showing deviations from the reference values of up to ±15%. The Ni values vary somewhat from each other as well as from the literature values when different methods of determination are used. The internal variation could be due to the standards used; the ICP values are based on standards used by a research group at the Department of Scientific and Industrial Research (DSIR), Palmerston North, New Zealand. However, the 10 μg/mL Ni standard used in flame-AAS work agreed well with the ICP-AES standard (Table VI.2). However, in general, the values determined by these two methods are within acceptable errors for each instrumental method for this element. Two additional sources of error are in the digestion of the sample or in the sampling of the meteorite.

Nickel metal is soluble in dilute HNO_3 and slightly soluble in HCl, but the Ni in iron meteorites dissolved equally well in both solutions. The values presented in Table VI.2 were obtained from samples digested in HCl. The values on Table VI.1 were obtained from samples digested in HNO_3 or in aqua regia, with no difference in the amounts or types of error seen for each set of tests. The trouble appears to lie with the sampling of the meteorites.

VI.4. Discussion

The sampling of iron meteorites presents problems in that two phases of Ni-Fe alloy exist: α (kamacite) and γ (taenite). A phase diagram for a mixture of Fe and Ni at various concentrations and temperatures is shown in Figure VI.2. With slow cooling from temperatures at which the meteorite is in the γ phase, kamacite will separate from the mixture according to its position relative to the composition boundaries at the expense of taenite, which loses volume but becomes richer in Ni content. The kamacite will precipitate along the octahedral planes of the parent taenite crystal. This mode of crystallization, continuing at relatively low temperatures over long periods of time, can account for the regular geometric (Widmanstätten) patterns observed in polished and etched sections of the octahedrite meteorites (Uhlig, 1954). This creates regions and zones of Ni-rich and Ni-poor areas.

Figure VI.3a shows a microscopic view of the Widmanstätten pattern

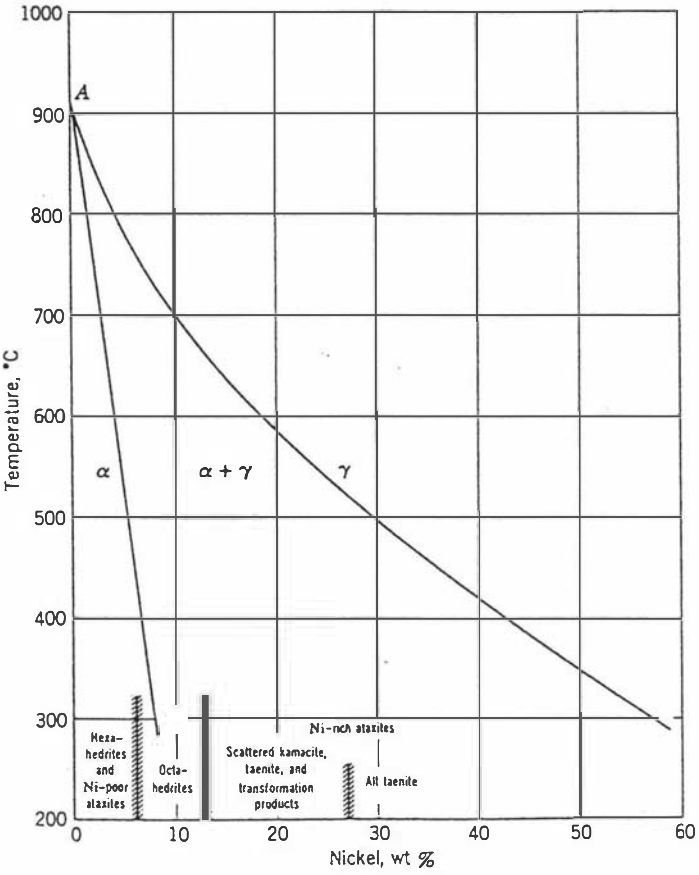


Figure XI.2. Phase diagram for iron-nickel alloys at 1 atomosphere pressure combined with iron meteorite classification (Owen and Liu, 1949)

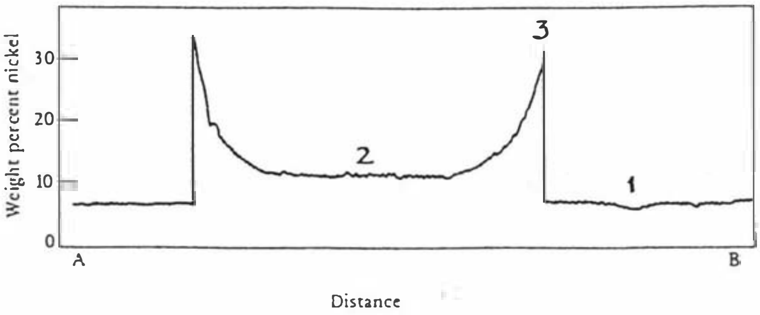


Figure VI.3a. (Top) A microscopic view of the Widmanstätten pattern in the Drum Mountains iron meteorite shown in reflected light. (McSween, 1987)

Figure VI.3.b. (Bottom) An electron-microprobe traverse measusring the Ni content across the region A--B. (McSween, 1987)

Table VI.3. Differences in Ni content between parts of a kamacite crystal (Refer to Figure VI. 3)

Region Number	≈ % Ni	Difference from Region #1
#1	6.88	--
#2	11.9	73.0%
#3	21.1	208%

in the Drum Mountains iron. Points A and B are on a kamacite area (in grey) and the transect between the points crosses through a white area of taenite and an acicular region of plessite ($\alpha + \gamma$ intergrowth). An electron microprobe traverse measuring the Ni content along this line has a distinctive M-shaped profile (Figure VI.3b). The Ni content decreases away from the margins of the taenite grain due to slower diffusion resulting from cooling, which produces an inhomogeneous grain. The difference in Ni content in the labelled portions of the graph of the microprobe traverse is given in Table VI.3.

Clearly, careful sampling is necessary to get a representative sample. For analysis, it is often tempting to cut or break the meteorite sample along planes of cleavage formed by the intergrowth of the α and γ phases. Clearly, this can cause large differences in apparent Ni concentrations for the same sample. An example of this was seen when Scott and Wasson (1976) resampled and reanalyzed the St. François County (IC) iron because they believed this meteorite was a member of group IC. However, the Ni content previously reported by Wasson (1970a) seemed too low to include St. François County in this group. Microscopic examination showed the previous analysis was performed on a single kamacite plate, causing the low values for Ni. Wasson (1990) had warned that because Ni is frequently used as a taxonomic indicator, it is perhaps necessary to accept and use the Ni values from the literature instead of attempting to obtain a piece of meteorite large enough to be representative for the whole meteorite and destroying it for the sake of a value which has already been established in the literature. The Ni values reported in Appendix 1 are thus taken from Wasson (1974) or from Graham *et al.* (1985).

VI.5. Subsampling Procedure

The inhomogeneity of iron meteorites caused concern regarding the values determined here and by Ryan *et al.* (1990). Subsamples for these determinations were taken from the same meteorite specimen. When the sample was received, it was first polished and etched with a 5% HNO_3 in ethanol (nital) solution (Appendix 4) to reveal the Widmanstätten pattern and/or Neumann bands. The samples were then sawn across these patterns rather than parallel to them. It was hoped that the 2-5g piece sent to the TARC group for INAA and the resultant sawings would then be as representative as possible within the 5-10g sample sent to us by the museums and individuals listed in Appendix 1. The sawings were used to determine Ru, Pd and Pt. No detectable differences were observed when these three elements were determined in either sawings or in carefully cleaned whole pieces of meteorite. In addition, it is desirable not to waste this material in single element, destructive methods of determination of these often rare samples. Clean metal was used in the Ga and Tl studies, as contamination from the steel in the hacksaw blade could cause enhancement of signals for Ga and Tl.

VI.6. Conclusion

Nickel cannot be determined with acceptable accuracy and precision using the small samples received by this laboratory. The meteorites are not homogeneous with regard to Ni content. Values for Ni established in the literature will be used in this study and are presented in Appendix 1.

The inhomogeneity of iron meteorites opens up other possible topics for research, namely the study of the distribution of Ru, Pd and Pt in meteorites, and the critical sample size necessary for a confident determination for Ni. It is hoped that these topics will be studied as research projects in the near future.

Chapter Seven

Instrumental Specifications

VII.1. Atomic Absorption Spectrometry

Free atoms cannot undergo rotation or vibrational transitions as do molecules. Only electronic transitions can take place when energy is absorbed or emitted. The quantized nature of the transitions allows the observation of line spectra (Christian, 1978).

In order to make measurements in atomic absorption, it is necessary to convert material to a population of ground state atoms and then pass resonance radiation of the element to be measured through that population. Spectrophotometric analysis is the determination of the concentration of a substance according to its absorption of specific monochromatic radiation (Pinta, 1966). Ideally, the measuring device should "see" only the wavelength which is being absorbed as the presence of other radiation lowers the proportion of absorbed radiation, resulting in decreased sensitivity (Price, 1979).

Aspiration into a flame is the most convenient and reproducible means of obtaining atomic vapor in AAS (Christian, 1978). However, it is one of the least efficient in terms of converting all of the sample elements into atomic vapor and presenting this to the optical path. The overall efficiency of conversion and measurement of atoms presented has been estimated at as little as 0.1%. In addition, aspiration methods require several mL of solution for analysis.

Furnace atomizers have higher conversion efficiencies than flame atomizers. Absolute detection limits are typically 100-1000 times improved over flame aspiration methods. For flame-AAS with an analyte concentration of 10^{-6}M, the density of atoms produced (n) in the vapor is of the order of 10^{15} atoms/cm^3. For a non-flame situation, the density is $\approx 10^{18}$ atoms/cm^3 (equations from Zeegers *et al.*, 1968-- shown in Appendix 5).

The general principles of atomization in a temperature programmed furnace have been discussed by Fuller (1977) and Price (1979). The graphite tube is held between two electrodes through which voltage is applied. By varying the voltage across the electrodes, the temperature of the atomizer can be controlled. The unit is sheathed in a stream of inert gas (oxygen-free nitrogen for all of the work presented in this thesis) which prevents the oxidation of the graphite atomizer and also removes vapor as it diffuses from the furnace. The generation of a population of free atoms whose absorption is measured is achieved in three stages:

1) drying--solvent removal
2) ashing--organic matrix and reagent removal
3) atomization--atom production.

The heating process for each stage is controlled by setting three parameters: final temperature, ramp time,and hold time. The initial temperature is assumed to be the final temperature of the previous step. The advantage of ramp heating over fixed heating allows the sample to be dried more reliably and prevents the possibility of mechanical loss of analyte by spluttering.

VII.2. Instrumentation

The main difference in instrumentation and procedure between GFAAS and conventional flame-AAS is the use of an electrothermal atomizer as the atomization source in place of a flame. Automated sampling is desirable in GFAAS to obtain better reproducibility.

Graphite furnace AAS was carried out by the use of a GBC-1000 graphite furnace instrument coupled to a GBC-902 double-beam atomic absorption spectrometer with the option of automatic background correction. Automatic sampling was performed using a PAL-1000 automatic sampler capable of delivering up to 5 μL of sample with the option of ten multiple loadings. Traces of the peak height were plotted with an Epson LX-80 printer. Hollow cathode lamps were used as line sources for all of the elements discussed in the previous chapters.

Flame-AAS was performed using an IL457 instrument with manual sampling.

VII.3. Instrument Parameters

The selection of furnace conditions and development of the thermal program depends on the nature of the sample matrix as well as the element to be determined. To obtain the best results for any analysis, these parameters should be studied. In addition, the instrumental parameters must be selected to give optimum performance in the detection of the analyte. This refers to the lowest limit of detection (LOD) coupled with the smallest possible errors (reproducibility). However, in general, compromises must be accepted.

VII.3.i. Lamp Current

The Ru, Pd and Pt lamps used for this project were subjected to increasing current (1-20mA) for the same standard samples. The results of the signals caused by the analyte and the background noise as a function of the lamp current are shown in Figures VII.1. The signal to noise ratio (S/N) as a function of the lamp current is plotted in Figure VII.2.

Platinum shows the best S/N ratio at 10 mA; Ru at 14 mA; Pd at 18 mA. However, currents must be chosen with consideration to the life of the lamp, and it is inadvisable to use higher currents if they are not necessary. With this in mind, the lamp current used for Ru is 10 mA, as this current actually produced the largest absorbance signal, with a fairly low background signal. Palladium signals actually decrease with increasing lamp current, perhaps due to this element's ability to absorb inert gases at higher temperatures (Livingstone, 1973). As a compromise, a current of 5 mA was selected to avoid the excessive noise of the background signal at the smallest possible input of power. The current chosen for the Pt lamp is the one displaying the best S/N ratio at 10 mA.

The currents selected here are the same as those recommended by the manufacturer.

Figure VII.1a. Ru absorbance and background noise as a function of lamp current

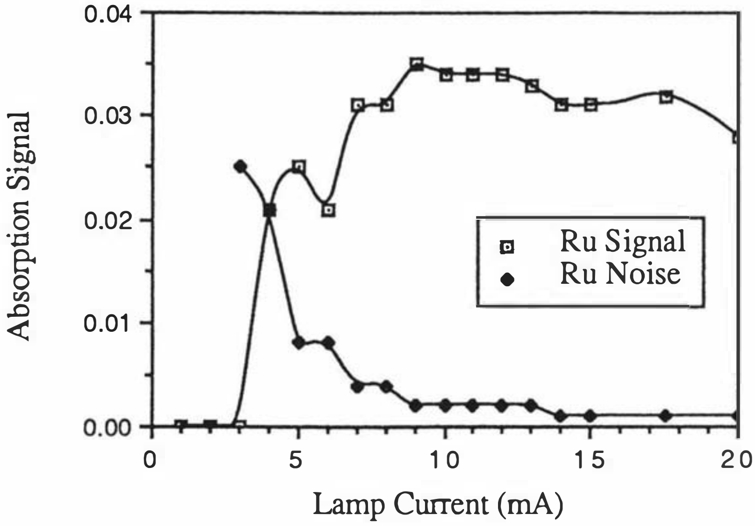


Figure VII.1b. Pd absorption signal and background noise as a function of lamp current

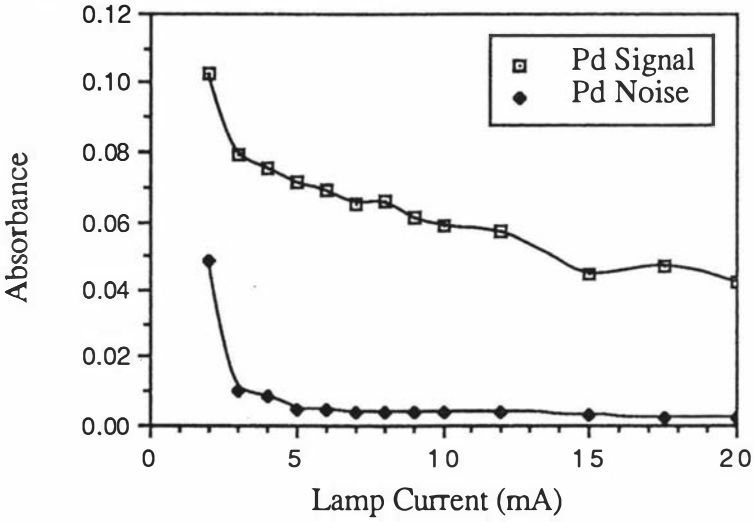


Figure VII.1c. Pt absorption signal and background noise as a function of lamp current

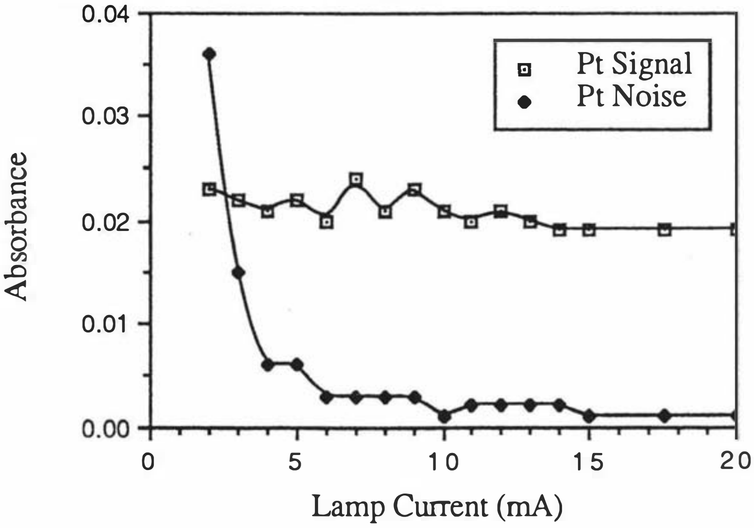
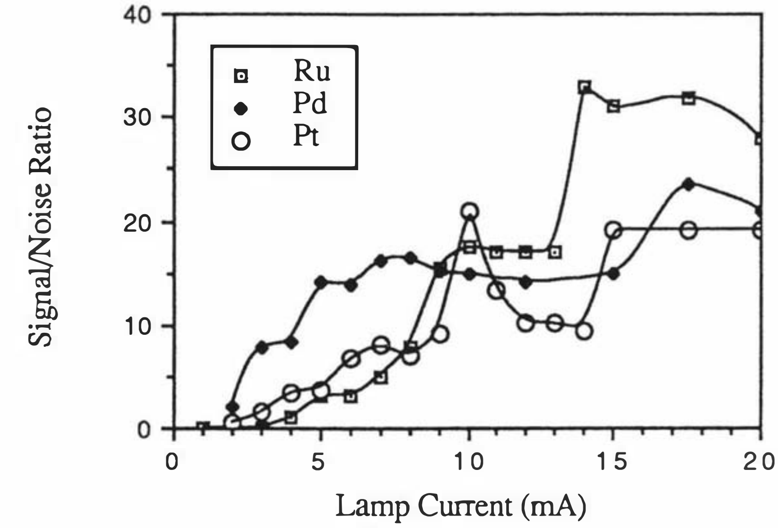


Figure VII.2. Signal to Noise ratio as a function of lamp current



VII.3.ii. Slit Width

The curved mirrors within the monochromator comprise the focussing elements by which an image of the entrance slit is formed on the focal plane (Slavin, 1978). The length of the slit is limited by the diameter of the detector window. The width of both the entrance and exit slits are usually adjustable.

The slit widths can control certain spectral interferences, including unabsorbed lines of the fill gas in the lamp, or the unresolved and unabsorbed lines of the cathode material, or molecular absorbances. Mechanical and spectral considerations impose a lower limit on the narrowness of the slit. In the GBC-902 instrument, this minimum is 0.2 mm.

As a slit is narrowed, the background signal (noise) becomes less intense and so does the desired absorption signal. The intensity of the noise decreases more than that of the elemental signal, resulting in an increased S/N ratio. A slit width must be chosen to balance the removal of interferences and the sensitivity of the desired signal.

For Pt, a slit width of 0.5 mm was chosen as very little background noise was observed. As the LOD of Pt is approximately four times less that

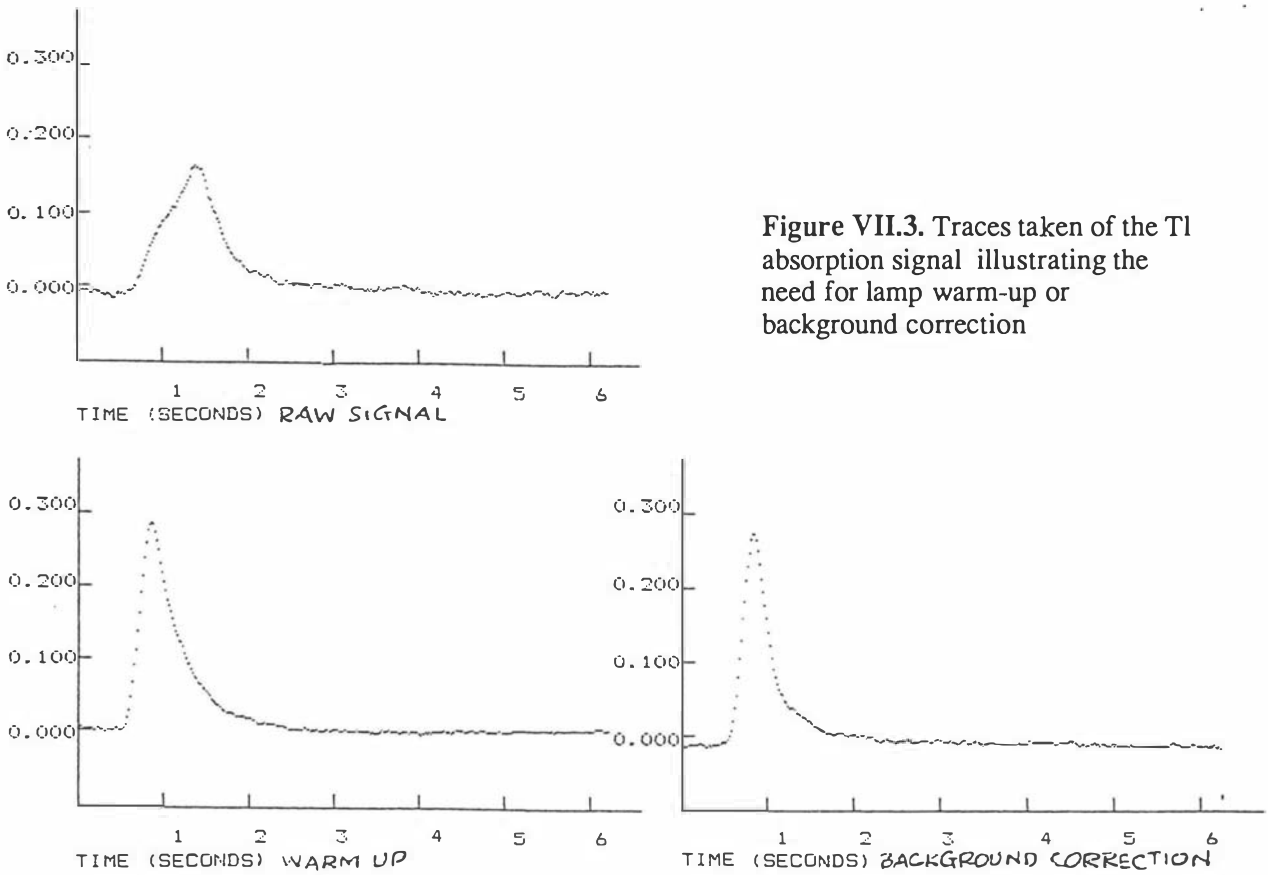


Figure VII.3. Traces taken of the Tl absorption signal illustrating the need for lamp warm-up or background correction

that of Pd (Brooks and Lee, 1989) it is desirable to try and maximize the absorbance signal as much as possible. A slit width of 0.2 mm was used for Pd determinations to balance its good sensitivity by GFAAS with its high level of background noise. This noise increases as a function of the usage of the Pd hollow cathode lamp.

For the same reasons as for Pt, a 0.5 mm slit width was chosen for Ru, Ga and Tl determinations.

VII.3.iii. Lamp Warm-up

The primary instability in the GFAAS system is the source lamp, which requires time to come to thermal equilibrium and a constant, stable emission (Slavin, 1978). Even if this point is reached, some lamps have a tendency to drift or to increase the value of the background noise as a function of operating time, as in the case of Pd stated in the previous section.

Table VII.3. Spectral Lines used in this study

Element	Wavelength (nm)
Ru	349.9
Pd	247.6
Pt	265.9
Ga	287.4
Tl	276.7

The signal for Tl was improved after a 15 minute warm-up time prior to sample analysis (Figure VII.3). The other lamps did not appear to drift or show instability as a function of warm-up time. To prevent unnecessary wear on the lamps, only 5 minutes of warm-up was allowed before the first sample was analyzed for Ru, Pt, Pd and Ga. The Tl lamp was ignited and allowed to run for 15 minutes prior to analysis of samples.

VII.3.iv. Wavelength Selection

The strongest lines for each of the five elements determined by GFAAS were selected for use in their detection (Table VII.1). Because these elements were analyzed in simplified matrices, no problems were observed with interference lines.

VIII.3.v. Background Correction

The Tl absorbance signal shape was improved with the use of background correction. In the separation of Tl from the matrix, Cl^- is necessary which must subsequently be removed to avoid volatization of $TlCl_4^-$ (Hoashi, 1988). Silver nitrate is employed to remove Cl^-, but excess Ag^+ causes a potentially interfering peak to be observed, the result of incomplete sample ashing (Figure VII.4). The use of background correction not only cuts down on warm-up time for the Tl lamp, but also eliminates background due to Ag salt volatilization.

For Ru, Pt, Pd and Ga, the simplicity of the matrices made the use of background correction unnecessary.

VII.4. Development of Furnace Programs

Atomization temperatures were investigated with an unvarying amount of sample and the results for Ru, Pd, Pt, Ga and Tl are presented in Figure VII.5. The temperatures selected were the same as those recommended by the GFAAS manufacturer.

Ashing temperatures for charring the organic matrix must be as high as possible without affecting the analyte. The temperatures listed in the GBC operator's manual were used with no problems.

For the drying stage, a temperature of 120°C was used. The ramp time to reach this temperature is chosen to be slow enough to prevent spluttering of the sample and the possible loss of analyte. A slow increase in temperature produces a more reproducible result, as does a longer hold time for both the drying and the ashing stages (Brooks and Lee, 1988). The same slow ramp and hold times were also used for the ashing stage.

For atomization, ramp times of 1-1.3 seconds were chosen in order to generate a population of free atoms as rapidly as possible. A three second hold time was selected to remove all analyte atoms and to reduce memory effects (Sighinolfi, 1973).

The furnace programs used for the determination of Ru, Pd, Pt, Ga and Tl are presented in Table VII.2.

Figure VII.5a. Ru absorption signal as a function of atomization temperature

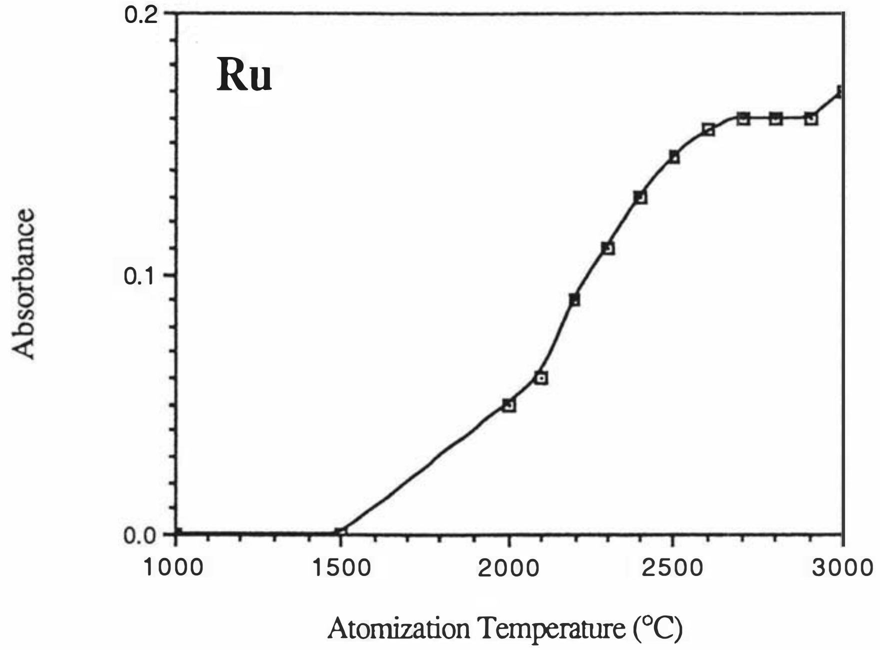


Figure VII.5b. Pd absorption signal as a function of atomization temperature

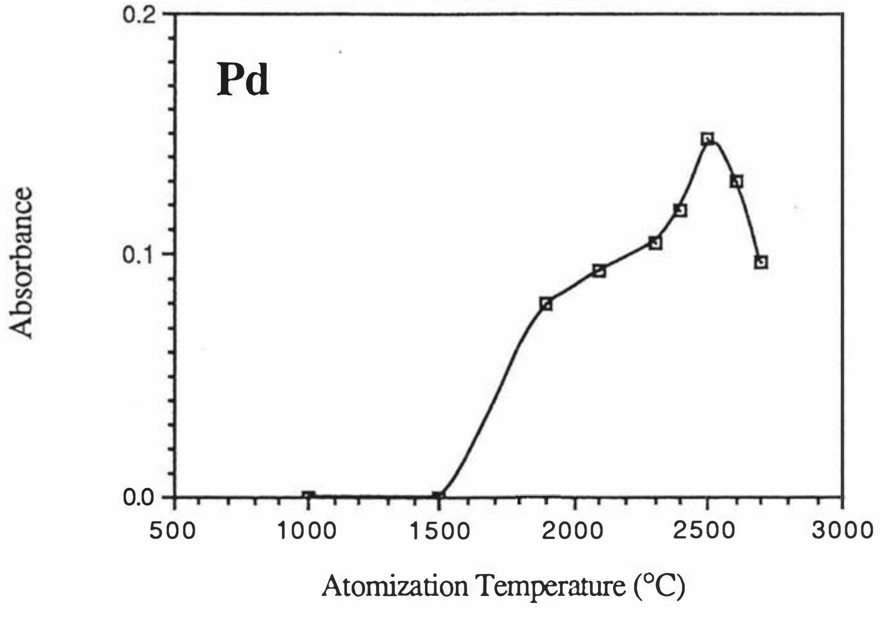


Figure VII.5c. Pt absorption signal as a function of atomization temperature

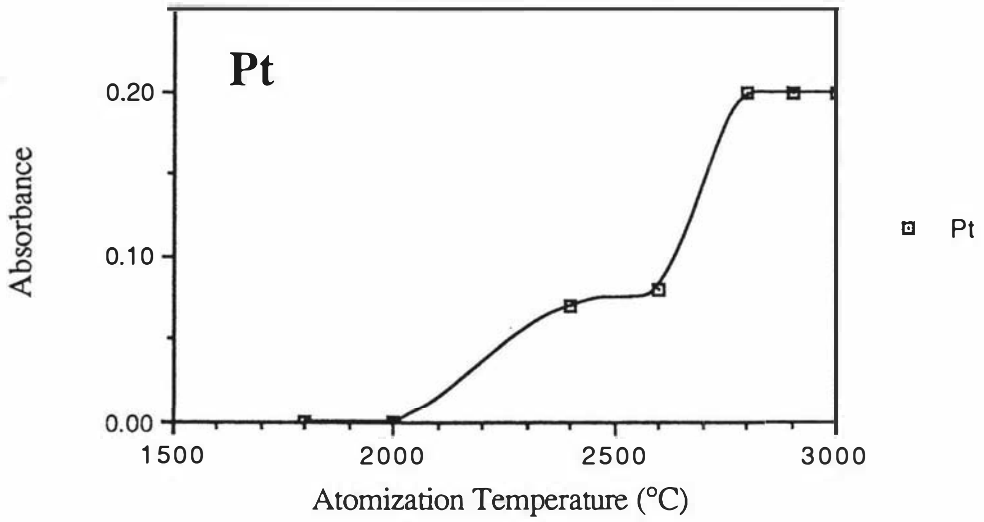


Figure VII.5d. Ga absorption signal as a function of atomization temperature

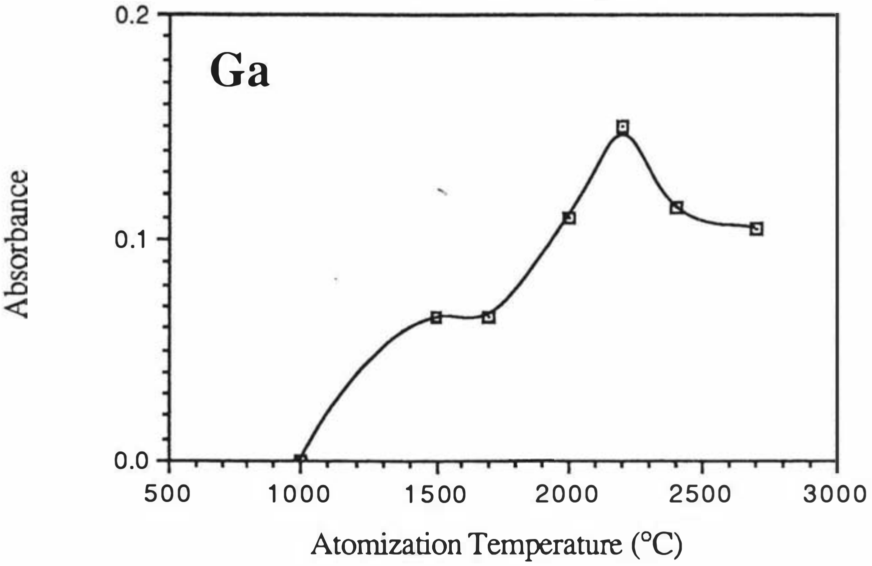


Figure VII.5e. Tl absorption signal as a function of atomization temperature

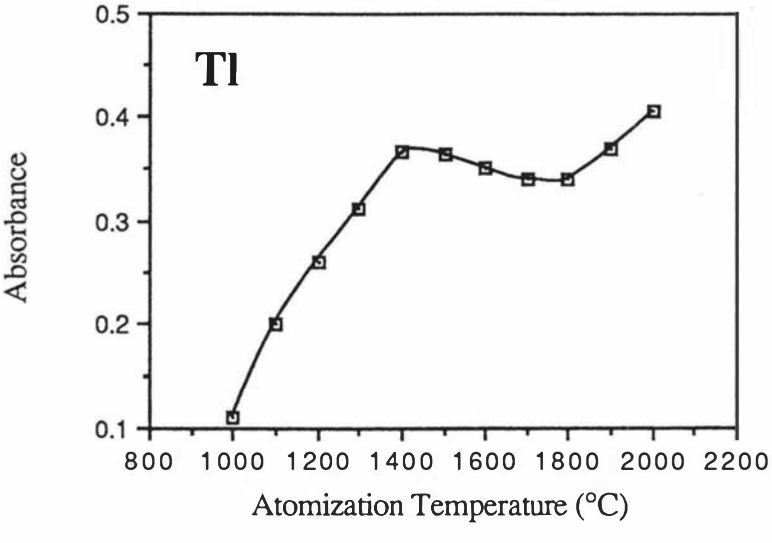


Table VII.1a. GFAAS program for Ru

Step	Stage	Final Temp (°C)	Time (sec) Ramp	Time (sec) Hold	Gas Inert	Gas Auxiliary	Read	Pen
1	Dry	120	10.0	5.0	No	No	No	No
2	Ash/Char	400	10.0	5.0	Yes	No	No	No
3	Atomize	2800	1.3	3.0	Yes	No	Yes	No

Table VII.1b. GFAAS program for Pd

Step	Stage	Final Temp (°C)	Time (sec) Ramp	Time (sec) Hold	Gas Inert	Gas Auxiliary	Read	Pen
1	Dry	120	10.0	5.0	No	No	No	No
2	Ash/Char	500	10.0	5.0	Yes	No	No	No
3	Atomize	2500	1.3	3.0	Yes	No	Yes	No

Table VII.1c. GFAAS program for Pt

Step	Stage	Final Temp (°C)	Time (sec) Ramp	Time (sec) Hold	Gas Inert	Gas Auxiliary	Read	Pen
1	Dry	120	10.0	5.0	No	No	No	No
2	Ash/Char	500	10.0	5.0	Yes	No	No	No
3	Atomize	2800	1.3	3.0	Yes	No	Yes	No

Table VII.1d. GFAAS program for Ga

Step	Stage	Final Temp (°C)	Time (sec) Ramp	Time (sec) Hold	Gas Inert	Gas Auxiliary	Read	Pen
1	Dry	120	10.0	5.0	No	No	No	No
2	Ash/Char	400	10.0	5.0	Yes	No	No	No
3	Atomize	2200	1.0	3.0	Yes	No	Yes	No

Table VII.1e. GFAAS program for Tl

Step	Stage	Final Temp (°C)	Time (sec) Ramp	Time (sec) Hold	Gas Inert	Gas Auxiliary	Read	Pen
1	Dry	120	10.0	5.0	No	No	No	No
2	Ash/Char	400	10.0	5.0	Yes	No	No	No
3	Atomize	1500	1.0	3.0	Yes	No	Yes	No

VII.5. The Multiple Loading Capacity

The use of the multiple loading option allowed a larger amount of sample to be placed into the graphite furnace tube prior to atomization. This 50 µL total loading is very useful in the determination of small amounts of analyte which effectively lowers the LOD in terms of concentration of the original sample for any element. If the original sample is very dilute, or the amount of sample available is small, the multiple loading feature may be extended past its designed capacity, as in the extreme case of the determination of Ru in the ungrouped iron meteorite, Bellsbank.

The 5 µL aliquot of sample solution in $CHCl_3$ is automatically pipetted into the furnace. The temperature of the graphite tube is raised to 120°C in order to dry the sample. The furnace is then cooled and another 5 µL aliquot pipetted into the furnace and the process repeated for 10 loadings (total 50 µL). After the tenth drying, the program is halted to prevent it from raising the temperature further to the charring and atomization steps. The program is then restarted, and another 50 µL of sample pipetted and dried in 5 µL aliquots. This is repeated as often as necessary or until there is no more sample. From experience, a total loading of 500 µL of sample solution should not be exceeded because of two considerations: 1) A rime eventually forms on the inside of the graphite furnace tube, which could cause problems in the charring and atomization stages through the formation of smoke (Sighinolfi, 1973); 2) The $CHCl_3$ in the sample vial (see next section) evaporates slightly in the time required to load larger amounts of sample into the furnace. This small loss of solvent is sufficient to make a change in the Ru concentration, rendering the determination uncertain. This, of course, indicates that only one determination may be accomplished for very dilute samples. In this manner, it was possible to bring the LOD of Ru down to 0.5 ng, and allowed the Ru content of the Bellsbank meteorite to be estimated at <0.5 ng/g.

VII.6. The Sampling Vial

The sampling vials supplied by the GFAAS manufacturer could not be used when an organic solvent is to be analyzed. The bottom of the plastic vials are glued rather than machined and MIBK readily dissolves this glue. The plastic vials were also readily softened and eventually dissolved by $CHCl_3$. To overcome these objections, glass test tubes that fit into the automatic sampling carousel were cut to a height of 25 mm and initially used in place of the plastic vials. However, this vial requires 2 mL of sample and the relatively large exposed surface area allows rapid evaporation of the solvents used in these studies.

The drilled Teflon plug described by Brooks and Lee (1988) was considered, but it proved to be difficult to clean thoroughly and it was expensive to produce the number necessary to perform these analyses.

Another sampling vial was devised using the manufacturers plastic vials and caps with Durham tubes. A hole was punched into the cap with a cork borer and a Durham tube inserted. This cap was then placed over the plastic vial and the sample placed into the tube with a Pasteur pipette. This vial requires 0.25-0.50 mL of sample, will not distintegrate with use of solvents or acids, and the Durham tubes can be discarded after each use. The main disadvantage of this vial is that the sampling arm of the PAL-1000 auto-sampler does not come down into the center of the sampling surface. To accomodate this, holes were punched in the plastic caps with a #3 cork borer off-center and the sampler was watched carefully to ensure that the Durham tube was in the correct position for the syringe to descend into it for sampling.

Because of the long amounts of time needed to analyze some samples with the multiple loading capacity, it is advisable to introduce the sample into the vials just before they are required by the sampler. This prevents any excessive evaporation and resultant changes in concentration of the analyte-bearing organic solvent.

VII.7. The Furnace Tube

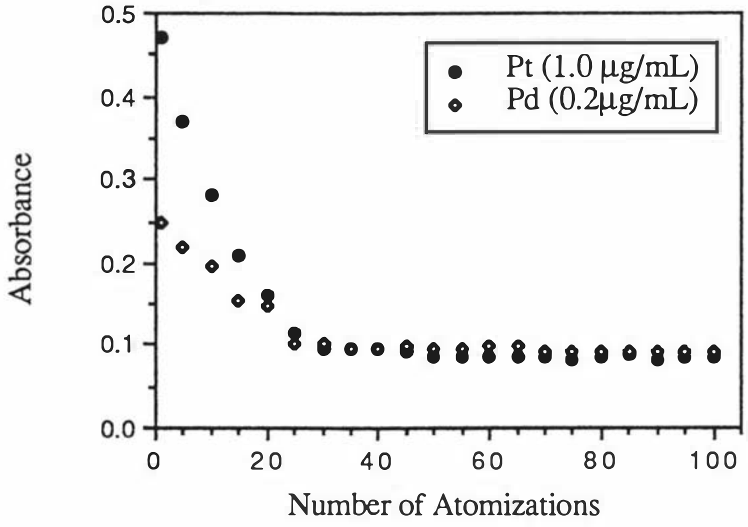
Although the pyrrolytic coating on the furnace tube should be clearly visible to the eye for optimum sensitivity for any element, the use of new or nearly new tubes was not always practical or even necessary. With every atomization, the surface conditions in the furnace will change, especially after the intense heating required for the determination of more refractory elements. In general, when the coating wears off, the result is a wetting of the furnace by sample solutions, which in turn lowers sensitivity and precision and can increase memory effect problems due to contamination.

Ruthenium is determined in the $CHCl_3$ phase, which dries quickly and efficiently in the furnace tube. The result is better sensitivity for Ru than can be found if the analyte were presented to the GFAAS in an aqueous medium. There were small, barely significant losses in signal peak height between a new furnace and a very worn one when using $CHCl_3$ as the sample medium. In this case, the condition of the furnace was mostly irrelevant to the production of reproducible Ru data.

Platinum and Pd signals decayed markedly between one atomization and the next, but stabilized after about 25 atomizations (Figure VII.6). The stable, reproducible signal in the worn furnace is approximately five times smaller than the irreproducible signal in the new furnace. The concentrations of Pd and Pt in the MIBK sample solutions could be controlled by decreasing the organic phase volume in the extraction or by increasing the sample size to be extracted. In addition, multiple loadings could be utilized to make up for losses in sensitivity in exchange for improved reproducibility. For these reasons, a moderately worn furnace is preferable for the analysis of samples containing Pd and Pt.

A study to check the effect of furnace wear on Ga showed no significant loss of peak height signal in 25 atomizations when using nearly new or worn furnaces.

Figure VII.6. Pt and Pd absorption signal as a function of furnace wear



The atomization temperature for Tl is quite low (1500°C) and the furnace tube does not wear as quickly as for the other elements in this study. No change in the peak height signal was observed after 25 atomizations.

An attempt was made to recover worn graphite furnace tubes with a refractory coating of Ta_2O_5 using the method of Brooks *et al.* (1981) in which a mixture of Ta_2O_5, water and detergent is repeatedly pipetted into the furnace tube and heated to 3000°C until an even, bronze coating was visible. The method did not result in an even coating as the particle size of the Ta_2O_5 was not sufficiently small to encourage an even distribution over the surface of the tube. Even when the particles were ground to -100 mesh, the coating described by Brooks *et al.*, (1981) could not be effected.

However, the recovery of furnaces stripped of their pyrrolytic coating from excessive use is not necessary, as a worn furnace is preferable for the determination of Pd and Pt, and is of little or no consequence for Ru, Ga and Tl.

Part Two

The Determination of Ruthenium, Palladium and Platinum in Iron Meteorites

Chapter Eight

Introduction

VIII.1. Introduction

The Earth is approximately chondritic in its bulk chemical composition (Morgan and Anders, 1980), meaning that the most important element by weight is Fe which composes nearly 40% of the whole planet (Mason, 1971). This metal is located in the Earth's core which forms from differentiation on melting of the planet. As samples of the core are inaccessible for direct study, the study of the iron meteorites is important as these specimens are thought to be remnants of cores of other planets, albeit smaller ones than the Earth.

Iron meteorites have a deceptively simple appearance that masks a complex history, indicated by the marked variations in trace element chemistry (Kelly and Larimer, 1977). Vinogradov (1971) reported that more than 70 elements are known to be soluble in native Fe, the most abundant element in iron meteorites.

Core formation, whether in planets or planetesimals, has the effect of scavenging siderophile elements, especially Fe, Ni, Co, Au and all of the platinum group metals (PGMs). Only Fe and Ni are present in high concentrations (>1%), but the others, along with Ge and Ga, are important for classification purposes (McSween, 1987).

The purpose of a classification scheme is to group together related objects in order to facilitate comparative investigations. A classification should consist of as few categories as possible without forcing together specimens for which the evidence of a relationship is inadequate (Wasson, 1974).

Goldberg *et al.* (1951) and Lovering *et al.* (1957) showed that Ga and Ge contents in iron meteorites vary by a factor of 1000 (Figure VIII.1). Within this range, the data tended to cluster into four Ga-Ge groups which approximately parallelled the earlier structural classification schemes (see Chapter one), and these clusters were numbered I to IV. Since then, in a series of papers entitled "The Chemical Classification of Iron Meteorites" (see references), Wasson and his colleagues resolved 17 chemical groups

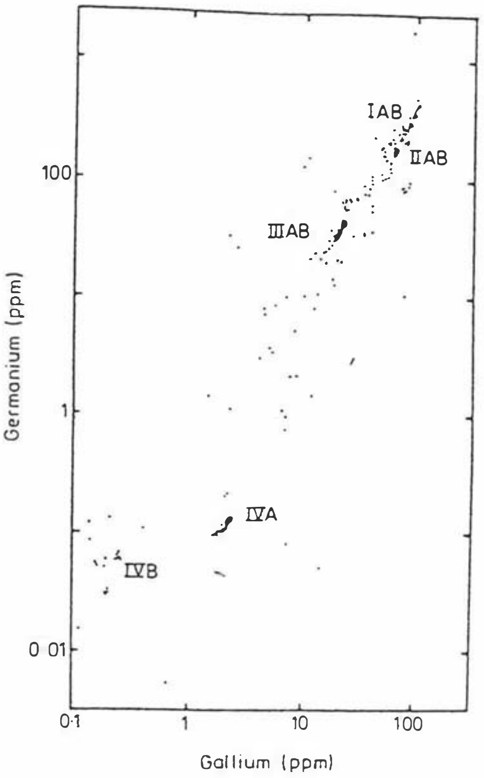


Figure VIII.1. Plot of Ge and Ga abundances in iron meteorites (Sears, 1978)

based on the abundances of Ga, Ge, Ir and Ni in individual irons. Scott (1972) pooled available data and showed that other elements also classify the meteorites in the same 17 groups, though not as well as the original four selected by Wasson. A few groups have been combined after the discovery of transitional members, and groups IVA and IVB, which have similar $^{Ga}/_{Ge}$ abundances have been shown to be totally unrelated. Meteorites which do not plot within well-defined chemical clusters are called anomalous or ungrouped. In principle, a separate group for each unique sample is a correct solution to the problem of classification, but the number of such samples is so great that these objects are best lumped together in a catch-all group and labelled as anomalous (Wasson, 1974).

VIII.2. Mislabelled Meteorites

In many cases, experienced meteorite researchers can assign an unknown sample to a group on the basis of its morphology in hand samples. However, detailed chemical and mineralogical studies are desirable, both to confirm the classification and to increase the amount of available data on that group of meteorites and for that particular sample. Mislabelling of meteorites must be avoided and takes several forms:

1) **Paired falls**--These are members of the same meteorite shower that have been mistakenly labelled as separate falls. The original location of the sample and a similarity in the resultant chemical and mineralogical analyses will usually indicate a paired fall. An example of this is the Cape York meteorite, which entered the Earth's atmosphere and broke up before landing, scattering many pieces over Greenland. This resulted in different names and dates of discovery for each of the individual parts of the original meteorite. A "fall" is defined as a witnessed siting of the meteorite's progress through the earth's atmosphere and subsequent recovery. A "find" is just that--no fall conditions can be established and the sample could have landed on earth at any time prior to its discovery. Finds are usually subjected to terrestrial corrosion and perhaps depletion of elements. Therefore, to meteorite researchers, a fall is preferable to a find (Buchwald, 1975).

Another possibility is the removal of samples by man or other forces to new locations, thus erasing any location data for a given specimen. Careful detective work is sometimes necessary in this case. For example, of the 13 medium to coarse octahedrites recovered throughout Arizona, 11 have the same composition and appear to be fragments of the Cañon Diablo mass, despite reported recovery sites being as much as 350 km away from its impact site--the famous Meteor Crater (Wasson, 1968).

2) **Mistaken identity**--This occurs when an individual specimen is mislabelled in collections. For instance, the Paneth's Iron (IIIE) sample in the British Museum of Natural History was mistakenly labelled Toluca (IAB) until the 1970's when disparate chemical analyses showed it to be a member of the rare IIIE group of irons. Details of this particular case of mislabelling will be discussed in Section X.3.iv.

3) **Frauds**--In some unfortunate cases, pieces of steel or slag are included in collections as meteorites (not always deliberately) until chemical and structural analyses prove otherwise. This occurs mainly in group IIAB, whose members do not display a Widmanstätten pattern. The IIABs are hexahedrites, or large kamacite (α-Ni) crystals, with no apparent taenite (γ -Ni) parent crystal still present. The absence of one of these phases allows false samples to masquerade as iron meteorites because of the lack of a resultant structural pattern.

Frauds can also be produced when a meteorite sample is brought forward as a new find, but is actually a piece of a previously known fall or find. Careful consideration of all available data is needed to avoid reporting the sample as a separate find. This fraud is different from a paired fall, as the provenance and movement of the sample since the fall has been deliberately and continuously destroyed or falsified. This type of fraud is unfortunately very common in meteoritics (Buchwald, 1975).

VIII.3. The Naming of Meteorites

Hey (1966) emphasized that the chief value of a meteorite's name is as a label of a scientific sample. Previously, meteorites were named after the nearest settlement large enough to have a post office (Wasson, 1974). The suggestions of Buchwald and Wasson (1972) are now followed, and meteorites are given unique names based on any permanent, named landmark in the vicinity of the discovery site.

The naming of meteorites in Antarctica raises a serious problem of terminology, for they come from very few geographic areas (Dodd, 1981). The solution comes from a precedent set by the lunar program for the recovery of selenological samples, and a modified version is applied to meteorites recovered "from the ice." Each sample is designated by a geographic area and a 5-digit number. The first two digits indicate the collection season (year) and the last 3 are reserved for the order in which that sample was collected. Thus, the 99th sample recovered in the Yamato Mountains area collected in the 1976 season is labelled Yamato 76099.

The clear classification of meteorites and the recognition of paired and mislabelled samples is important for the understanding of meteorites. A mislabelled sample could extend the borders that constrain the classification of members within a group. Paired samples that are regarded as two separate specimens could alter the probability and statistical treatments of data by assigning greater weight to a group because of the occurrence of an "extra" member. Also, five members with similar chemical, structural and mineralogical features are necessary to elevate those formerly ungrouped and anomalous members to separate group status. Including a paired set of samples could allow unjustified group assignment; two paired samples would mean there are actually only four members instead of the regulation five, and assign unjustified significance to those meteorites.

VIII.4. The Analysis of Iron Meteorites

The 108 iron meteorites held at the Brian Mason Meteorite Research Unit (BMMRU) were analyzed for Ir, Os, Rh, As and Au by TARC using the technique of INAA. The abundances of Ru, Pd and Pt were determined using the GFAAS technique and the methods detailed in chapters II and III. The Ge values, where necessary, were determined using hydride generation-AAS using the methods presented in Guo (1989). Values for Ni, Ga and Ge were taken from the literature.

The data generated by the above procedures are presented in Appendix 1 and are the basis for the discussions that follow.

Chapter Nine

Statistical and Graphical Treatment of Data

IX.1. Introduction

As is traditional in meteorite work, the logarithms of elemental concentrations are plotted against Ni abundances. For completeness, every other binary combination is also plotted and the results are located in Appendix 6. Initially, it was felt that using log-log plots of values would result in the poorer resolution of groups, especially if log Ni-log element plots were employed rather than if linear Ni-log element plots. This is because the Ni concentrations in meteorites tend to cluster together at 6-12%. However, there seems to be no loss of group resolution with the use of log-log axes (compare Figure IX.1). Ahrens (1954) showed that many elements in nature are distributed lognormally, especially if they are present in trace amounts. In Appendix 6, where all of the data points are plotted to show the relationships amongst groups, the graphs are presented with log-log axes. Within a group, the distribution and relationship of data points is sometimes seen more clearly if one of the axes (usually Ni) is linear. For discussions concerning individual members within a single group, a semi-log graph is employed.

With a large pool of abundance data having been obtained for all six PGMs in 108 meteorites, it becomes possible to reassess the chemical classification of iron meteorites by statistical analysis of the data. The procedures generally preserve and confirm the fundamental integrity of the classification system developed by Wasson and his colleagues over the past 25 years, but they do raise questions as to the confidence of the classification of several individual meteorites.

Figure IX.1a. Plotting of data for log Ni vs. log Ir

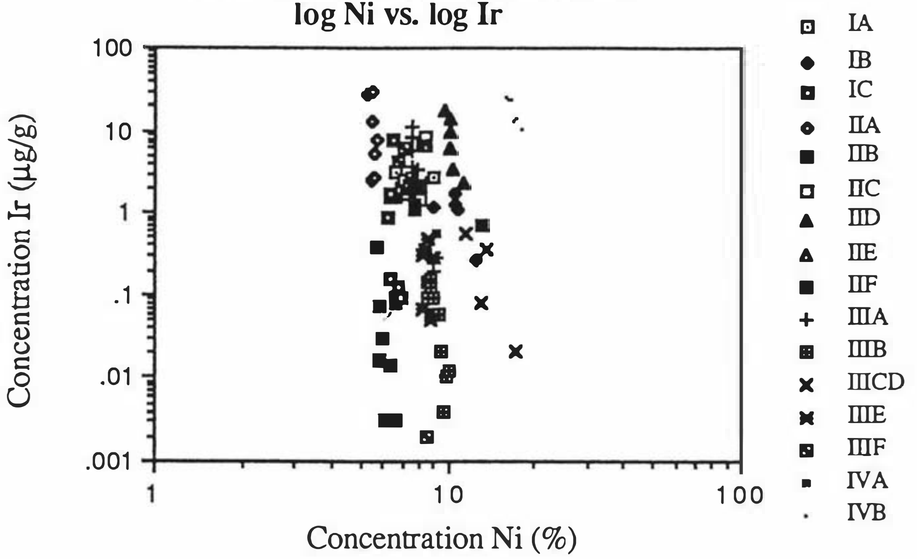
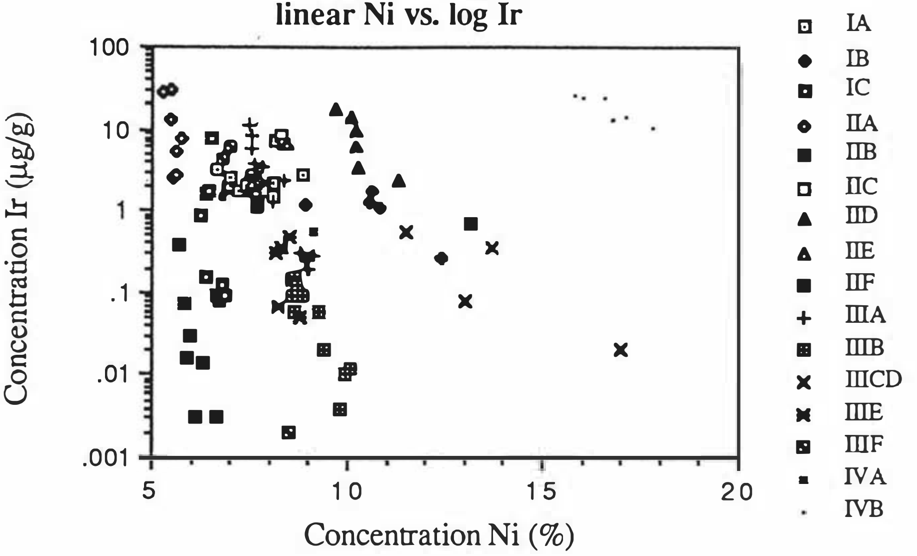


Figure IX.1b. Plotting of data for linear Ni vs. log Ir



IX.2. Correlation Coefficients

Correlation coefficients were calculated for any two of the abundances using the equation:

$$r = \frac{\Sigma x_i y_i - (\Sigma x_i \Sigma y_i)/_n}{[\{\Sigma x_i^2 - (\Sigma x_i)^2/_n\}\ \{\Sigma y_i^2 - (\Sigma y_i)^2/_n\}]^{1/2}}$$

where r is the Pearson's product moment correlation coefficient, n= 108 (106 degrees of freedom), and x and y are the concentrations of any two elements determined in a single meteorite. The results are listed in Table IX.1.

An impression of the degree of correlation of any two elements with each other can be assessed by visual inspection of the graphs in Appendix 6. In general, it appears that calculation of correlation coefficients is not sufficient to indicate the usefulness of any combination of two elements for classification purposes. Apparently, if the value of r indicates a strong correlation between two elements, it could either mean that all points on such a graph will plot along a straight line with no resolution of groups (eg.--As vs. Au) or will plot in clusters along the straight plotted line (eg.--Ga vs. Ge). Likewise, a binary combination that supports the null hypothesis could either mean that the data is spread on a graph in a totally random manner or in a quantized spread of values (eg.--Ni vs. Ir). In essence, the value of r cannot be used to judge the usefulness of any combination of elements towards the classification of iron meteorites. Plotting of the data points and visual inspection of the resulting graph is a more useful procedure.

Table IX.1. Correlation coefficients for pairs of elements determined in the iron meteorite data (Appendix 1)

	Ni	Ru	Os	Ir	Rh	Pd	Pt	Au
Ru	-0.113							
Os	0.141	0.482						
Ir	0.017	0.588	0.841					
Rh	-0.021	0.710	0.282	0.374				
Pd	0.770	-0.358	-0.138	-0.238	-0.145			
Pt	-0.057	0.882	0.574	0.726	0.716	-0.375		
Au	-0.075	-0.407	-0.558	-0.525	-0.311	0.258	-0.582	
As	-0.029	-0.376	-0.512	-0.489	-0.236	0.293	-0.553	0.933

	Ni	Ru	Os	Ir	Rh	Pd	Pt	Au
Ru	NS							
Os	NS	P**						
Ir	NS	P**	P**					
Rh	NS	P**	P**	P**				
Pd	P**	-P**	NS	-P**	NS			
Pt	NS	P**	P**	P**	P**	-P**		
Au	NS	-P**	-P**	-P**	-P**	P**	-P**	
As	NS	-P**	-P**	-P**	-P*	P**	-P**	P**

degrees of freedom (n-2)	106
Not Significant (NS)	<0.158
Possibly Significant (PS)	0.158-0.188
Significant (P)	0.188-0.223
Highly Significant (P*)	0.223-0.246
Very Highly Significant (P**)	>0.246

IX.3. Principal Components Analysis

Principal Components Analysis (PCA) was used to determine the contribution of the abundance of each element towards the total variance of the system (Sas, 1987). From the eigenvalues of the covariance matrix, it is possible to isolate a small number of components accounting for most of the variance in the system (Harman, 1976). The results are presented in Table IX.2.

The procedure was of little use for direct discrimination of the different groups, but was of use in identifying those elements that were the most variable among the different groups. These might then have the greatest potential for discrimination using a different statistical procedure.

The statistical process was carried out over all meteorite groups except those considered to be ungrouped. Tests were performed with and without inclusion of data for Ga and Ge. These two elements are excluded first to assess the effects of Au, As and the PGMs as Ga and Ge are considered to be the most diagnostic of chemical groups for iron meteorites (Wasson, 1974). The inclusion of Ga and Ge would have "diluted" the effects of the other elements in this analysis.

The result of PCA for PGMs, Au and As is that Ir, Os, Pt and Ru in principal component #1 account for 72.9% of the total variance of the system. A further 12.4% is accounted for by a combination of the abundances of Ru, Pt, Os and Rh in principal component #2. In these two principal components, very little of the variance is accounted for by Ni, Pd, Au and As. The data show that Ir, which initially was chosen arbitrarily because of its ease of quantification and low limit of detection (LOD) by RNAA (Wasson, 1974) is fortuitously the PGM accounting for the greatest amount of variance in the system.

If Ga and Ge are included in the data set, the value of Ge as a group-diagnostic parameter is highlighted, since it then becomes the most important constituent of principal components #1 and #2, in which the

Table IX.2. Principal components analysis of elemental abundances in iron meteorites. Only the first four components are shown. (All values shown in µg/g except for Ni)

	Excluding Ga and Ge			
	Component 1	Component 2	Component 3	Component 4
%Ni	+0.006	-0.053	-0.053	+0.050
Ru	+0.279	+0.606	+0.106	+0.039
Os	+0.562	-0.477	-0.270	+0.597
Ir	+0.666	-0.179	+0.474	-0.515
Rh	+0.098	+0.305	0.000	+0.138
Pd	-0.044	-0.136	-0.019	+0.065
Pt	+0.307	+0.488	+0.003	-0.025
Au	-0.155	-0.081	+0.539	+0.277
As	-0.176	-0.113	+0.629	+0.348
Cumulative % Variance	72.9	85.3	91.5	95.7

	Including Ga and Ge			
	Component 1	Component 2	Component 3	Component 4
%Ni	+0.027	-0.037	+0.026	+0.013
Ru	+0.164	+0.274	-0.561	+0.253
Os	+0.468	+0.288	+0.449	+0.691
Ir	+0.482	+0.479	+0.251	-0.663
Rh	+0.062	+0.089	-0.301	+0.073
Pd	-0.001	-0.088	+0.101	-0.029
Pt	+0.213	+0.240	-0.475	-0.058
Au	-0.169	-0.006	+0.168	-0.044
As	-0.202	+0.011	+0.219	-0.010
Cumulative % Variance	51.7	85.1	92.4	95.0

most significant other elemental abundances are those of Ir, Os and Ga. Principal component #3 shows the predominance of Ru, Pt and Os.

The results indicate that the principal components (in descending order) for the chemical classification of iron meteorites within this data set are Ga, Ge, Ir, Os, Ru and Pt. From these values, it is possible to decide which given binary element concentration plots are able to separate the different groups from each other, and this is confirmed by the graphs in Appendix 6.

IX.4. Discriminant Analysis

Reclassification of some meteorites can be considered using Discriminant Analysis (DA) (Sas, 1987). The form of the DA used in this study involved the creation of a linear combination of all variables in the form:

$$Z = a_1[\mathrm{Ni}] + a_2[\mathrm{Ga}] + a_3[\mathrm{Ge}] + a_4[\mathrm{Ru}] + a_5[\mathrm{Os}] + a_6[\mathrm{Ir}] + a_7[\mathrm{Rh}] + a_8[\mathrm{Pd}] + a_9[\mathrm{Pt}] + a_{10}[\mathrm{Au}] + a_{11}[\mathrm{As}] + C$$

The weights a_1-a_{11} and the constant C are selected by the program to give factor scores (Z) for each specimen. The degree of discrimination is calculated from the D^2 statistic determined from the means, variances and covariances of the variables measured in replicate samples from each group (Mahalanobis, 1936). It is in effect a measure of the "distance" between groups. The larger the value of D^2, the greater the degree of discrimination. The program determines the probability that each individual meteorite can be assigned to a particular group on the basis of chemical analysis alone.

The statistical procedure involved DA of abundance data for all elements determined in this study, plus Ni, Ga and Ge. The tests were first carried out over all groups excluding ungrouped irons. The second stage involved reassigning the meteorites to their new groups when changes

Table IX.3. Proposed reassignment (>90% probability) of iron meteorites following discriminant analysis

Meteorite	Group		Probability of Correct Assignment (%)								
	Original	Proposed	IAB	IC	IIAB	IIE	IIIAB	IIICD	IIIE	IIIF	IVA
Mesa Verde Park	IAB	IIE	0.7	--	--	96.1	3.2	--	--	--	--
El Burro	IIAB	IC	--	90.7	8.2	--	--	--	0.3	0.8	--
Sam's Valley	IIIAB	IAB	--	--	--	--	0.2	--	94.9	4.9	--
Lonaconing	AN	IAB	98.0	--	--	0.7	0.6	0.7	--	--	--
Cranbourne	IIICD	IAB	94.6	--	--	3.5	--	1.6	--	--	0.3
Nantan	IIICD	IAB	95.6	--	--	3.7	--	0.7	--	--	--
Mundrabilla	IIICD-AN	IAB	98.7	--	--	--	1.0	0.3	--	--	--
De Hoek	AN	IVA	--	--	--	--	--	--	--	--	100

appeared to be warranted and then recalculating the new distribution fields. The third stage involved addition of the ungrouped irons to the abundance data pool and establishing which, if any, of these could be assigned to a group with a high degree of probability. The results of these statistical analyses are shown in Table IX.3. In the final stage of the procedure, the morphological characteristics of these reclassified meteorites were considered, as described in Buchwald (1975), and specific recommendations made as to the reclassification of these samples.

IX.4.i. Mesa Verde Park

Mesa Verde Park is a polycrystalline, medium octahedrite (Om) with a bandwidth of 0.60 ± 0.10 mm. Taenite and plessite cover approximately 50% by area of a given section, and the kamacite is straight and long with a length/width ($^L/_W$) ratio of about 15. Schreibersite occurs as monocrystalline, brecciated units and is enveloped in rims of swathing kamacite. Troilite is present and 50 μm daubréelite blebs occur locally. Graphite is common as imperfect cliftonite crystals and in formation of oriented, acicular platelets, the latter completely embedded in schreibersite crystals. (A glossary of common minerals in iron meteorites is located in Appendix 7.)

Mesa Verde Park is rather an unusual medium octahedrite and is related to Colfax and Four Corners, both members, like Mesa Verde Park, of the subgroup IB. Mesa Verde Park lacks the silicates of Four Corners, but Buchwald (1975) notes that only small sections of this meteorite have been studied, and larger sections might yet reveal the presence of silicates.

There is no typical structure or mineralogy for group IIE, and it is possible that Mesa Verde Park should be reassigned to this group. Group IIE, to which the D^2 program assigns Mesa Verde Park, is not as well defined as other groups are. Scott and Wasson (1976) admit that their strict requirements that group members have similar structure and mineralogy were relaxed in order to establish group IIE. They justified this with the use of additional elemental parameters or, as in the case of IIE, that a larger membership supports the establishment of a proposed group. As a result, the strength of genetic links between members of IIE are considerably weaker than for members of other groups. Scott and Wasson (1976) state that the advantages in identifying a cluster of related irons outweighs the disadvantages that the members of the group did not share entirely identical formation conditions. The purpose in establishing a group is to assist the investigation of the origin of its members.

Malvin *et al.* (1984) noted that the IIE irons do not show elemental patterns typical of magmatic groups and stated that further study was needed to better define this group. Wasson and Wang (1986) require that data on genetically related iron meteorites should form smooth arrays on all siderophile-Ni diagrams.

Unfortunately, the BMMRU has only managed to obtain samples of two members of the IIE group, Weekeroo Station and Arlington. Values for Ni, Ga, Ge, As, Ir and Au for other members of IIE were taken from Wasson and Wang (1986) and listed in Table IX.5. Since Ru, Pd, Pt, Rh and Os data are not acquired routinely from samples by RNAA, Figure IX.2 shows the relationship Mesa Verde Park has with members of the IIE group by plotting available data against Ni.

Table IX.4. Data for members of IIE arranged in the order of increasing Ni values-- from Wasson and Wang, 1986 (all values in μg/g except Ni)

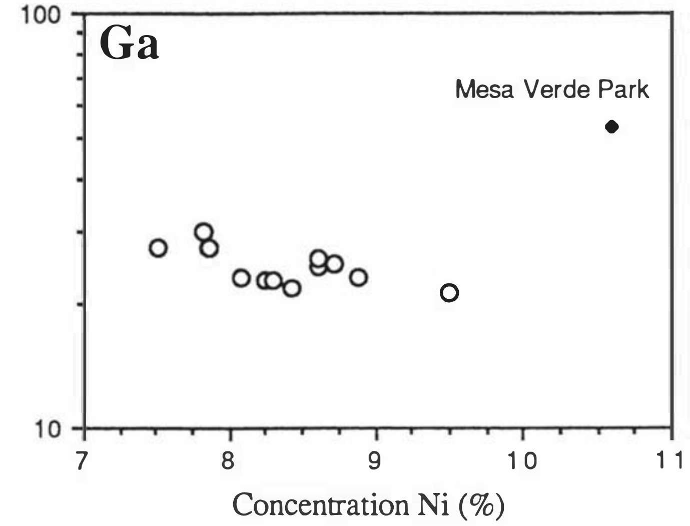
Meteorite	Classification	Silicates	%Ni	Ga	Ge	Ir	Au	As
Weekeroo Station†	IIE-AN	Differentiated	7.51	27.4	67.0	3.0	0.81	5.7
Tobychan	IIE		7.82	29.9	75.0	6.2	0.91	7.7
Colomera	IIE	Differentiated	7.86	27.3	75.0	7.9	0.95	8.0
Barranca Blanca	IIE-AN	None	8.07	23.2	64.0	5.6	1.16	10.8
Elga	IIE		8.25	22.8	72	4.0	1.18	10.3
Garhi Yasin	IIE		8.30	22.8	65	6.1	1.14	10.6
Arlington†	IIE-AN	None	8.42	21.9	64.9	6.2	1.51	14.6
Verkhne Dnieprovsk	IIE		8.60	24.6	70	7.2	1.33	11.7
Netschaëvo	IIE-AN	Chondritic	8.60	25.8	66	3.1	1.27	11.4
Kodaikanal	IIE		8.71	25.0	68.7	5.6	1.26	11.5
Techado	IIE		8.88	23.2	70.2	4.9	1.72	15.5
Leshan	IIE		9.50	21.3	68.9	4.1	1.79	18.0
Mesa Verde Park *	IB	None	10.6	53.0	142	1.24	1.20	9.46

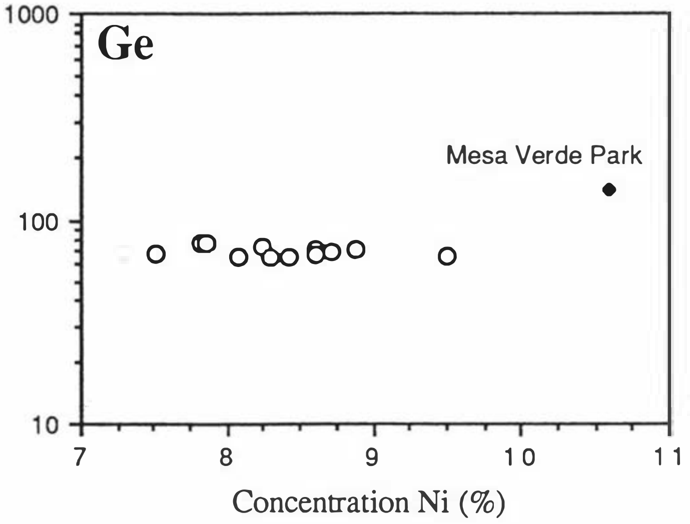
† Sample held in the BMMRU collection
* Presented by the DA program for reclassification into group IIE

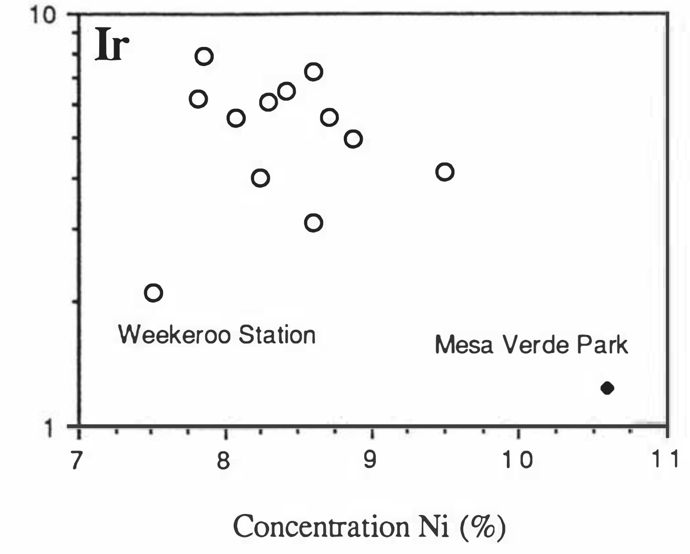
None of the Mesa Verde Park values fall on any of the elemental trends for IIE, as scattered as some of the badly defined trends appear to be. This is probably due to data being obtained for only Weekeroo Station and Arlington, so in the statistical procedure, these two points defined the field for the D^2 calculations. In addition, these two samples are not considered to be typical IIE samples, as the IIE-AN label indicates.

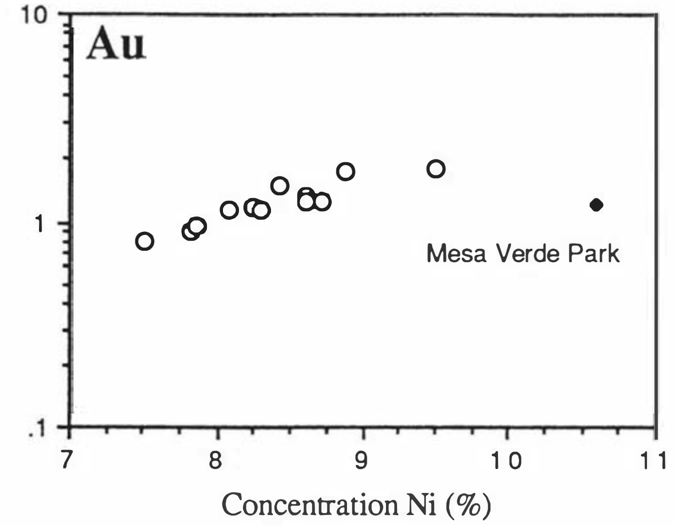
With this in mind, the reclassification of Mesa Verde Park by the DA program is rejected and this meteorite should remain in subgroup IB.

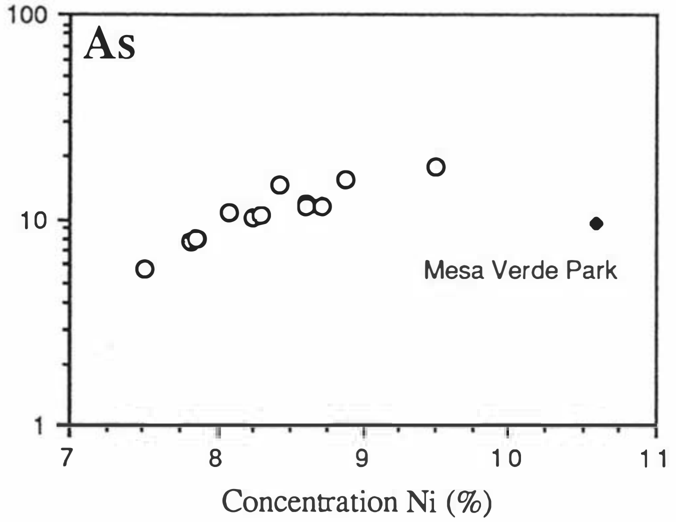
Figure IX.2. Group IIE data and Mesa Verde Park








Au
10
1
.1
7
8
9
10
11
Mesa Verde Park
Concentration Ni (%)


As
100
10
1
7
8
9
10
11
Mesa Verde Park
Concentration Ni (%)

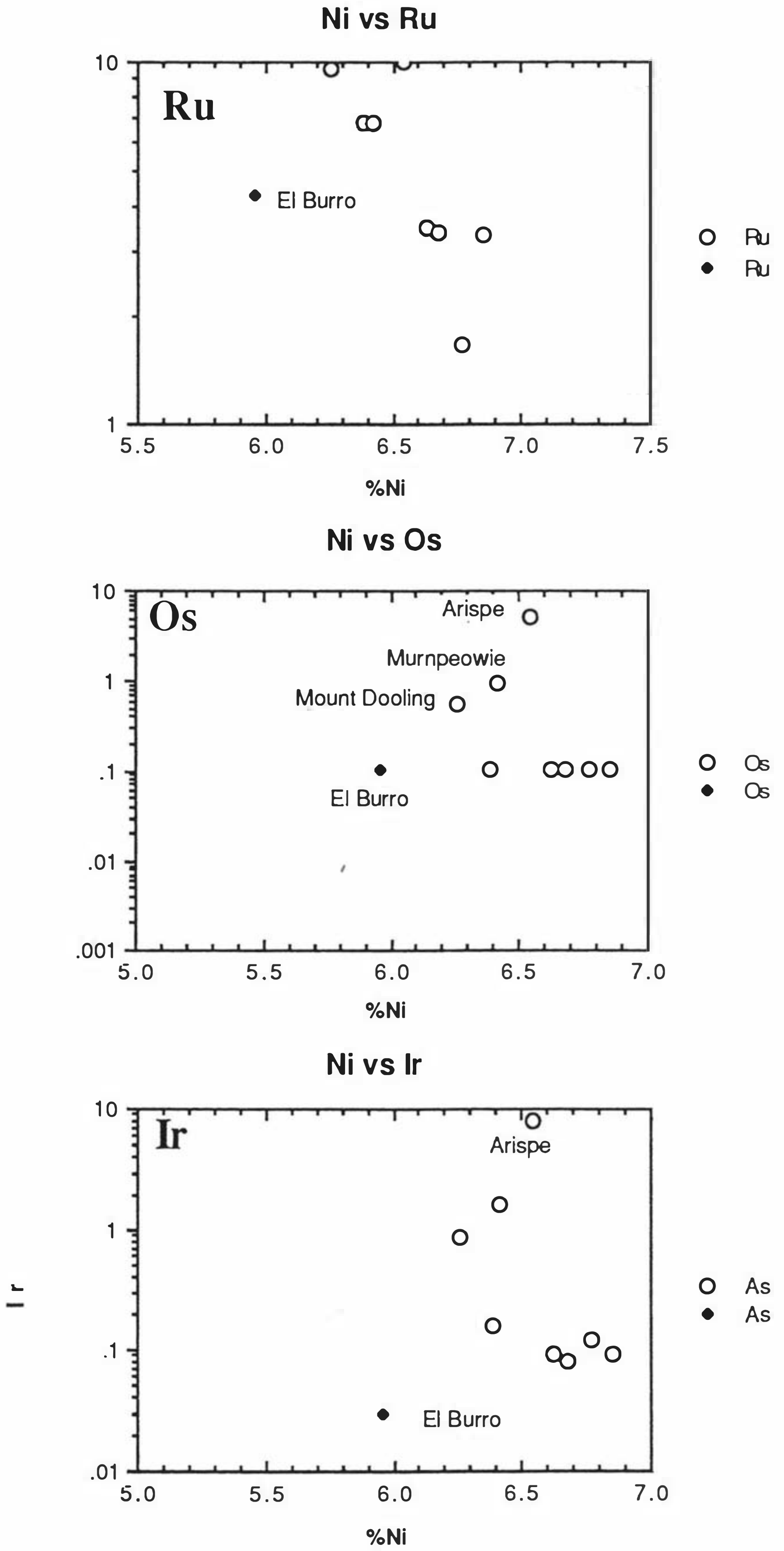
IX.4.ii. El Burro

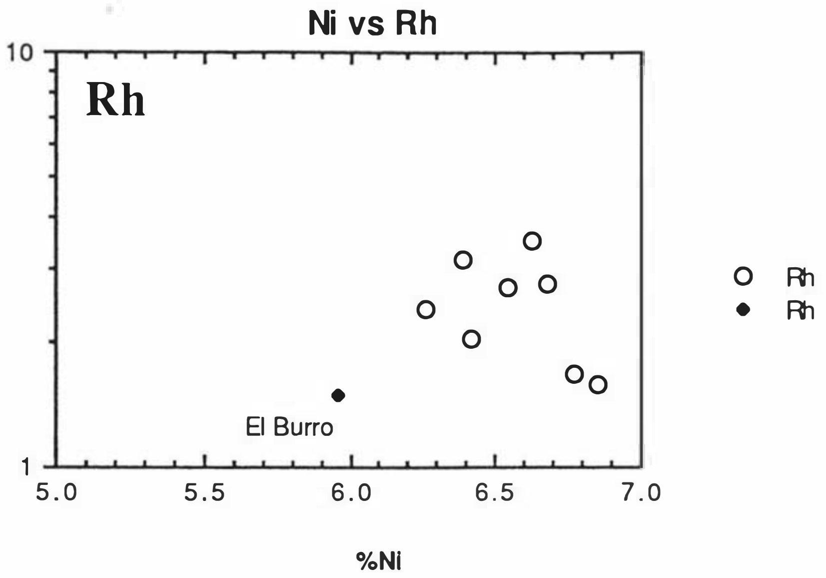
El Burro is a coarsest octahedrite (Ogg) with an average kamacite bandwidth of 10 mm with a few remnants of taenite. Neumann bands and rhabdites are common. Schreibersite, troilite, and cohenite are all present. Structurally, El Burro is closely related to Ainsworth and Sikhote-Alin, both subgroup IIB members.

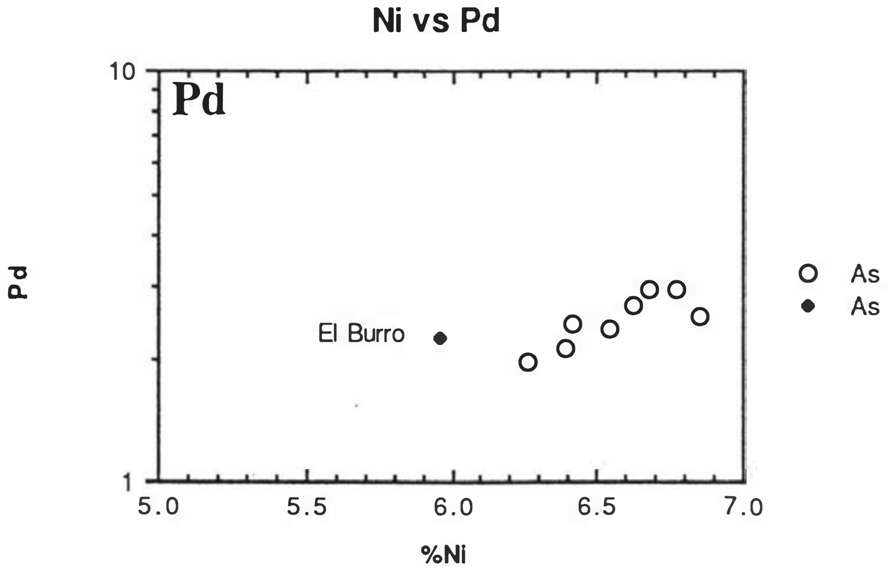
El Burro is assigned by the D^2 program to group IC, which, like group IIE, is not well defined (Scott and Wasson, 1976). In the case of IC, the abundances of Au and As are used to classify members of this group in addition to Ga, Ge, Ni and Ir contents. Structurally, group IC shows a great diversity ranging from slowly cooled coarse octahedrites to rapidly cooled polycrystalline structures with a very fine, faint octahedral structure. Mineralogically, group IC has abundant cohenite (which may have decayed to graphite) and sparse amounts of large phosphides.

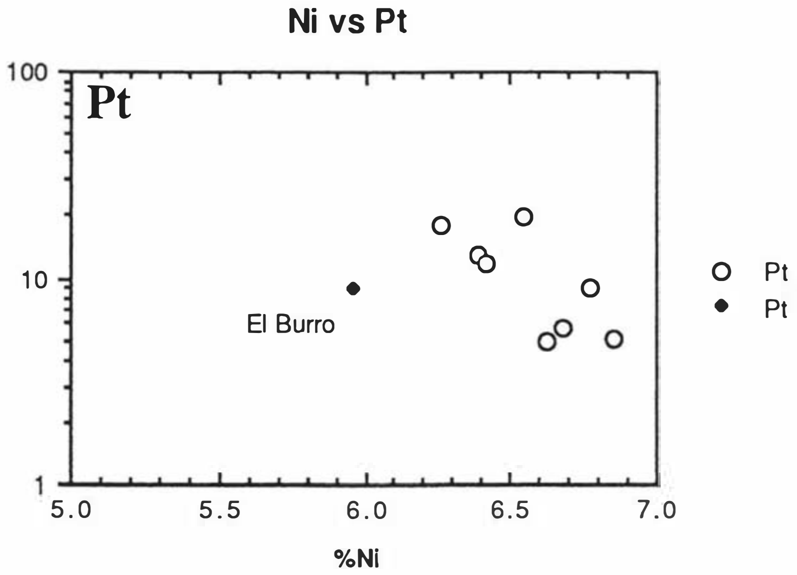
The data for the group IC members analyzed by the BMMRU were taken from Appendix 1. From the plots of the elemental concentrations against Ni abundance (Figure IX.3), the El Burro sample analyzed might be considered a low-Ni extension of the Ni-Ga and Ni-Ge trends for IC and shows a somewhat stronger relationship to members of IC than does Arispe (IC-AN). The plots of Ni-Au and Ni-As which were used by Scott and Wasson (1976) to define group IC in the absence of a stronger relationship between members using only Ni, Ga, Ge and Ir did not support the program's reassignment of El Burro to IC. Since the criteria for the inclusion of meteorites to this groups has not been met as defined by Scott and Wasson (1976), the reassignment of El Burro to IC is rejected.

Figure IX.3. Group IC data and El Burro

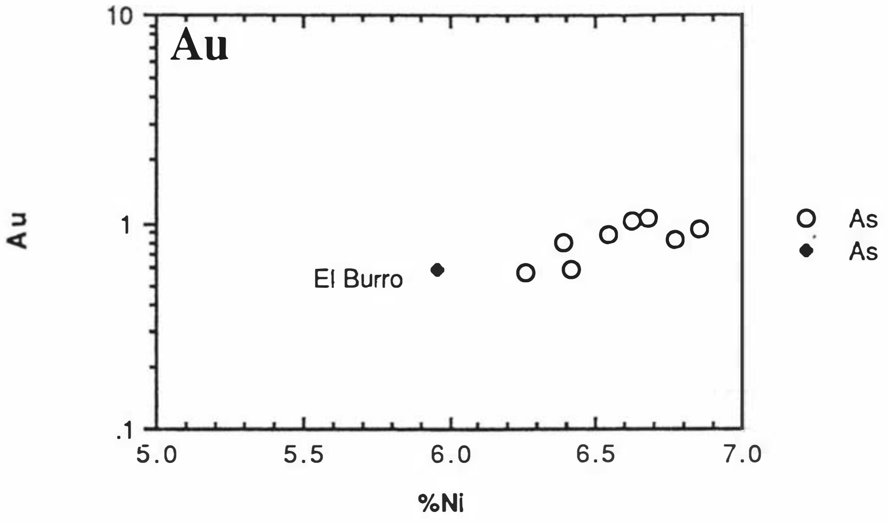



Ni vs Rh

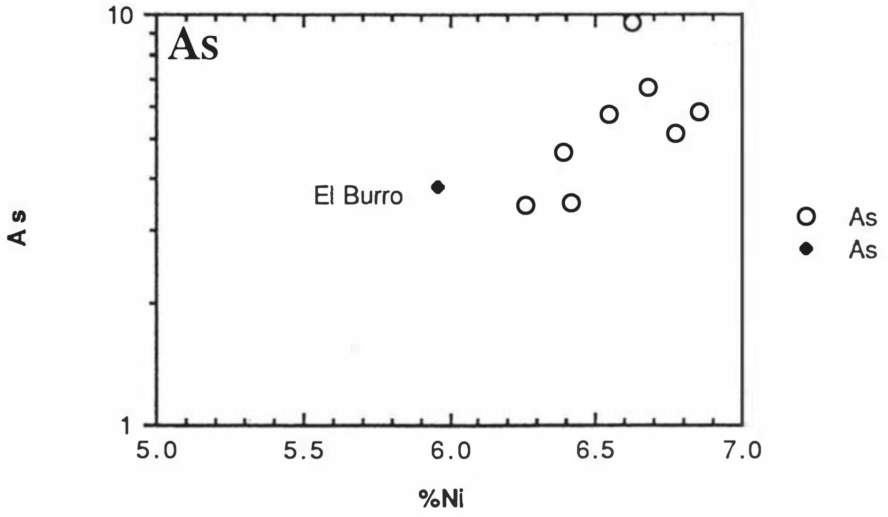

Ni vs Pd


Ni vs Pt

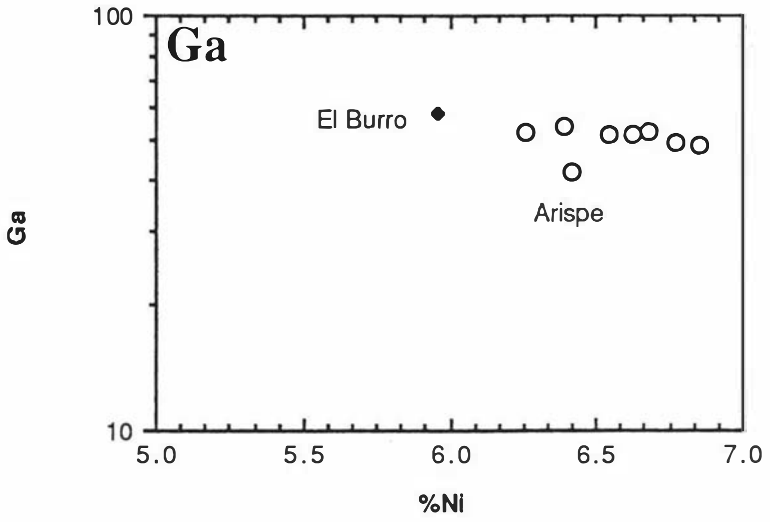
Ni vs Au

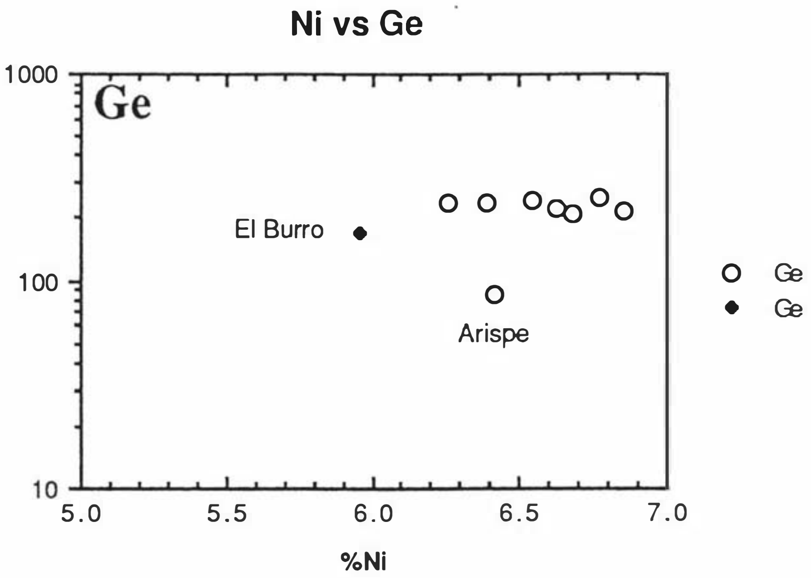


Ni vs As



Ni vs Ga





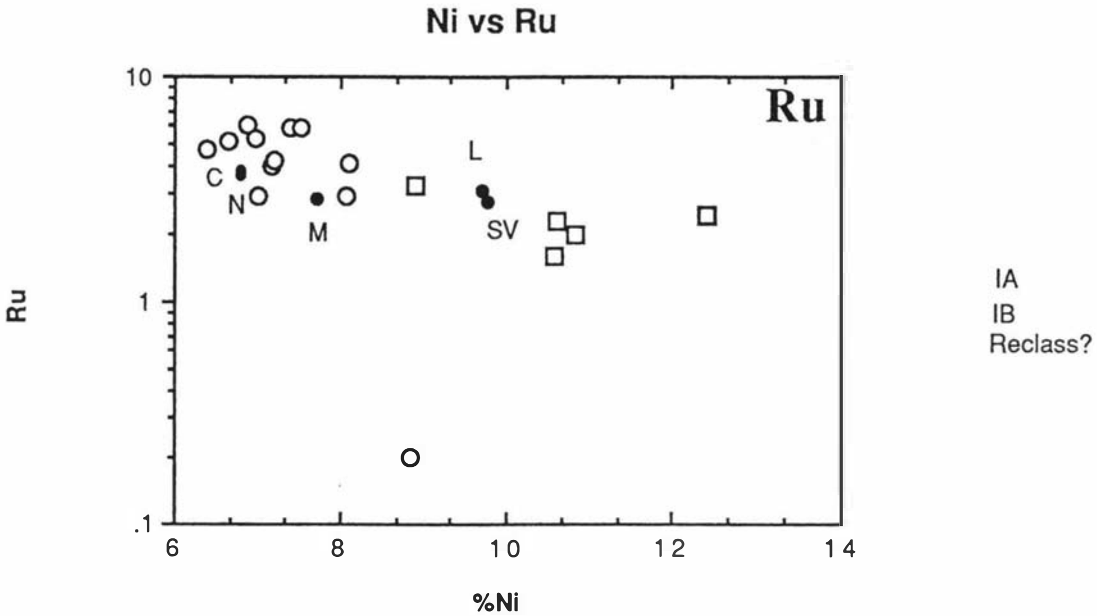
IX.4.iii. Sam's Valley

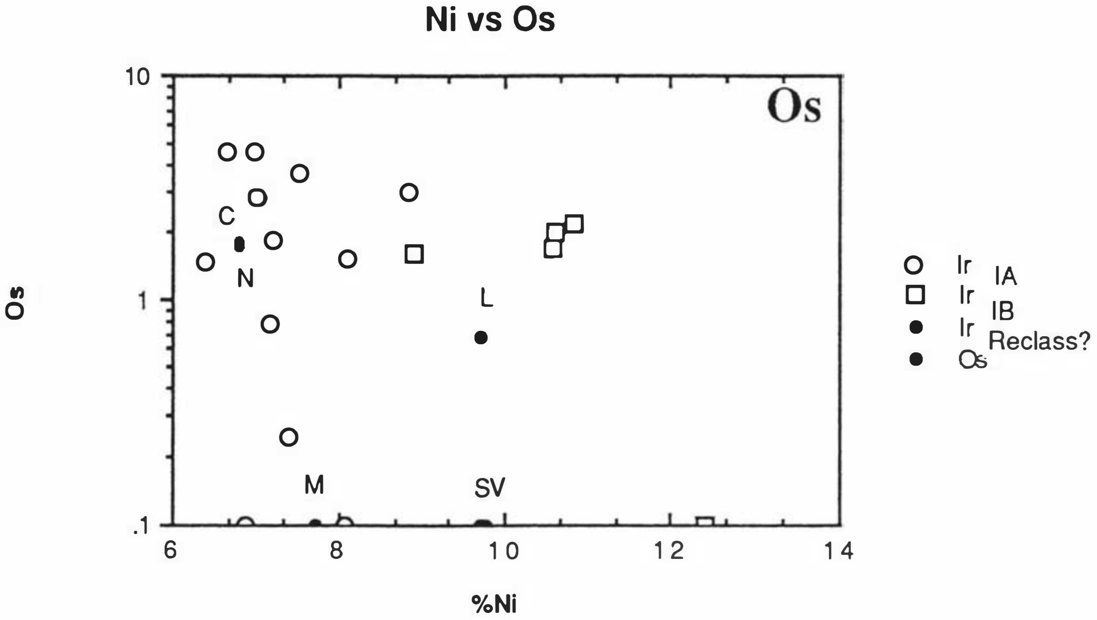
Sam's Valley is a medium octahedrite (Om) with a bandwidth of 0.75 ± 0.10 mm. The long crystals of kamacite ($^{L}/_{W}$ ≈25) contain phosphides. Taenite and plessite cover about 35% of the area of a cross section. Large schreibersite and troilite veins are present, and rhabdites are not observed.

Cañon Diablo is a typical IAB iron (Wasson, 1985). This meteorite is a coarse octahedrite with troilite-graphite-silicate nodules with schreibersite-cohenite rims. The bandwidth varies, but is generally 2.0 ± 0.5mm. Diamonds have been noted in Cañon Diablo samples, but they are most likely to have been formed from graphite during the passage of shock waves produced in the meteorites upon collision with the earth (Lipschutz and Anders, 1961) rather than being present in the meteorite since its formation (Urey, 1956). The precurser, graphite, is a feature of IAB irons.

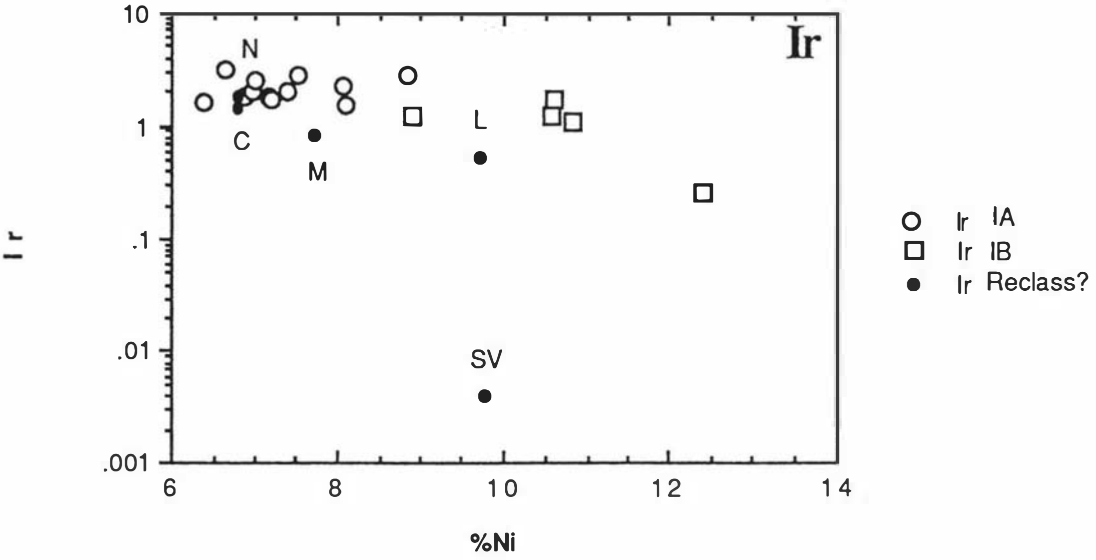
Also present in IAB samples are haxonite, phosphates and sphalerite (Dodd, 1981). The structural and mineralogical descriptions for Sam's Valley appears to place it into group IAB. However, the chemistry does not support this because Sam's Valley does not fit into plots of Ni against values for Ga, Ge, Os, Ir and Pt (Figure IX.4). It does, however, fit rather well in the trends for Ni vs. Ru, Rh, Pd, Au and As. Since IAB is a well-defined group with respect to the usual four-element classification parameters and the graphs into which it does not fit are graphs of the principal component elements, Sam's Valley should remain in group IIIB.

Figure IX.4. Group IAB and Sam's Valley (SV), Lonaconing (L), Cranbourne (C), Nantan (N) and Mundrabilla (M)

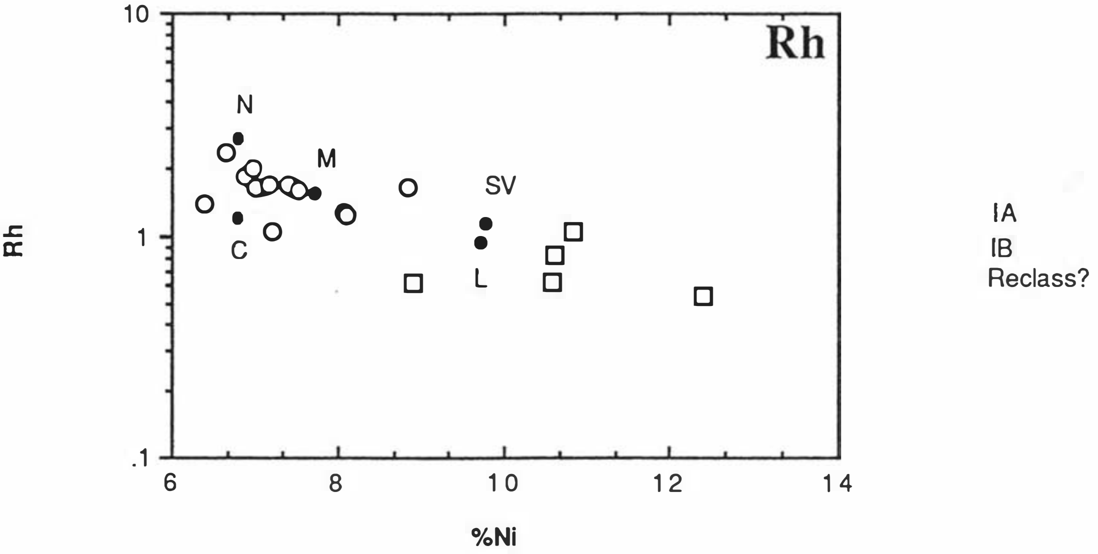




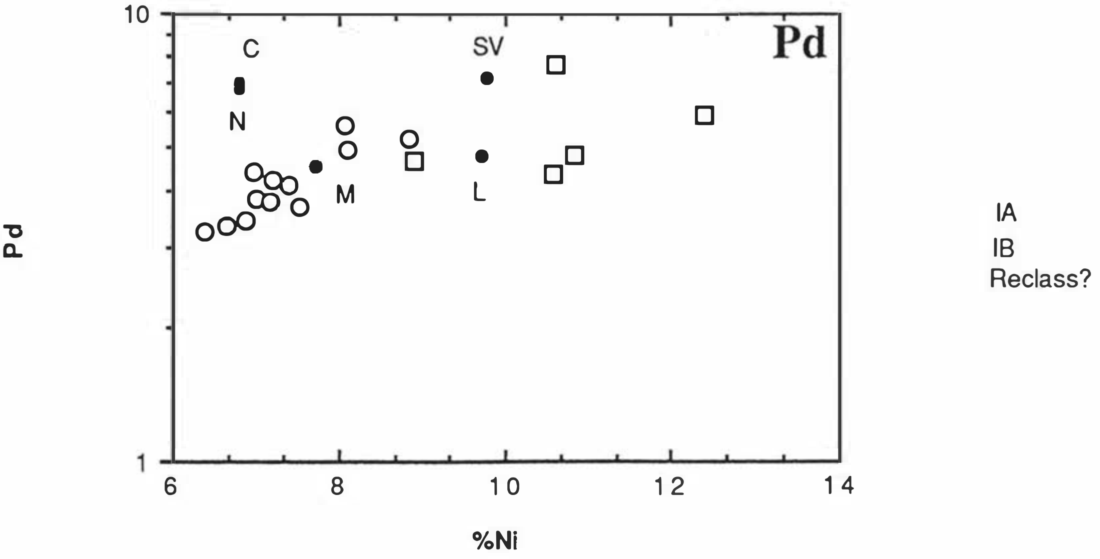
Ni vs Ir

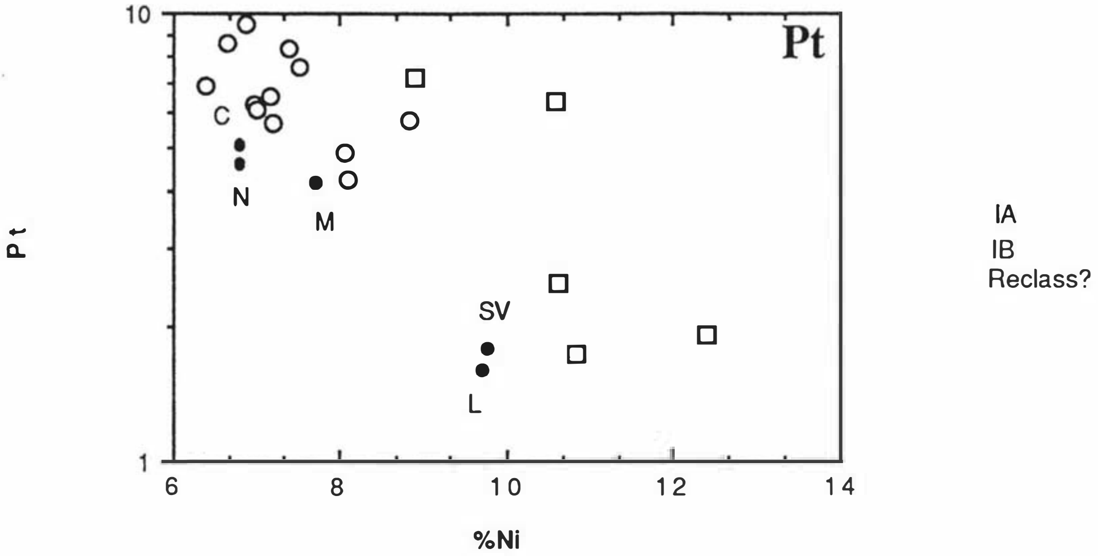


Ni vs Rh

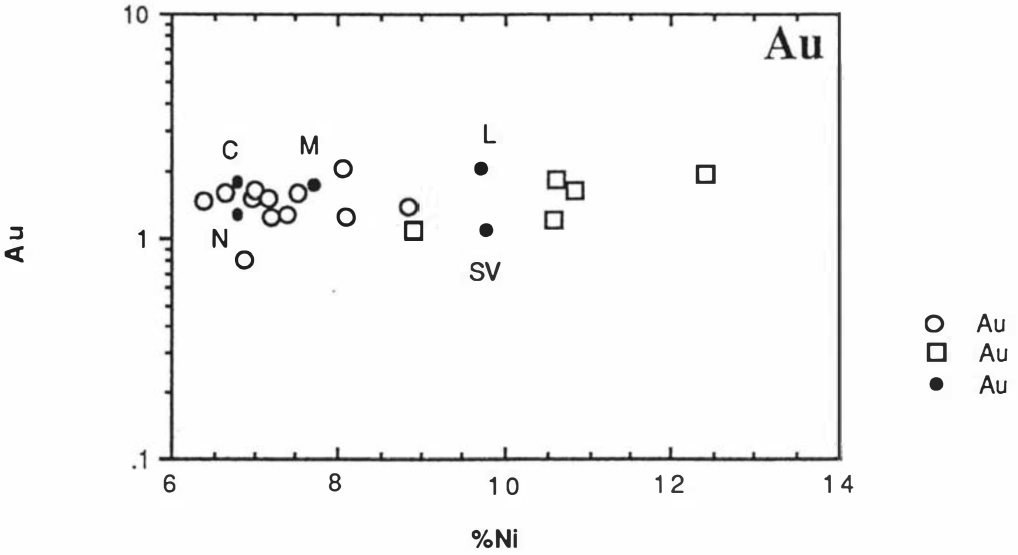


Ni vs Pd

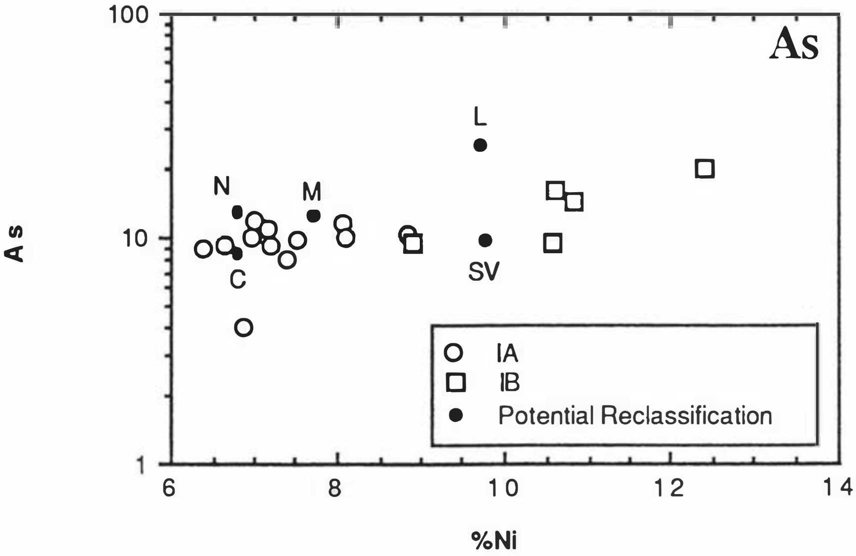




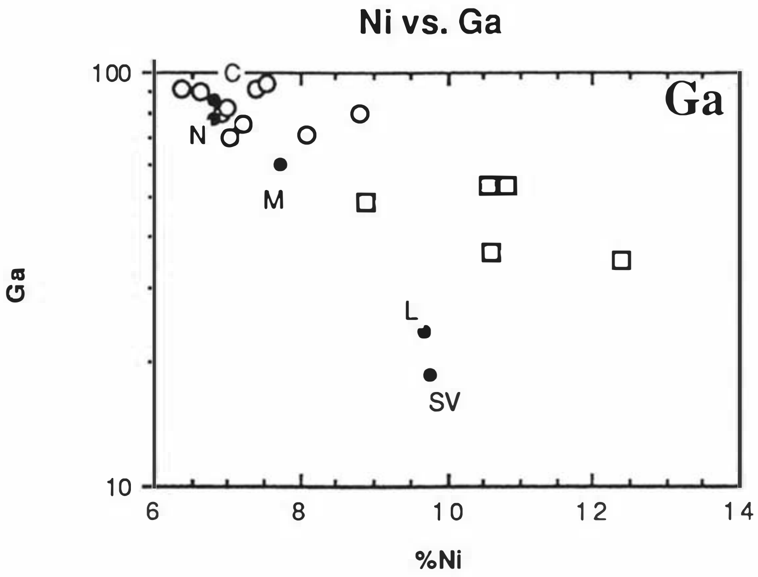
Ni vs Pt

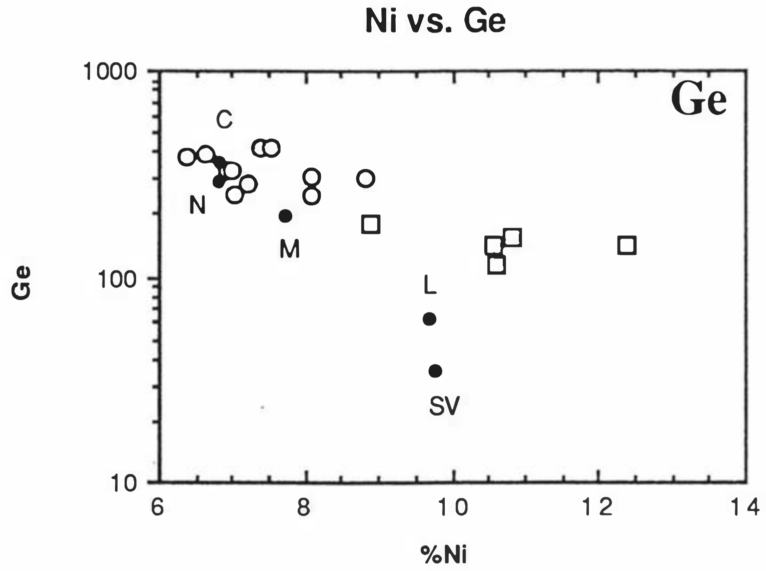


Ni vs Au



Ni vs As





IA
IB
Reclass?

IX.4.iv. Lonaconing

Lonaconing displays an anomalous Widmanstätten structure with few but broad kamacite lamellae of 2.0 ± 0.3mm, with $^{L}/_{W} \approx 15$. Although a coarse octahedrite, Lonaconing shows a very different structural development from samples with similar bandwidths (eg.--Cañon Diablo) with 40-50% by area as taenite and plessite fields. Cohenite is not observed, though schreibersite, phosphates and troilite are. Rhabdite precipitates are common.

Chemically, Lonaconing, like Sam's Valley, does not plot on group IAB Ni-element trends, though it sometimes appears to plot in the IB portion of the slope (Figure IX.4). This meteorite was classified as a IIE by Scott and

Wasson (1976) but was later removed by Wasson and Wang (1986) and reclassified as an ungrouped iron. Despite its apparently good fit for some elements, Lonaconing is chemically and structurally unusual and is probably not a member of group IAB. It should remain designated as an ungrouped iron meteorite.

IX.4.v. Cranbourne and Nantan

Cranbourne was classified as a IAB member similar to Cañon Diablo, Magura and Youndegin. It is a coarse octahedrite (Og) with a bandwidth of 2.2 ± 0.5mm. The total 8.5 tonne mass is polycrystalline, the original taenite crystals being 20-30 cm in size. Plessite occurs in the cross sections as 1-5% of the total area. Schreibersite is common, as are cohenite, rhabdite and troilite, along with cliftonitic graphite. This description agrees very well with the description of Cañon Diablo (section IX.4.iii).

Nantan was not studied by Buchwald (1975), but its chemistry and apparent structure is similar to Cañon Diablo. Buchwald (1990) believes Nantan to be a IAB iron similar in composition to Cranbourne.

Kracher *et al.* (1980) reclassified Nantan and other IAB irons into group IIICD because the Ni vs. Ga, Ge, W, Re and Ir contents for these meteorites plotted lower in the graph than the IAB field and higher for Ni vs. As. Cranbourne was removed from IAB and placed into IIICD by Pernicka and Wasson (1987) for similar reasons.

The low-Ni IAB and low-Ni IIICD irons are not only similar in composition, but they are very similar in texture and structure (metallography, inclusions, cooling rates, etc.) and no reported structural observations can resolve them (Pernicka and Wasson, 1987). The two subgroups resemble each other closely and it appears that they are formed by the same processes on closely related parent bodies or even on the same parent body. Pernicka and Wasson (1987) could not resolve low-Ni IIICD from low-Ni IAB using Ru, Re, Os and Pt abundances. Ryan *et al.* (1990) could not resolve these two subgroups using Rh, Ir, Os and Au.

Cranbourne and Nantan were included in the data set and presented to the DA program as IIICD irons. Therefore, these two samples were used with the high-Ni IIICD members to define the IIICD field. Even so, the DA program rejected these two irons as IIICD and reassigned them as IAB with nearly 100% certainty. As the structural and mineralogical observations comply with the chemical data (Figure IX.4), the reassignment of Cranbourne and Nantan into group IAB is accepted.

IX.4.vi. Mundrabilla

Polished and etched sections of the Mundrabilla meteorite display a very unusual structure. The meteorite is composed of a large number of precursor taenite crystals, each 2-5 cm across, which are apparently randomly oriented and separated by 0.5-5 mm wide troilite veins. At the junction of many taenite crystals, the troilite-graphite aggregates assume globular shapes and increase to 20 x 30 mm in size. This gives the mass a "raisin bread" appearance, with the plentiful troilite nodes dispersed throughout the meteorite. The Widmanstätten structure is indistinct, and the bandwidth is cautiously estimated at 0.55 ± 0.10 mm. The kamacite crystals are long and straight ($^{L}/_{W} \approx 20$), occur in bundles and are decorated with numerous µm-sized rhabdites. Taenite and plessite cover 15-20% of a cross section by area and an unusually large proportion occurs in an open-meshed comb structure. Schreibersite and daubréelite are common.

Mundrabilla was originally classified as an anomalous iron in Wasson (1974) and later as a IAB-AN by Kracher *et al.* (1980), based on rather weak chemical and mineralogical evidence. Scott and Wasson (1976) reclassified this iron as a IIICD-AN rather than a IAB-AN because, like Cranbourne and Nantan, Mundrabilla plots slightly outside the IAB field. Kracher *et al.* (1980) felt that Mundrabilla could never be considered a normal member of either group because of its unusual structures and ambiguous compositions.

The DA program assigns Mundrabilla to group IAB based on its chemical composition with only 90% certainty, indicating that it does not fit into this group very well (Figure IX.4). The structural observations of Buchwald (1975) do not comply with the assignment of Mundrabilla to either group IAB or IIICD. It is concluded here that the assignment of Mundrabilla to group IAB is coincidental; Mundrabilla's structure indicates that this iron did not originate in the same way as the group IAB irons, though it could have come from a parent body with a similar elemental composition as the IAB group parent. The PGM data do not strongly support reclassification of Mundrabilla to group IAB, and this meteorite should be returned to its original classification as an anomalous iron.

IX.4.vii. De Hoek

De Hoek is a troilite-rich ataxite. Sections through the specimen show an unusual macro-structure that may be compared to Mundrabilla, which has abundant troilite nodules. The matrix is a polycrystalline aggregate of parent taenite grains which are separated by nearly continuous veins and films of troilite. Occasional kamacite spindles (bandwidth 8 ± 4 mm) occur in a Widmanstätten arrangement. Phosphate and chromite fragments occur in the troilite nodules. Schreibersite and rhabdites are not observed, and the meteorite seems never to have existed as a equilibrated melt. The maximum temperature De Hoek has experienced is probably about 1000-1200°C. The small, cm-sized grains indicate that this temperature was not maintained for long, ie.--the cooling rate was high.

The DA program assigns De Hoek, an anomalous iron meteorite, to group IVA with 100% certainty. Wasson (1985) cites Gibeon as a typical example of a IVA meteorite. Due to its low P content, schreibersite and rhabdites are not present and cohenite is absent, resulting in the very pure metallic matrix which is distinctive of Gibeon and the IVA meteorites. Etched sections display a fine Widmanstätten structure of straight, long kamacite lamellae (L/W ≈40) with a bandwidth of 0.30 ± 0.05 mm. Taenite and plessite cover 50-60% by area in cross sections and troilite is ubiquitous as 0.5-25 mm nodules. Chromite is sparse, daubréelite is common and silicates, present as enstatite and rare tridymite, are occasionally found. Gibeon's marked polycrystallinity is very characteristic. It is composed of many taenite grains ranging in size from 10-50 cm. Repeated twinning is common.

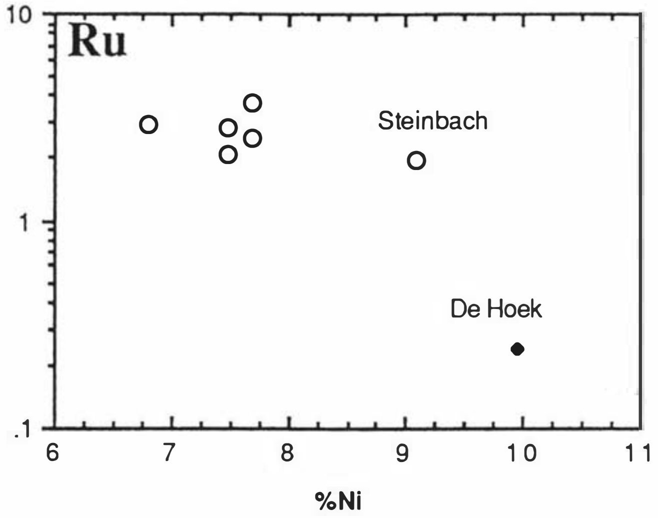
Structurally, De Hoek does not display the fine Widmanstätten structure shown in Gibeon, and though both samples are polycrystalline, De Hoek's small grains do not compare with Gibeon's much larger ones. Mineralogically, phosphates are present in De Hoek, but not in Gibeon. The veins and films of troilite indicate that the parent body of De Hoek was heated to a temperature sufficient to soften and squash the FeS between crystals, but not enough to actually melt and trap them throughout the metal as blebs, as evidenced in Gibeon.

As seen in Figure IX.5, De Hoek does not generally plot in the IVA field. This would not be the case if Steinbach was excluded from the plots. The IVA field is extended to accomodate Steinbach, and could not be stretched in an opposing direction to accomodate De Hoek as well. Steinbach is a IVA-AN iron with silicate inclusions consisting of 11% forsterite pyroxenitic olivine (Graham *et al.*, 1985). Gibeon also has silicates, albeit different minerals, and no silicates are noted by Buchwald (1975) in De Hoek. This is not surprising considering that the maximum temperature of the parent melt of De Hoek as indicated by its structure is calculated at about 1100°C. If this is so, then De Hoek could not even be considered as a fast-cooling member of IVA.

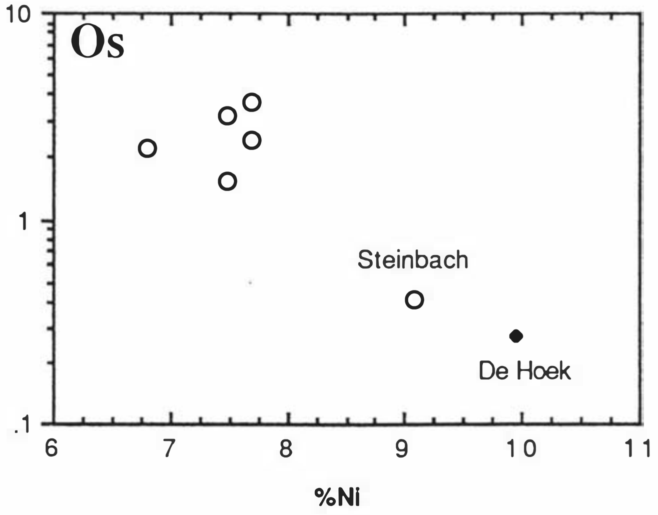
Chemically, De Hoek and Steinbach could possibly be called anomalous members of group IVA, but the two meteorites could not be considered members of the same group as each other. Therefore, acceptance of Steinbach as a member of IVA excludes De Hoek from entry into IVA. Since the DA program accepted Steinbach as a member of IVA, De Hoek's reassignment to group IVA must be rejected.

Figure IX.5. Group IVA and De Hoek

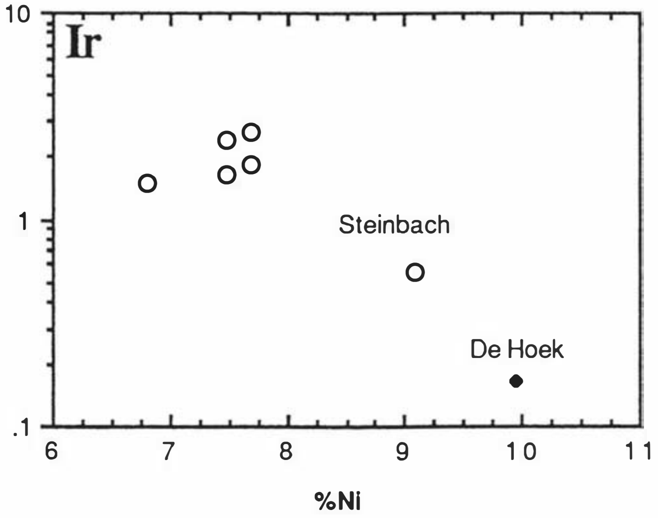
Ni vs Ru



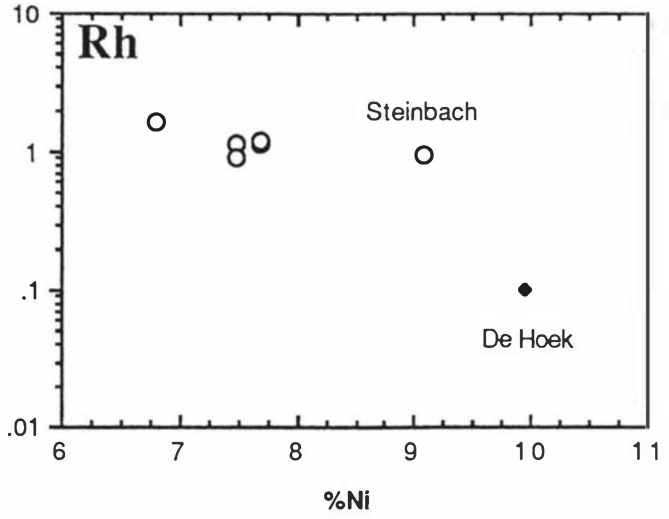
Ni vs Os



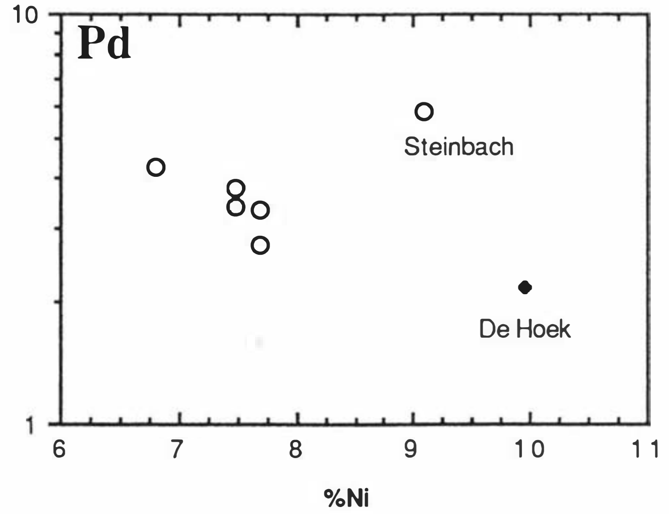
Ni vs Ir



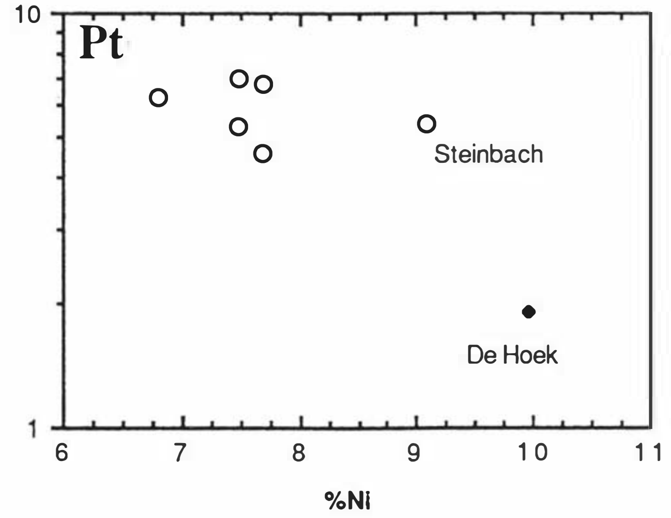
Ni vs Rh



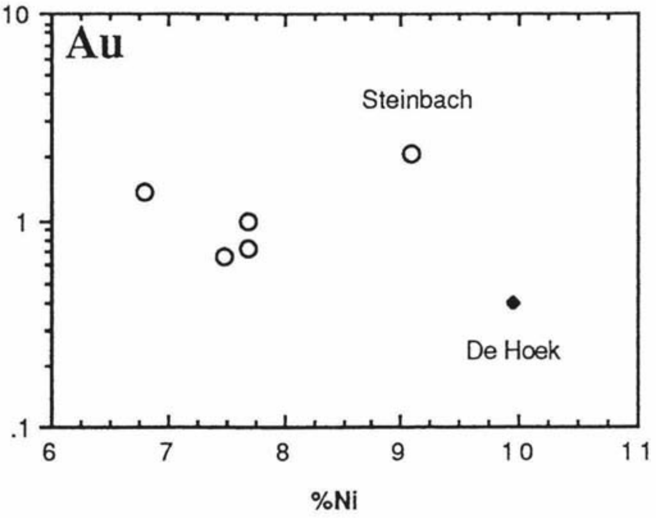
Ni vs Pd



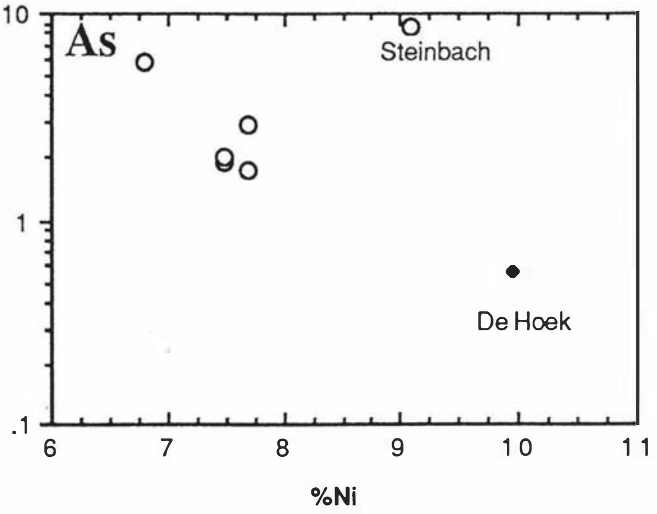
Ni vs Pt



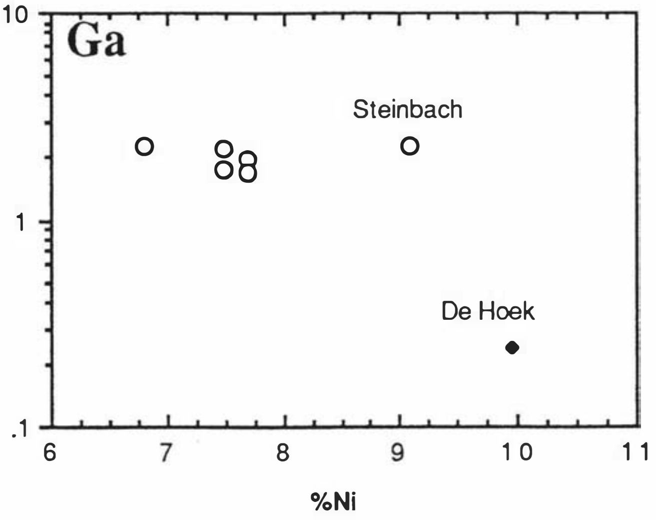
Ni vs Au



Ni vs As



Ni vs Ga



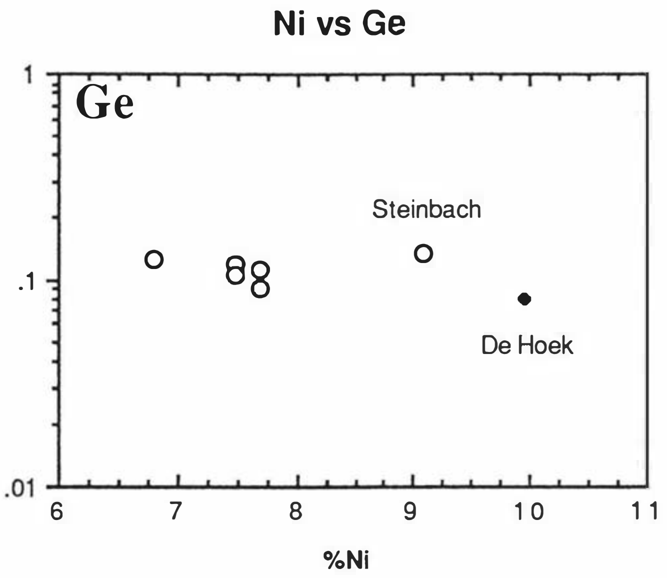


Table IX.5. Reclassification of iron meteorites by D^2 analysis with <90% probability

Meteorite	Present Classification	D^2 Reclassification	Probability
Dunganville	IAB	IC	73%
Woodbine	IAB	IIE	64%
Arispe	IC	IIE	76%
Sikhote-Alin	IIAB	IC	56%
Kumerina	IIC	IIE	89%
Arlington	IIE	IIIAB	76%
Weekeroo Station	IIE	IIIAB	86%
Willow Creek	IIIE	IIIAB	54%

IX.4.viii. Anomalous Members of Established Groups.

The DA program also indicated the poor fit for some meteorites within their groups. They are not considered here but the reassignments are rejected because of the low (<90%) calculated probability that these samples can be reclassified. Nonetheless, it highlights the anomalous behavior of the meteorites in question, and the meteorites listed in Table IX.6 should be labelled as anomalous members of their groups (e.g.--Arispe IIC-AN) if they are not already labelled this way. This also applies Mesa Verde Park, El Burro and Sam's Valley, which were considered in this chapter for possible reclassification, but were retained in their original groups.

Chapter Ten

Mislabelled and Paired Iron Meteorites

X.1. Introduction

It is very important when making comments about the properties of a related-group of meteorites that all of the samples analyzed for that group are authentic ones. A mislabelled iron meteorite sample may escape detection as such and confuse the interpretation of the resulting pooled data. As mentioned previously, Hey (1966) regarded the names of iron meteorites, as quaint and romantic as they seem, to be labels for the purposes of scientific research. As such, these labels must represent an authentic sample, or else the label and the sample become meaningless.

Graham (1990) has indicated that museum curators cannot always be diligent about distributing authentic specimens and therefore the ultimate onus is on the researcher to verify the identity of a given sample. To an extent, the kamacite bandwidth and the nature of inclusions that appear when preparing a section by etching provides a rough check on a sample's identity. Unless the researcher is very experienced, gross structural observations are not sufficient to classify or identify a meteorite sample (Wasson, 1974).

Whenever it was practical, abundance data determined in this study were checked against literature values to establish beyond doubt that the samples held and analyzed by the BMMRU are authentic.

X.2 Steels as Meteorites

This section deals with samples that are not meteorites. The purported Walker County (IIAB) sample #297 was donated by the American Museum of Natural History (AMNH) who had performed no previous analyses on the sample and were unaware that this sample was anything but a meteorite. The IIAB group of meteorites do not display Widmanstätten features, so the identity of this sample was not doubted because of its lack of crystal pattern. Suspicion was cast on the sample supplied to us when it was first cut using a hacksaw. The sample cut very

Table X.1. Results of analyses of mislabelled samples compared to data for authentic samples (all values in μg/g except for Ni)

Meteorite Sample	Donor & Catalog #	%Ni	Ga	Ge	Ir	Cr	Au	As	Co	Rh	Ru
Walker County[1]		5.46	58.2	189	3.0						
Walker County	AMNH 297	<0.02	--	<0.03	<0.002	16	<0.002	18.6	61.6	<0.06	<0.001
Unknown	MGS G314	<0.02	--	10	<0.004	459	0.250	338	195	<0.2	<0.001

[1] Wasson, 1974

easily and was softer than other meteorites; cutting a meteorite manually requires time and strength and this Walker County sample needed very little of either. When digested in HNO_3 for Ni and Ge determination, the solution was not the usual yellow-green color associated with the presence of Ni in NO_3^-, but was pink, indicating a lack of Ni. The results of the analysis are compared to results for Walker County (IIAB) from Wasson (1974) in Table X.1. It is clear that AMNH 297 contains such small concentrations of Ni, Ge, Co and PGMs that it does not compare to Wasson's analysis of an authentic sample of the Walker County meteorite.

Sample G314 from the Museum of the Geological Survey (MGS) in Pretoria, South Africa did not appear to be meteoritic. Its appearance is similar to that of iron slags, and analysis of the sample showed it to contain non-meteoritic abundances of Ni, Ir, Cr, As and Co (Table X.1).

It is concluded here that Walker County AMNH 297 and MGS G314 are pieces of terrestrial, man-made Fe steel samples and should be removed from any catalog of meteorites.

X.3. Paired Meteorites

Wasson (1974) defines a paired set of meteorites to be samples accorded separate entries in catalogs, but which on detailed study appear to be parts of the same fall. Hey (1966) uses the word "paired" in a less restrictive sense to indicate meteorites which are possibly fragments of the same fall. In any case, separate samples of the same fall are accorded separate status for a variety of reasons. The most common reason is the removal of a piece of a fall from the area where a meteorite shower landed on the Earth's surface. Many meteorites are similar in chemical and structural composition; this, after all, is the basis for them to be classified together into groups. It is thus often difficult to establish pairings for samples that have been removed from other members of the same shower.

Some tribes of American Indians carried pieces of iron meteorite with them on their travels or nomadic wanderings, believing them to bestow the carrier with supernatural powers. In this way, pieces of the Cañon Diablo meteorite were scattered throughout Arizona (Wasson, 1968). The eskimos of Greenland traded pieces of the Cape York meteorite to others, and samples of this meteorite have been found by archeologists as cold-worked tools as far away as Hudson Bay in Canada (Buchwald, 1975). In his *Handbook*, Buchwald (1975) includes a list of venerated iron meteorites, some of which have been wrapped or mummified and buried in graves or reworked into jewellery and tools. Careful chemical and structural investigations can disclose the probable source of the meteoritic metal.

Table X.2. Analysis of Carlton and Lamesa IIICD (All values in µg/g except for Ni)

Meteorite and source	%Ni	Ga	Ge	Ru	Os	Ir	Rh	Pd	Pt	Au	As	Co
Carlton AMNH 3851	13.0	11.4	8.6	0.098	--	0.079	0.36	15.2	0.104	1.76	19.2	6280
Lamesa WZ(MU)	13.7	13.3	11.8	0.105	0.53	0.036	0.30	14.4	0.106	1.75	6.79	6100

X.3.i. Carlton and Lamesa, Texas

The Lamesa IIICD iron was purchased from a private collector. The sample on analysis was found to have elemental abundances very similar to those of Carlton (Table X.2). This is not a mere coincidence, as analyses for other IIICD samples showed that though the values of elements were similar, they were not identical (Appendix 1), and rather than clustering together, the IIICD meteorites fall along a curve. Both Carlton and Lamesa are finds rather than falls (Buchwald, 1975). Carlton was ploughed up as a 80kg mass by a farmer in Texas in 1887. Lamesa (17kg) was located in 1981 about 300 km away from the site where Carlton was unearthed. Though this appears to be a large distance, Wasson (1968) showed Cañon Diablo samples of comparable weights to Lamesa had been transported for similar distances. Likewise, Buchwald (1975) did not think a mass this size would cause the carriers much difficulty in removing it to where it was eventually found. The century that had elapsed between the discovery of the two masses has no significance.

Graham *et al.* (1985) mention that these two meteorite samples may be paired based on the abundances of Ni, Ga, Ge and Ir. The determinations of other elements strengthens this possibility with the exception of As. This may be due to the expected inhomogeneity within any given meteorite mass. Esbensen *et al.* (1982) have found evidence for inhomogeneity in the Agpalilik (Cape York, IIIAB) mass for some elements, though the PGMs, determined in this study, appear to be uniformly distributed between Carlton and Lamesa in this study.

The pairing of Carlton and Lamesa is therefore supported. It is recommended, in future, that only the values from one of these samples is used, or an average of their individual values.

X.3.ii. Derrick Peak and Onnum Valley, Antarctica

Antarctic meteorites are often located in the blue ice fields on the windward side of mountain ranges. Here, the wind ablates the ice away, leaving behind meteorites and other rocks that have been moved by the glacier to the mountain range from points throughout its length (Dodd, 1986). This movement of the ice and the effect it has of concentrating meteorites into one area means that it is highly unlikely that any of the meteorites found on the ice in proximity to each other are in any way related or paired.

The Derrick Peak irons are different in that they were found on a remote nunatak free of ice and snow (McSween, 1985). These sixteen meteorites (Derrick Peak 78001-78016) have been shown to be related to each other, and therefore parts of the same fall (Clarke, 1982). Another two small irons were found by a New Zealand geological field party in the mid-1980's in Onnum Valley, near Derrick Peak. They are held at the Canterbury Museum in Christchurch, New Zealand and are provisionally labelled Derrick Peak CM66 and Onnum Valley. To establish their relationship to the Derrick Peak irons, they were analyzed with the results shown in Table X.3.

Unlike Lamesa and Carlton, the Derrick Peak irons have not been transported. Establishing the identity of like members is less troublesome for these Antarctic samples.

Onnum Valley and CM66 have similar elemental abundances and are members of the subgroup IIB. They display no Widmanstätten pattern. Detailed structural and mineralogical studies were not performed here, as the samples provided were very small (<5 g), but chemically, these two meteorites are members of the Derrick Peak shower, and are paired by Hey's (1966) definition.

Table X.3. Analysis of Derrick Peak, Antarctica meteorites (all values in μg/g except Ni)

Meteorite	%Ni	Ge	Ru	Pd	Pt
Derrick Peak 78012	6.54	160	3.94	3.32	2.84
Onnum Valley	6.5	159	3.24	3.18	2.32
Derrick Peak CM#66	6.5	162	3.91	2.46	2.52

X.3.iii. MGS G2011, Railway and Gibeon, Namibia

The Museum of the Geological Survey in Pretoria presented the BMMRU with samples labelled G2011 and of Railway (IVA) found in South West Africa (Namibia). The location and appearance of the find suggested that both could be pieces of Gibeon. The data in Table X.4 generally confirm this, though results for Ge, Ru and Pd for G2011 and Ru, As and Co for Railway are not very convincing. If G2011 has been mistreated or has suffered deformation caused by the force of impact (very common in Gibeon samples) them some of the more volatile elements might be expected to volatilize. This is evident in the Railway sample which Buchwald paired structurally with Gibeon, though it had been violently deformed, displaying severely twisted, bent and overfolded textures. In addition, Railway is enriched in Pd and Pt relative to a sample of Gibeon, but removal of some elements could result in enrichment of others. Alternatively and more credibly, because of the great size of the original Gibeon mass (there are presently about 75 known masses, each averaging 280kg for a total possible weight of at least 21 tonnes), the question of homogeneity of these elements must be raised. When considering the size of the original body, there seems to be no serious reason to doubt the conclusions of Buchwald (1975) regarding the pairing of Railway and Gibeon. Neither is there much fault doubt that most IVA iron meteorites located in South West Africa are pieces of the Gibeon mass which disintegrated in the upper atmosphere prior to impact with the Earth. Indeed, of all of the iron meteorites found in South West Africa, only

Table X.4. Analysis of G2011, Railway and Gibeon samples
(all values in μg/g except for Ni)

Meteorite and source	%Ni	Ga	Ge	Ru	Os	Ir	Rh	Pd	Pt	Au	As	Co
MGS G2011	7.58	--	<0.01	2.01	2.25	1.88	0.97	4.30	6.58	0.98	3.86	4220
Railway MGS	7.82	1.99	0.119	1.90	2.08	1.53	0.80	4.76	8.16	0.72	2.25	3330
Gibeon CMS 4010	7.68	1.97	0.111	3.70	2.43	1.86	1.16	3.32	6.72	1.00	2.87	

Karasburg (IIIAB) is a fall independent of Gibeon. It is thus proposed that MGS G2011 and Railway be considered as part of the Gibeon shower.

X.3.iv. Paneth's Iron(origin unknown) and Coopertown, Tennessee

The three existing slices of Paneth's Iron have until recently been regarded as specimens of Toluca (IAB) since both meteorites are coarse octahedrites (Og). Buchwald (1975) was puzzled by the structures of the samples held in the British Museum of Natural History (BMNH), the Institute of Geological Science, London (IGSL) and in the Max-Planck-Institut-für-Chemie, Mainz (MPICM). He did not believe that they were slices of the Toluca iron and undertook a rigorous search for their origins.

Buchwald concluded from structural observations that the meteorite from which the slices were taken is a member of group IIIE, not IAB, and proposed that these slices be cataloged as "Paneth's Iron" to honor one of the early investigators of this mass. Chemical analyses by Smales *et al.* (1967) for "Toluca" were in disagreement with those of other workers. This is surprising, as Smales was an analyst of a high standard and his determinations are generally dependable. The controversial analysis was probably performed not on a Toluca sample, but on the British Museum's Paneth's Iron slice. Wasson (1974) also noted the disparate results and cataloged this slice as "Pseudo Toluca" (Table X.5).

Table X.5. Data for Paneth's Iron and Toluca (all values in μg/g except Ni)

Element	"Toluca" Smales *et al.*, 1967	"Pseudo Toluca" Wasson, 1974	Toluca	Paneth's Iron
%Ni	--	8.98	8.07	9.04
Ga	18.2	16.9	70.6	16.9
Ge	36	34.1	246	35.1
Ru	--	--	2.96	4.36
Os	--	--	<0.2	<0.2
Ir	--	0.37	1.86	0.29
Rh	--	--	1.28	2.15
Pd	3.0	--	5.56	4.12
Pt	--	--	4.84	8.86
Au	--	--	1.52	0.714
As	5.1	--	13.6	4.15
Co	--	--	4890	1930
Sb	0.06	--	0.44	--
Cu	124	--	186	127
Cr	38	--	<20	45

Calvert, the owner and purported discoverer of the slices was an eccentric autodidact and was not known for his integrity (Buchwald, 1975). He reported the slabs to be from 3 different meteorites found in Africa, Brazil and Dartmoor. Buchwald provides convincing evidence that the 3 slabs are from the same mass and furthermore notes that the exterior crust of the samples is corroded and artificially reworked, suggesting instead an origin in the United States or Mexico. The North Americans are apparently notorious in the eyes of meteorite workers for their desire to turn any piece of metal into implements or anvils. When attempting to reassemble the 3 existing slices from the BMNH, MPICM, and IGSL, Buchwald found that a fourth slice was missing, as well as a 5-10kg chunk taken off the end of the original mass prior to slicing of the meteorite. The entire mass probably originally weighed 100-150kg.

In order to establish the origin of the mass, Buchwald compared analytical data for Paneth's Iron against other IIIE meteorites. Fortunately, there are not too many meteorites of this type known and for historical and geographical reasons, Buchwald thought that Paneth's Iron could be a part of the Burlington (IIIE) mass. Burlington was found in New York State in 1819 and weighed 50-100kg when ploughed up by a farmer. The bulk of the material had disappeared before 1844 and only 5kg of heated and altered material survives. The remainder probably was manufactured into iron implements by the blacksmith to whom the mass was taken after its discovery. Paneth's Iron's presence in collections (labelled as Toluca) was established by 1873 and the missing 5-10kg chunk of pre-slicing material mentioned above could be the presently known pieces of Burlington.

The BMMRU possesses the three American IIIE irons known to have been part of collections in the mid-to-late 1800's. Our analyses indicate that the data (including PGM values) do not agree as well between Burlington and Paneth's Iron as for they do Coopertown and Paneth's Iron (Table X.6). The total mass of Coopertown makes it insufficiently small for it to be considered as the parent mass for Paneth's Iron, and besides, Coopertown's entire mass is accounted for in collections. However, Buchwald (1975) does not rule out the possibility that Paneth's Iron could be a paired fall with either Coopertown, which fell in Tennessee, or Staunton, which fell in Virginia. The chemical evidence presented in Figure X.1 seem to indicate that Paneth's Iron is indeed a paired fall with Coopertown, and that Calvert may have discovered, or otherwise acquired, a large mass in or from Tennessee (a fairly rural and sparsely populated state, even today) and produced his frauds with it. With this evidence at hand, it is perhaps now unwise to include both Paneth's Iron and Coopertown in statistical treatments of group IIIE.

Table X.6. Comparison of data for all American IIIE iron meteorites discovered or known before 1873 (all values in µg/g except for Ni)

Element	Paneth's Iron origin unk. 1873 (≈100-150 kg)	Burlington, New York 1819 (≈50-100 kg)	Coopertown, Tennesse 1860 (16.8 kg)	Staunton, Virginia 1869 (≈44 kg)
%Ni	8.98	8.34	8.47	8.62
Ga	17	16.9	17	18.9
Ge	34	34.9	35	36.6
Ru	4.36	5.40	4.42	2.57
Os	<0.20	<0.20	<0.20	<0.20
Ir	0.20	0.301	0.51	0.068
Rh	2.15	1.27	1.90	1.76
Pd	4.12	7.72	3.96	3.40
Pt	8.86	10.8	9.24	6.52
Au	0.71	0.57	0.66	0.67
As	4.15	2.88	5.12	4.03
Co	4930	4190	4690	4460

Figure X.1a. Comparison of Paneth's Iron data to Burlington data

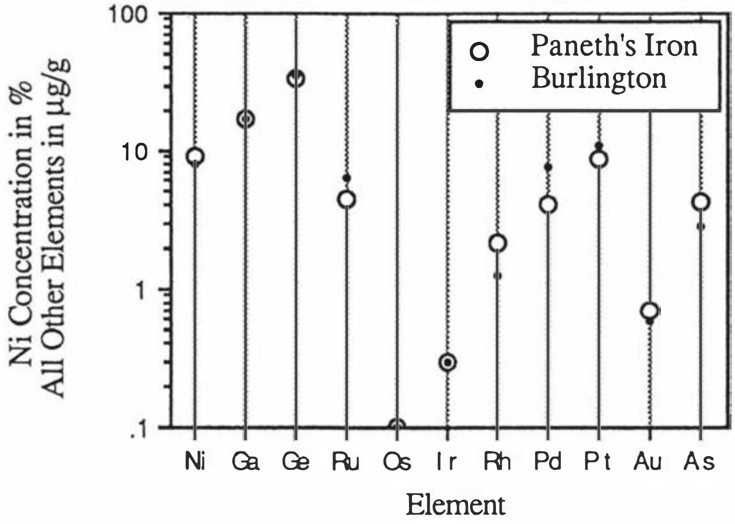


Figure X.1b. Comparison of Paneth's Iron data to Coopertown data

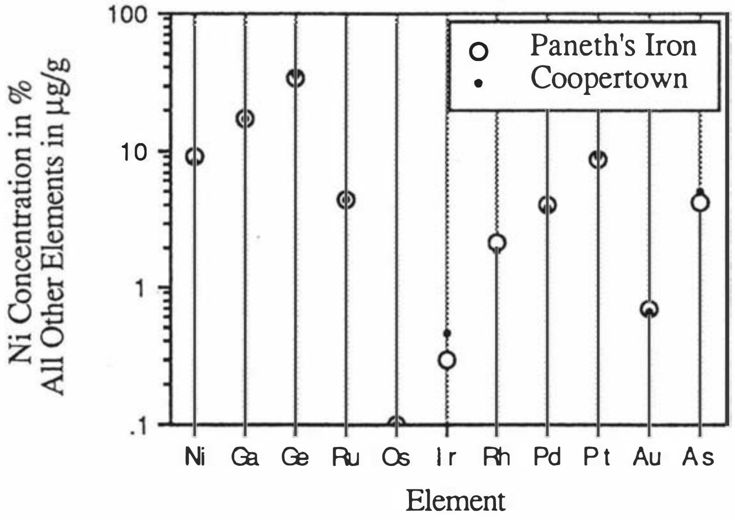
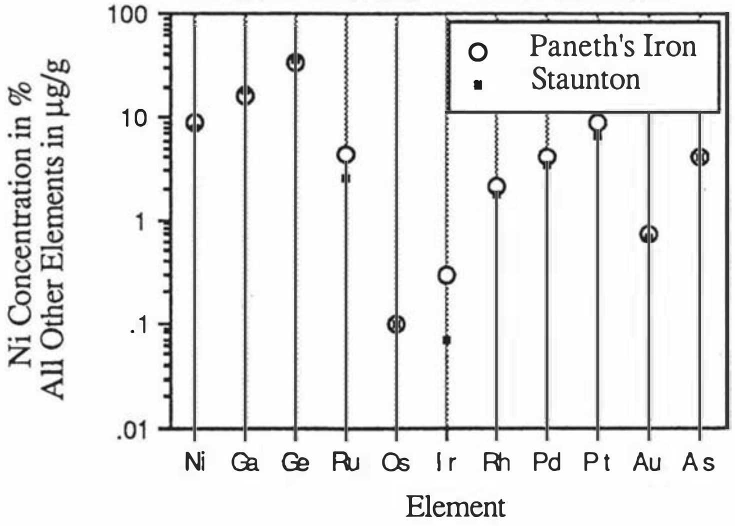


Figure X.1c. Comparison of Paneth's Iron data to Staunton data



X.3.v. Hanau Harbor, Germany and Cañon Diablo, Arizona, USA

An iron meteorite weighing 86g was purportedly recovered from a mound of river gravel that was the result of dredging operations from the River Main near Hanau, Germany in April, 1988. The sample was presented to the BMMRU by the collector for analysis. Because of its discovery location, it was thought that the iron could have landed anywhere within 20km of the gravel heap, limited by the strength of the river current and the extent of the commercial dredging operation. It was provisionally named Hanau Harbor, as a previously discovered chondrite was already named Hanau.

Suspicions were cast on the sample because its surface did not show signs of corrosion normally associated with pieces of Fe in a river bottom. Buchwald (1990) showed that terrestrial corrosion by groundwater action is very severe, causing the conversion of Fe to limonite and akaganeite, thereby efficiently destroying the sample. The Hanau Harbor sample looked like a typical rounded river pebble, and the amount of time needed to round this hard material to such a shape is probably equivalent to the time needed to rust it completely (Selley, 1982).

Nevertheless, a chemical analysis was performed and indicated this specimen to be a IAB iron meteorite. This type of meteorite is very common, comprising 17% of all investigated meteorites (Wasson, 1974). When compared to data from other IAB meteorites, Hanau Harbor could be potentially paired based on chemical analysis with over a dozen established candidates. When this meteorite was cut and polished in this laboratory, no Widmanstätten pattern was observed, just serrated bands of cohenite. In all but the tiniest of sections, IAB samples should show a Widmanstätten pattern.

The advice of V.F. Buchwald was sought, and the report of his inspection of Hanau Harbor appears below (Buchwald, 1988):

> The structure of Hanau Harbor is that of a medium to coarse octahedrite with numerous cohenite crystals, typically 1.5 x 4.0 mm in size, but one attaining 12 x 0.7 mm. The Widmanstätten structure is blurred due to secondary reheating that has obliterated all Neumann bands...The secondary reheating has transformed cohenite which is under decomposition to graphite, schreibersite to eutectics and taenite and cohenite are surrounded by continuous dark rims of baritic carbon-rich transformation products. Secondary reheating is a result of a violent event and the shock features are indicative of crater-impact transformation products. In addition, the state of corrosion is that of the Arizona desert, not that of a European river bottom. Type IAB irons are very common, but a IAB iron showing *impact features is next to unique* and has so far been found only in small slugs (50-300g) of reheated stage VI-VII Cañon Diablo. If the sample is genuine, I suggest we search for a substantial crater in the vicinity of Frankfurt!

Further, it was revealed that the collector of Hanau Harbor had initially approached Buchwald (1989) with the sample. The shocked structures mentioned in Buchwald's report are unique to crater-producing meteorites. In light of the sample's similarity to Cañon Diablo and the collector's inability to provide hard evidence of the find, a case of mislabelling was concluded.

With the possibility of a hoax at hand, samples of Hanau Harbor and Cañon Diablo were reanalyzed(Table X.7). Taking into account that Cañon Diablo is not a homogeneous meteorite (Wasson, 1968), the agreement between the two samples is excellent. The two meteorites probably belong to the same fall, and it is concluded that Hanau Harbor did not originate in Europe and does not exist as an independent meteorite.

Table X.7. Chemical data for Cañon Diablo and Hanau Harbor (all values in µg/g except for Ni)

Element	Cañon Diablo	Hanau Harbor
%Ni	6.9-7.9	7.5
Ga	82	---
Ge	320	299
Ru	5.24	5.16
Os	2.13	1.70
Ir	2.01	1.90
Rh	2.00	1.90
Pd	4.40	4.24
Pt	6.20	6.31
Au	1.52	1.50
As	10.1	11.6
Co	4830	4900
Cu	169	163
Cr	10.0	10.3

X.4. Unresolved Cases

Four meteorites donated to the BMMRU for this classification project have shown themselves to be mislabelled specimens. Three of the samples are from large institutions with reputable curators; the fourth is from a private collector who, as far as had been indicated, is also reputable. The catalog numbers from the respective collections which held the mislabelled specimens are given in Table X.8 along with the results of our analyses.

X.4.i. "Cape of Good Hope"

The "Cape of Good Hope" sample arrived bearing two labels. One was marked with the name of the sample and what I assumed to be the catalog numbers, 1950. This number could, however, be a date of discovery of this particular sample. The Cape of Good Hope mass has been known since 1801 (Buchwald, 1975). The other label was marked "Capland." According to Graham *et al.* (1985) the name "Capland" has also been applied to the Hex River Mountain meteorite as well as to Cape of Good Hope. The data from various sources is presented in Table X.8 for Cape of Good Hope, Hex River Mountain and the RB "1950" sample. Clearly, the alleged sample of "Cape of Good Hope" analyzed here is not a piece of either of the authentic meteorites. According to the criteria of Wasson (1974), RB"1950" is probably an anomalous iron as the Ni, Ge and Ir values do not place it in any established group. When compared to values of anomalous irons known up to 1973, this sample does not match any of them within the limits of experimental and sampling errors.

It is tempting to announce RB"1950" as a new meteorite, but not enough is yet known about the provenance and subsequent history of this sample to assume that it is indeed a hitherto unrecorded meteorite. As advised by Clarke (1990), the collector has been contacted for more information as to the source of this sample.

X.4.ii. "Jaralito"

The "Jaralito" sample analyzed here is not the same University of California at Los Angeles (UCLA) sample analyzed by Wasson and co-workers (Kracher *et al.*, 1980; Pernicka and Wasson, 1987). Their sample is labelled UCLA1026, whereas the sample held at the BMMRU arrived with the catalog number UCLA1026B. The latter piece was presumably acquired by UCLA at a later date after establishing the catalog number on the first sample of Jaralito held by them. The difference between our analysis and their published values is not as large as for the previous case (RB"1950"), but it is apparent that UCLA1026 is not the same as 1026B. The values for Ni, Ge and Ru differ by a larger amount than experienced for other meteorites, and is certainly outside analytical error. The Ru determination was repeated five time with similar results. The Ni content for this sample is too low to consider it a IAB or IIICD iron based on the parameters set by Wasson (1974). It is quite possibly an anomalous iron. Discussions are presently underway with the curator of the UCLA meteorite collection to decide the origin and fate of this sample.

X.4.iii. "Zacatecas"

"Zacatecas" can either be the "1969" mass or the "1792" (Rancho de la Pila) mass (Graham *et al.*, 1985) and when the sample arrived, no indication was given as to which of these two it might have been, though we had requested the IIIB iron and assumed it to be so. The 1969 sample is a IIIB iron and the 1792 mass is a IIIA, indicating that the two are genetically related to each other. However, our analysis shows that the sample received from the United States National Musuem (USNM1780) is related to neither of the known Zacatecas masses. The provenance and history of this sample is yet to be established.

X.4.v. "Chupaderos"

"Chupaderos" was donated without labels or catalog numbers from the Field Museum of Natural History (FMNH). According to the chemical analysis, this sample is a IIIB iron, as is the authentic Chupaderos, but the values for Ni and Ir are very different for the two samples. Chupaderos fell as a shower. Many members have different names (Graham *et al.*, 1985) but they have been established as pieces of this meteorite. It is possible that a meteorite was collected in the general area of the Chupaderos strewn field and was assumed, without adequate inspection, to be a member of the fall.

The IIIAB group is large, and comparing this iron with data for all of the established IIIAB irons requires some narrowing of the many possible choices. Once again, the provenance of this sample needs to be investigated before any action can be taken towards deciding on the relationship of this sample to others.

Table X.8. Comparison of data for mislabelled meteorites with data from authentic specimens (all values in µg/g except for Ni)

Table X.8a. Cape of Good Hope

Element	RB "1950" This Work	Schaudy *et al.*, 1972 (NMW)	Nichiporuk & Brown, 1965	Hex Riv Mtn Wasson, 1969 (NMV)	Hex River Mtn(NMV) This Work
%Ni	9.8	16.92	--	5.59	--
Ga	--	0.198	--	60.7	--
Ge	<0.01	0.059	--	181	--
Ru	0.682	--	13.3	--	12.9
Os	<0.20	--	--	--	1.20
Ir	0.018	36	--	4.4	2.63
Rh	1.13	--	1.7	--	2.75
Pd	4.38	--	4.1	--	2.42
Pt	2.98	--	11.8	--	19.4
Au	1.97	--	--	--	0.496
As	18.8	--	--	--	2.98

Table X.8b. Jaralito

Element	UCLA1026B This Work	Kracher *et al.*, 1980 (UCLA1026)	Pernicka & Wasson, 1987 (UCLA)
%Ni	5.0	6.52	--
Ga	--	9.16	--
Ge	254	376	--
Ru	2.20	--	6.0
Os	0.71	--	1.31
Ir	0.98	1.5	--
Rh	2.04	--	--
Pd	3.84	--	--
Pt	5.06	--	7.6
Au	1.30	--	1.40
As	7.07	--	--

Table X.8c. Zacatecas and Chupaderos (values not from this work are from Scott *et al.*, 1972)

Element	"Zacatecas" USNM1780 This Work	Zacatecas (1969) USNM5291	Zacatecas (1792, Rancho de la Pila) BMNH55253	"Chupaderos" FMNH This Work	Chupaderos FMNHMe1045
%Ni	6.0	9.0	7.93	8.2	9.7
Ga	--	20.3	20.8	--	17.2
Ge	--	38.3	42.4	--	29.6
Ru	8.62	--	--	3.14	--
Os	0.40	--	--	2.72	--
Ir	1.46	0.029	0.070	2.14	0.020
Rh	2.04	--	--	1.44	--
Pd	3.66	--	--	3.88	--
Pt	37.0	--	--	5.34	--
Au	0.64	--	--	1.70	--
As	4.38	--	--	14.0	--

X.4.vi. Conclusions

Even considering inhomogeneity within a meteorite, the chemical analyses do not match previously determined values for authentic samples of these meteorites, and I conclude that these four samples are mislabelled specimens. There lies a remote possibility that the previously analyzed specimens are not authentic, whereas the BMMRU samples are. This case has occurred when the Mount Sir Charles (IVA) sample was accidentally interchanged with Yardea (IAB) by Reed (1972), resulting in the labelling of Mount Sir Charles as a IAB sample by Buchwald (1975) and Wasson (1974). To be fair, neither of the later workers had access to a Mount Sir Charles sample and would have undoubtedly questioned the label if they had. One hopes that this example of accidental mislabelling is a rare and unlikely one, and is not repeated here.

The samples with the labels and catalog numbers listed in Table X.8 should not be distributed as authentic samples. Further examinations into the chemistry and structure of the samples as well as their histories may reveal them to be pieces of already established irons, or to be completely new and unique meteorites.

Chapter Eleven

Thoughts on Some Iron Meteorite Groups with Reference to the Platinum Group Metals, Gold, Arsenic, Gallium and Germanium

XI.1. Combination and Separation of Groups

As stated in the introduction, some iron meteorite groups have been combined upon discovery of members with intermediate chemical values between the two groups. To check that these combinations are justified, recombined groups are plotted separately (eg.--IAB as IA and IB) for each of the elements determined by the BMMRU. It is important that potentially related objects are not separated by implying differences and gaps in information that may not actually exist. Likewise, objects should not be thrown together because they superficially resemble each other.

XI.1.i. Group IAB

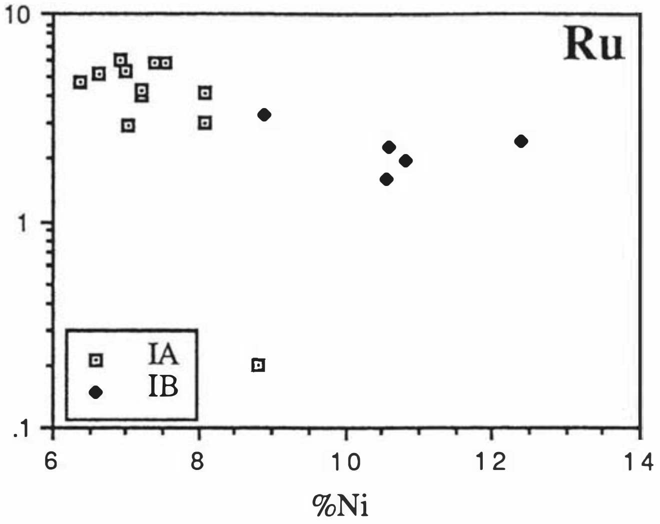
Annaheim was included in the subgroup IA as an anomalous member (IA-AN) because it generally provides intermediate chemical values bridging the groups IA and IB (Wasson, 1970a). For all elements studied here, except Os and Ru, the two subgroups merge together along the same trend (Figure XI.1).

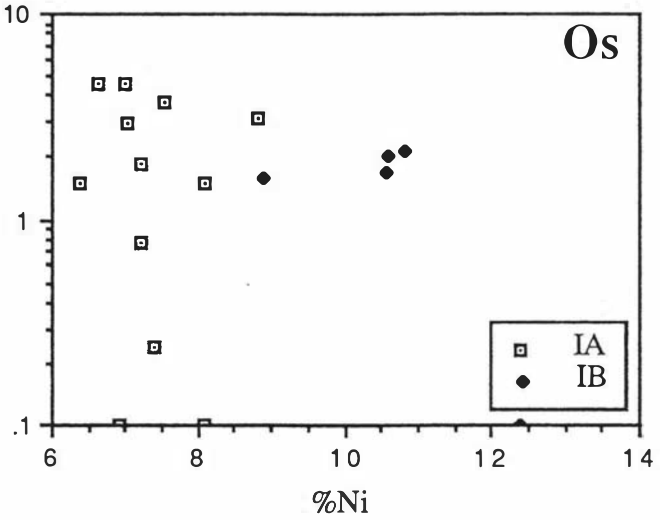
The value for Annaheim does not plot on the IA-IB trend for the Ni-Ru graph or on any of the Ru-element graphs in Appendix 6. Wasson (1970a) had suspected that Annaheim was somewhat anomalous by its slightly high Ga and Ge values. The Ru value for this sample confirms this, though the structure of Annaheim is similar to that of Toluca (IAB).

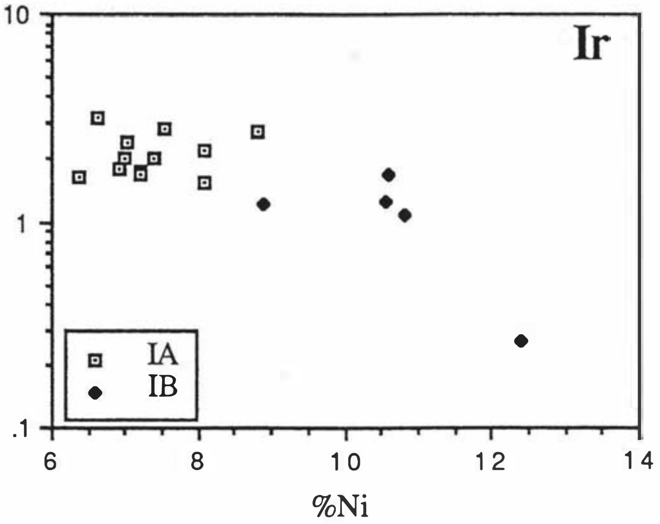
The Ni-Os plot shows several meteorites falling off the expected IAB trend. Of these, the DA program had singled out Dunganville as a poor-fitting IAB member, but the others were confirmed by the program. Though Os is considered to be a member of principal components #1, 2 and 3, it is perhaps not very good for the classification of the members of group IAB. The low Os values might be indicative of the subsequent heating of those particular masses by collisions in space or by terrestrial decay in an oxidizing environment. Osmium is more easily lost than Ru as the tetroxide. Then, too, the LOD of the INAA method for determining Os is not very low (0.20 μg/g), and perhaps if larger samples were available, Os could be determined more precisely.

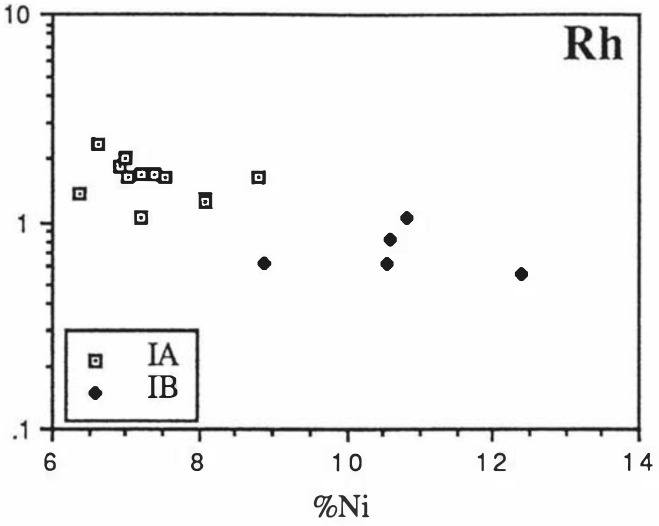
For the other Ni-PGM plots, groups IA and IB merge together smoothly, indicating that they are not actually two separate groups. This confirms the combination of these two groups to form group IAB.

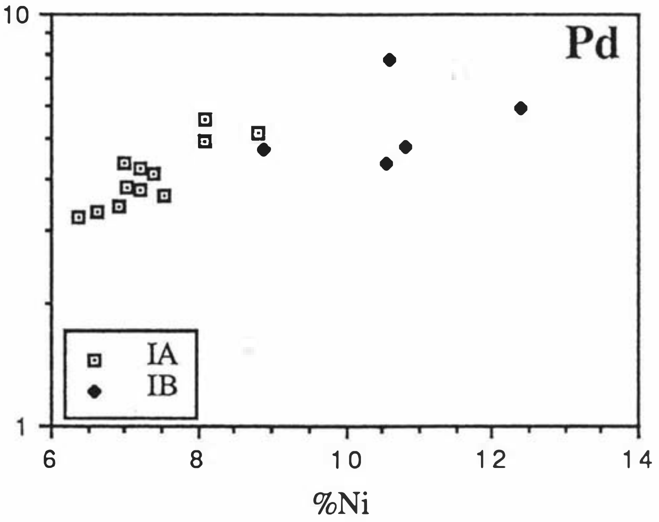
Figure XI.1. Ni vs. Element plots for groups IA and IB

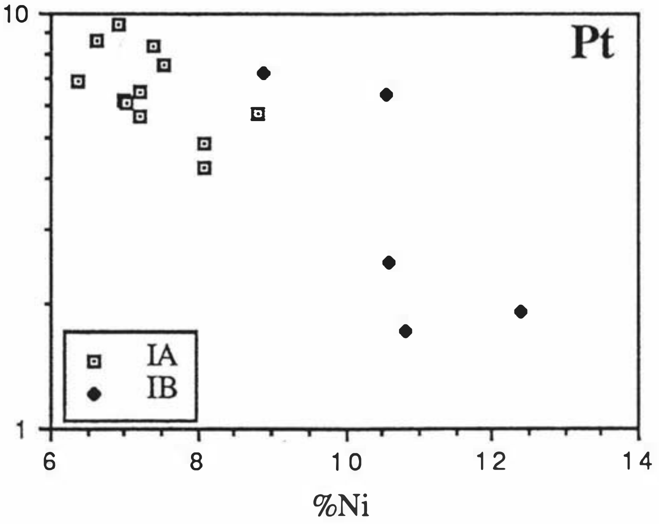


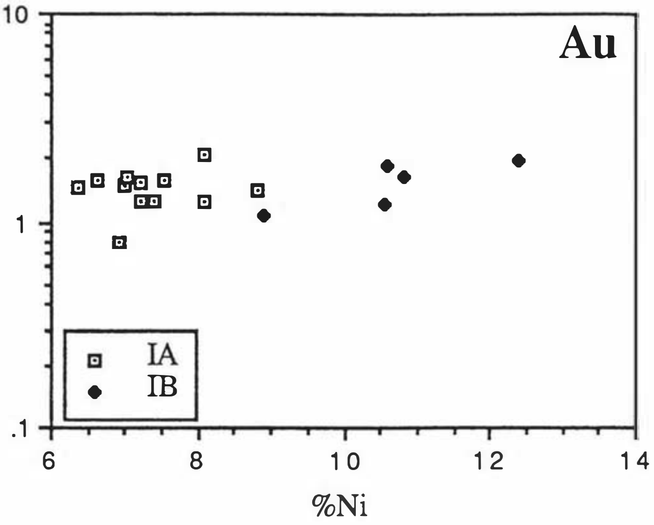


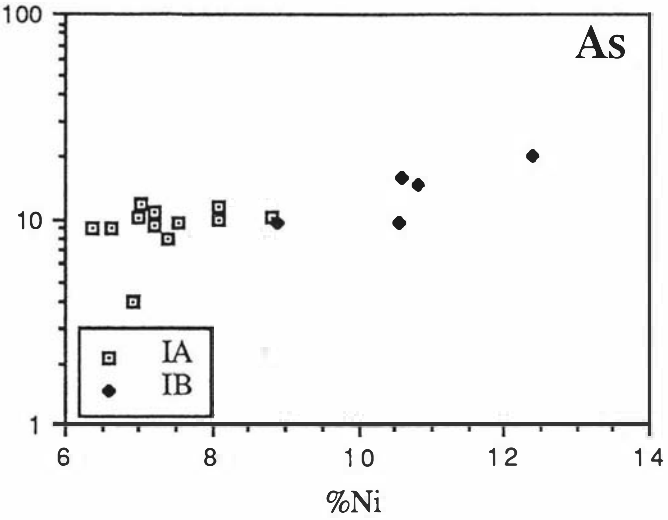


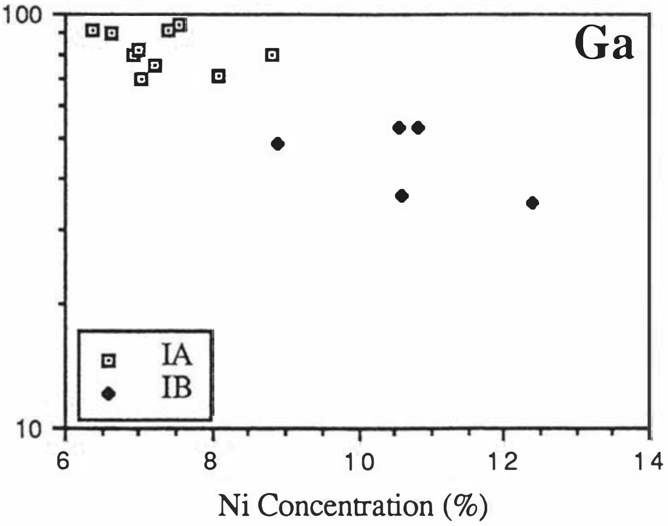

Rh
10
1
.1
6
8
10
12
14
%Ni
IA
IB

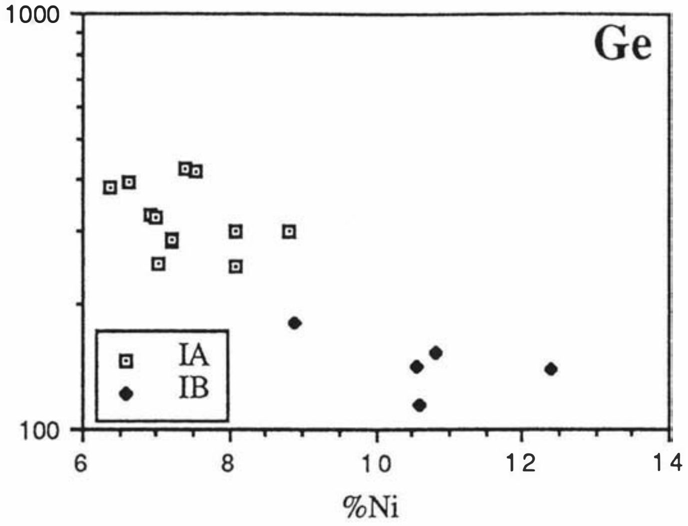

Pd
10
1
6
8
10
12
14
%Ni
IA
IB


Pt
10
1
6
8
10
12
14
%Ni
IA
IB


Au
10
1
.1
6
8
10
12
14
%Ni
IA
IB


As
100
10
1
6
8
10
12
14
%Ni
IA
IB


Ga
100
10
6
8
10
12
14
Ni Concentration (%)
IA
IB

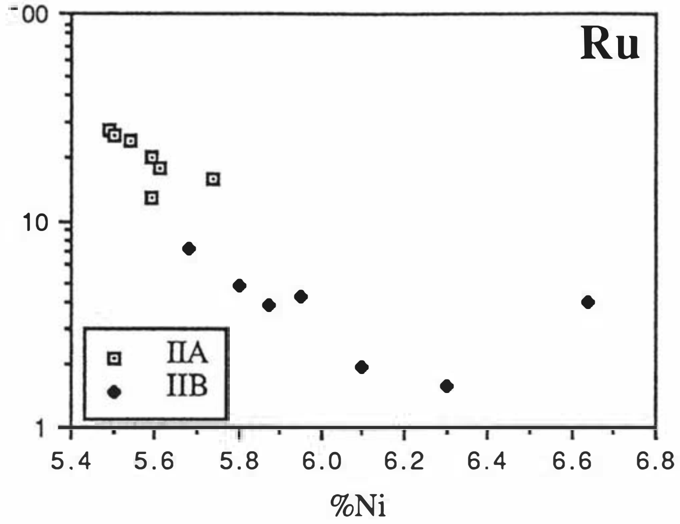

Ge
1000
100
6
8
10
12
14
%Ni
IA
IB

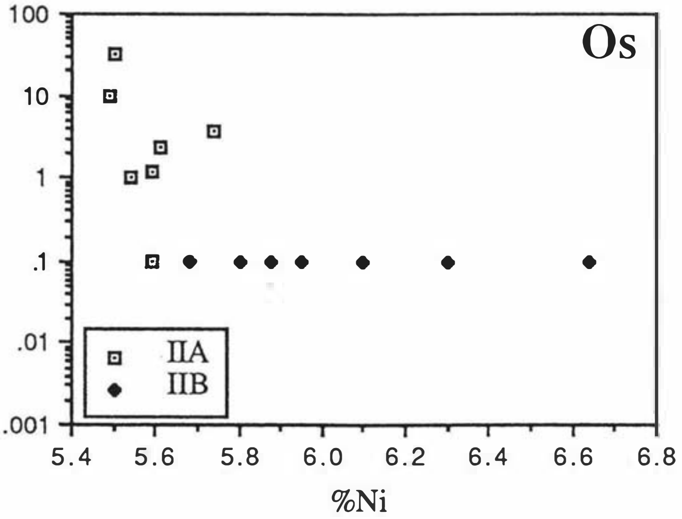
XI.1.ii. Group IIAB

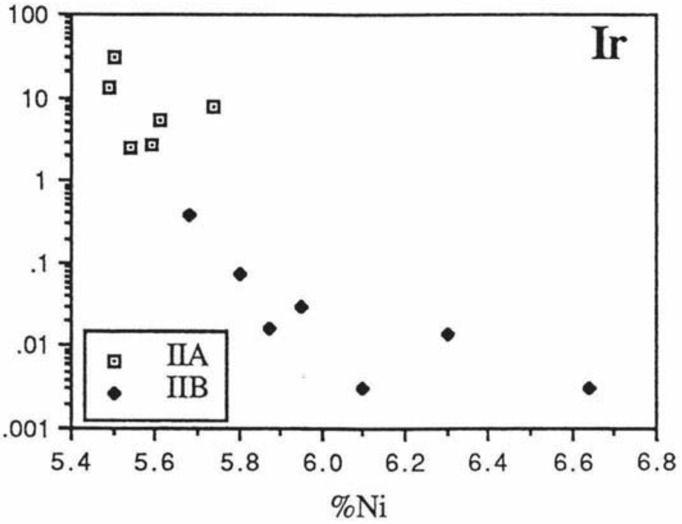
In the Ni-element plots, subgroups IIA and IIB cannot be resolved (Figure XI.2). Scott and Wasson (1975), in an effort to separate the subgroup members, placed an arbitrary cut-off at 1ppm Ir; members containing more are called IIA, and those containing less are IIB. Of the PGMs, the Ni-Pt plot shows a slight clustering of the IIA members, and Pt could be used to differentiate between the subgroups more effectively than Ir does. Otherwise, it is difficult to tell the two groups apart and the merging of these groups is supported.

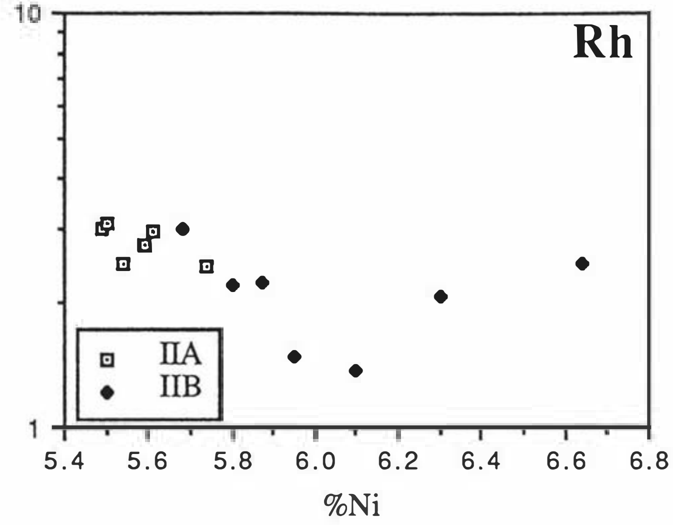
Some of the Derrick Peak 78012 values seem rather high for the amount of Ni the meteorite contains. This is true for Ge, Ru, Rh, Pt and As, and were it not for its hexahedrite structure, Derrick Peak might have been considered to be a group IA iron instead. Experimental and sampling errors are not responsible for this, as the disparate values are the result of three different instrumental techniques (GFAAS, INAA and hydride generation AAS) and performed by three separate operators. Guo (1989) determined Ge in seven members of the Derrick Peak shower and found them all to contain 161 ± 2 μg/g Ge, indicating that his data, at least, do not result from meteorite inhomogeneity. It might be labelled IIB-AN, except that the anomalous tag indicates fulfillment of most classificatory parameters; Derrick Peak fulfills very few of the requirements of membership into group IIB and so an anomalous tag is not appropriate. It is probably best to remove the Derrick Peak irons from the IIB field and to study them further to establish the true classification.

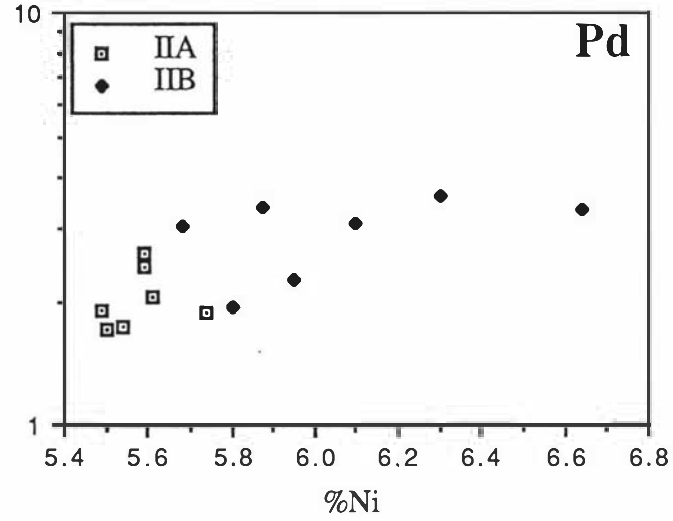
Figure XI.2. Ni-Element plots for groups IIA and IIB

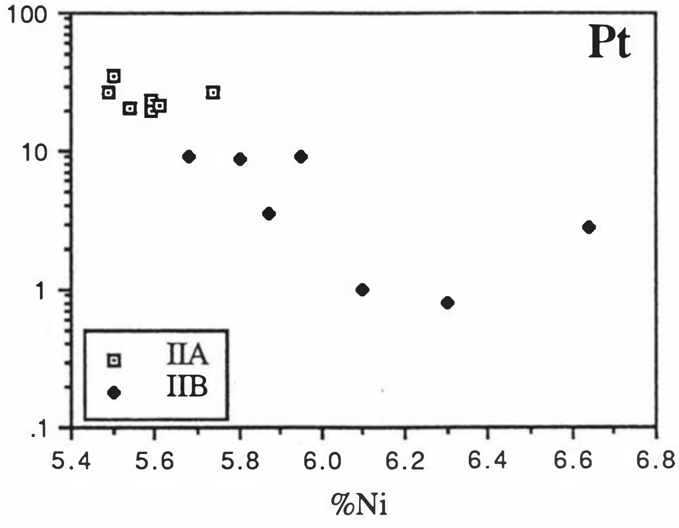


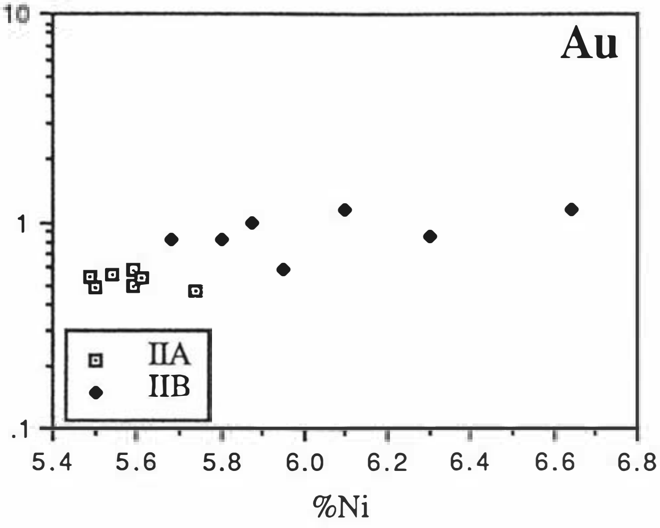


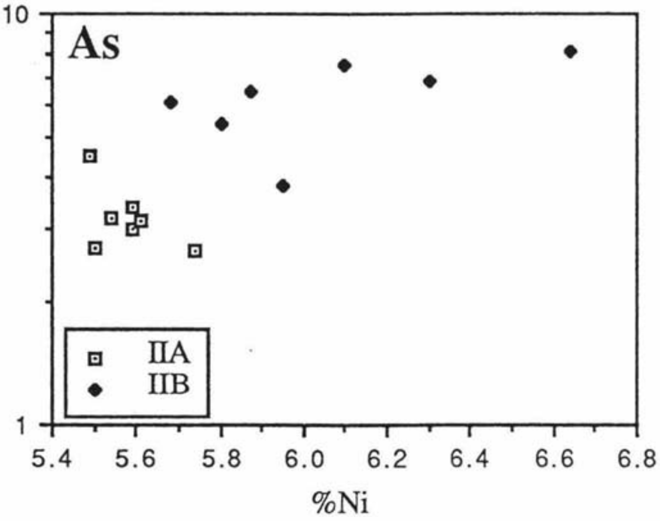


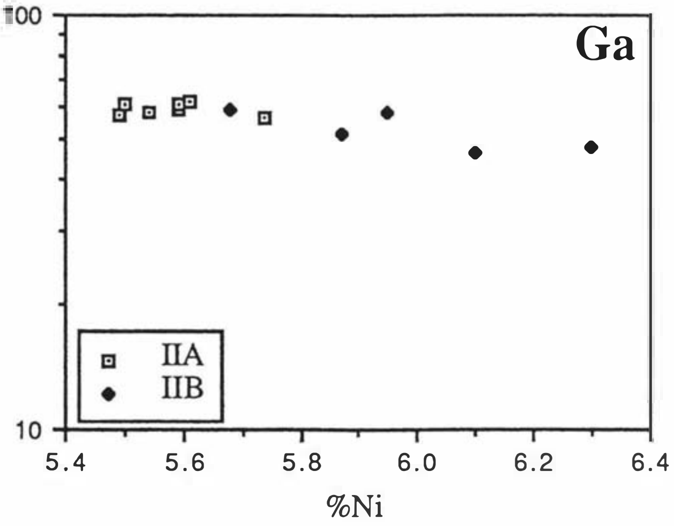

Rh
IIA
IIB
10
1
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
%Ni

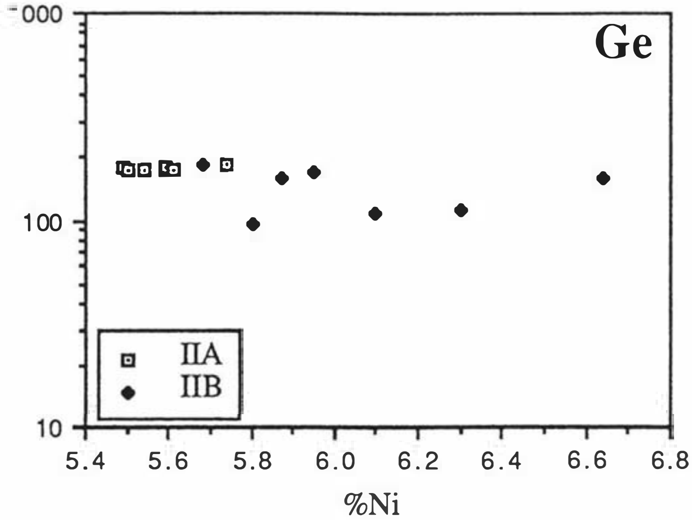

Pd
IIA
IIB
10
1
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
%Ni


Pt
IIA
IIB
100
10
1
.1
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
%Ni


Au
10
1
.1
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
%Ni
IIA
IIB


As
10
1
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
%Ni
IIA
IIB

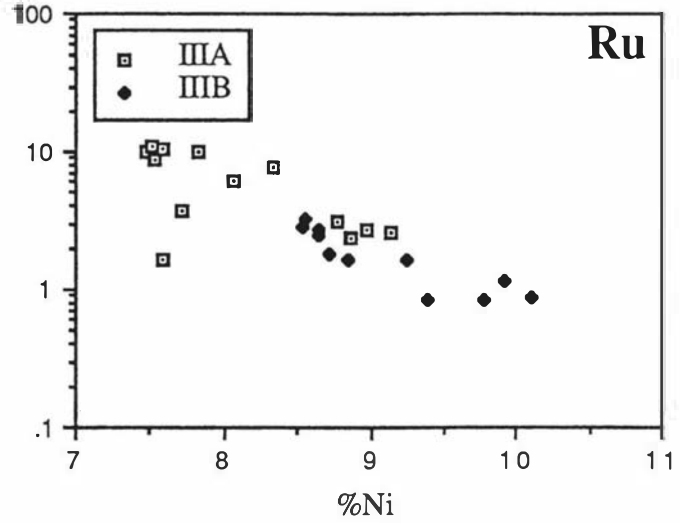

Ga
100
10
5.4
5.6
5.8
6.0
6.2
6.4
%Ni
IIA
IIB

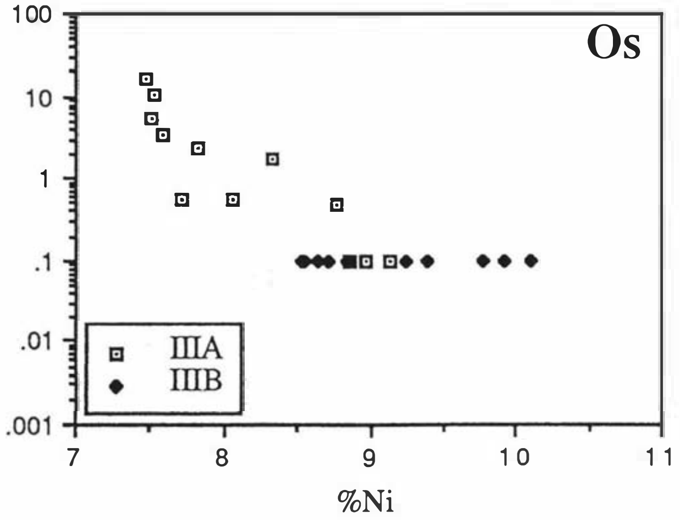

Ge
1000
100
10
IIA
IIB
5.4
5.6
5.8
6.0
6.2
6.4
6.6
6.8
%Ni

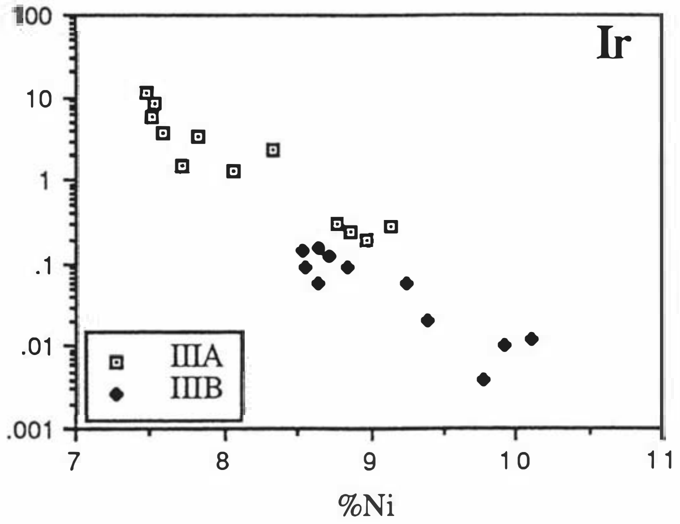
XI.1.iii. Group IIIAB

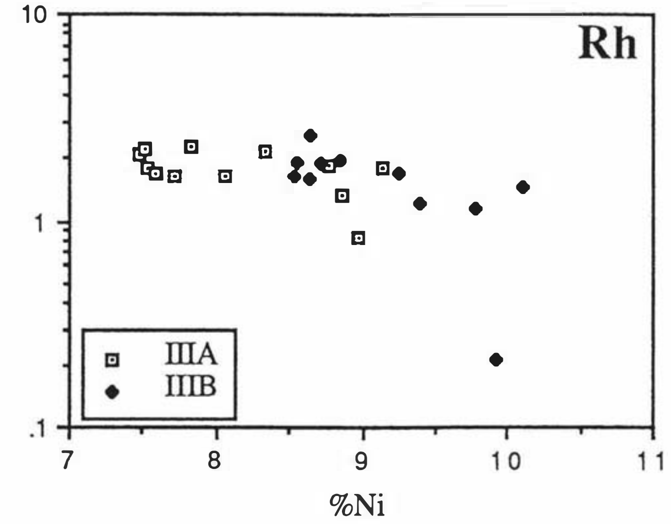
Subgroups IIIA and IIIB are easily resolved by Pt and Pd as the subgroup trends for Ni against these elements differ. The values for Henbury, Madoc, Chambord and Cape York are in line with the IIIB slope, but the rest of the IIIA members are not, giving the IIIAB group a "zigzag" appearance in these graphs (Figure XI.3). This kink occurs at exactly where the Ni-Ge and Ni-Ga plots of IIIAB change from a positive slope to one with a value of zero. This is thought to be due to the influence of an increase in phosphide content with increasing Ni (Scott *et al.*, 1973). The amount of P in the melt controls, to some extent, the accretion of some metals during core formation. As critical concentrations of P are reached, varied by fractional solidification of the melt, elements change their behavior so that they become more, or less, siderophilic. Haack (1990) hypothesized that the Cape York meteorite was a fragment of a stalactitic dendrite growing from the ceiling of the IIIAB magma chamber. If large dendrites separate from the ceiling and fall back into the magma, it would alter, at least locally, the concentration of elements in the melt. It is possible that the kink observed in the Ni-Pd and Ni-Pt plots is due to a subtle change in magma composition; perhaps Pd and Pt are more sensitive to changes in P composition than the other PGMs. Likewise, Ni appears to also be affected. The boundary between subgroup IIIA and IIIB is defined as an Ir/Ni ratio of 0.02, or of 8.6% Ni where Ir data are not available (Scott *et al.*, 1973). Compliance with the ratio explains why some meteorites with >8.6% Ni are considered IIIA meteorites and some <8.6% Ni ones are classified as IIIB. When the meteorites are listed within their subgroups in the order of increasing Ni content, the Ni values also appear to display a kink like the values for Pd and Pt (this is probably one of the few observed behaviors that Ni shares with Pd and Pt). This behavior, if Haack's model is accepted, indicates that remelting of solids probably occurred during processes that occurred in the IIIAB parent body.

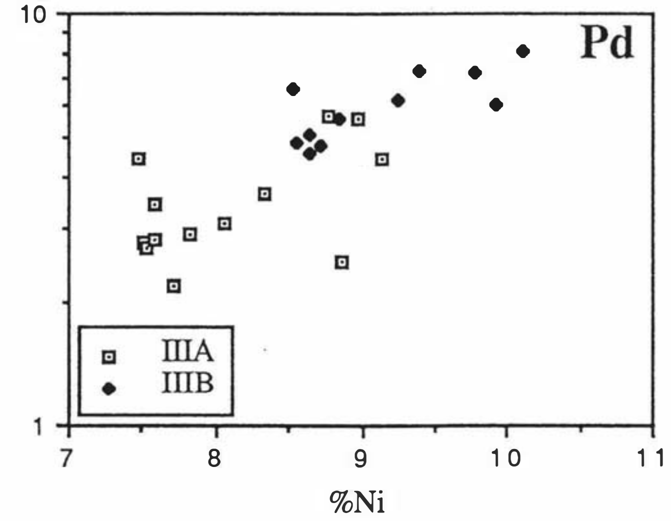
Figure XI.3. Ni-Element plots for groups IIIA and IIIB

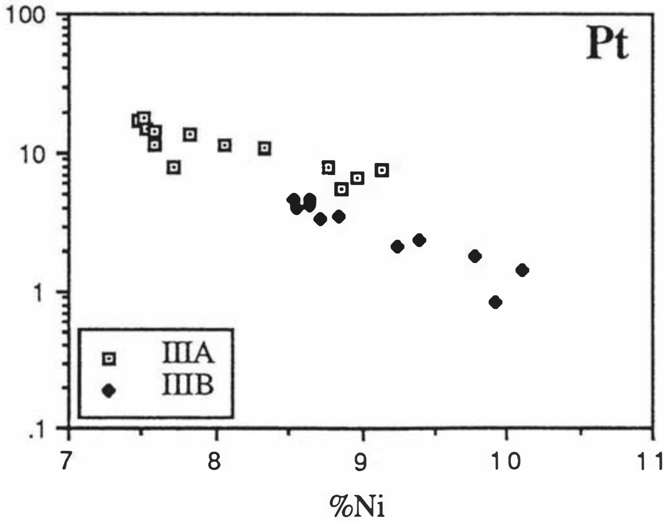


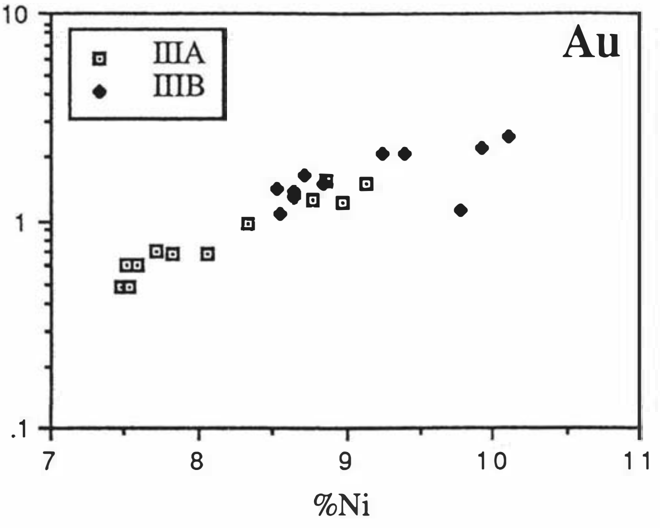


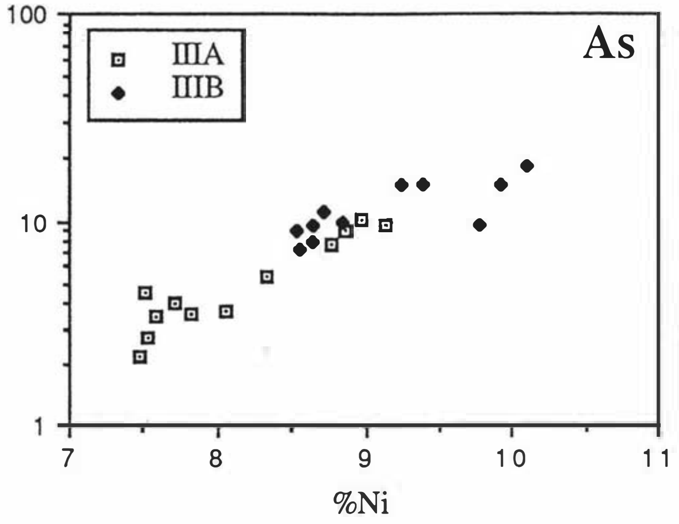


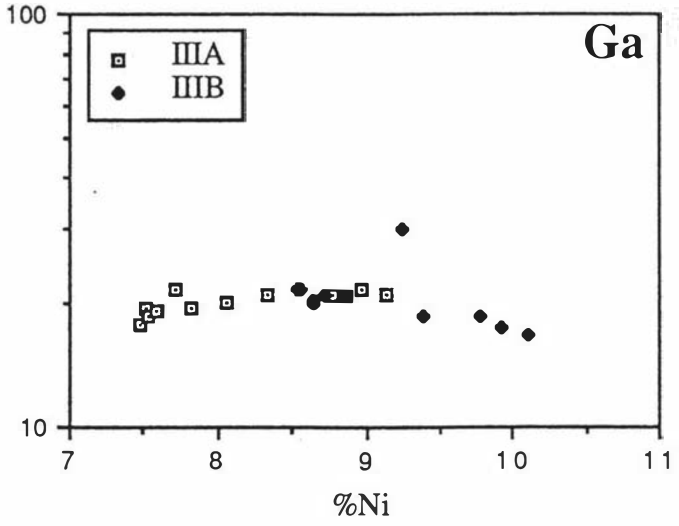

Rh
10
1
.1
7
8
9
10
11
%Ni
IIIA
IIIB

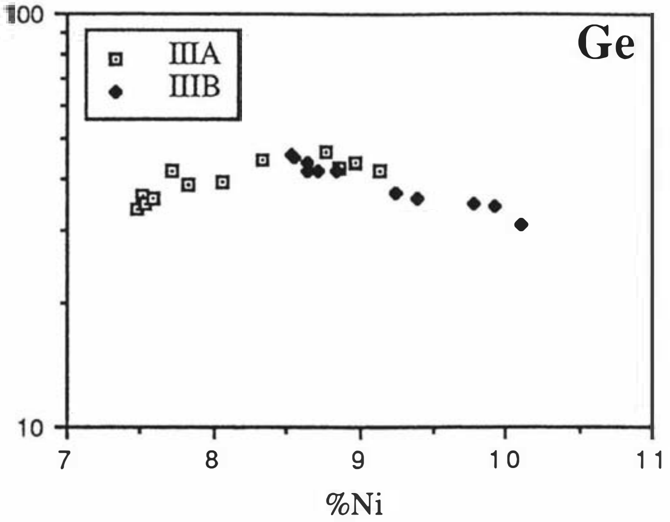

Pd
10
1
7
8
9
10
11
%Ni
IIIA
IIIB


Pt
100
10
1
.1
7
8
9
10
11
%Ni
IIIA
IIIB


Au
IIIA
IIIB
10
1
.1
7
8
9
10
11
%Ni


As
IIIA
IIIB
100
10
1
7
8
9
10
11
%Ni


Ga
IIIA
IIIB
100
10
7
8
9
10
11
%Ni

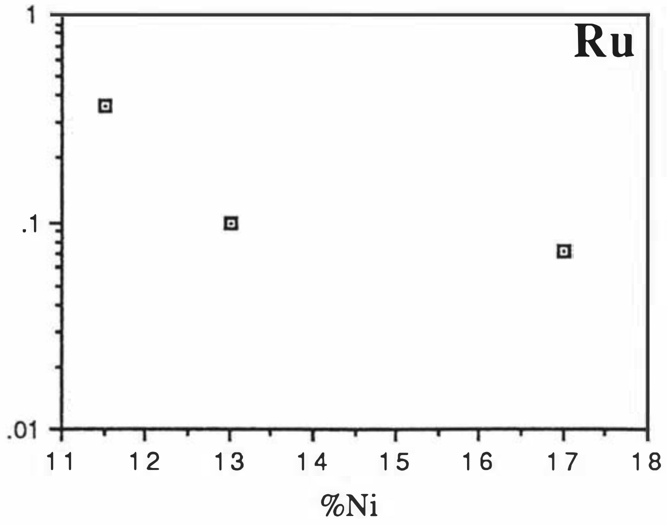


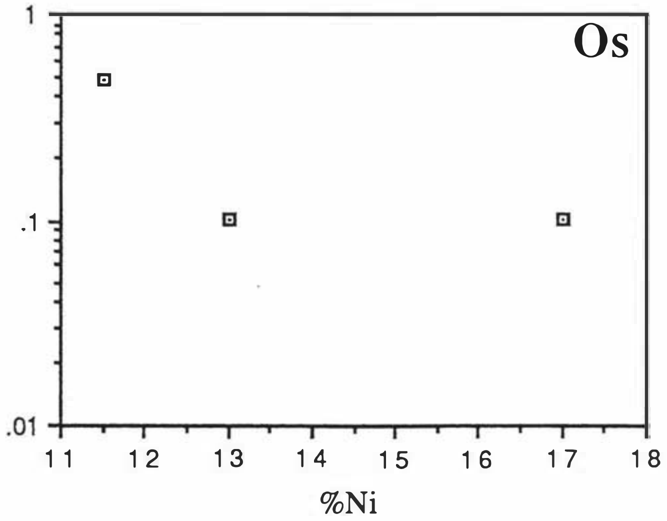
XI.1.iv. Group IIICD

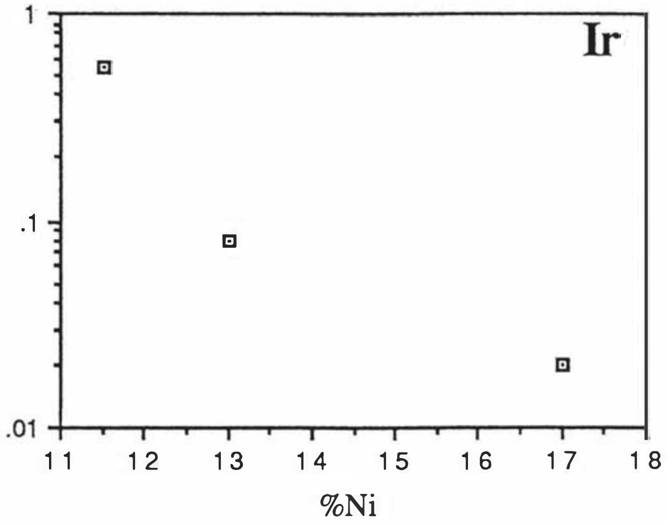
Wasson and Schaudy (1971) established groups IIIC and IIID, but did not combine them despite the fairly continuous and smooth curve that could connect the data on Ni Ge and Ga-Ge plots. A discontinuity was present on their Ni-Ir plot, which prevented them from combining the members into one group. Scott and Bild (1974) nevertheless felt that the designations IIIC and IIID merely represented two ends of the same group and referred to them as the combined group IIICD.

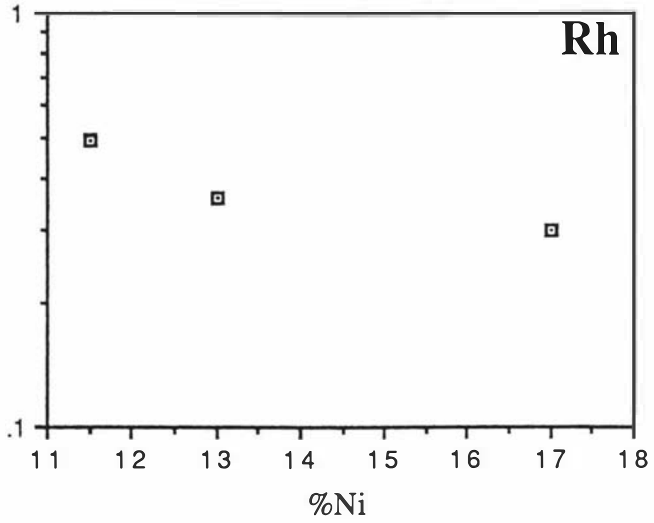
Unfortunately, the BMMRU collection possesses only three of the original IIICD members; of them, Dayton is the only IIID member. Inspection of the plots of log Ni vs. log element shows a generally sickle-shaped, smooth transition along the curve that joins these three members (Figure XI.4). Although the small number of data points does not confer very much confidence, Scott and Bild's (1974) combination of groups IIIC and IIID is probably justified. It is possible that the Ir data of Wasson and Schaudy (1971) were not determined with sufficient accuracy.

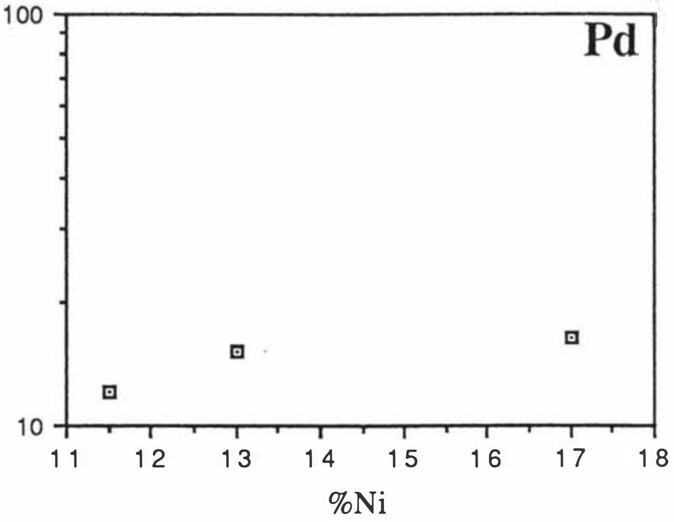
Figure XI.4. Ni-Element plots for group IIICD

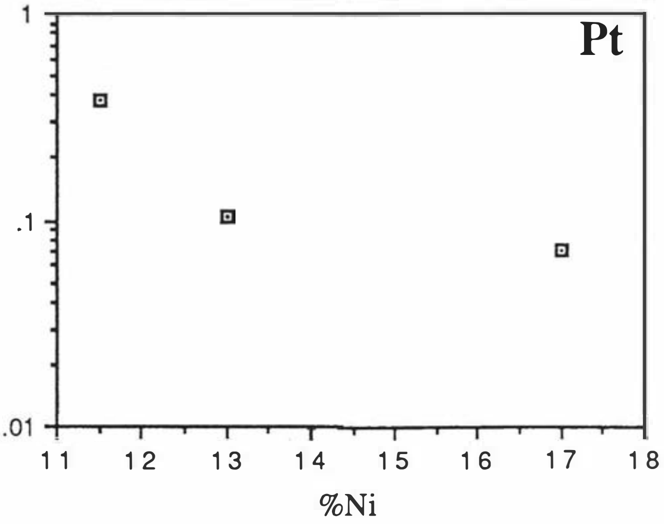


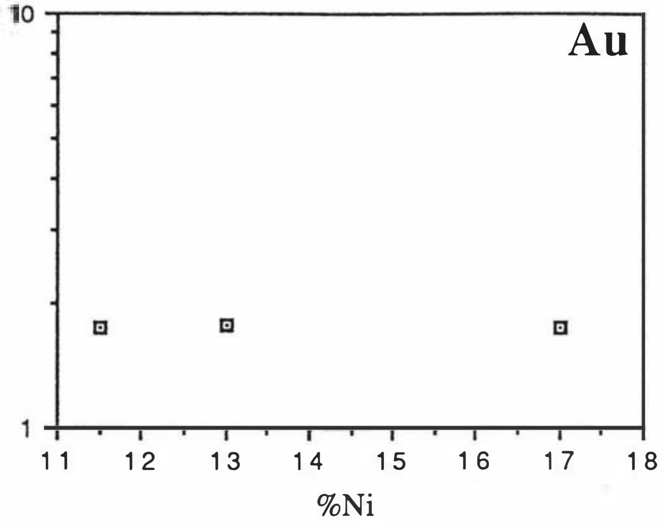


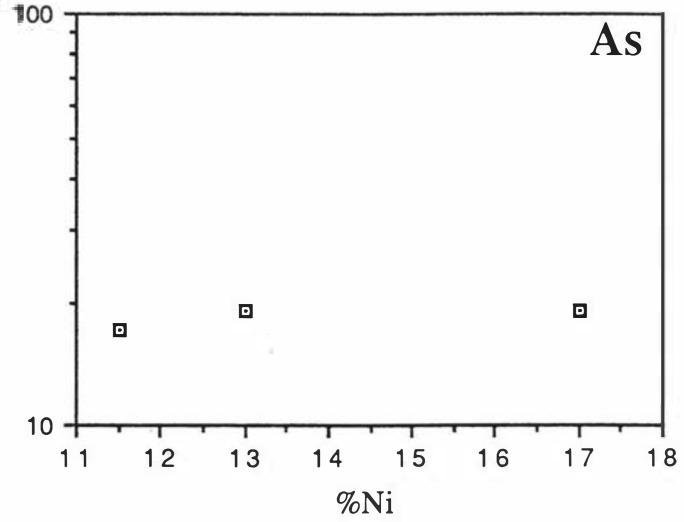


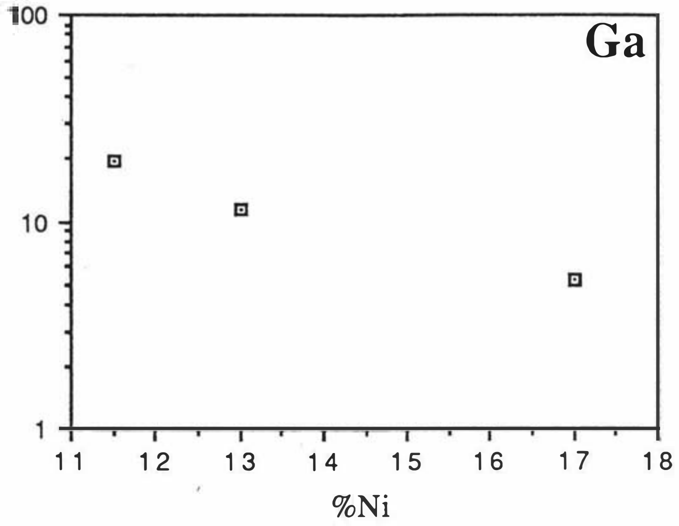

Rh
1
.1
11
12
13
14
15
16
17
18
%Ni

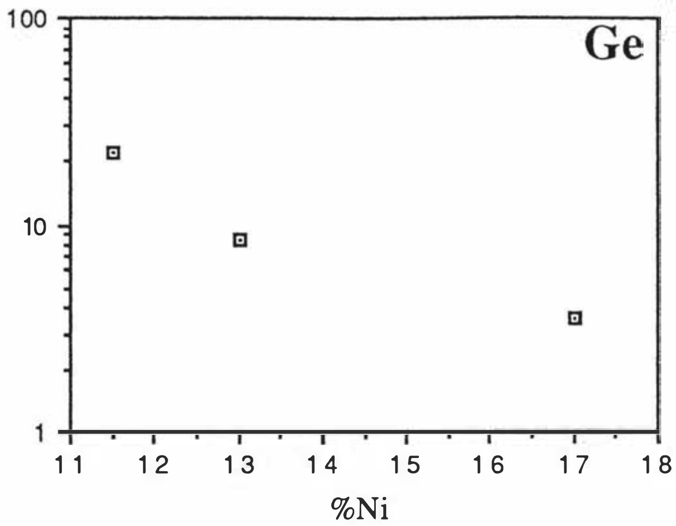

Pd
100
10
11
12
13
14
15
16
17
18
%Ni


Pt
1
.1
.01
11
12
13
14
15
16
17
18
%Ni


Au
10
1
11
12
13
14
15
16
17
18
%Ni


As
100
10
11
12
13
14
15
16
17
18
%Ni


Ga
100
10
1
11
12
13
14
15
16
17
18
%Ni



XI.1.v. Low-Ni IIICD and Low-Ni IAB

The low-Ni boundary of group IIICD was extended by Wasson *et al.* (1980) from 10.5% down to 6.1% by inclusion of some members of IAB. The observed slope for IIICD was extrapolated to where it intersected the low-Ni IA cluster and Pittsburg, Ballinger, Carrizalillo, Jaralito, Nantan, Zaffra (Wasson *et al.*, 1980) and Cranbourne (Pernicka and Wasson, 1987) were removed from group IAB and included as members of IIICD. At >10.5% Ni, it is easy to distinguish between the two groups. However, at lower Ni concentrations, it is very difficult to separate low-Ni IIICD from low-Ni IAB (Figure XI.5).

Undoubtedly, both IAB and IIICD resulted from non-magmatic differentiation processes (Wasson *et al.*, 1980). Group IAB probably never existed as a single, homogeneous melt. Large IAB meteorites like Cañon Diablo preserve the resultant chemical inhomogeneity (Wasson, 1968). Wasson *et al.* (1980) proposed shock melting of an unequilibrated chondrite as the mode of formation for both groups IAB and IIICD. The impact would generate sufficient heat to melt a local portion of the chondrite. The low-Ni values are results of more intense shock events; low temperature melts would form high-Ni members. This also explains the low abundances of refractory elements in high-Ni samples. The IAB and

IIICD meteorites represent individual melt pools formed by impacts of chondrite parent bodies and Wasson *et al.* (1980) even propose that these two groups may actually share the same parent body.

This model fails to explain why IB irons with Ni values comparable to IIICD irons do not show similar structures or chemical compositions (Table XI.1). The values for the refractory Ir and the volatile Ge are rather different. If these two groups were formed on an unequilibrated parent body, the heat of the impact that produced similar Ni-concentrations should also produce similar refractory and volatile element abundances, and perhaps more similar structures.

If impact melting is the mode of formation of these two groups, then it is wholly possible that low-Ni IIICD members exist, as the magnitude of impacts and the resultant heat generated should occur equally for both of the bodies. It is possible, however, that IAB and IIICD were formed on different parent bodies with different mean near-surface concentrations of elements as evidenced by the disparate abundances and structures at the high-Ni ends of the groups. If the initial bulk compositions of the two planets were different, perhaps more differences than the ones shown by the IAB meteorites designated IIICD by Wasson and his co-workers would exist.

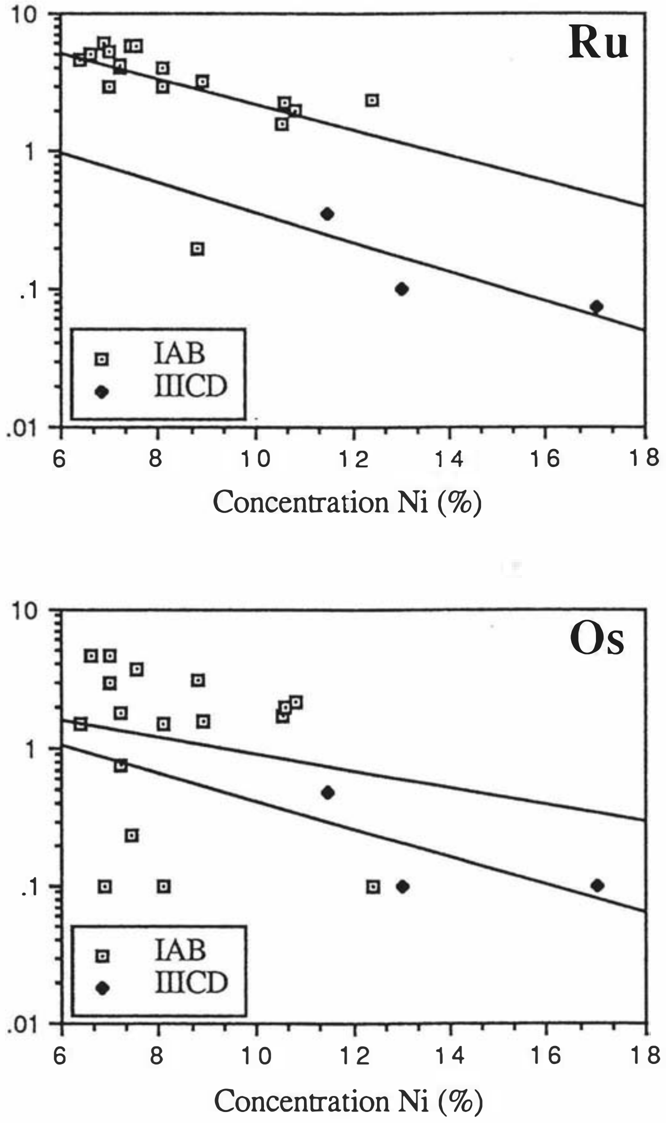
At this point, data for IIICD are insufficient to predict its low-Ni terminus. However, Buchwald (1990a,b) firmly maintains that Cranbourne and probably Jaralito and Nantan are typical IAB iron meteorites, and should never have been reassigned to group IIICD based on what he considers to be weak evidence. The elemental abundances for these meteorites agree well with Buchwald's structural observations (Section IX.4.v).

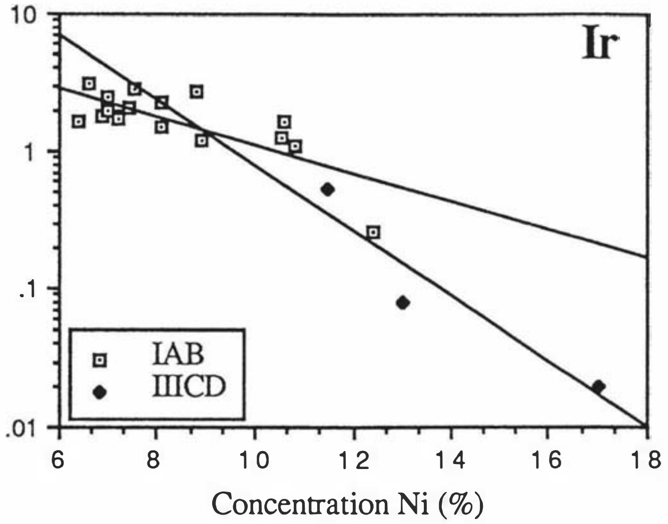
The celestial delivery of a true low-Ni IIICD meteorite would end this controversy. Although low-Ni IIICD members probably exist if impact melting was their mode of formation, we have yet to come across such a sample, and should not create them out of the desire to have them.

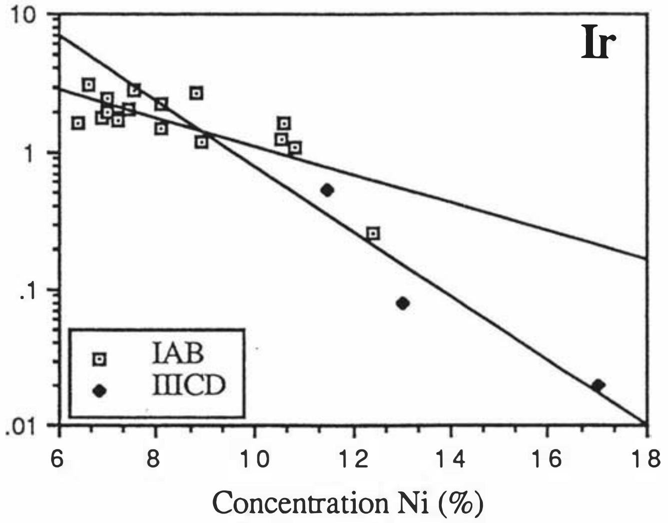
Table XI.1. Comparison of data for IAB and IIICD iron meteorites with similar Ni values (all values in µg/g except for Ni)

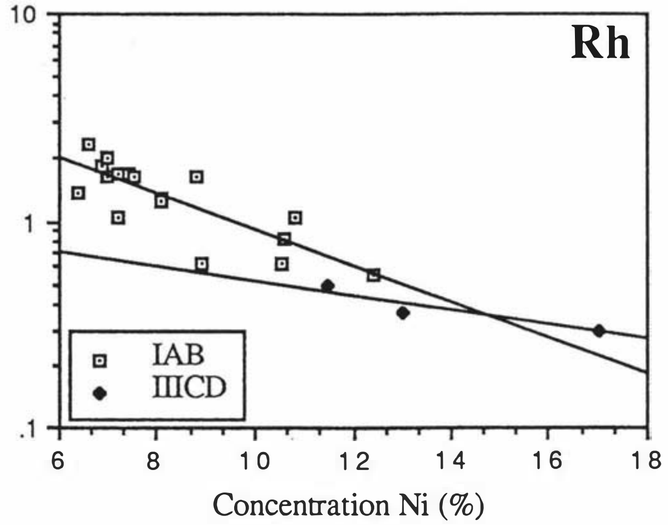
Meteorite	Group	Structure	%Ni	Ga	Ge	Ir
Colfax	IB	Om	10.5	55.1	155	1.5
Hassi-Jekna	IIICD	Of	10.5	27	70	0.18

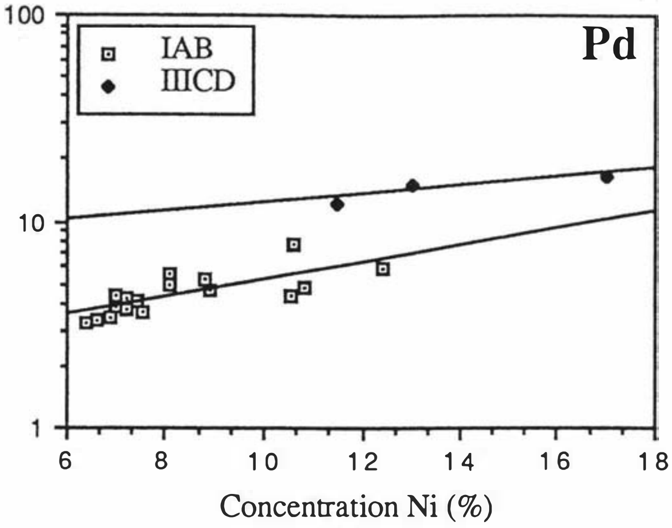
Figure XI.5. Ni-Element plots and regression lines for groups IAB and IIICD

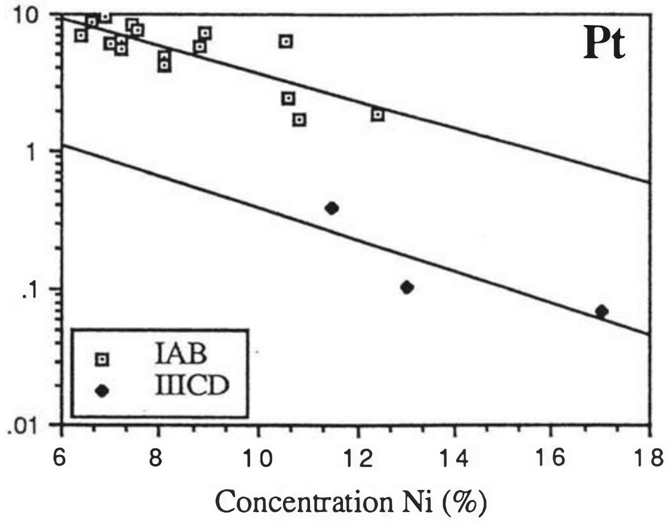


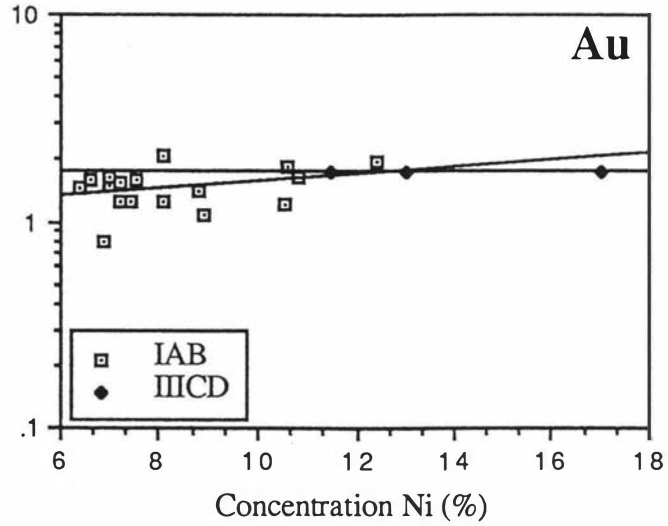

Ir
10
1
.1
.01
6
8
10
12
14
16
18
Concentration Ni (%)
IAB
IIICD

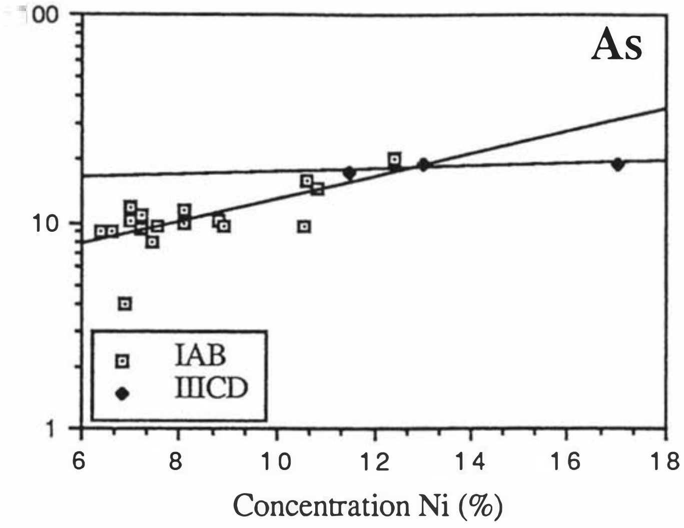

Ir
10
1
.1
.01
6
8
10
12
14
16
18
Concentration Ni (%)
IAB
IIICD

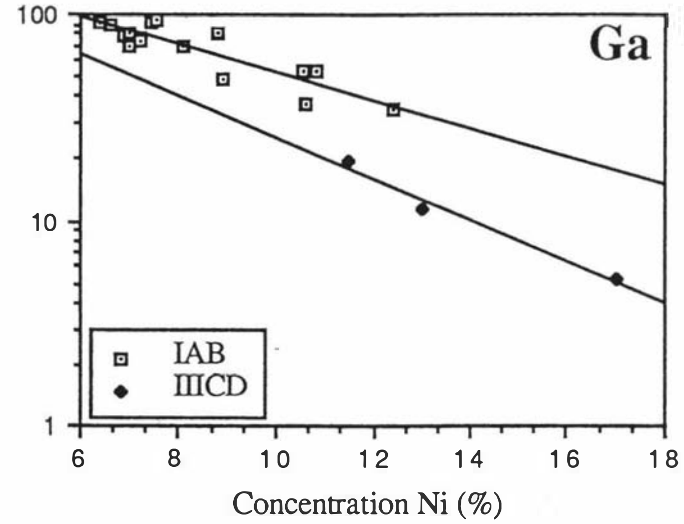

Rh
10
1
.1
6
8
10
12
14
16
18
Concentration Ni (%)
IAB
IIICD

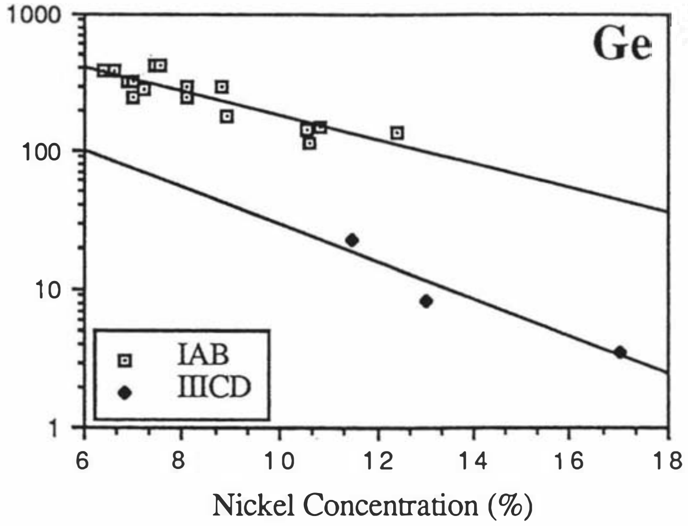

Pd
IAB
IIICD
100
10
1
6
8
10
12
14
16
18
Concentration Ni (%)


Pt
IAB
IIICD
10
1
.1
.01
6
8
10
12
14
16
18
Concentration Ni (%)


Au
IAB
IIICD
10
1
.1
6
8
10
12
14
16
18
Concentration Ni (%)


As
100
10
1
6
8
10
12
14
16
18
IAB
IIICD
Concentration Ni (%)


Ga
100
10
1
6
8
10
12
14
16
18
IAB
IIICD
Concentration Ni (%)


Ge
1000
100
10
1
6
8
10
12
14
16
18
IAB
IIICD
Nickel Concentration (%)

XI.2. The Need for Intermediate Members Within Group IIIF

Scott and Wasson (1976) established the group IIIF, whose members have the following morphologies. Large sections of IIIF members show a notable scarcity of macroscopic inclusions of phosphide or sulfide. Millimeter-sized troilite and schreibersite are rare, whereas microscopic daubréelite precipitates are unusually abundant. Carbides, graphites and silicates have not been reported. The kamacite bandwidth is generally 0.5 mm, although bands of greater width are sometimes apparent due to plate impingement during formation of the crystals.

Klamath Falls was recognized as a member of IIIF by Kracher *et al.* (1980) because it plotted on or near an extrapolated slope projected from the original members of IIIF for most elements (Figure XI.6). However, for Ru and Pt, the other members of this group form a well-defined cluster with an implausibly shallow slope similar to that of IAB or IIICD. If this was believed, it would make IIIF another non-magmatic group; however, the other elements determined do not display similar behavior. Pernicka and Wasson (1987) attributed this stochastic clumping to experimental or sampling errors. The addition of Klamath Falls to the Ni-Ru and Ni-Pt plots decreased the slope of the IIIF group for these elements, allowing the group to be regarded as a normal magmatically-differentiated one.

In the present work, the data obtained for Ru and Pt are more clustered than for the other elements, as found by Pernicka and Wason (1987). This is probably not the result of the errors noted above for two reasons: 1) The samples analyzed by Pernicka and Wasson (1987) were not from the same sources as the ones analyzed here, making the repetition of the same sampling errors unlikely; 2) The methodologies used here for the determination of Ru and Pt were different from those of Pernicka and Wasson (1987), ruling out analytical errors.

This clustering highlights the need to find intermediate values between the original IIIF members and Klamath Falls. The clustering could be the result of unfortunate sampling, or it could indicate that Klamath

Falls may be an anomalous member of IIIF, if it is one at all.

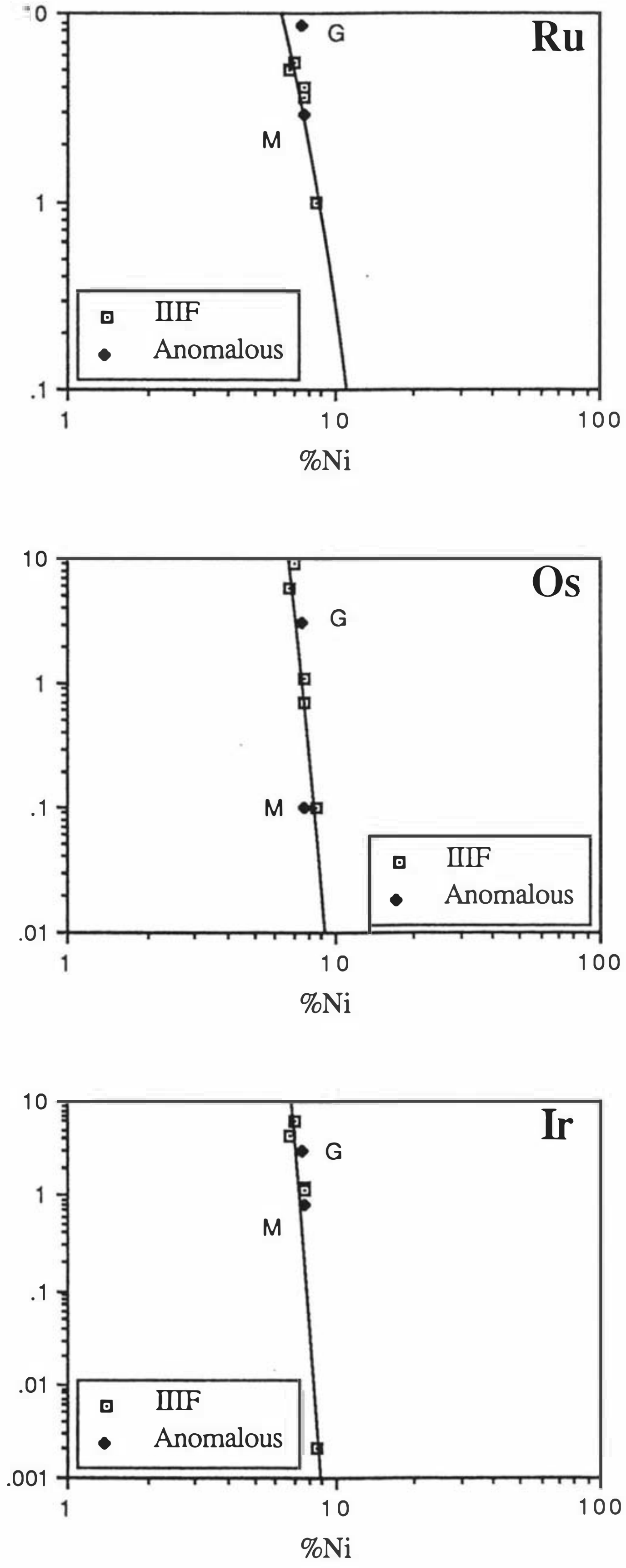
A visual inspection of data for all of the ungrouped meteorites analyzed in group IIIF, indicates that chemically, Glenormiston and Mundrabilla could fit onto the interpolated lines on Ni-element plots, usually falling between Klamath Falls and the main cluster. The only exceptions are the Ni-Ga and Ni-Ge plots.

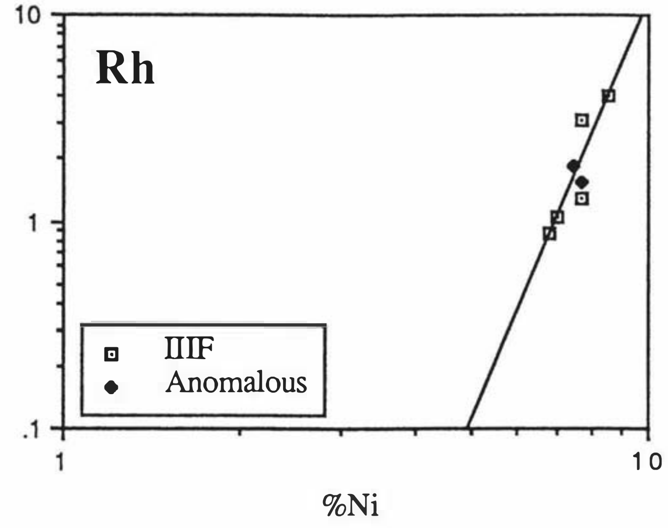
Structurally, Mundrabilla is not at all similar to members of IIIF. Mundrabilla is an unusual meteorite possessing large and abundant troilite nodules, resulting in an almost pallasitic structure for this iron, with the troilite present instead of olivine (Buchwald, 1975). Group IIIF members have much smaller and sparser troilite nodules.

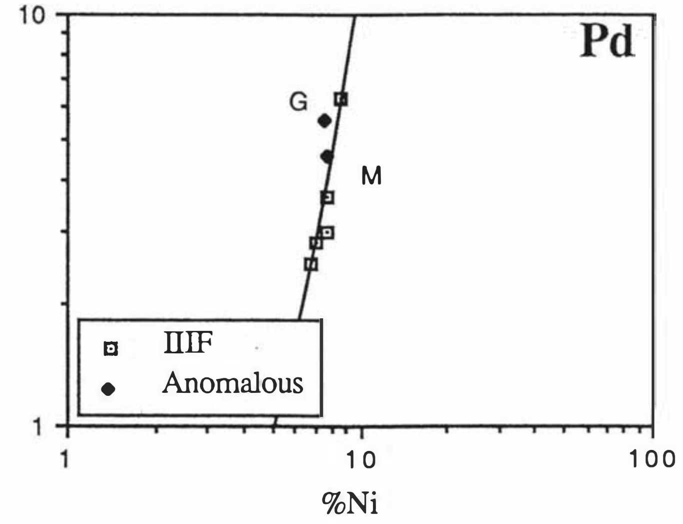
The kamacite bandwidth of Glenormiston averages 6 mm. Schreibersite and troilite nodules are abundant but unevenly distributed and graphite, carbides and silicate are not identified (Richards, 1930).

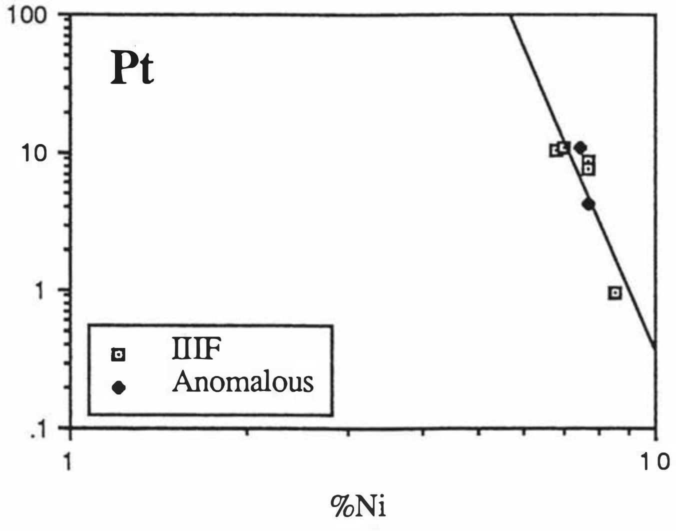
From the descriptions, neither of the meteorites will completely fit chemically into group IIIF and not at all structurally or mineralogically. A search among new and anomalous meteorites might reveal the existence of an intermediate member between the two extremes of IIIF. If the structure and mineralogy of Mundrabilla and Glenormiston had agreed, the Ga and Ge concentrations could have been overlooked using the argument of Scott and Wasson (1976) that the advantages of identifying a cluster of related irons can outweigh the disadvantages that its members might not have shared entirely identical formation conditions. On the other hand, one should obey the caveat in the previous section (XI.1.v) against "wishing" samples into groups.

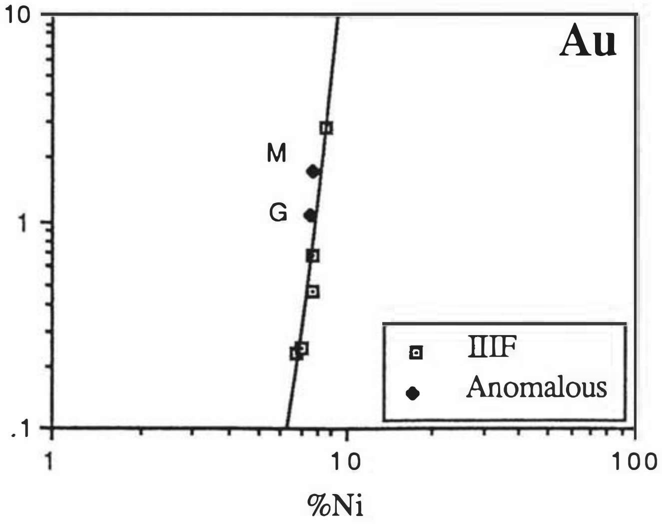
Figure XI.6. Ni-Element Plots for group IIIF including the anomalous meteorites Glenormiston (G) and Mundrabilla (M)

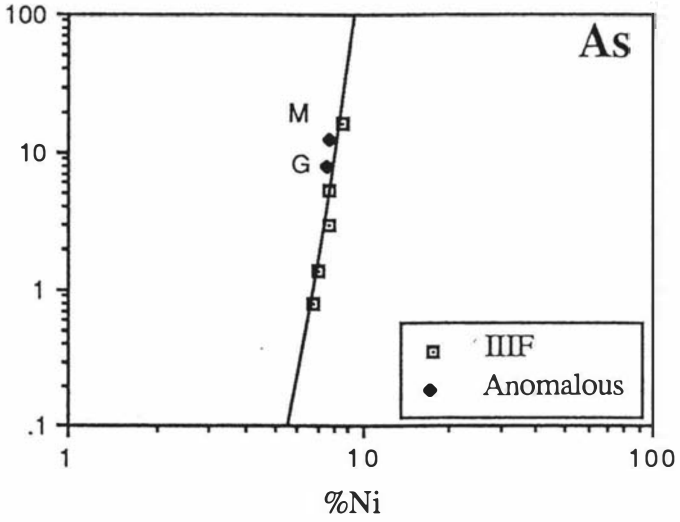


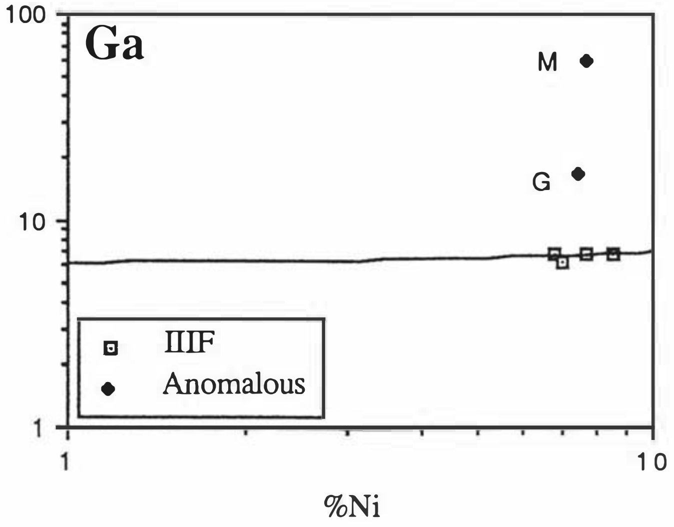

Rh
10
1
.1
1
10
%Ni
IIIF
Anomalous

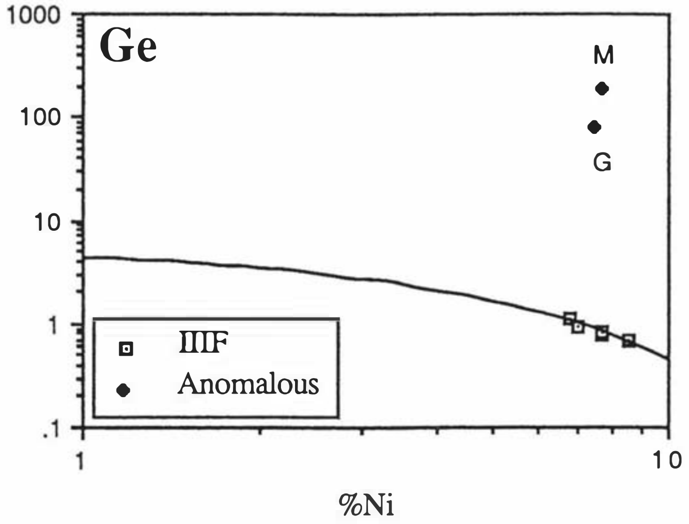

Pd
10
1
G
M
1
10
100
%Ni
IIIF
Anomalous


Pt
100
10
1
.1
1
10
%Ni
IIIF
Anomalous


Au
M
G
IIIF
Anomalous
10
1
.1
1
10
100
%Ni


As
M
G
IIIF
Anomalous
100
10
1
.1
1
10
100
%Ni


Ga
M
G
IIIF
Anomalous
100
10
1
1
10
%Ni



XI.3. Temperature of Formation of the Group IVB Parent Body

As indicated by Scott (1972), refractory elements with high melting points correlate negatively with Ni abundance, and low melting point volatile elements correlate positively with Ni. This implies that Ni can be treated as a volatile element as well. Using this generalization, it is possible to designate the elements studied here using the correlation coefficient data of Table IX.1: Ru, Os, Rh, Ir and Pt are refractory and Pd, Au, As, Ga and Ge are volatile. When the cosmic abundance ratios of %Ni/ppm-element (calculated from the data of Anders and Grevesse, 1989, Appendix 8) are compared to the Ni-element graphs, the refractories are depleted relative to Ni, whereas the volatile elements parallel this ratio for all meteorite groups. The only exception is group IVB. Vinogradov (1971) notes that this unusual group is high in refractories and low in volatiles and this points to a high temperature origin. However, the high abundances of Pd and Ni do not follow the general pattern of low volatile element concentrations. Kelly and Larimer (1977) suggest that this group became isolated from the nebular gases that were the starting material of the solar system shortly after the metal began to condense.

Because the Pd and Ni content is high in group IVB, the temperature at which the IVB parent body became isolated from the starting material could be lower than generalized by Vinogradov (1971). Kelly and Larimer (1977) imply that the removal of the IVB body from contact with the nebular gases perhaps occurred by accretion of the solidifying masses. This can be taken to mean that the isolation of the body would protect it from further changes in composition. In this way, it remains enriched in refractories and depleted in volatiles. The outermost rind of the accreted mass would be rich in volatile condensates and perhaps these outer layers were separated from the original protected mass prior to the start of core formation processes.

From reported boiling points of pure metals (Ni 2730°C, Pd 2970°C --Hammond, 1990), it can be estimated that the IVB parent body was first isolated from chemical interactions with the primeval nebular gases at a temperature of approximately 2700°C.

Chapter Twelve

Summary and General Conclusions

XII.1. Summary and General Conclusions

The first section of this thesis showed that careful consideration of the chemical behavior of Ru is necessary for the development of a methodology for the determination of this element in iron meteorites. Conventional methods of digestion for ores and alloys containing large amounts of Ru are too harsh and result in loss of the μg quantitites of Ru in iron meteorites as the volatile tetroxide. A gentler digestion procedure involves refluxing of the sample with HCl only. The isolation of Ru from matrix and cross-element interferences is accomplished using solvent extraction. The procedure entails the oxidation of the Ru(III) in solution with $NaIO_4$ to RuO_4 which is selectively and nearly completely (D = 670) extracted into $CHCl_3$. Studies on the behavior of RuO_4 in $CHCl_3$ revealed the need to remove the organic phase from contact with the aqueous HCl, as RuO_4 is a powerful oxidant and causes chloride to oxidize to chlorine at the aqueous-organic phase interface. This reaction reduces RuO_4 into a lower valence species not soluble in $CHCl_3$. This problem was solved by separating the $CHCl_3$ phase immediately after extraction, placing it in contact with a "keeper" solution of $HNO_3 + NaIO_4$. The RuO_4 could not oxidize the components in this solution and the Ru remained quantitatively in the organic phase for at least 16 hours.

Methods were also developed for the quantitative determinations of Pd and Pt in iron meteorites. This required a rather severe oxidative attack, entailing successive additions of aqua regia and of H_2O_2 and boiling to dissolve all of the Pd and Pt, and finally fuming the solution with HCl to remove all traces of NO_3^-. The two metals were concentrated into methylisobutyl ketone (MIBK) as the iodocomplexes $[PdI_4]^{2-}$ and $[PtI_6]^{2-}$ after the removal of Fe(III) and other elements as extractable chlorocomplexes into MIBK. There is no detectable extraction of Pd and Pt as chlorocomplexes.

All three elements were determined using the technique of graphite furnace atomic absorption spectrometry with careful selection of instrumental parameters. Very low concentrations of Ru, Pd and Pt may be quantified by making use of the automated multiple-loading capacity of the instrument. Actual limits of detection can be lowered if required by increasing the total volume of the charge placed in the furnace. The smallest absolute detection limits that were necessary in this study were 0.5 ng for Ru, 0.5 ng for Pd and 5 ng for Pt.

The developed methods are rapid, sensitive and relatively inexpensive and allow for the routine determination of these elements in iron meteorites. By a fortunate coincidence, INAA (which was the instrumental technique utilized by TARC) is capable of determining Os, Ir and Rh, but not Ru, Pd and Pt. The two techniques of GFAAS and INAA complemented each other perfectly for the quantification of all PGMs in iron meteorites.

It was possible to detect ng amounts of Tl in the metal phase of the Toluca (IAB) iron meteorite, and though it is not likely that this chalcophilic element would be helpful for the classification of iron meteorites, the method utilized may be of use in the calculation of partition coefficients for Tl between the metal (Fe/Ni--kamacite and taenite) and the sulfide (FeS--troilite) phases.

Attempts were made to develop a reliable method for the determination of Ga using the GFAAS technique. This was not possible, as Ga could not be completely separated from Fe using solvent extraction methods. Iron causes the suppression of the Ga absorbance signal. No single method is suitable for determination of all elements, as shown in the complementary capabilities of GFAAS and INAA for the quantification of the PGMs. Unfortunately, Ga cannot yet be determined by either of these methods with good and acceptable precision.

Sampling of the iron meteorites proved to be a problem, especially for the determination of Ni. The presence of two phases of Fe-Ni alloy with large differences in metal content means that iron meteorites have to be sampled for analysis with a knowledge of their metallographic structures. In addition, samples were donated to the BMMRU as small (1-10 g) slugs or turnings and there was no guarantee that the pieces received were truly representative.

A procedure was developed to ensure the most representative sample possible from the 1-10 g pieces. The surfaces of the meteorites that were free from fusion crust were etched with a 5% nital solution (Appendix 4) to reveal the Widmanstätten pattern or Neumann bands. The specimen was sawn across or through the patterns. If possible, a piece of approximately 2 g was sent to TARC, and the remainder was reserved for any necessary replicate analyses and for display. The sawings were reserved for use in the determinations for Ru, Pd and Pt. These are normally discarded because of the possible contamination from the hacksaw blade for some elements. However, determination of Ru, Pd and Pt in clean pieces and in sawings showed no detectable difference in the apparent concentrations of these elements. In addition to reducing wastage of rare samples, the sawings were easier to weigh and digest and probably were as representative as was possible of the small samples donated to the BMMRU.

The procedures developed in the methodology section were then applied to all irons received by the BMMRU purported to be meteorites. The resulting pool of PGM data allowed recognition of fraudulent specimens and their exclusion from statistical treatment of the data.

The statistical procedures included calculation of correlation coefficients and the application of principal components and discriminant analysis programs. Along with the visual inspection of binary plots, the statistical programs revealed a few problems with the classification scheme and the generalizations associated with acceptance of the scheme, including:

1) Justification for combination of groups and discussions on the shapes of the group field;

2) Highlighting poor fits of some meteorites within their groups and discussion towards the relabelling or reclassification of these members;

3) The incorrect assumption that Pd and (by inference) Ni are volatile elements with respect to their supposed behavior in the primeval nebula during the formation of our solar system. Their behavior is refractory in iron meteorites, as judged by their parallel abundance patterns.

In addition, evidence was examined for the pairing of some meteorites and the following pairings are recommended based on chemical and morphological evidence:

1) Lamesa with Carlton (IIICD)
2) Paneth's Iron with Coopertown (IIIE)
3) Onnum Valley and Derrick Peak CM66 with the Derrick Peak (AN?) shower
4) MGS G2011 and Railway with Gibeon (IVA)
5) Hanau Harbor with Cañon Diablo (IAB)

The following specimens are mislabelled irons whose origins are not yet known. No conclusions can be drawn about their potential pairings with established meteorites, or whether they represent completely separate falls:

1) RB"1950"--purported to be Cape of Good Hope (IVB)
2) UCLA1026B--purported to be Jaralito (IAB-IIICD)
3) USNM1780--purported to be Zacatecas "1969" (IIIB)
4) FMNH--purported to be Chupaderos (IIIB)

It is important to determine as many elements as possible in iron meteorites. Lack of sufficient data for the PGMs have led to generalizations of their individual behaviors based on Ir abundances as Ir is the only PGM routinely and unfailingly determined in irons. The PGM values reveal that the classification scheme for iron meteorites is generally sound. These values also allow for some insights into the assignments of individual specimens into groups, as well as of their modes and conditions of formation.

XII.2. Recommendations for Further Research

Towards the use of the methods developed here and towards the better understanding of iron meteorites, I consider that further work is needed along the following lines:

1) I suspect that there is a critical amount of sample needed for a given structural type of iron meteorite to accomplish an accurate determination of Ni. A relationship should be sought between bandwidth and/or presence of kamacite crystals and the amount of sample required for a reliable value of Ni to be obtained.

2) Thallium should be determined in iron meteorites. I believe the method used for the Toluca(IAB) sample could also be used to quantify Tl in stony meteorites and in troilite nodules.

3) Rhodium is very easily determined using the GFAAS technique, with a sensitivity at least as good as for Pt. A method should be sought for the determination of Rh using such a technique as a more sensitive alternative to INAA.

4) Use of the methods developed here for Ru, Pd and Pt should be applied to the determination of the elements in other samples, including sediments, ores, doped steels and alloys, plants and biological tissues. The current market prices of the PGMs indicate that even low-grade ores (PGM content in the ppm and ppb range) may soon be mined lucratively. These analytical methods can be used as an aid to prospecting and recovery studies. Electrical and metallurgical engineering require accurate determinations of the PGM content as do clinical laboratories because the PGMs (Pt in particular) are the basis of several effective anti-cancer complexes.

5) The determination of Ru is limited in that the severe oxidative attack often needed to bring silicates, ores and biological tissues into

solution cannot be used. Alternative digestion procedures need to be developed so that the Ru will not oxidize and volatilize as RuO_4. The same problems with volatility also apply to Os.

6) A method for the determination of Ga by GFAAS should be sought, ie.--a method must be developed for the hitherto unattainable quantitative separation of Ga(III) and Fe(III) in the relative quantities found in iron meteorites.

7) The quantification of Os for this project was accomplished using the INAA technique. The LOD for Os by INAA is >0.20 μg/g, meaning that 42 iron meteorites were not satisfactorily analyzed for Os in this study. The GFAAS technique cannot yet be used for the effective determination of Os. Radiochemical NAA and ICP-MS are so far the only methods available for determining minute quantities of Os effectively. Cheaper and more accessible methods should be sought.

8) Further negotiations must be entered into to acquire more samples of the rare iron meteorite groups IIICD, IIF, IIE and IIC in order to better establish their PGM contents and trends. In addition, more ungrouped irons should be sought in an attempt to find members of low-Ni IIICD or intermediate members of IIIF. These ungrouped irons could also potentially be similar to each other. Five such similar ungrouped irons would justify the establishment of a new group.

9) In order to more firmly establish mislabellings and pairings, the homogeneity of the PGMs within any given meteorite body or group must be established. The pairings proposed here are based on the similarities of abundances within analytical errors. Other potential pairings would be revealed if the limits of the distribution of many different elements, including the PGMs, were known. Evidence of some variation was revealed in the Cape York Agpalilik (IIIAB) mass by Esbensen *et al.* (1982) but not in the Armanty (IIIE) mass by Wasson *et al.* (1988), indicating that homogeneity within masses is variable for different groups. This research

could be done by acquiring samples from within one large mass, or with individual members of a single established meteorite shower.

10) Other elements not yet determined in iron meteorites should be studied. It is likely that other elements will not make a difference to the presently accepted classification scheme, but they may classify the iron meteorites more clearly, or at least separate some groups (such as low-Ni IIICD and low-Ni IAB) from each other more completely and thus more convincingly.

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Appendices

APPENDIX 1. Meteorites, BMMRU catalogue numbers, their sources (and their catalogue numbers) and data used in this study. Meteorites arranged alphabetically within in each group. All values in µg/g except for Ni. Values for Ni, Ga, Ge from Wasson (1974) and Grahame *et al.* (1985). unless indicated in the text.

Source abbreviations:

AMNH	American Museum of Natural History, New York, New York, USA
AS	Academy of Science, Moscow, USSR
AUSM	Australian Museum, Sydney, Australia
BMNH	British Museum (Natural History), London, UK
CM	Canterbury Museum, Christchurch, New Zealand
CMS	American Meteorite Center (Center for Meteorite Studies) Tempe, USA
EDM	Ecole des Mines, Paris, France
FMNH	Field Museum of Natural History, Chicago, USA
GSC	Geological Survery of Canada, Ottawa, Canada
HBG	Hubei Provincial Bureau of Geology & Mineral Resources, Hubei, China
IFM	Instituttet Fur Metallære, Lyngby, Denmark
IGG	Institute of Geochemistry, Guiyang, China
MGS	Museum of the Geological Survey, Pretoria, South Africa
MOV	Museum of Victoria, Melbourne, Australia
NZGS	New Zealand Geological Survey, Lower Hutt, New Zealand
PPS	Paul P. Sipiera
RB	Rainer Bartoschewitz
SAM	South Australian Museum, Adelaide, Australia
QM	Queensland Museum, Brisbaine, Australia
UCLA	University of California at Los Angeles, Los Angeles, USA
UNMx	University of New Mexico, Albuquerque, USA
UW	University of Waikato, Hamilton, New Zealand
WAM	Western Australia Museum, Perth, Australia
WZ	Walter Zeitschel

Legend:

⋈	Paired with each other (Hanau Harbor is the result of a fraud and does not exist)
🤖	Mislabelled specimen
Ÿ	Paired with each other and possibly misclassified into subgroup IIB
🖥	Probably paired with each other
‡	In the course of this work, these meteorites were reclassified from group IIICD to group IAB
¤	Probably paired with each other
✱	Probably paired with each other
○	Listed with the ungrouped irons as no firm classification exists for this meteorite
🕯	Badly corroded specimen--results therefore not reliable

APPENDIX 1 (Continued)

	BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	Ru	Os	Ir	Rh	Pd	Pt
IA	88	Annaheim	GSC-0116-4	7.74	79.8	3.5	1.40	10.3	0.696	3.05	2.76	1.66	5.18	5.76
	3	Campo del Cielo	AMNH-3957	6.62	90.0	392	1.59	9.08	5.12	4.62	3.15	2.39	3.33	8.64
	6	Cañon Diablo ⧓	USNM	7.0	81.8	324	1.52	10.1	5.24	2.13	2.01	2.00	4.40	6.20
	2	Coolac	MOV-E4957	7.40	91.5	423	1.27	8.02	5.90	0.24	2.02	1.70	4.10	8.30
	8	Copiapo	USNM	7.01	69.8	252	1.66	11.7	2.91	2.90	2.43	1.65	3.84	6.10
	5	Dunganville	NZGS	6.90	79.7	330	0.80	4.04	6.03	<0.20	1.81	1.86	3.45	9.48
	94	Gladstone #2	QM	7.53	93.7	418	1.61	9.60	5.88	3.69	2.80	1.62	3.66	7.54
	70	Hanau Harbor ⧓	WZ	7.5	---	299	1.50	11.6	5.16	1.70	1.90	1.90	4.24	6.31
	89	Mayerthorpe	GSC-1327-3	7.19	75.5	283	1.53	10.8	4.01	0.78	1.76	1.69	3.78	6.50
	1	Odessa	PPS	7.20	74.7	285	1.25	9.25	4.29	1.83	1.60	1.06	4.21	5.67
	131	Tassajara	AMC	8.10	---	300	1.26	10.0	4.12	1.51	1.53	1.25	4.96	4.22
	67	Toluca	FMNH	8.07	70.6	246	2.06	11.5	2.96	<0.20	2.22	1.28	5.56	4.84
	157	Youndegin	MOV-E11613	6.38	90.8	383	1.47	8.99	4.71	1.49	1.62	1.39	3.24	6.86
IB	73	Bitburg	USNM	12.4	34.8	140	1.95	20.0	2.41	<0.20	1.26	0.55	5.93	1.92
	72	Colfax	USNM	10.82	52.8	153	1.65	14.4	1.99	2.16	1.08	1.06	4.78	1.73
	9	Four Corners	USNM-728	8.90	48.7	179	1.08	9.47	3.36	1.60	1.21	0.63	4.68	7.18
	8	Mesa Verde Park	USNM-649	10.56	53.0	142	1.20	9.46	1.60	1.69	1.24	0.63	4.36	6.34
	7	Woodbine	USNM	10.60	36.7	114	1.84	15.9	2.28	2.01	1.68	0.83	7.72	2.49

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	Ru	Os	Ir	Rh	Pd	Pt
IC 49	Arispe	GSC-2638	6.54	50.3	243	0.88	5.72	9.99	5.26	7.98	2.71	2.36	19.8
75	Bendegó	USNM	6.39	54.0	234	0.81	4.65	6.79	<0.20	0.16	3.13	2.12	13.0
76	Chihuahua City	FMNH	6.68	52.7	212	1.04	6.62	3.39	<0.20	0.08	2.73	2.96	5.76
144	Etosha	MGS	6.85	48.9	217	0.93	5.79	3.35	<0.20	0.09	1.57	2.55	5.12
83	Mount Dooling	WAM	6.26	52.0	234	0.58	3.41	9.60	0.55	0.88	2.38	1.96	17.8
160	Murnpeowie	MOV	6.42	41.8	85.4	0.59	3.48	6.76	0.97	1.67	2.02	2.42	11.8
74	Santa Rosa	USNM	6.63	50.6	222	1.03	9.54	3.49	<0.20	0.09	3.49	2.72	4.86
77	St. François Co.	FMNH	6.77	49.2	217	0.83	5.12	1.67	<0.20	0.12	1.67	2.96	8.98
IIA 10	Coahuila	USNM	5.49	57.6	178	0.540	4.50	27.8	9.78	12.9	2.99	1.92	26.4
123	Forsyth County	AMNH-39	5.50	60.8	176	0.485	2.71	25.6	32.6	28.9	3.11	1.72	35.4
124	Gressk	AMNH-3862	5.61	62.1	177	0.540	3.12	18.2	2.41	5.18	2.96	2.07	21.2
125	Hex River Mtn.	AMNH-753	5.59	60.7	181	0.496	2.98	12.9	1.20	2.63	2.75	2.42	19.4
50	North Chile	CMS-1325	5.59	58.9	177	0.582	3.18	20.0	<0.20	2.67	2.75	2.63	23.1
145	Okahandja	MGS	5.74	56.3	186	0.466	2.66	16.0	3.78	7.62	2.43	1.88	26.4
126	Sierra Gorda	AMNH-3779	5.27	57.4	170	0.385	2.47	24.9	33.5	28.2	2.88	1.75	32.2
13	Tocopilla	MOV-E11105	5.54	58.6	176	0.548	3.18	24.0	0.98	2.49	2.46	1.74	20.7

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	Ru	Os	Ir	Rh	Pd	Pt
IIB 15	Bilibino	WZ	5.80	---	95.9	0.832	5.39	7.29	<0.20	0.075	2.18	1.94	8.72
17	Derrick Peak Ÿ 78012	UW	6.64	---	160	3.94	<0.20	3.94	<0.20	<0.01	2.45	3.32	2.84
127	Derrick Peak Ÿ	CM-66	7.0	---	162	---	---	3.91	---	---	---	2.46	2.26
23	El Burro	USNM-1345	5.95	58.1	167	0.585	3.80	4.24	<0.20	0.03	1.49	2.24	9.04
21	Mount Joy	AMNH-2516	5.68	59.1	183	0.820	6.05	7.29	<0.20	0.38	2.98	3.03	8.94
128	Onnum Valley Ÿ	CM	7.0	---	159	---	---	3.24	---	---	---	3.18	2.32
14	Santa Luzia	USNM-772	6.3	47.9	110	0.846	6.90	1.57	<0.20	0.014	2.06	3.62	0.801
69	São Julião de de Moreira	WZ	6.1	46.2	107	1.13	7.56	1.95	<0.20	<0.006	1.37	3.08	1.02
22	Sikhote-Alin	MOV-E11171	5.87	51.8	161	0.975	6.44	3.86	<0.20	0.016	2.21	3.36	3.50
IIC 99	Ballinoo	FMNH	8.32	39.0	94.4	1.18	13.3	8.32	12.1	8.65	2.99	4.13	15.0
82	Kumerina	WAM	8.33	36.8	93.4	0.796	5.46	8.33	8.71	6.87	1.57	4.22	15.5
24	Perryville	USNM-428	8.18	37.0	88.0	0.632	3.72	8.18	0.51	7.18	5.70	3.81	15.6
IID 28	Arltunga	MOV-E4883	9.64	77.1	83.1	0.531	6.72	11.9	27.4	17.1	2.63	2.84	20.2
25	Carbo	FMNH	10.2	70.0	87.2	0.494	1.94	10.8	13.6	9.68	1.46	3.22	21.1
100	Needles	FMNH	10.3	77.2	92.7	1.06	7.77	7.01	3.91	3.38	2.33	4.31	12.4
95	Puquios	GSC-1609-1	10.1	77.0	87.9	0.810	4.30	9.33	19.1	14.4	1.69	2.61	22.5
79	Rodeo	GSC-1802-1	10.2	82.1	93.0	0.791	5.59	8.10	7.38	6.20	1.90	4.54	15.2
26	Wallapai	USNM-1444	11.3	82.9	98.3	1.23	8.36	6.12	2.90	2.40	1.75	4.14	12.5

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	
			Ru	Os	Ir	Rh	Pd	Pt
IIE27	Arlington	USNM-3281	8.42	21.9	64.9	1.51	14.6	
			5.20	9.48	6.50	1.67	4.63	12.6
101	Weekeroo Station	FMNH	7.51	27.4	67.0	0.81	5.7	
			2.56	1.60	2.10	1.69	2.96	10.3
IIF158	Corowa	MOV	13.13	10.1	159	1.82	13.1	
			1.73	1.91	0.68	2.05	6.65	5.72
IIIA31	Cape York--Agpalilik	IFM	7.58	19.2	36.0	---	---	
			1.61	---	---	---	3.42	11.4
32	Cape York--Woman	AMNH-2632	7.58	19.2	36.0	---	---	
			10.3	3.44	3.73	1.67	2.83	14.6
78	Chambord	GSC-0331-3	7.53	18.4	35.0	0.476	2.70	
			8.60	10.1	8.53	1.82	2.72	15.3
33	Henbury	CMS-19314	7.47	17.7	33.7	0.474	2.18	
			10.2	16.0	11.0	2.11	4.44	17.0
12	Kyancutta	MOV-E4911	8.06	19.9	39.5	0.677	3.64	
			6.08	0.54	1.26	1.64	3.10	11.4
91	Madoc	GSC-1301-4	7.52	19.4	36.4	0.600	4.57	
			10.9	5.19	5.76	2.20	2.77	18.3
90	Merceditas	GSC-1309-2	7.82	19.5	38.9	0.687	3.50	
			10.2	2.30	3.34	2.29	2.89	14.0
95	Moorumbunna	SAM-G-7942A	8.98	21.7	44	1.20	10.3	
			2.66	<0.20	0.20	0.82	5.52	6.62
152	Red Rock	UCLA-LC1071H	7.71	21.6	41.8	0.70	4.04	
			3.74	0.57	1.45	1.62	3.19	8.08
87	Trenton	GSC-2010-3	8.34	20.8	44.5	0.957	5.42	
			7.56	1.78	2.38	2.17	3.66	10.9
29	View Hill	CM-22	8.87	21.0	42.6	1.54	9.09	
			2.34	<0.20	0.25	1.33	2.52	5.65
30	Waingaromia	CM-36	9.14	20.9	41.6	1.48	9.67	
			2.62	<0.20	0.28	1.79	4.45	7.58
86	Welland	GSC-2304-2	8.77	21.0	46.7	1.27	7.76	
			3.03	0.48	0.30	1.83	5.65	7.89

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.		%Ni	Ga	Ge	Au	As
			Ru	Os	Ir	Rh	Pd	Pt
IIIB109	Apoala	FMNH		9.39	18.4	35.7	2.11	14.9
			0.82	<0.20	0.02	1.22	7.26	2.38
107	Bella Roca	FMNH		10.1	16.7	31.1	2.47	18.6
			0.89	<0.20	0.012	1.45	8.10	1.42
153	Buenaventura	UCLA-LC947J		9.92	17.4	34.5	2.19	14.9
			1.16	<0.20	0.010	0.21	5.98	2.19
35	Campbellsville	USNM-2572		8.65	20.4	43.8	1.28	8.02
			2.47	<0.20	0.06	1.61	5.10	4.30
110	Chupaderos	FMNH		---	---	---	1.70	14.0
			3.14	2.72	2.14	1.44	3.88	5.34
111	Cleveland	FMNH		8.85	21.0	41.9	1.48	10.0
			1.62	<0.20	0.09	1.98	5.58	3.56
112	El Capitan	FMNH		8.56	21.5	45.1	1.09	7.34
			3.17	<0.20	0.094	1.90	4.82	4.14
105	Grant	FMNH		9.24	19.8	37.0	2.11	14.9
			1.63	<0.20	0.06	1.70	6.22	2.14
106	Los Reyes	FMNH		8.71	20.9	40.7	1.64	11.0
			1.76	<0.20	0.12	1.92	4.80	3.37
108	Luis Lopez	FMNH		8.64	20.1	41.9	1.38	9.44
			2.75	<0.20	0.15	2.60	4.54	4.54
34	Owens Valley	AMNH-4480		8.53	21.5	45.9	1.40	8.98
			2.82	<0.20	0.14	1.64	6.54	4.68
81	Sam's Valley	GSC-1904-1		9.77	18.4	35.1	2.19	14.9
			0.82	<0.20	0.004	1.16	7.15	1.78
36	Zacatecas	USNM-1780		---	---	---	0.638	4.38
			8.62	0.40	1.46	2.04	3.66	37.0

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	
			Ru	Os	Ir	Rh	Pd	Pt
IIICD37	Carlton 💻	AMNH-3851	13.0	11.4	8.5	1.76	19.2	
			0.098	<0.20	0.08	0.36	15.2	0.104
4	Cranbourne ‡	MOV-E12227	6.8	85.4	358	1.27	8.49	
			3.77	1.79	1.43	1.21	6.97	5.04
38	Dayton	USNM-1592	17.0	5.16	3.52	1.74	19.2	
			0.073	<0.20	0.02	0.30	16.4	0.071
151	Jaralito 🤖	USNM-LC1026B	5.0	--	254	1.30	7.07	
			2.20	0.71	0.976	1.55	3.84	5.06
113	Lamesa 💻	WZ	13.7	13.3	11.8	1.75	6.67	
			0.105	0.53	0.36	0.30	14.4	0.106
102	Mungindi	FMNH	11.5	19.4	22.1	1.74	17.2	
			0.361	0.49	0.54	0.49	12.2	0.38
116	Nantan ‡	IGG	6.8	77	293	1.81	12.6	
			3.67	1.75	1.78	2.69	6.76	4.59
IIIE149	Burlington	USNM-978	8.15	16.9	34.9	0.57	2.88	
			6.50	<0.20	0.30	1.27	7.72	10.8
104	Cachiyuyal	FMNH	7.88	16.9	30.3	0.51	3.33	
			6.28	1.19	2.11	2.00	3.50	11.0
120	Coopertown ¤	AMNH-101	8.47	17.0	34.9	0.66	5.12	
			4.42	<0.20	0.47	1.90	3.96	9.24
156	Kokstad (Matatiele)	UCLA-LC900	8.32	17.7	34.4	0.54	2.68	
			2.60	<0.20	0.36	1.34	3.52	9.25
115	Paneth's Iron ¤	BMNH-47192	8.98	16.9	34.1	0.71	4.15	
			4.36	<0.20	0.29	2.15	4.12	8.86
114	Staunton	BMNH-44761	8.21	18.9	36.6	0.67	4.03	
			2.57	<0.20	0.07	1.76	3.40	6.52
39	Willow Creek	USNM-900	8.76	16.9	36.4	0.998	5.12	
			3.56	<0.20	0.05	1.54	3.17	6.11

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	Ru	Os	Ir	Rh	Pd	Pt
IIIF40	Clark County	USNM-1304	6.79	6.92	1.11	0.231	0.793	5.03	5.69	4.18	0.88	2.49	10.6
151	Klamath Falls	UNMx	8.50	6.79	0.701	2.80	16.7	0.989	<0.20	<0.004	4.02	6.24	0.946
97	Moonbi	AUSM-DR1253	7.70	6.84	0.831	0.688	5.42	4.11	0.69	1.12	1.28	3.67	7.76
103	Nelson County	FMNH	7.02	6.33	0.92	0.25	1.36	5.42	8.98	6.25	1.05	2.82	10.9
121	St. Genevieve Co.	AMNH-66	7.68	6.86	0.781	0.462	2.90	3.60	1.11	1.19	3.06	3.02	8.90
IVA41	Gibeon *	CMS-5065a	7.68	1.97	0.111	3.70	2.43	3.70	2.43	1.86	1.16	3.32	6.72
132	Guanghua	HBGM	7.70	1.71	0.091	0.72	1.74	2.47	3.69	2.70	1.22	2.76	4.59
122	Huizopa	AMNH-2232	7.48	2.22	0.118	0.67	1.93	2.82	1.55	1.62	1.13	3.39	6.96
96	Mount Sir Charles	SAM-G5994E	6.80	2.32	0.126	1.39	5.80	2.93	2.23	1.51	1.61	4.26	6.28
147	--- *	MGS-G2011	---	---	<0.03	0.983	3.86	2.01	2.25	1.88	0.97	4.30	6.58
143	Railway *	MGS	7.82	1.99	0.119	0.715	2.25	1.90	2.08	1.53	0.80	4.76	8.16
42	Steinbach	USNM	9.08	2.27	0.132	2.06	8.49	1.98	0.41	0.56	0.95	5.80	5.38
155	Yanhuitlan	UCLA-LC60	7.49	1.75	0.105	0.67	2.04	2.07	3.14	2.43	0.92	3.74	5.28

APPENDIX 1 (Continued)

BMMRU Cat. No.	Meteorite	Source Cat. No.	%Ni	Ga	Ge	Au	As	
			Ru	Os	Ir	Rh	Pd	Pt
IVB138	Cape of Good Hope 🤖	RB	---	---	<0.01	1.97	18.8	
			2.81	<0.20	0.018	1.13	4.38	2.98
92	Hoba	GSC-0811-2	16.56	0.192	0.047	0.078	0.6	
			13.0	43.0	23.8	4.94	5.15	80.6
137	Iquique	RB	16.03	0.170	0.051	0.081	0.64	
			20.0	41.3	24.4	2.99	4.81	86.4
84	Skookum Gulch	GSC-1916-3	17.12	0.272	0.057	0.135	1.07	
			21.4	19.3	14.0	5.33	14.9	38.3
43	Tlacotepec	AMNH-2640	15.82	0.195	0.031	0.057	0.478	
			8.85	52.3	26.4	5.90	8.59	39.2
159	Warburton Range	MOV	17.80	0.244	0.064	0.165	0.66	
			9.92	12.5	10.3	3.66	12.4	30.6
44	Weaver Mountains	CMS-313	16.81	0.233	0.058	0.112	---	
			11.2	18.9	13.0	4.67	11.0	29.5
Anomalous								
146	Bellsbank	MGS	4.13	39.2	54.6	0.708	7.55	
			<0.001	<0.02	0.049	0.501	2.78	0.344
129	Butler	CM-11	15.5	87.1	1970	6.30	36.0	
			26.8	<0.20	1.24	17.4	16.9	48.6
142	De Hoek	MGS	9.95	0.236	0.079	0.397	0.560	
			0.241	0.27	0.166	<0.20	2.14	1.92
154	Denver City	UCLA-LC951C	8.40	1.03	0.5	0.419	2.08	
			4.35	3.20	2.95	1.15	4.00	7.44
80	Gay Gulch	GSC-0701-1	15.06	6.68	10.7	3.09	23.7	
			2.29	<0.20	0.08	1.17	12.6	3.40
93	Glenormiston	QM	7.45	16.9	79.4	1.09	8.06	
			8.55	3.10	3.03	1.85	5.56	11.0
162	Lonaconing	EDM	9.7	23.5	62.1	2.08	25.4	
			3.08	0.682	0.530	0.95	4.79	1.61
51	Mundrabilla ◇	CMS-1022s	7.72	59.5	190	1.76	12.5	
			2.88	<0.20	0.81	1.56	4.56	4.20
130	Santa Catharina 🕯	CM-7	33.6	5.28	8.94	5.24	44.0	
			0.482	---	0.020	---	44.2	0.461

APPENDIX 2 Abundance data for iron meteorites, compared to literature values for the same meteorites (Iron meteorites arranged alphabetically within a group)

APPENDIX 2a: Ruthenium

BMMRU Catalog Number	Meteorite	Abundance (μg/g)		Reference
		This Work	Literature	
IA				
88	Annaheim	0.696	6.3	Sen Gupta,1968
3	Campo del Cielo	5.12	8.1	Crocket,1972
6	Cañon Diablo	5.24	5.7	Pernicka&Wasson,1987
			5.2	Crocket,1972
			6.4	Nichiporuk&Brown,1965
			5.9	Hara&Sandell,1960
			5.37	Hermann *et al.*,1971
			3.46	Bate&Huizinga,1963
2	Coolac	5.90		
68	Copiapo	2.91		
5	Dunganville	6.03		
94	Gladstone#2	5.88		
89	Mayerthorpe	4.01		
1	Odessa	4.29	4.7	Pernicka&Wasson,1987
			6.0	Nichiporuk&Brown,1965
			4.94	Hermann *et al.*, 1971
131	Tassajara	4.12		
67	Toluca	2.96	5.3*	Nichiporuk&Brown,1965
			6.70*	Seitner *et al.*, 1971
157	Youndegin	4.71	6.1	Crocket,1972
IB				
73	Bitburg	2.41		
72	Colfax	1.99	2.1	Crocket,1972
9	Four Corners	3.26		
8	Mesa Verde Park	1.60		
7	Woodbine	2.28	2.49	Pernicka&Wasson,1987

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* These analyses were probably performed on Paneth's Iron (See Section X.3.iv)

APPENDIX **2a** (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g)		Reference
		This Work	Literature	
IC				
49	Arispe	9.99	13.7	Nichiporuk&Brown,1965
			10.0	Hara&Sandell,1960
75	Bendegó	6.79	8.5	Crocket,1972
			11.9	Nichiporuk&Brown,1965
76	Chihuahua City	3.39		
144	Etosha	3.35		
83	Mount Dooling	9.60		
160	Murnpeowie	6.76		
74	Santa Rosa	3.80		
77	St. François County	5.74		
IIA				
10	Coahuila	27.8	25.4	Pernicka&Wasson,1987
			23.7	Nichiporuk&Brown,1965
			23.40	Seitner *et al.*, 1971
			26.60	Seitner *er al.*, 1971
123	Forsyth County	25.6		
124	Gressk	18.2		
125	Hex River Mountain	12.9		
50	North Chile	20.0	19.3	Pernicka&Wasson,1987
145	Okahandja	16.0		
126	Sierra Gorda	24.9		
13	Tocopilla	24.0		
IIB				
15	Bilibino	4.75		
17 Ÿ	Derrick Peak 78012	3.94		
127 Ÿ	Derrick Peak CM#66	3.91		
23	El Burro	4.24		
21	Mount Joy	7.29	9.1	Hara&Sandell,1960
			9.05	Hermann *et al.*, 1971
			9.05	Seitner *et al.*, 1971
128 Ÿ	Onnum Valley	3.24		
14	Santa Luzia	1.57		
69	São Julião de Moreira	1.95	1.4	Crocket,1972
			0.92	Herman *et al.*, 1971
22	Sikhote-Alin	3.86	5.0	Nichiporuk&Brown,1965
			5.7	Yavnel,1950

Ÿ Paired with each other and misclassified as IIB (See Sections X.3.ii. and XI.1.ii.)

APPENDIX 2a (Continued)

BMMRU Catalog Number	Meteorite	Abundance (μg/g)		Reference
		This Work	Literature	
IIC				
99	Ballinoo	8.32	12	Crocket,1972
82	Kumerina	8.33		
24	Perryville	8.18		
IID				
28	Arltunga	11.9		
25	Carbo	10.8	14.5	Pernicka&Wasson,1987
			52.4	Herr *et al.*,1958
100	Needles	7.01	9.6	Pernicka&Wasson,1987
85	Puquios	9.33	17	Crocket,1972
79	Rodeo	8.10	11.9	Pernicka&Wasson,1987
26	Wallapai	6.12	8.3	Pernicka&Wasson,1987
IIE				
27	Arlington	5.20		
101	Weekeroo Station	2.56		
IIF				
158	Corowa	1.73		
IIIA				
31	Cape York-Agpalilik	1.61		
32	Cape York-Woman	10.3		
--	Cape York-Savik	--	12	Crocket,1972
78	Chambord	8.60		
33	Henbury	10.2	11.7	Pernicka&Wasoon,1987
			6.0	Nichiporuk&Brown,1965
			3.6	Hara&Sandell,1960
			5	SenGupta&Beamish,1963
			86.4	Hermann *et al.*,1971
12	Kyancutta	6.08		
91	Madoc	10.9	11.5	Sen Gupta,1968
90	Merceditas	10.2		
95	Moorumbunna	2.66		
152	Red Rock	3.74		
87	Trenton	7.56	7.0	Pernicka&Wasson,1987
			9.4	SenGupta&Beamish,1963
29	View Hill	2.34		
30	Waingaromia	2.62		
86	Welland	3.00		

APPENDIX **2a** (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g)		Reference
		This Work	Literature	
IIIB				
109	Apoala	0.815		
107	Bella Roca	0.891	1.15	Pernicka&Wasson,1987
153	Buenaventura	1.16		
35	Campbellsville	2.47	2.85	Pernicka&Wasson
			3.3	Crocket,1972
110🤖	Chupaderos	3.14		
111	Cleveland	1.62		
112	El Capitan	3.17		
105	Grant	1.63	1.96	Pernicka&Wasson,1987
			2.0	SenGupta&Beamish,1963
106	Los Reyes	1.76		
108	Luis Lopez	2.75		
34	Owens Valley	2.82		
81	Sam's Valley	0.821	1.2	Crocket,1972
36🤖	Zacatecas 1969	8.62		
IIICD				
37	Carlton	0.098	0.103	Pernicka&Wasson,1987
			0.19	Crocket,1972
			0.23	Seitner *et al.*,1971
4 ‡	Cranbourne	3.77	5.8	Pernicka&Wasson,1987
38	Dayton	0.073	0.045	Pernicka&Wasson,1987
151🤖	Jaralito	2.20	6.0	Pernicka&Wasson,1987
113	Lamesa	0.105		
102	Mungindi	0.361	0.35	Pernicka&Wasson,1987
116 ‡	Nantan	3.67	5.4	Pernicka&Wasson,1987
IIIE				
149	Burlington	6.50		
104	Cachiyuyal	6.28		
120🖥	Coopertown	4.42		
156	Kokstad(Matatiele)	2.60		
115🖥	Paneth's Iron	4.36	5.3*	Crocket,1972
			5.3*	Nichiporuk&Brown,1965
			6.70*	Seitner *et al.*, 1971
114	Staunton	2.57	11.70	Seitner *et al.*, 1971
39	Willow Creek	3.56	3.6	Hara&Sandell,1960

🤖 Mislabelled specimens (See Section X.3.vi)

‡ Reclassified as IAB irons (See Section IX.4.v)

* Mistakenly analyzed as Toluca IAB (See Section X.3.iv)

🖥 Possibly paired (See Section X.3.iv)

APPENDIX 2a--Ru (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g) This Work	Abundance (µg/g) Literature	Reference
IIIF				
40	Clark County	5.03	5.9	Pernicka&Wasson,1987
161	Klamath Falls	0.989	0.96	Pernicka&Wasson,1987
97	Moonbi	4.11	6.2	Nichiporuk&Brown,1965
103	Nelson County	5.42	5.7	Pernicka&Wasson,1987
			6.30	Seitner *et al.*, 1971
121	St. Genevieve County	3.60	5.5	Pernicka&Wasson,1987
IVA				
41🖥	Gibeon	3.70	4.7	Nichiporuk&Brown,1965
132	Guanghua	2.47		
122	Huizopa	2.82		
96	Mount Sir Charles	2.93		
147🖥	MGS G2011	2.01		
143🖥	Railway	1.90		
42	Steinbach	1.98		
155	Yanhuitlan	2.07		
IVB				
138🤖	Cape of Good Hope	2.81		
92	Hoba	13.0		
137	Iquique	20.0		
84	Skookum Gulch	21.4	34.2	Sen Gupta,1968
43	Tlacotepec	8.85		
159	Warburton Range	9.92		
44	Weaver Mountain	11.2		
Anomalous				
146	Bellsbank	<0.001		
129	Butler	26.8	21.80	Seitner *et al.*,1971
142	De Hoek	0.241		
154	Denver City	4.35		
80	Gay Gulch	2.29		
93	Glenormiston	8.55		
162	Lonaconing	3.08		
51◇	Mundrabilla	2.88	3.16	Pernicka&Wasson,1987
130🧪	Santa Catharina	0.482	0.19	Crocket,1972

🤖 Mislabelled specimen (See section X.3.vi)

🧪 Sample thoroughly corroded--results are not reliable

◇ Listed here as no firm classification exists (See Section IX.4.vi)

🖥 Paired with each other (See Section X.3.iii)

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APPENDIX 2b: Palladium

BMMRU Catalog Number	Meteorite	Abundance (µg/g) This Work	Abundance (µg/g) Literature	Reference
IAB				
88	Annaheim	5.18	5.2	Sen Gupta,1968
3	Campo del Cielo	3.33		
6	Cañon Diablo	4.40	3.6	Smales *et al.*,1967
			2.71	SenGupta&Beamish,1963
			5.17	SenGupta&Beamish,1963
			3.6	Nichiporuk&Brown,1965
			3.98	Goldberg *et al.*,1951
2	Coolac	4.10		
68	Copiapo	3.84		
5	Dunganville	3.45		
94	Gladstone#2	3.66	2.4	Smales *et al.*,1967
89	Mayerthorpe	3.78		
1	Odessa	4.21	3.7	Nichiporuk&Brown,1965
			4.15	Goldberg *et al.*,1951
131	Tassajara	4.96		
67	Toluca	5.56	3.0*	Smales *et al.*,1967
			4.0*	Nichiporuk&Brown,1965
			4.72*	Goldberg *et al.*,1951
157	Youndegin	3.24	3.9	Smales *et al.*,1967
IB				
73	Bitburg	5.93		
72	Colfax	4.78	4.6	Smales *et al.*,1967
9	Four Corners	4.68		
8	Mesa Verde Park	4.36		
7	Woodbine	7.72		

* These analyses were probably performed on a sample of Paneth's Iron (See Section X.3.iv)

APPENDIX **2b**--Pd (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g) This Work	Abundance (µg/g) Literature	Reference
IC				
49	Arispe	2.36	2.4	Smales *et al.*,1967
			3.1	Nichiporuk&Brown,1965
			2.69	Goldberg *et al.*,1951
75	Bendegó	2.12	3.1	Smales *et al.*,1967
			2.7	Nichiporuk&Brown,1965
76	Chihuahua City	2.96		
144	Etosha	2.55		
83	Mount Dooling	1.96		
160	Murnpeowie	2.42		
74	Santa Rosa	2.72	2.4	Smales *et al.*,1967
77	St. François County	2.76		
IIA				
10	Coahuila	1.92	2.0	Smales *et al.*,1967
			2.0	Nichiporuk&Brown,1965
123	Forsyth County	1.72		
124	Gressk	2.07		
125	Hex River Mountain	2.42		
50	North Chile	2.63		
145	Okahandja	1.88		
126	Sierra Gorda	1.75		
13	Tocopilla	1.74	2.1	Smales *et al.*,1967
IIB				
15	Bilibino	1.94		
17 Ÿ	Derrick Peak 78012	3.32		
127 Ÿ	Derrick Peak CM#66	2.46		
23	El Burro	2.24		
21	Mount Joy	3.03		
128 Ÿ	Onnum Valley	3.18		
14	Santa Luzia	3.62		
69	São Julião de Moreira	3.08	2.6	Smales *et al.*,1967
22	Sikhote-Alin	3.36		

Ÿ Paired with each other and misclassified as IIB (See Section XI.1.ii)

APPENDIX 2b--Pd (Continued)

BMMRU Catalog Number	Meteorite	Abundance (μg/g)		Reference
		This Work	Literature	
IIC				
99	Ballinoo	4.13	3.8	Smales *et al.*,1967
82	Kumerina	4.22		
24	Perryville	3.81		
IID				
28	Arltunga	2.84		
25	Carbo	3.22		
100	Needles	4.31		
85	Puquios	2.61	3.5	Smales *et al.*,1967
79	Rodeo	4.54		
26	Wallapai	4.14		
IIE				
27	Arlington	4.63		
101	Weekeroo Station	2.96		
IIF				
158	Corowa	6.65		
IIIA				
31	Cape York--Agpalilik	3.42		
32	Cape York--Woman	2.83		
--	Cape York--Savik	--	2.5	Smales *et al.*,1967
78	Chambord	2.72		
33	Henbury	4.44	2.1	Smales *et al.*,1967
			2.2	SenGupta&Beamish,1963
			1.2	SenGupta&Beamish,1963
			3.4	Nichiporuk&Brown,1965
			2.02	Goldberg *et al.*,1951
12	Kyancutta	3.10		
91	Madoc	2.77	2.6	Sen Gupta,1968
90	Merceditas	2.89		
95	Moorumbunna	5.52		
152	Red Rock	3.19		
87	Trenton	3.66	6.6	SenGupta&Beamish,1963
29	View Hill	2.52		
30	Waigaromia	4.45		
86	Welland	5.65		

APPENDIX 2b--Pd (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g)		Reference
		This Work	Literature	
IIIB				
109	Apoala	7.26		
107	Bella Roca	8.10		
153	Buenaventura	5.98		
35	Campbellsville	5.10	3.8	Smales *et al.*,1967
110🤖	Chupaderos	3.88		
111	Cleveland	5.58		
112	El Capitan	4.82		
105	Grant	6.22	1.66	SenGupta&Beamish,1963
106	Los Reyes	4.80		
108	Luis Lopez	4.54		
34	Owens Valley	6.54		
81	Sam's Valley	7.15	4.7	Smales *et al.*,1967
36🤖	Zacatecas 1969	3.66		
IIICD				
37🖥	Carlton	15.2	6.7	Smales *et al.*,1967
4 ‡	Cranborne	6.97	4.8	Smales *et al.*,1967
38	Dayton	16.4		
151🤖	Jaralito	3.84		
113🖥	Lamesa	14.4		
102	Mungindi	12.2		
116 ‡	Nantan	6.76		
IIIE				
149	Burlington	7.72		
104	Cachiyuyal	3.50		
120🖥	Coopertown	3.96		
156	Kokstad(Matatiele)	3.51		
115🖥	Paneth's Iron	4.12	3.0* 4.0* 4.72*	Smales *et al.*,1967 Nichiporuk&Brown,1965 Goldberg *et al.*,1951
114	Staunton	3.40		
39	Willow Creek	3.17		

🤖 Mislabelled specimens (See section X.3.vi)

‡ Reclassified in the course of this work to group IAB (See section IX.4.v)

🖥 Possibly paired (See section X.3.i)

🖥 Possibly paired (See section X.3.iv)

* Data for Toluca--mistakenly performed on samples of Paneth's Iron IIIE (See section X.3.iv)

APPENDIX 2b--Pd (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g) This Work	Abundance (µg/g) Literature	Reference
IIIF				
40	Clark County	2.49	2.7	Smales *et al.*,1967
161	Klamath Falls	6.24		
97	Moonbi	3.67	3.9 3.5	Smales *et al.*,1967 Nichiporuk&Brown,1965
103	Nelson County	2.82		
121	St. Genevieve County	3.02		
IVA				
41🖥	Gibeon	3.32	3.5	Smales *et al.*,1967
132	Guanghua	2.76		
122	Huizopa	3.39	3.6 4.8	Smales *et al.*,1967 Nichiporuk&Brown,1965
96	Mount Sir Charles	4.26		
147🖥	MGS G2011	4.30		
143🖥	Railway	4.76		
42	Steinbach	5.80		
155	Yanhuitlan	3.74		
IVB				
138🤖	Cape of Good Hope	4.38	4.1 7.07	Nichiporuk&Brown,1965 Goldberg *et al.*,1951
92	Hoba	5.15	6.6	Smales *et al.*,1967
137	Iquique	4.81		
84	Skookum Gulch	14.9	13.2	Sen Gupta,1968
43	Tlacotepec	8.59		
159	Warburton Range	12.4		
44	Weaver Mountains	11.0		
Anomalous				
146	Bellsbank	2.78		
126	Butler	16.9		
142	De Hoek	2.14		
154	Denver City	4.00		
80	Gay Gulch	12.6		
93	Glenormiston	5.56		
162	Lonaconing	4.79		
51◇	Mundrabilla	4.56		
130🧪	Santa Catharina	44.2	19.7	Smales *et al.*,1967

🤖 Mislabelled specimen (See section X.3.vi)

🧪 Sample thoroughly corroded--result not reliable

◇ Listed here as no firm classification apparent (See section IX.4.vi)

🖥 Paired with each other (See section X.3.iii)

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APPENDIX 2c: Platinum

BMMRU Catalog Number	Meteorite	Abundance (µg/g)		Reference
		This Work	Literature	
IA				
88	Annaheim	5.76	3.35	Sen Gupta,1968
3	Campo del Cielo	8.64	9.7	Crocket,1972
6	Cañon Diablo	6.20	5.8	Pernicka&Wasson,1987
			5.17	SenGupta&Beamish,1963
			1.86	SenGupta&Beamish,1963
			7.4	Nichiporuk&Brown,1965
			8.0	Crocket,1972
			5.7	Baedecker&Ehmann,1965
2	Coolac	8.30		
68	Copiapo	6.10		
5	Dunganville	9.48		
94	Gladstone#2	7.54		
89	Mayerthorpe	6.50		
1	Odessa	5.67	5.5	Pernicka&Wasson,1987
			8.5	Nichiporuk&Brown,1965
131	Tassajara	4.22		
67	Toluca	4.84	6.5*	Nichiporuk&Brown,1965
157	Youndegin	6.86	11.5	Crocket,1972
IB				
73	Bitburg	1.92		
72	Colfax	1.73		
9	Four Corners	7.18		
8	Mesa Verde	6.34		
7	Woodbine	2.49	1.9	Pernicka&Wasson,1987
IC				
49	Arispe	19.8	17.2	Nichiporuk&Brown,1965
75	Bendegó	13.0	9.8	Nichiporuk&Brown,1965
			10.9	Crocket,1972
76	Chihuahua City	5.76		
144	Etosha	5.12		
83	Mount Dooling	17.8		
160	Murnpeowie	11.8		
74	Santa Rosa	4.86		
77	St. François County	8.98		

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* Mislabelled sample of Paneth's Iron analyzed (See Section X.3.iv)

APPENDIX 2c--Pt (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g)		Reference
		This Work	Literature	
IIA				
10	Coahuila	26.4	30.1	Pernicka&Wasson,1987
			24.2	Nichiporuk&Brown,1965
123	Forsyth County	35.4		
124	Gressk	21.2		
125	Hex River Mountain	19.4		
50	North Chile	23.1	23.0	Pernicka&Wasson,1987
145	Okahandja	26.4		
126	Sierra Gorda	32.2		
13	Tocopilla	20.7		
IIB				
15	Bilibino	8.72		
17 Ÿ	Derrick Peak 78012	2.84		
127 Ÿ	Derrick Peak CM#66	4.52		
23	El Burro	9.04		
21	Mount Joy	8.94		
128 Ÿ	Onnum Valley	2.32		
14	Santa Luzia	0.801		
69	São Julião de Moreira	1.02	2.9	Crocket,1972
22	Sikhote-Alin	3.50	3.9	Nichiporuk&Brown,1965
			4.1	Baedecker&Ehmann,1965
IIC				
99	Ballinoo	15.0	13	Crocket,1972
82	Kumerina	15.5		
24	Perryville	15.6		
IID				
28	Arltunga	20.2		
25	Carbo	21.1	21.0	Pernicka&Wasson,1987
100	Needles	12.4	13.9	Pernicka&Wasson,1987
85	Puquios	22.5	20	Crocket,1972
79	Rodeo	15.2	16.2	Pernicka&Wasson,1987
26	Wallapai	12.5	12.6	Pernicka&Wasson,1987
IIE				
27	Arlington	12.6		
101	Weekeroo Station	10.3		
IIF				
158	Corowa	5.72		

Ÿ Paired with each other and misclassified as IIB (See Section XI.1.ii)

APPENDIX 2c--Pt (Continued)

BMMRU Catalog Number	Meteorite	Abundance (μg/g) This Work	Abundance (μg/g) Literature	Reference
IIIA				
31	Cape York--Agpalilik	11.4		
32	Cape York--Woman	14.6		
78	Chambord	15.3		
33	Henbury	17.0	16.1	Pernicka&Wasson,1987
			11.4	SenGupta&Beamish
			7.42	SenGupta&Beamish,1963
			5.6	Nichiporuk&Brown,1965
12	Kyancutta	11.4		
91	Madoc	18.3	6.5	Sen Gupta,1968
90	Merceditas	14.0		
95	Moorumbunna	6.62		
152	Red Rock	8.08		
87	Trenton	10.9	9.0	Pernicka&Wasson,1987
29	View Hill	5.65		
30	Waingaromia	7.58		
86	Welland	7.89		
IIIB				
109	Apoala	2.38		
107	Bella Roca	1.42	1.40	Pernicka&Wasson,1987
153	Buenaventura	0.828		
35	Campbellsville	4.30	4.40	Pernicka&Wasson,1987
110🤖	Chupaderos	5.34		
111	Cleveland	3.56		
112	El Capitan	4.14		
105	Grant	2.14	2.20	Pernicka&Wasson,1987
106	Los Reyes	3.37		
108	Luis Lopez	4.54		
34	Owens Valley	4.68		
81	Sam's Valley	1.78	3.0	Crocket,1972
36🤖	Zacatecas	37.0		

🤖 Mislabelled specimens (See Section X.3.vi)

APPENDIX 2c--Pt (Continued)

BMMRU Catalog Number	Meteorite	Abundance (µg/g)		Reference
		This Work	Literature	
IIICD				
37🖥	Carlton	0.104	0.35	Pernicka&Wasson,1987
4 ‡	Cranbourne	5.04	4.6	Pernicka&Wasson,1987
38	Dayton	0.071	0.10	Pernicka&Wasson,1987
151🤖	Jaralito	5.06	7.6	Pernicka&Wasson,1987
113🖥	Lamesa	0.106		
102	Mungindi	0.382	0.50	Pernicka&Wasson,1987
116 ‡	Nantan	4.59	6.4	Pernicka&Wasson,1987
IIIE				
149	Burlington	10.8		
104	Cachiyuyal	11.0		
120◘	Coopertown	9.24		
156	Kokstad(Matatiele)	9.25		
115◘	Paneth's Iron	8.86	6.5*	Crocket,1972
			6.5*	Nichiporuk&Brown,1965
114	Staunton	6.52		
39	Willow Creek	6.11		
IIIF				
40	Clark County	10.6	9.7	Pernicka&Wasson,1987
			16	Crocket,1972
161	Klamath Falls	0.946	1.2	Pernicka&Wasson,1987
97	Moonbi	7.76	9.2	Nichiporuk&Brown,1965
103	Nelson County	10.9	9.9	Pernicka&Wasson,1987
121	St. Genevieve County	8.90	8.5	Pernicka&Wasson,1987
IVA				
41**	Gibeon	6.72	8.0	Crocket,1972
132	Guanghua	4.59		
122	Huizopa	6.96	4.4	Nichiporuk&Brown,1965
96	Mount Sir Charles	6.28		
147**	MGS G2011	6.58		
143**	Railway	8.16		
42	Steinbach	5.38		
155	Yanhuitlan	5.28		

🖥 Possibly paired (See Section X.3.i)
‡ Reclassified in the course of this work as IAB irons (See Section IX.4.v)
🤖 Mislabelled specimens (See Section X.3.vi)
* Analyzed mistakenly as Toluca IAB (See Section X.3.iv)
◘ Possibly paired (See Section X.3.iv)
** Possibly paired (See Section X.3.iii)

APPENDIX 2c--Pt (Continued)

BMMRU Catalog Number	Meteorite	Abundance (μg/g)		Reference
		This Work	Literature	
IVB				
138🤖	Cape of Good Hope	2.98	11.8	Nichiporuk&Brown,1965
92	Hoba	80.6		
137	Iquique	86.4		
84	Skookum Gulch	38.3	23.5	Sen Gupta,1968
43	Tlacotepec	39.2		
159	Warburton Range	30.6		
44	Weaver Mountains	29.5		
Anomalous				
146	Bellsbank	0.344		
129	Butler	48.6		
142	De Hoek	1.92		
154	Denver City	7.44		
80	Gay Gulch	3.40		
93	Glenormiston	11.0		
162	Lonaconing	1.61		
51◇	Mundrabilla	4.20	3.16	Pernicka&Wasson,1987
130	Santa Catharina	0.461	<0.5	Crocket,1972

🤖 Mislabelled specimen (See Section X.3.vi)

◇ Listed as anomalous here as no firm classification can be made (See Section IX.4.v)

APPENDIX 3 Ni determinations by flame-AAS for iron meteorites digested in HNO_3

BMMRU Catalog #	Meteorite	Ni Abundance (%)	Literature Value
IA			
1	Odessa	8.76	7.20
2	Coolac	7.10	7.40
3	Campo del Cielo	7.98	6.62
5	Dunganville	4.71	6.9
6	Cañon Diablo	8.08	6.9-7.9*
67	Toluca	9.09	8.07
68	Copiapo	7.12	7.01
88	Annaheim	8.82	7.74
89	Mayerthorpe	7.26	7.19
94	Gladstone #2	7.53	6.53
131	Tassajara	8.81	8.10
IB			
7	Woodbine	10.57	10.6
8	Mesa Verde	11.76	10.6
9	Four Corners	10.41	8.90
72	Colfax	11.61	10.8
73	Bitburg	11.69	12.4
IC			
49	Arispe	7.22	6.54
74	Santa Rosa	8.04	6.63
75	Bendegó	7.53	6.39
76	Chihuahua City	7.17	6.68
77	St. François County	7.96	6.12
83	Mount Dooling	7.03	6.26
IIA			
10	Coahuila	6.34	5.49
11	Walker County 🐞	0.82	5.46
13	Tocopilla	6.59	5.54
50	North Chile	6.17	5.57
124	Gressk	6.12	5.61
123	Forsyth County	6.61	5.50
125	Hex River Mountain	6.00	5.59
126	Sierra Gorda	6.50	5.27

🐞 Mislabelled specimen (See Section X.2)

* Variable for this meteorite (Wasson, 1968)

APPENDIX 3 (Continued.)

BMMRU Catalog #	Meteorite	Ni Abundance (%)	Literature Value
IIB			
14	Santa Luzia	6.29	6.30
15	Bilibino	6.28	5.80
17	Derrick Peak 78012	6.60	5.54
21	Mount Joy	7.17	5.68
22	Sikhote-Alin	7.18	5.87
23	El Burro	6.40	5.96
69	São Julião de Moreira	7.58	6.10
127	Derrick Peak CM#66	7.39	5.54
128	Onnum Valley	6.30	5.54
IIC			
24	Perryville	9.77	9.27
82	Kumerina	10.30	9.69
99	Ballinoo	9.96	9.72
IID			
25	Carbo	10.81	10.2
26	Wallapai	11.86	11.3
28	Arltunga	10.95	9.64
79	Rodeo	10.51	10.2
85	Puquios	10.84	10.1
100	Needles	12.62	10.3
IIE			
27	Arlington	7.23	8.42
101	Weekeroo Station	7.92	7.51
IIIA			
12	Kyancutta	9.56	8.06
29	View Hill	10.60	8.87
30	Waingaromia	10.38	9.14
31	Cape York--Agpalilik	8.70	7.58
32	Cape York--Woman	8.46	7.58
33	Henbury	8.07	7.47
78	Chambord	7.70	7.53
86	Welland	9.10	8.77
87	Trenton	10.37	8.34
90	Merceditas	8.48	7.82
91	Madoc	8.76	7.52
95	Moorumbunna	9.31	8.98

APPENDIX 3 (Continued)

BMMRU Catalog #	Meteorite	Ni Abundance (%)	Literature Value
IIIB			
34	Owens Valley	9.90	8.53
35	Campbellsville	8.80	8.65
36	Zacatecas 🤖	6.00	9.00
81	Sam's Valley	9.63	9.77
105	Grant	10.45	9.24
106	Los Reyes	9.37	8.71
107	Bella Roca	10.13	10.1
108	Luis Lopez	9.31	8.64
109	Apoala	10.74	9.39
110	Chupaderos 🤖	8.68	9.70
111	Cleveland	9.18	8.85
112	El Capitan	9.12	8.56
IIICD			
4‡	Cranbourne	7.96	6.80
37🖥	Carlton	13.92	13.0
38	Dayton	16.91	17.0
102	Mungindi	12.23	11.5
113🖥	Lamesa	13.10	13.1
116‡	Nantan	7.33	6.80
IIIE			
39	Willow Creek	9.41	8.76
104	Cachiyuyal	8.75	7.88
114	Staunton	9.92	8.21
115□	Paneth's Iron	9.94	8.98
120□	Coopertown	9.57	8.47
IIIF			
40	Clark County	7.37	6.79
97	Moonbi	8.62	7.70
103	Nelson County	6.94	7.02
121	St. Genevieve County	8.83	7.68
IVA			
42	Steinbach	10.26	9.08
41	Gibeon	8.77	7.68
122	Huizopa	8.69	7.48

🤖 Mislabelled specimens (See Section X.3.vi)

‡ Reclassified in the course of this work as IAB irons (See Section IX.4.v)

🖥 Possibly paired (See Section X.3.iv)

□ Possibly paired (See Section X.3.iv)

APPENDIX 3 (Continued)

BMMRU Catalog #	Meteorite	Ni Abundance (%)	Literature Value
IVB			
44	Weaver Mountains	18.29	16.8
92	Hoba	16.94	16.6
43	Tlacotepec	15.64	15.8
84	Skookum Gulch	18.84	17.71
Anomalous			
51	Mundrabilla	8.38	7.72
80	Gay Gulch	15.61	15.1
93	Glenormiston	7.95	7.45
129	Butler	16.50	15.5
130	Santa Catharina ∮	18.90	33.62

∮ Specimen completely corroded, result not reliable

APPENDIX 4: Etching Iron Meteorites (from T. Thomas of the Smithsonian Institution, United States National Museum ,1988 personal communication)

Cut an iron meteorite and grind and polish the face. Generally speaking, with a high degree of polish, less etching time and etching solution is required. The specimen should be cleaned of any grinding or polishing compounds.

The best solution for etching iron meteorites is *nital*, a mixture of dilute nitric acid and ethanol. This solution minimizes oxidation and contamination and give good control over the depth and evenness of the etch. Nital is prepared by slowly adding 5% nitric acid to 95% ethanol in equal proportions with constant stirring. For convenience during the etching procedure, the nital should be stored in a wash bottle.

Thoroughly coat the meteorite surface with nital and gently wipe the surface with a cotton swab (Johnson and Johnson brand Q-Tips™ or Cotton Buds™ work well). Agitation of the solution is necessary to prevent staining of the meteorite surface. Thoroughly rinse the surface with ethanol and swab this solution. Dry the surface with compressed air and reapply the nital, swab, rinse with ethanol. When a pattern begins to show, swab in parallel directions to the Widmanstätten pattern or Neumann bands, if present. Repeat the procedure until the desired depth of etch is achieved.

When complete, thoroughly wash the meteorite with warm water for several minutes to remove all acid. With paper towels, pat the sample dry and rinse with acetone to remove all remaining water. Dry again and apply lacquer to the surface, if desired.

APPENDIX 5: Equations for the calculation of the density of analyte atoms produced in flame and non-flame situations (Based on Zeegers *et al.*, 1968)

$$n = \frac{N \beta \varepsilon F C}{(Q e_f)\, 0.001}$$

where n = number of analyte atoms per unit volume

N = Avogadro's number

β = atomization efficiency (1)

ε = aspiration efficiency (0.1)

F = solution flow rate (0.05 cm^3/s)

Q = unburned gas flow rate (100 cm^3/s)

e_f = flame expansion factor (10)

C = concentration of analyte (10^{-6} mol/L)

Production of atomic vapor in a non-flame situation

$$n = \frac{N \beta V_s C}{V}$$

where N = Avogadro's Number

β = atomization efficiency (1)

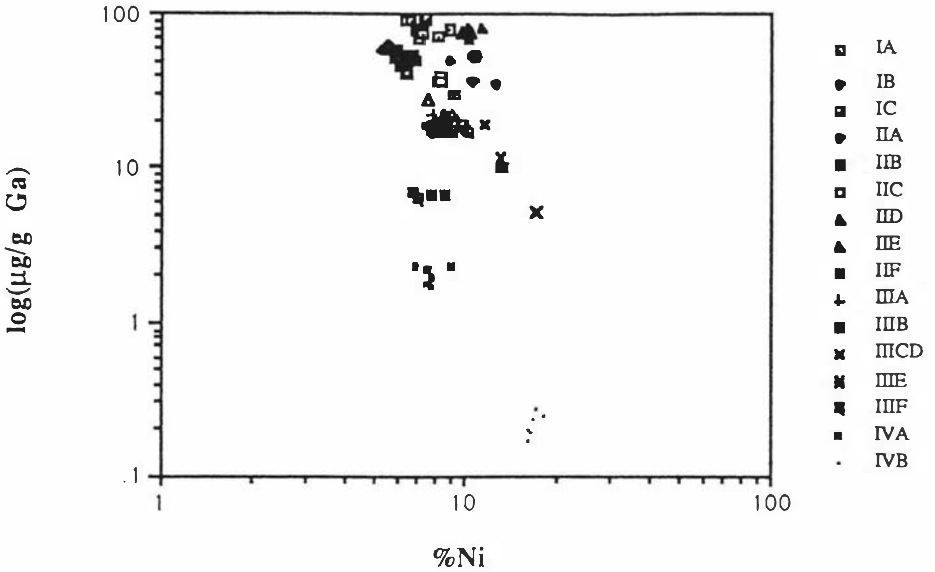
C = concentration of analyte (10^{-6} mol/L)

V_s = volume of solution ($5 mm^3$)

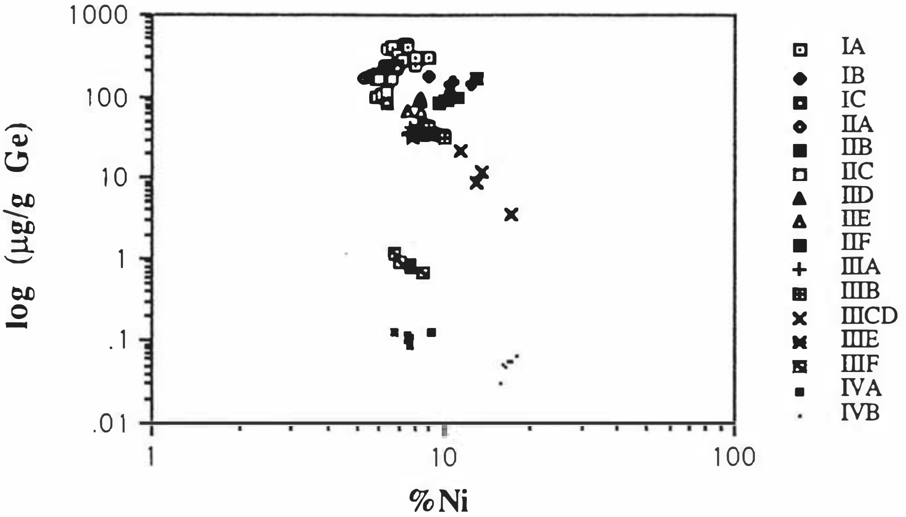
V = volume of gas phase ($1 cm^3$)

APPENDIX 6: Graphs of every binary combination for the data set presented in Appendix 1. (All values in µg/g except for % Ni)

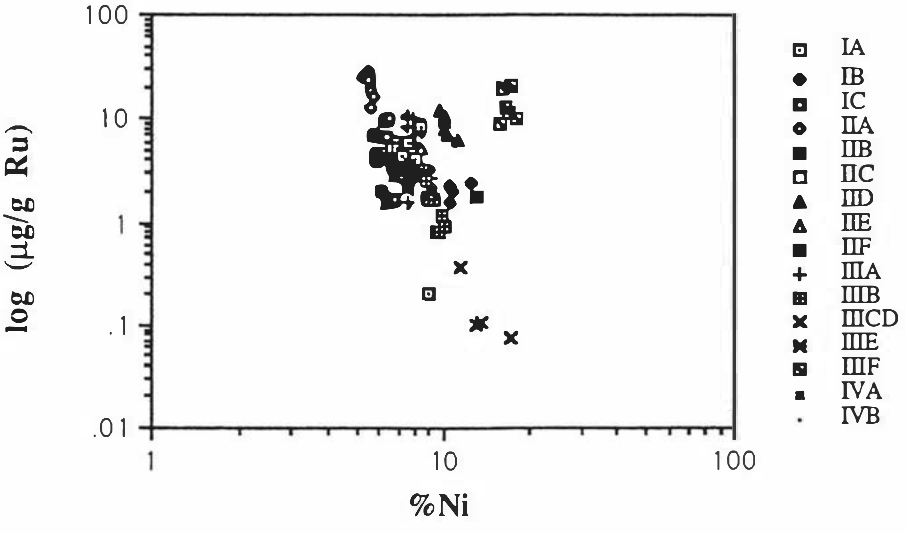
Ni vs. Ga



Ni vs. Ge

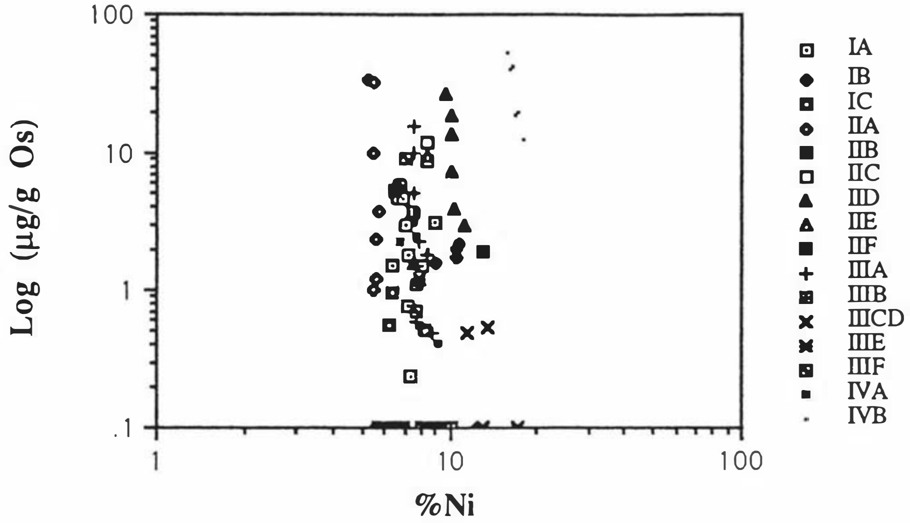


Ni vs Ru

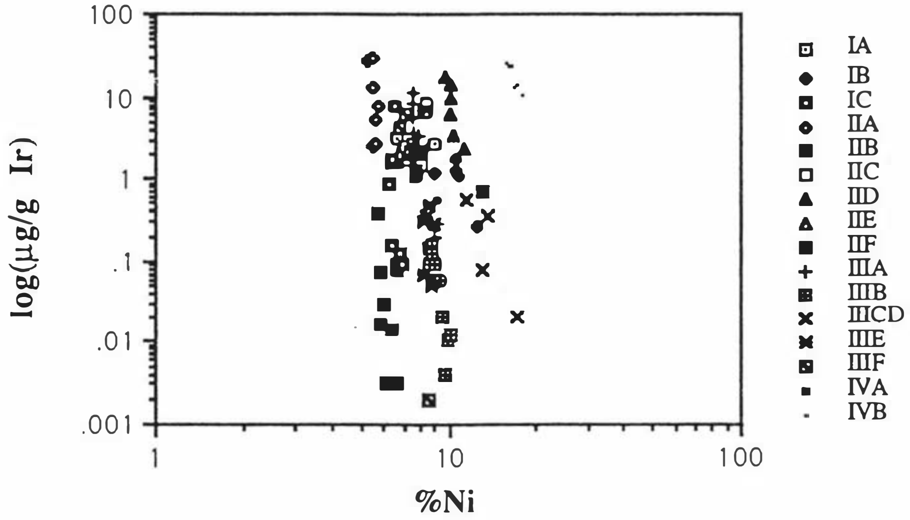


APPENDIX 6 (Continued)

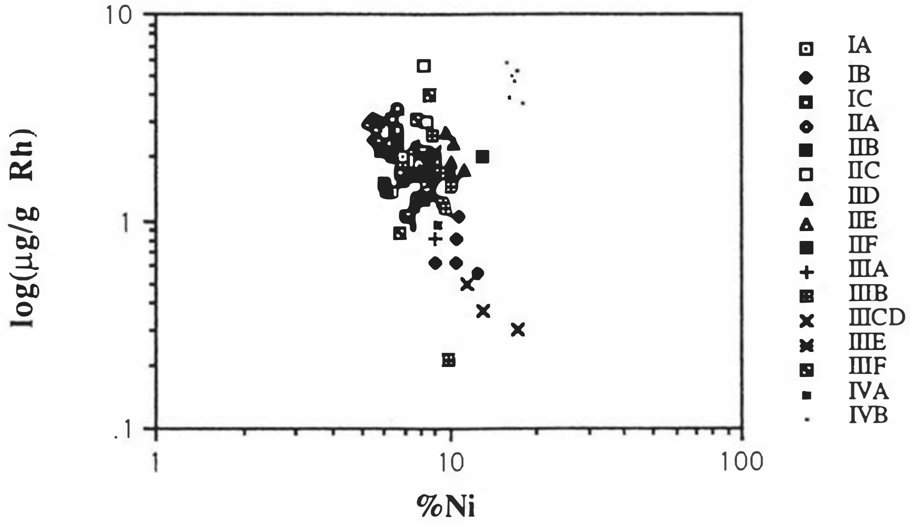
Ni vs. Os



Ni vs. Ir

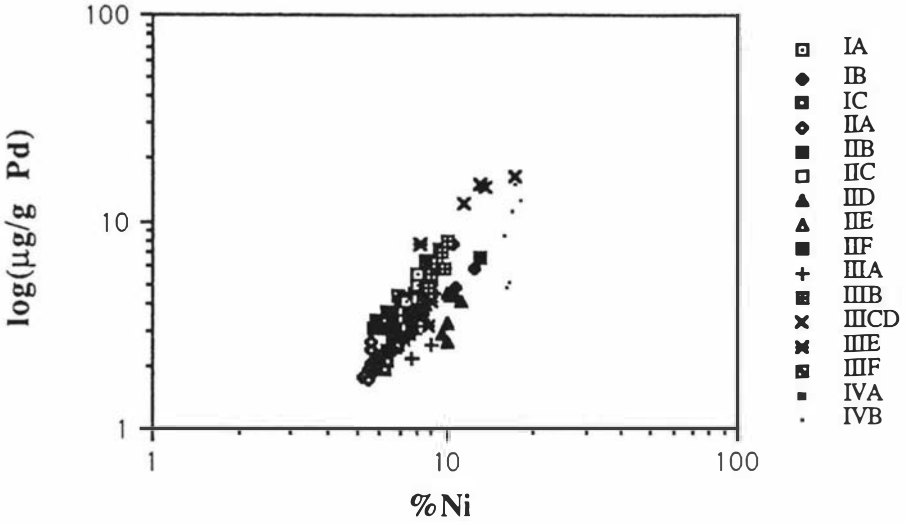


Ni vs. Rh

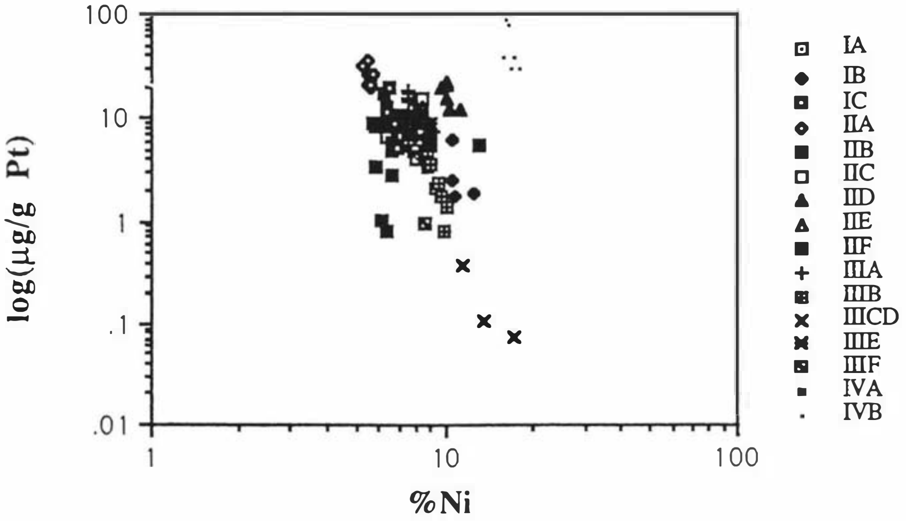


APPENDIX 6 (Continued)

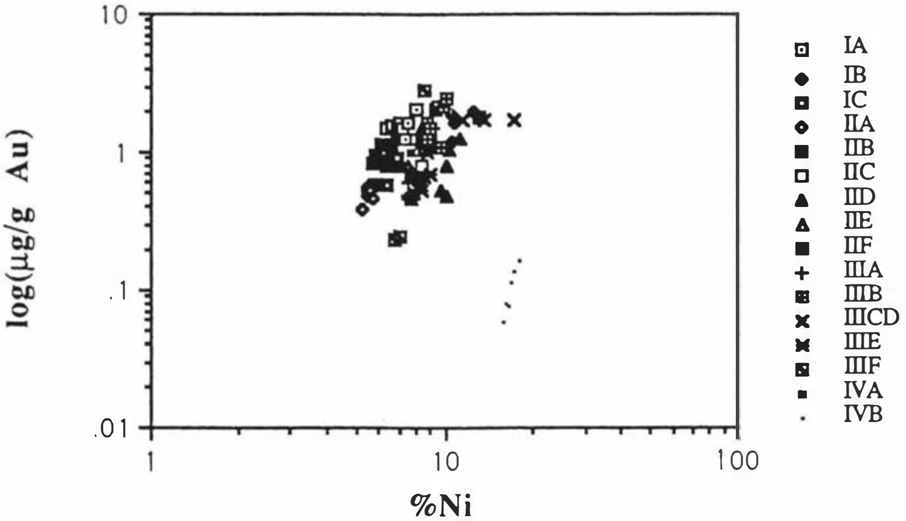
Ni vs. Pd



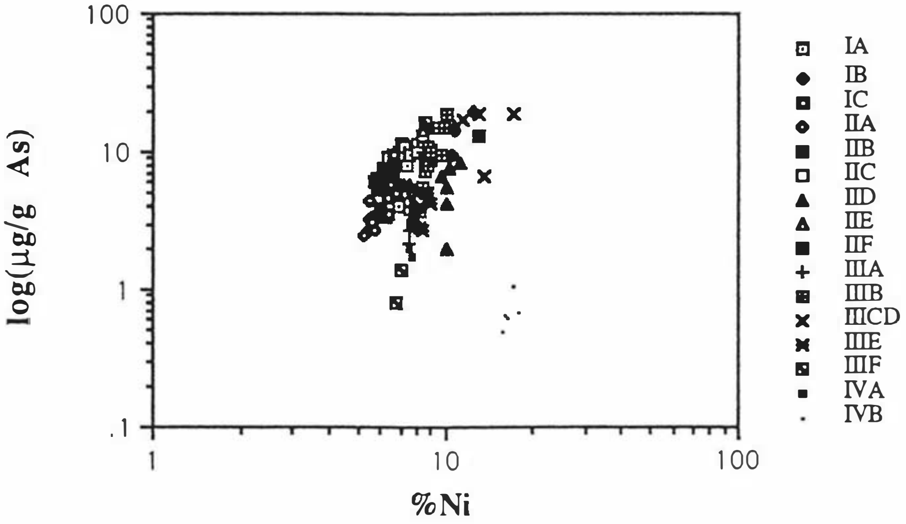
Ni vs. Pt

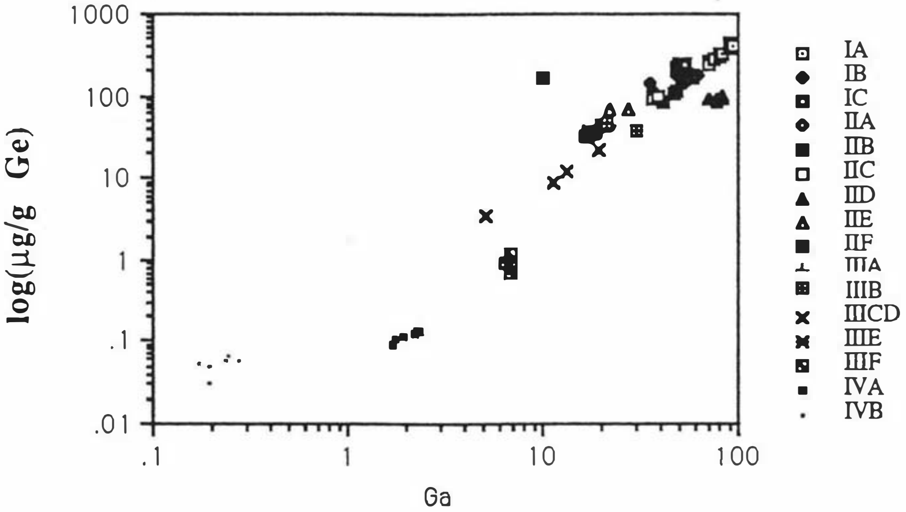


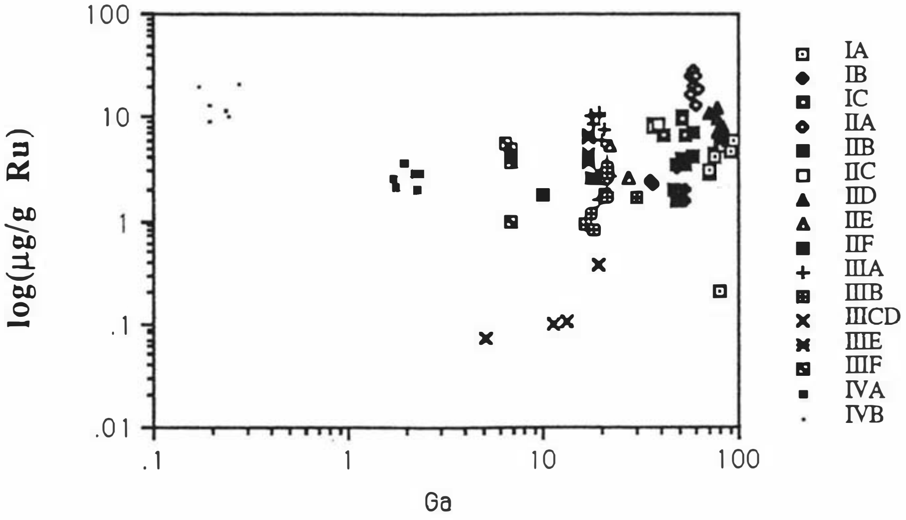
Ni vs. Au



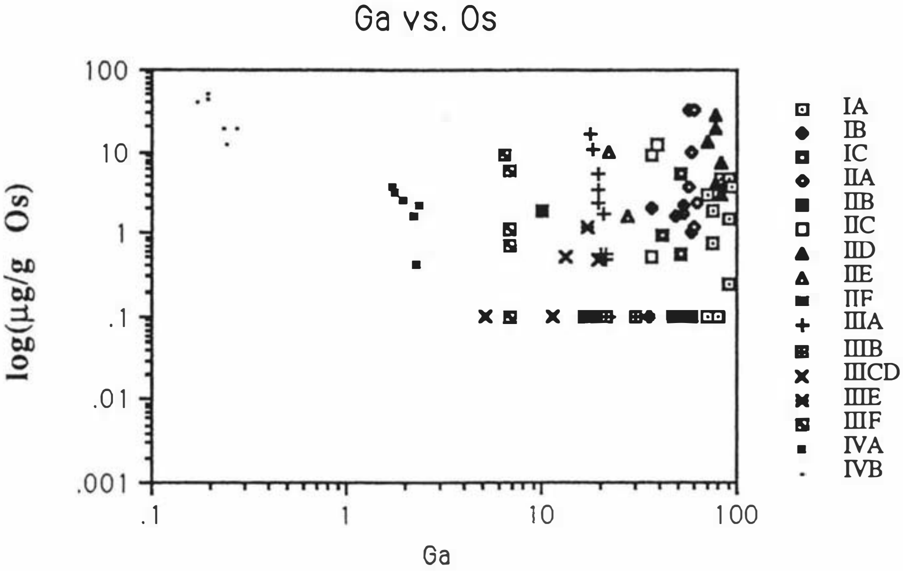
APPENDIX 6 (Continued)

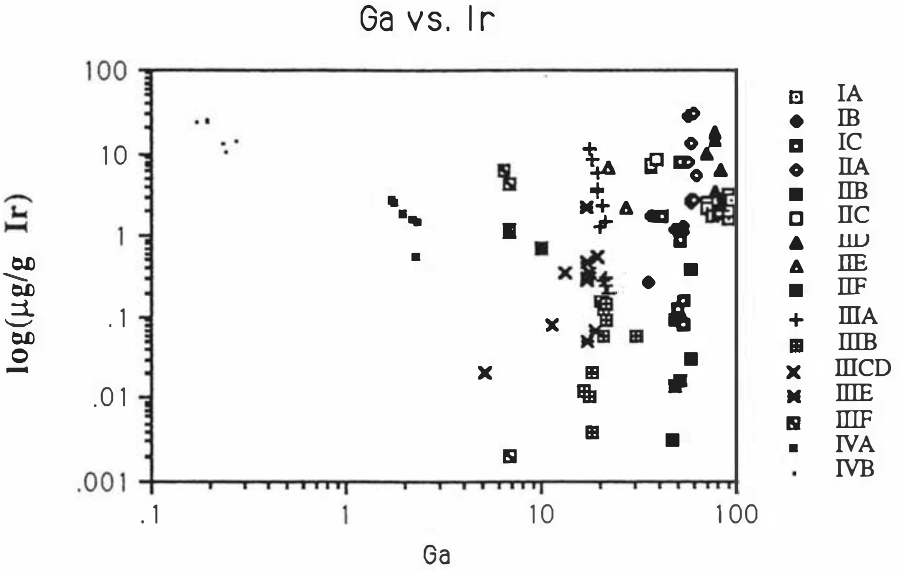

Ni vs. As

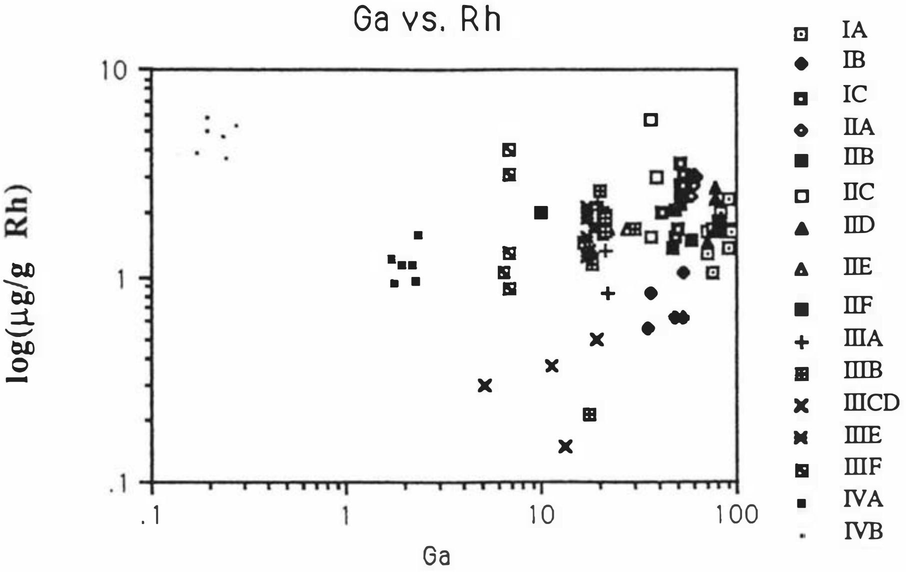

Ga vs. Ge


Ga vs. Ru

APPENDIX 6 (Continued)

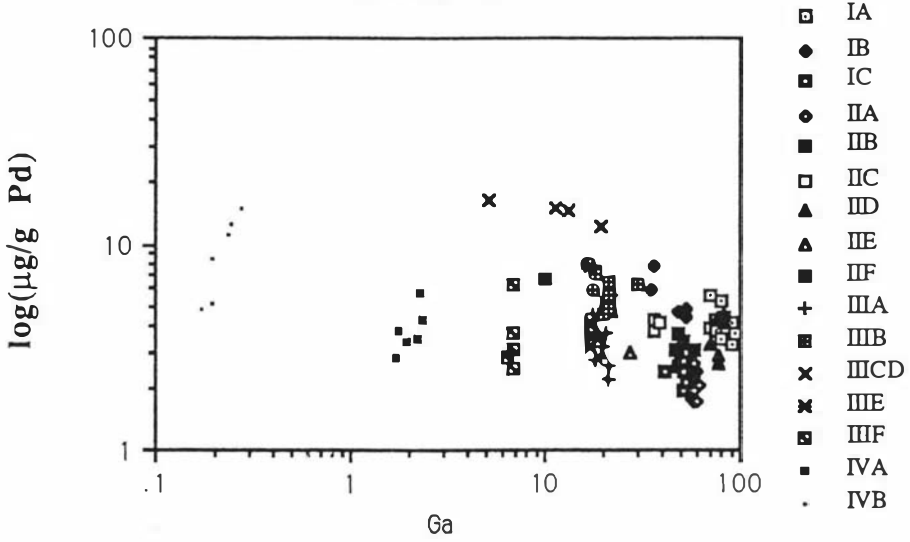




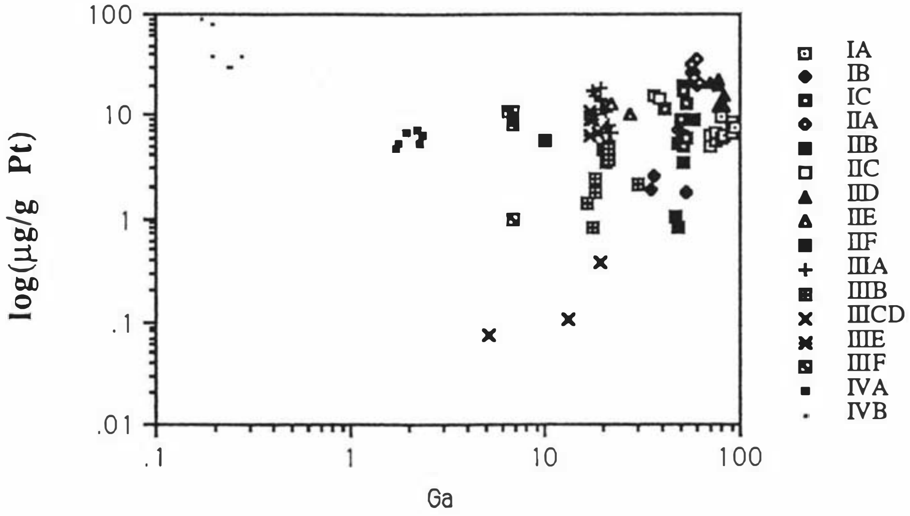


APPENDIX 6 (Continued)

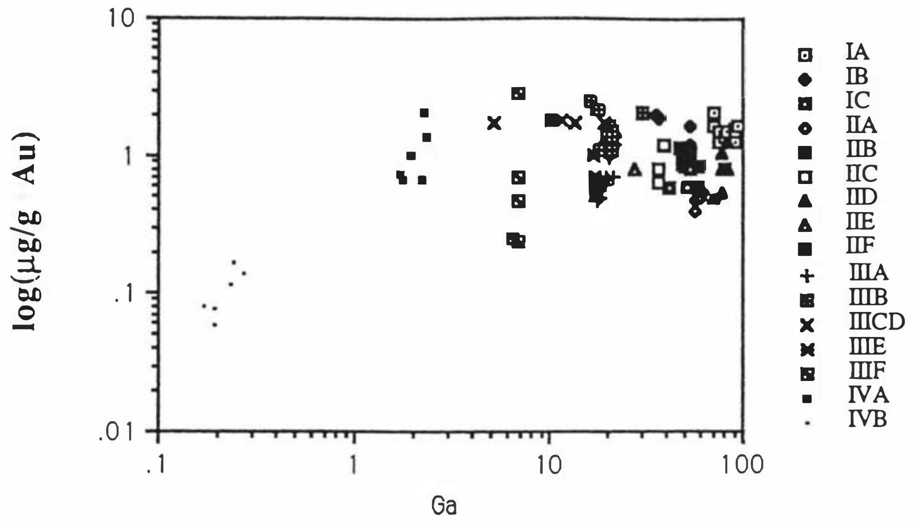
Ga vs. Pd



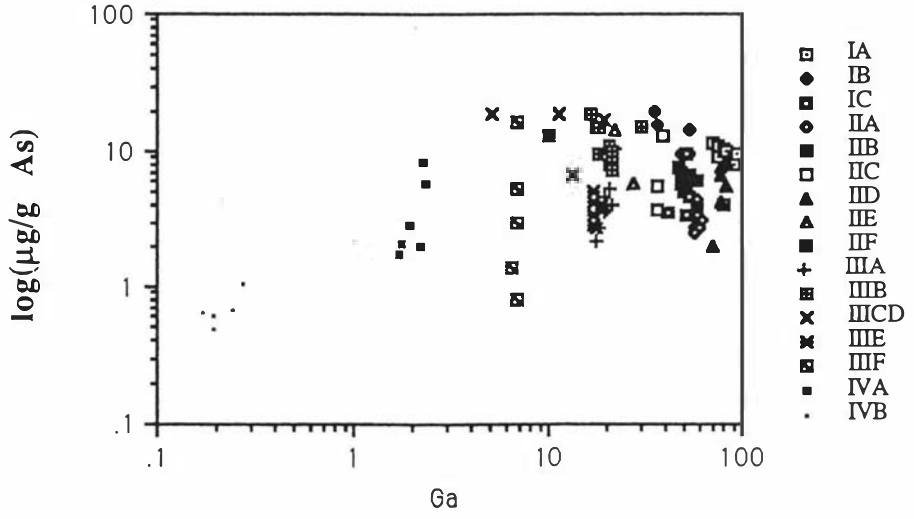
Ga vs. Pt



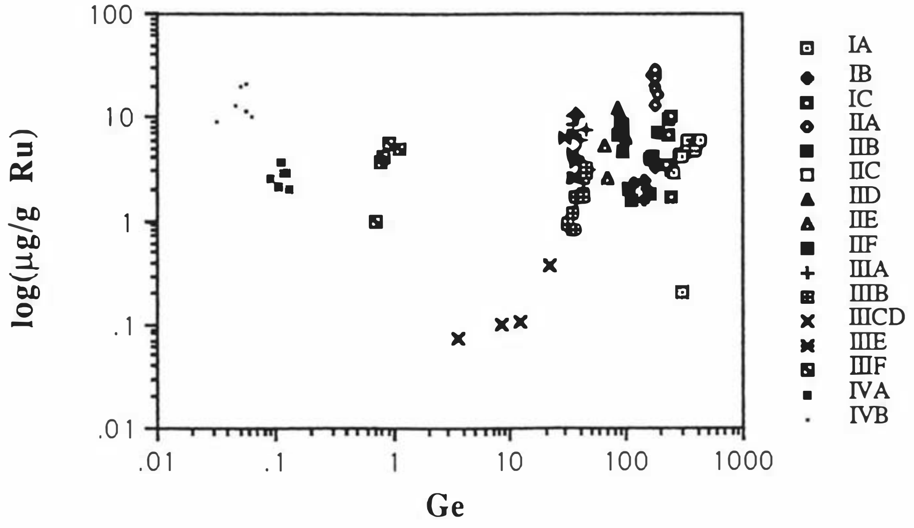
Ga vs. Au



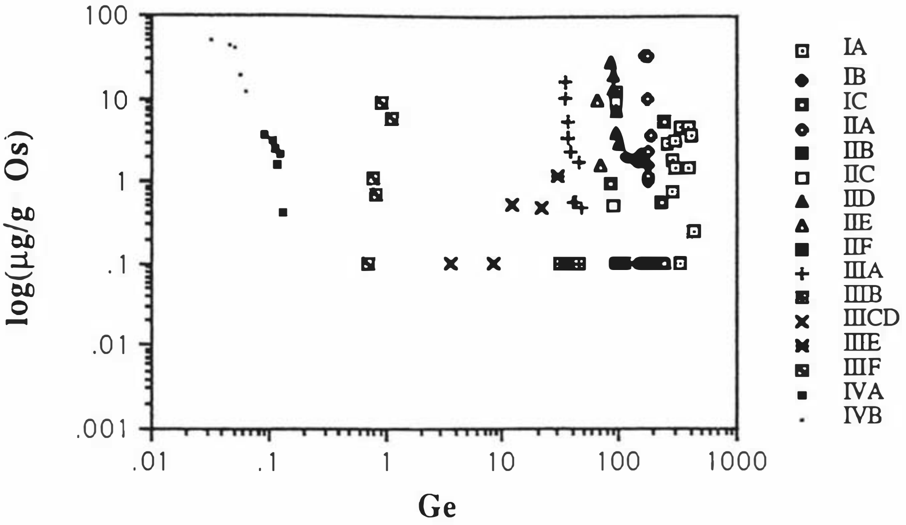
Ga vs. As



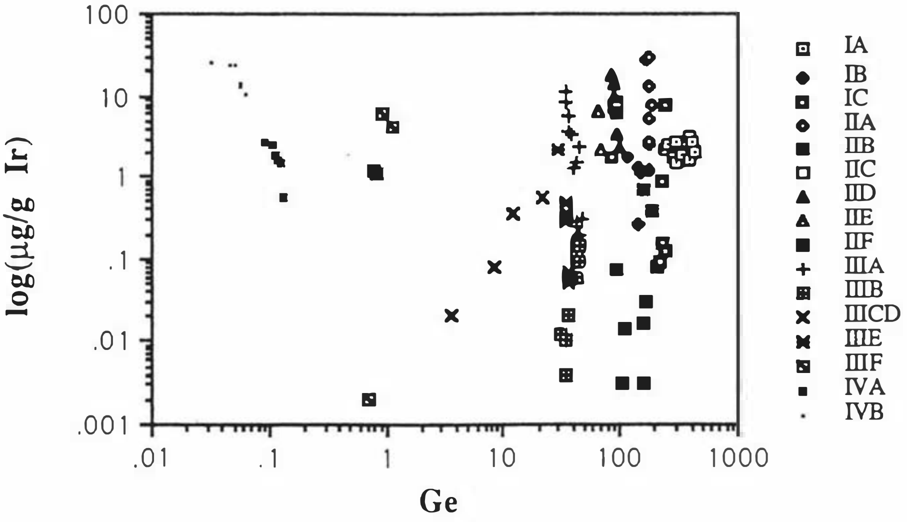
Ge vs. Ru

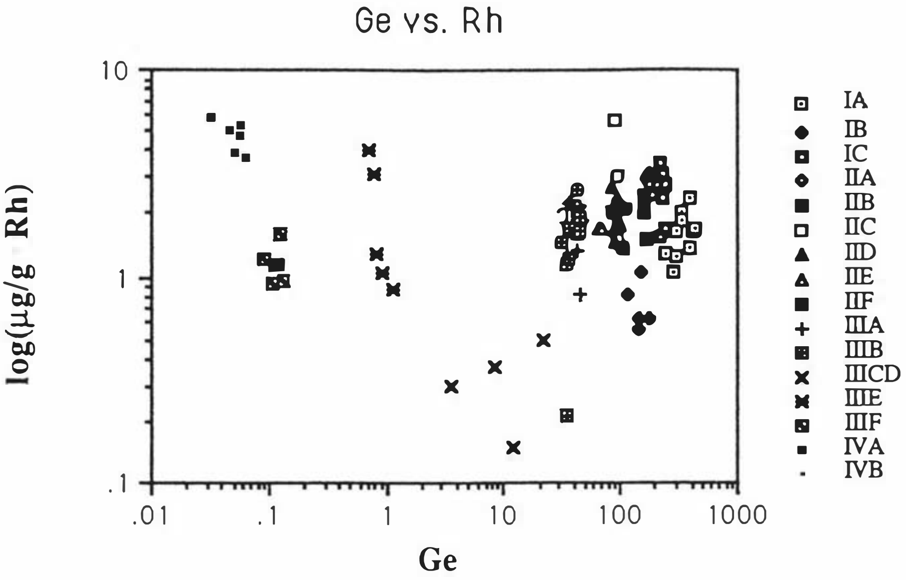


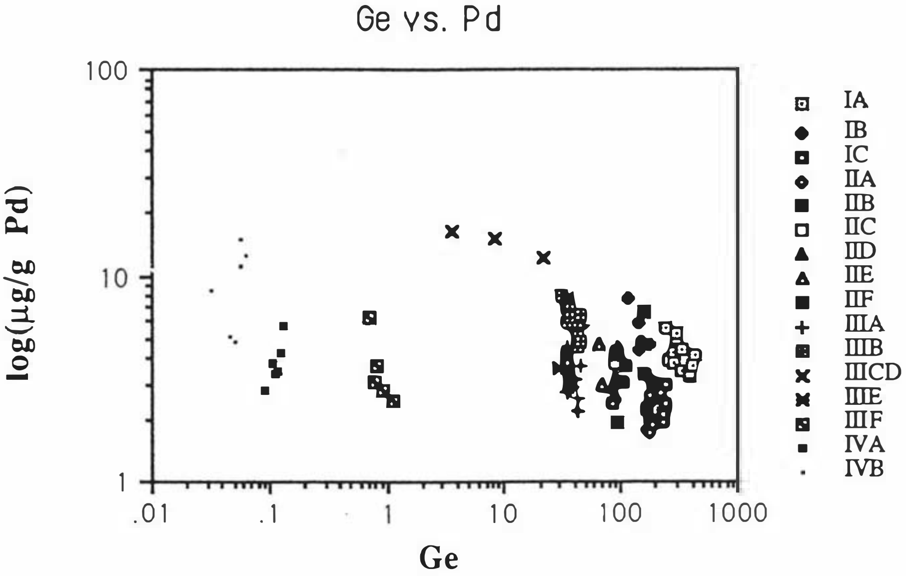
Ge vs. Os



Ge vs. Ir




Ge vs. Rh
10
1
.1
log(µg/g Rh)
.01
.1
1
10
100
1000
Ge
IA
IB
IC
IIA
IIB
IIC
IID
IIE
IIF
IIIA
IIIB
IIICD
IIIE
IIIF
IVA
IVB


Ge vs. Pd
100
10
1
log(µg/g Pd)
.01
.1
1
10
100
1000
Ge
IA
IB
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IIC
IID
IIE
IIF
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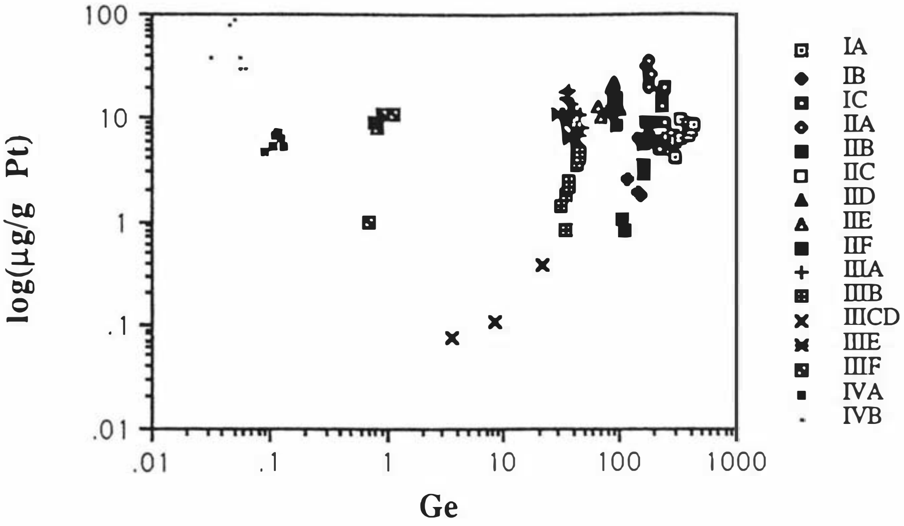
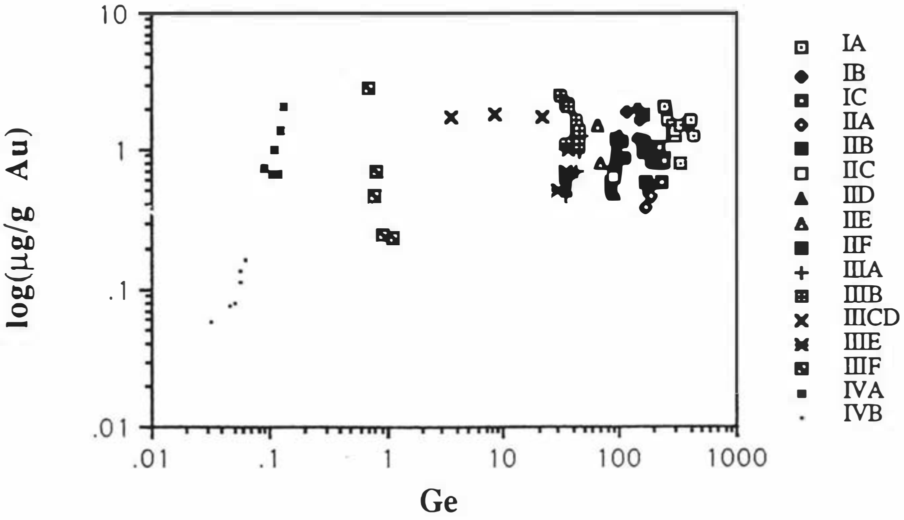
IIIB
IIICD
IIIE
IIIF
IVA
IVB

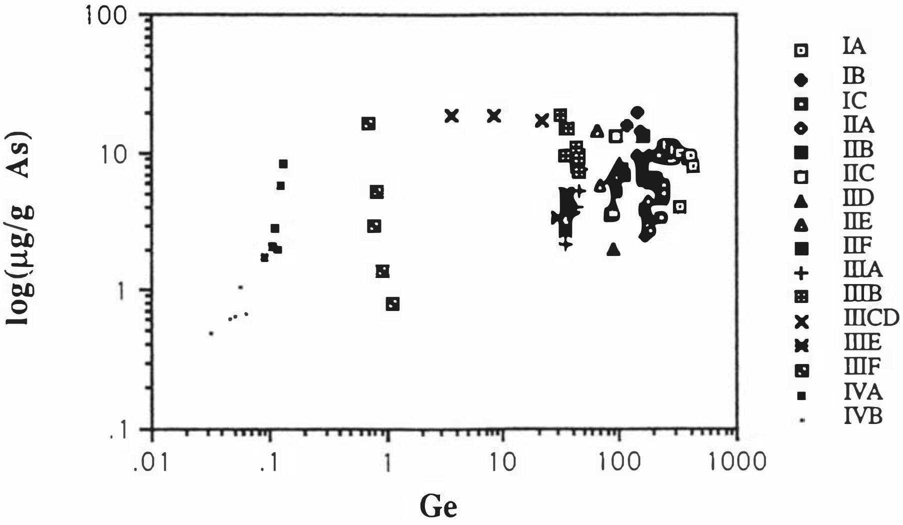
Ge vs. Pt

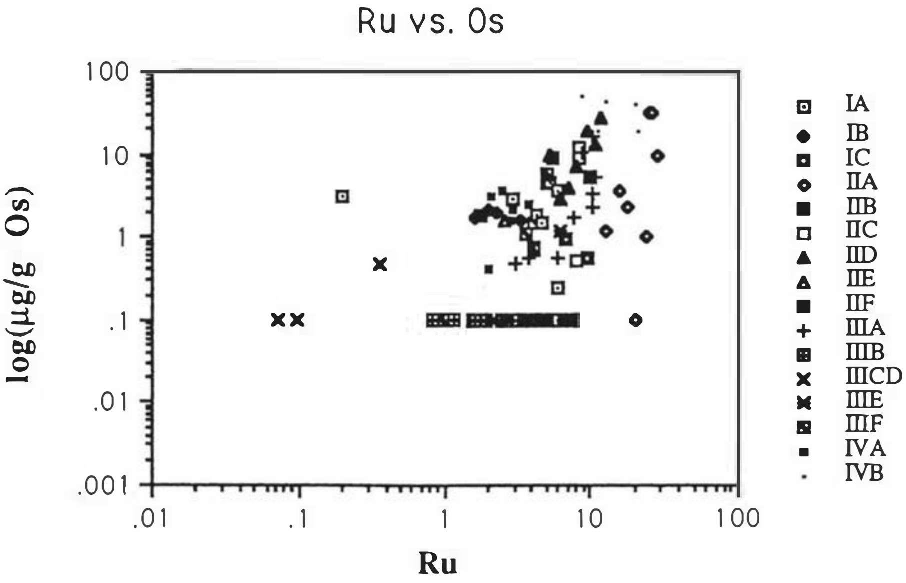


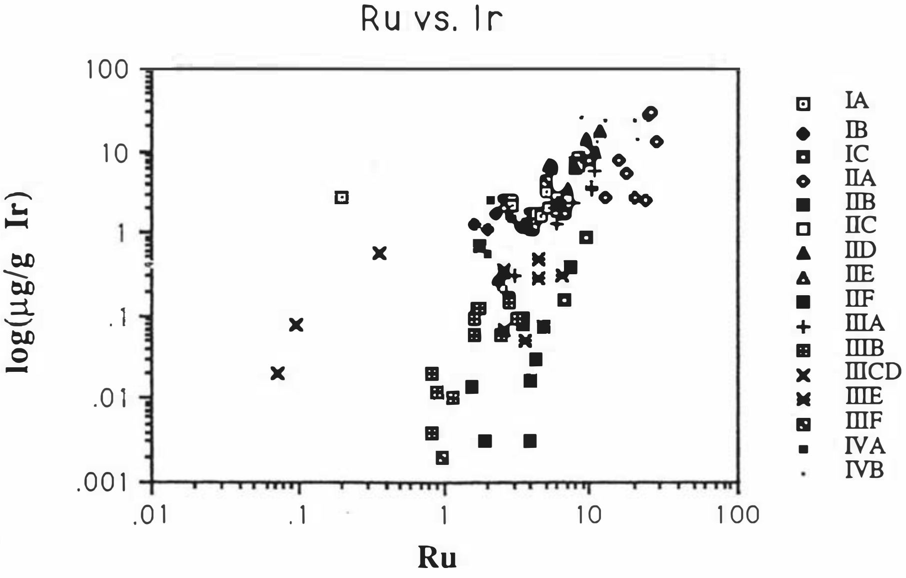
Ge vs. Au

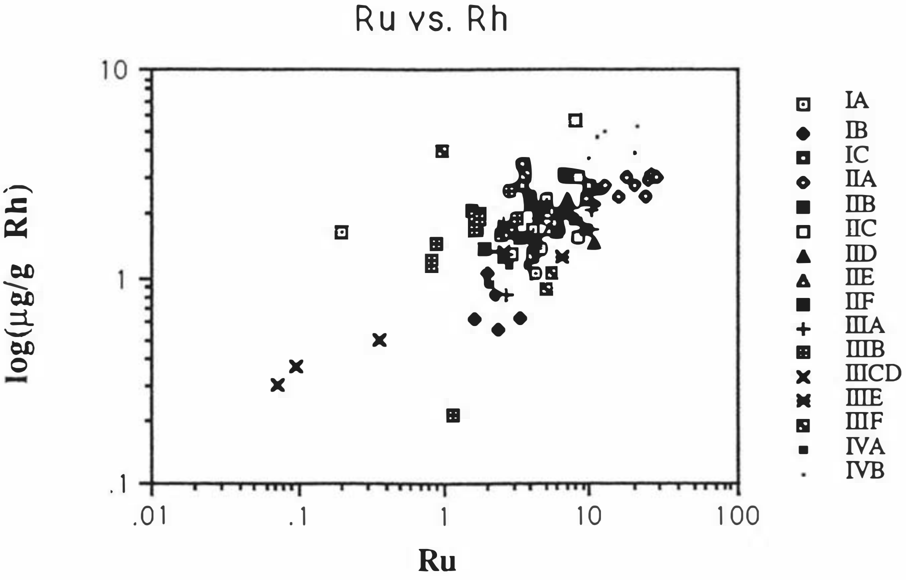


Ge vs. As

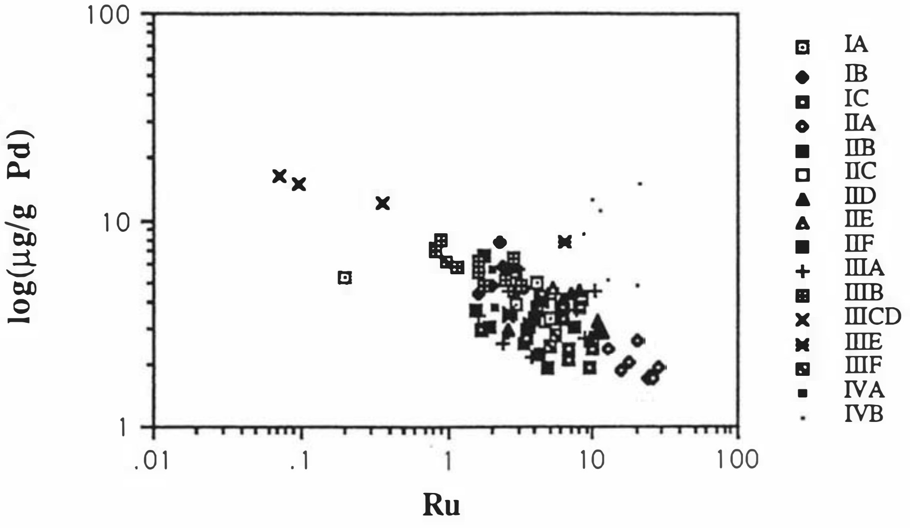


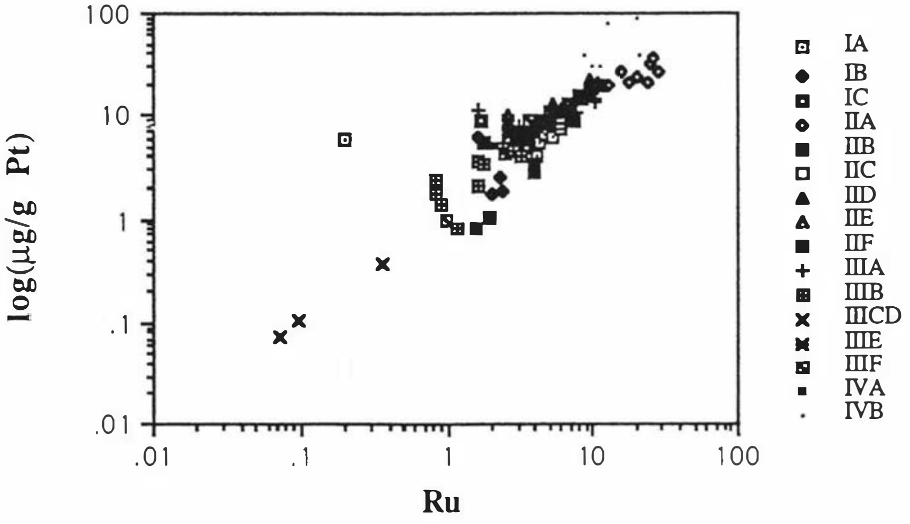

Ru vs. Os

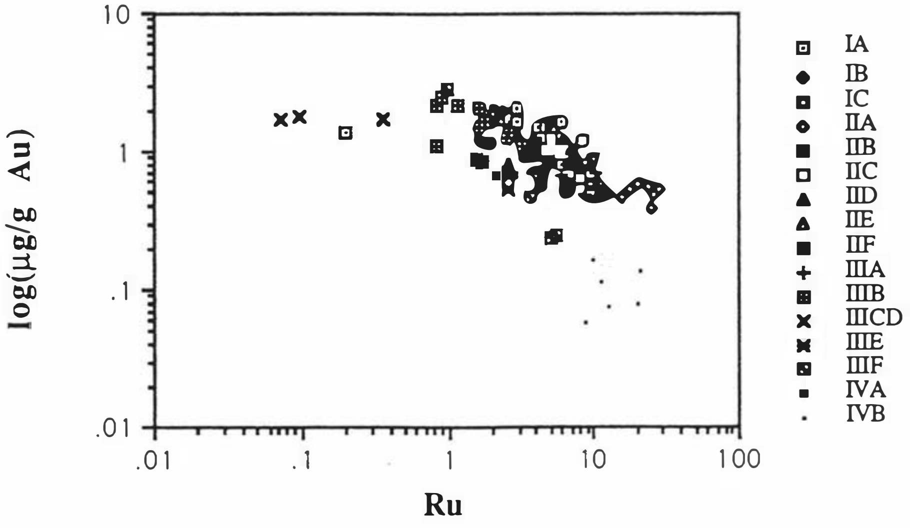

Ru vs. Ir


Ru vs. Rh

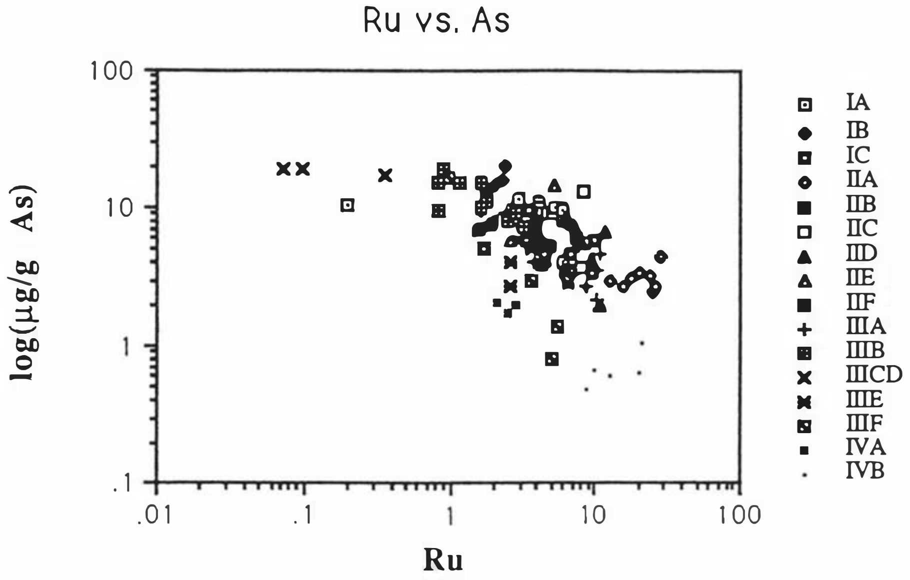
APPENDIX 6 (Continued)

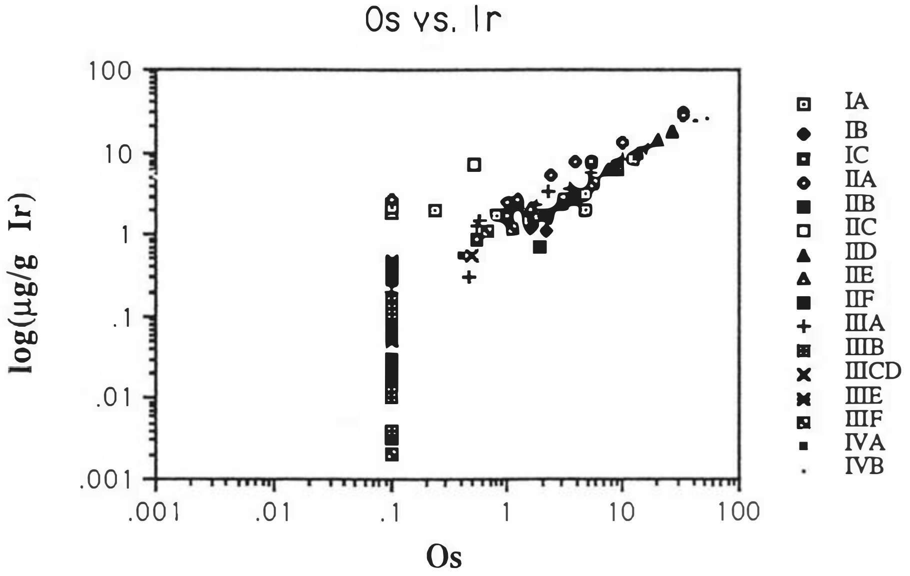

Ru vs. Pd

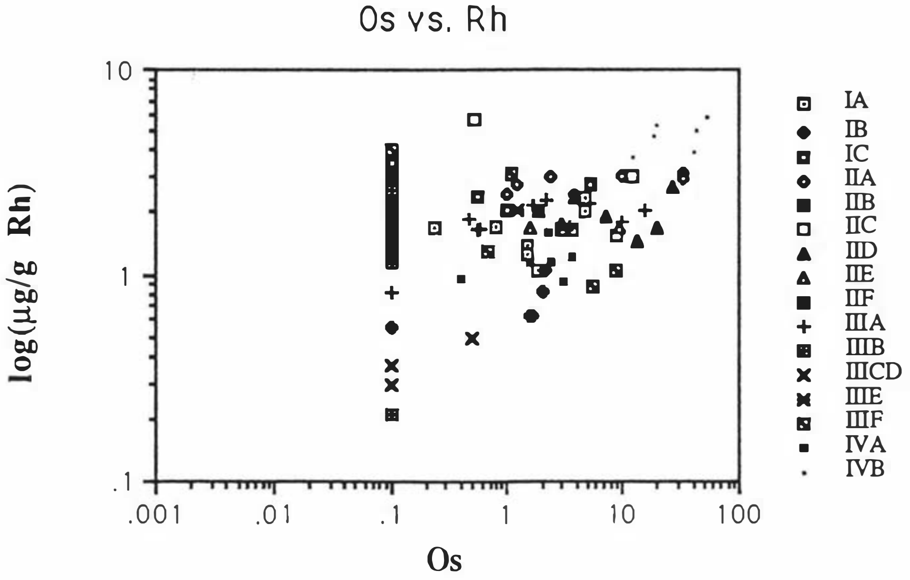

Ru vs. Pt


Ru vs. Au

APPENDIX 6 (Continued)

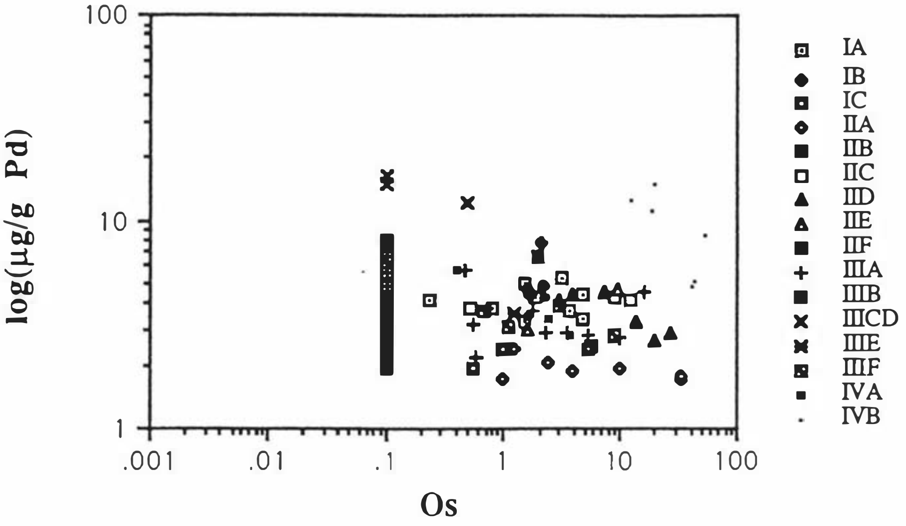




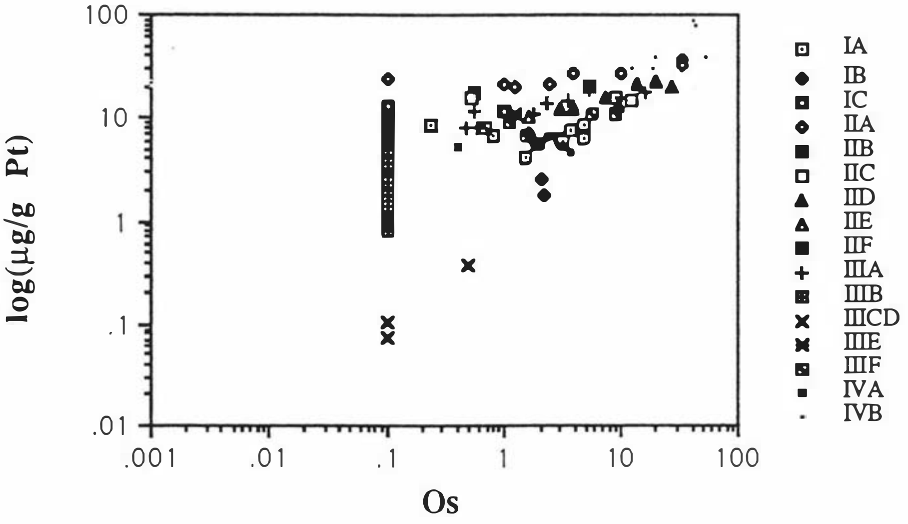


APPENDIX 6 (Continued)

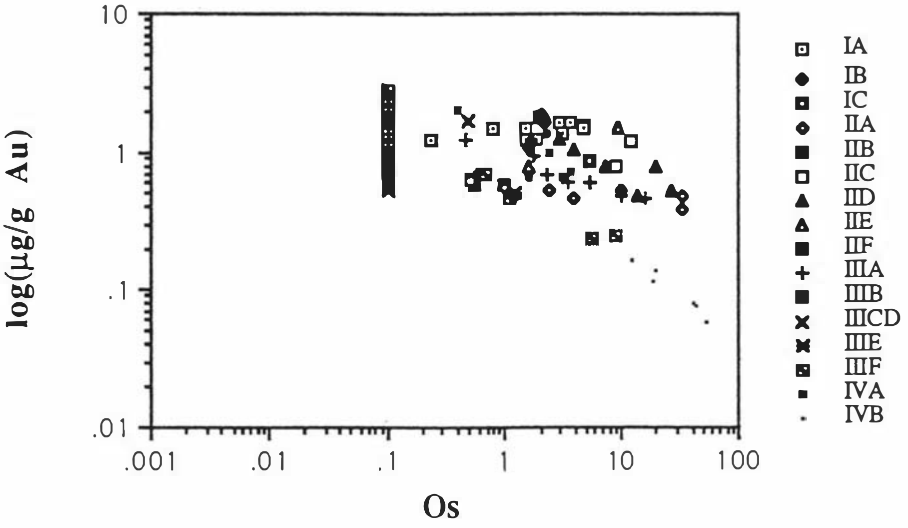
Os vs. Pd



Os vs. Pt

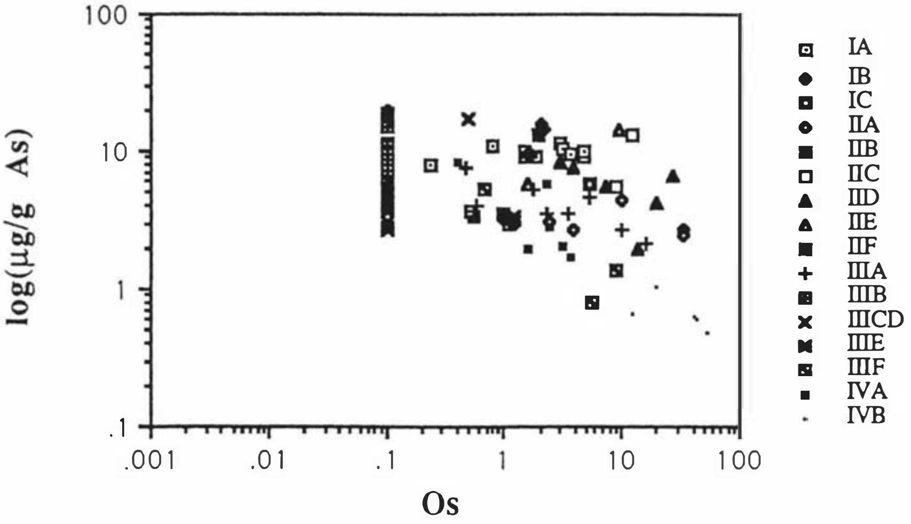


Os vs. Au

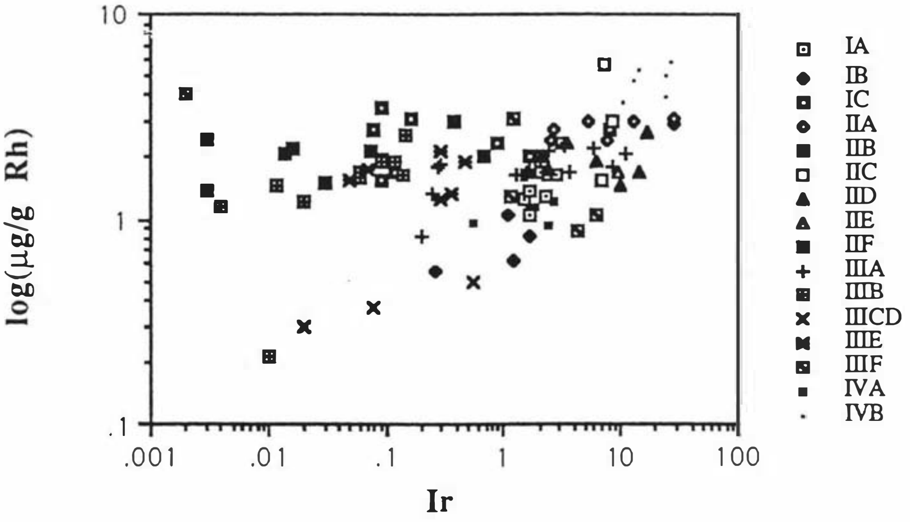


APPENDIX 6 (Continued)

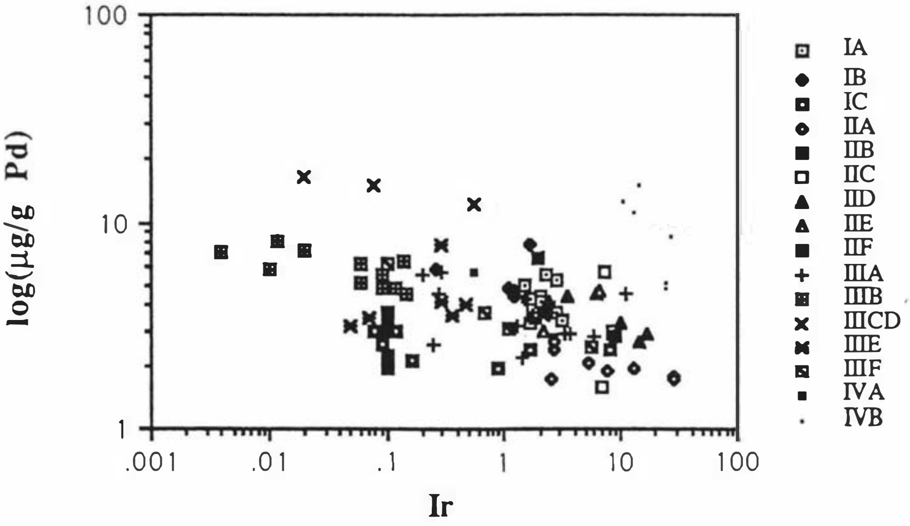
Os vs. As



Ir vs. Rh

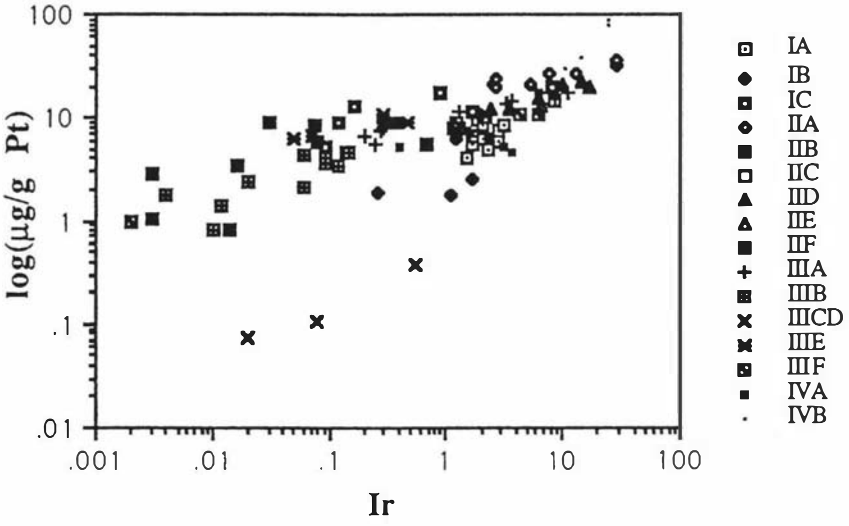


Ir vs. Pd

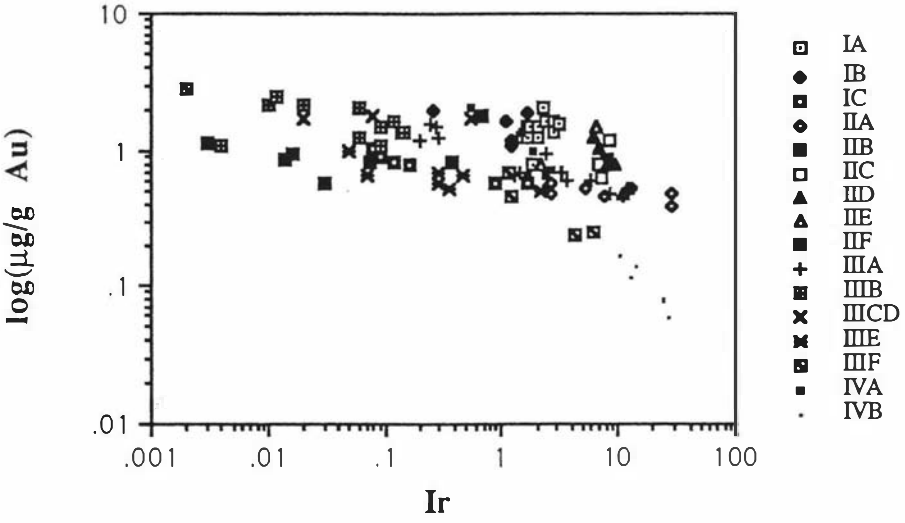


APPENDIX 6 (Continued)

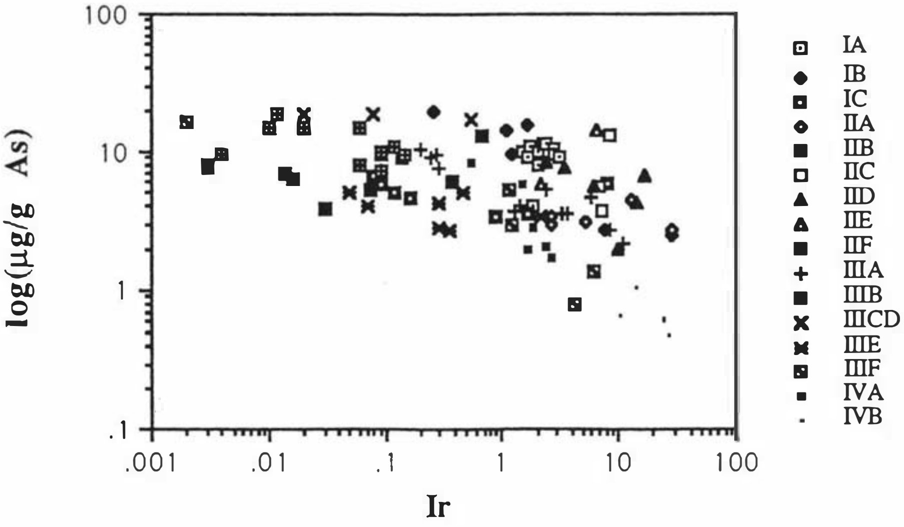
Ir vs. Pt



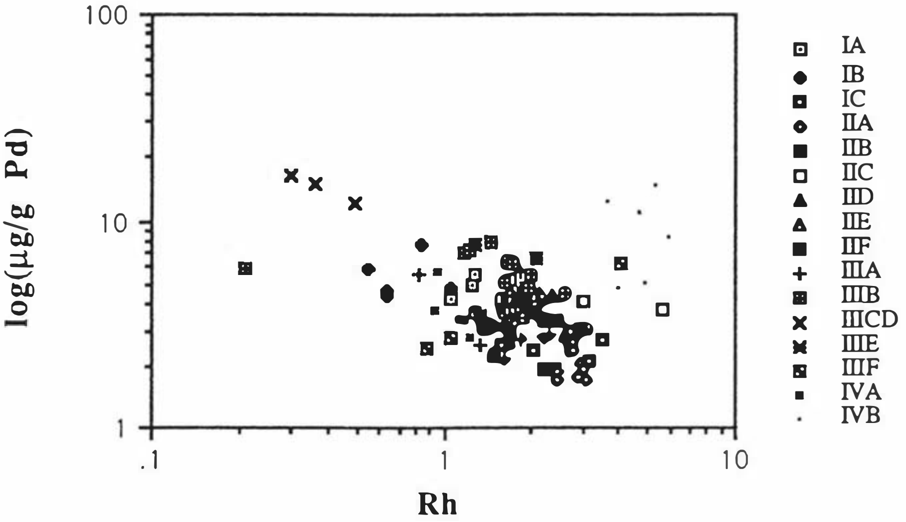
Ir vs. Au

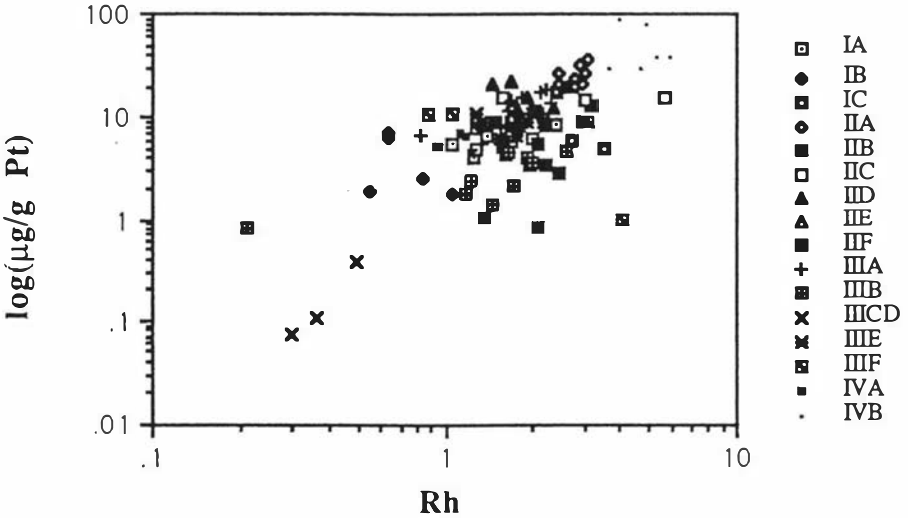


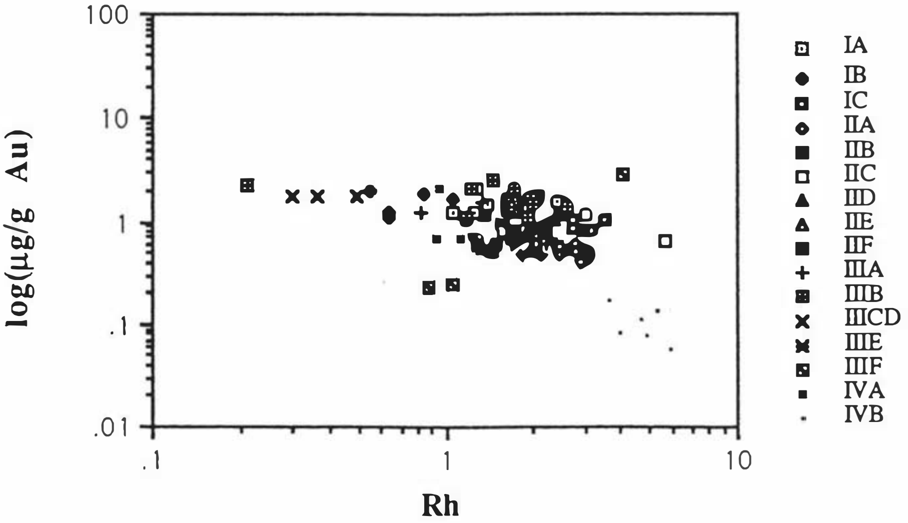
Ir vs. As



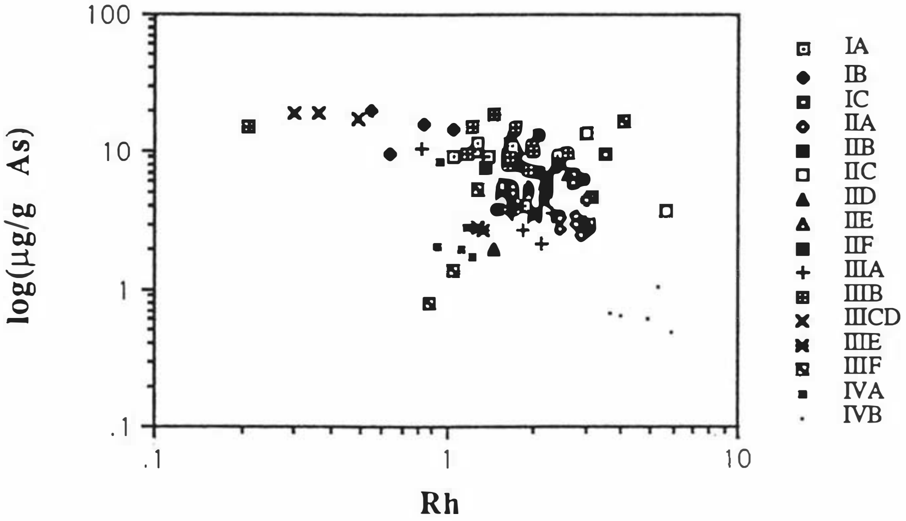
APPENDIX 6 (Continued)


Rh vs. Pd

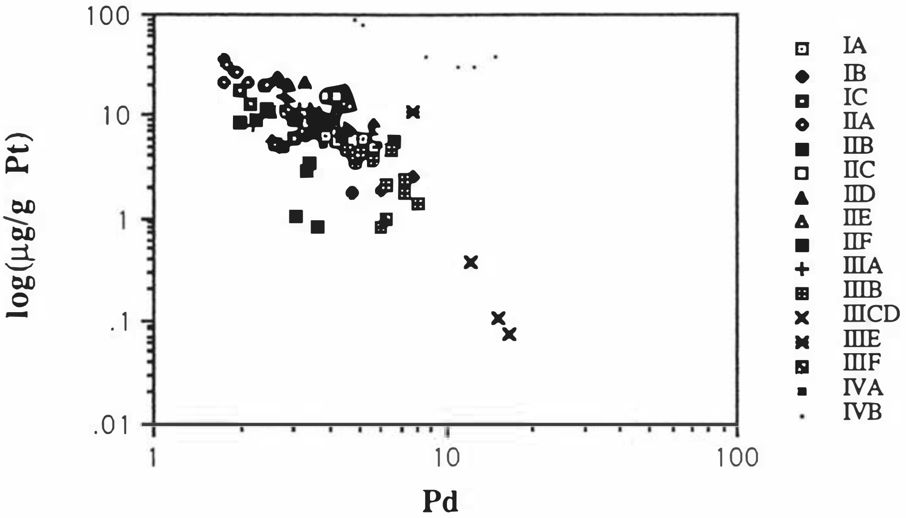

Rh vs. Pt


Rh vs. Au

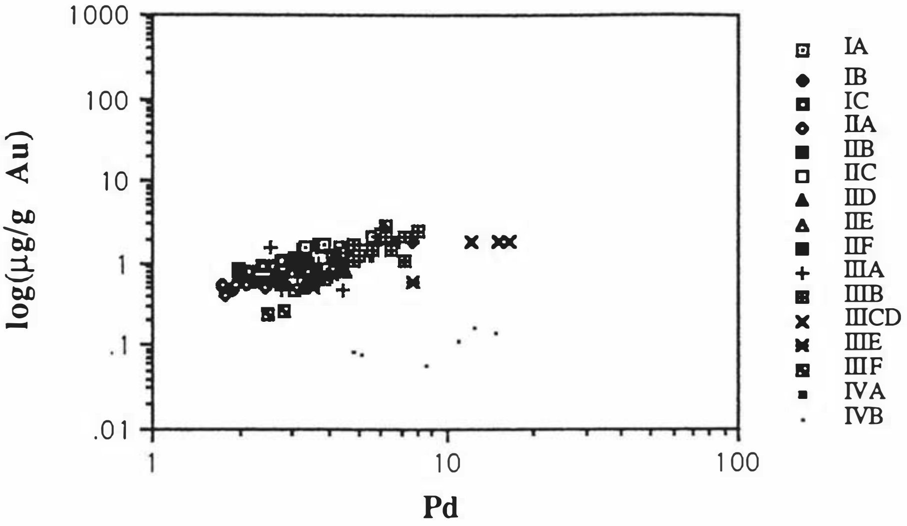
APPENDIX 6 (Continued)



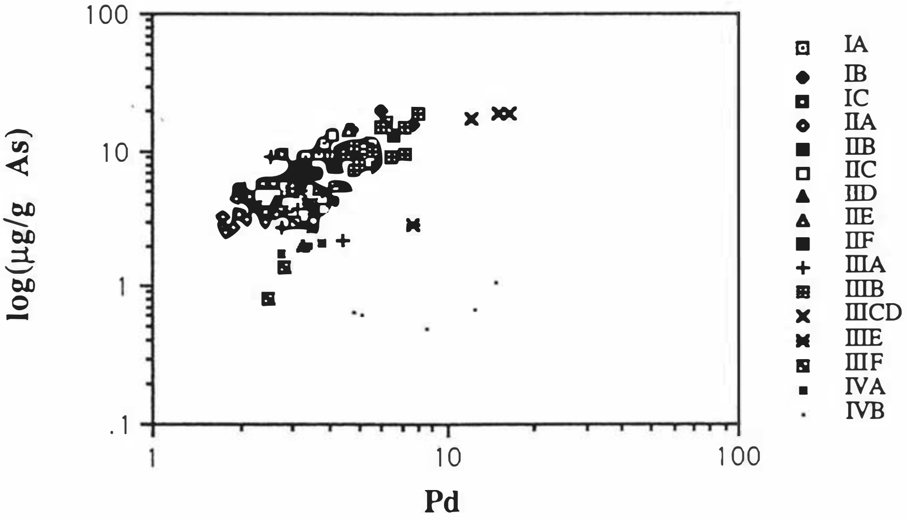
Rh vs. As



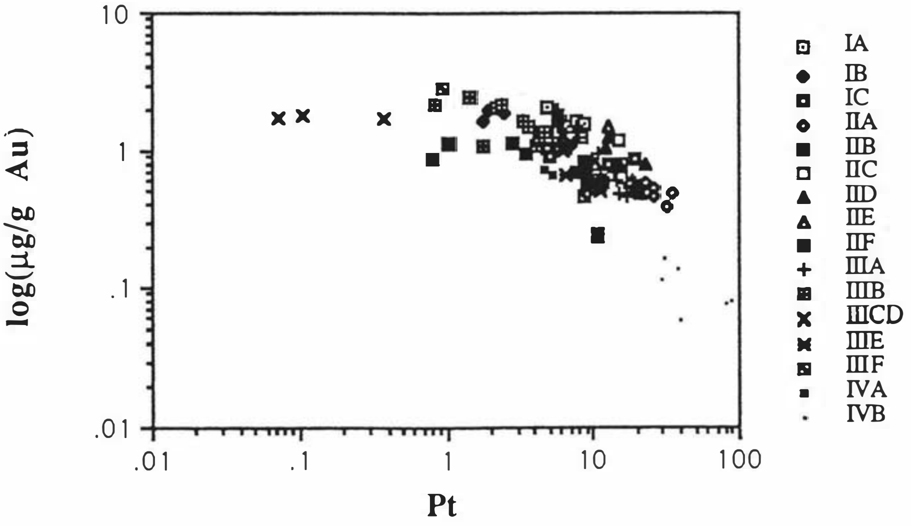
Pd vs. Pt



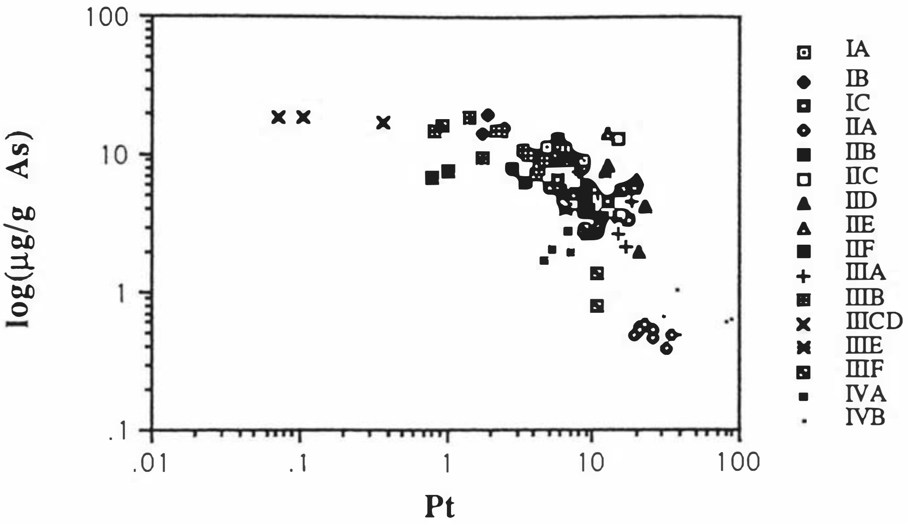
Pd vs. Au



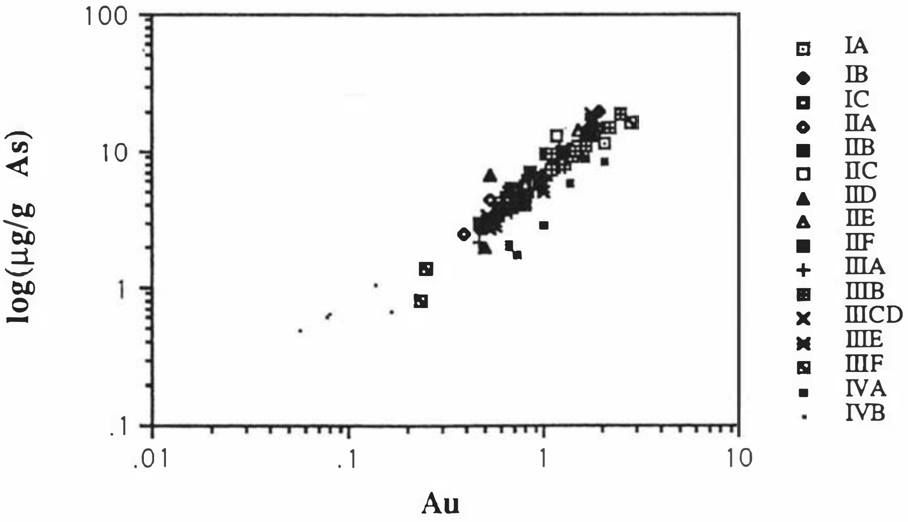
Pd vs. As



Pt vs. Au



Pt vs. As



Au vs. As

APPENDIX 7: Common minerals found in unweathered meteorites (from Buchwald, 1975)

Mineral	Formula	Structure and Remarks
Cohenite	$(Fe,Ni)_3$ C	rhombic Extremely rare as a terrestrial mineral.
Cristobalite	SiO_2	tetragonal, transforms at 270°C to cubic
Daubréelite	$FeCr_2S_4$	cubic Unknown as a terrestrial mineral.
Diamond	C	cubic
Graphite	C	hexagonal
Haxonite	$(Fe,Ni)_{23}$ C_6	cubic Unknown as a terrestrial mineral.
Kamacite	α-Fe(Ni), Ni <7.5%	body-centered cubic Extremely rare as terrestrial minerals.
Olivine	$(Mg_{1-x}Fe_x)SiO_4$	orthorhomic isomorphous group
Plessite	not a mineral	mixture of kamacite and taenite $(\alpha + \gamma)$ in varying proportions
Rhabdite	$(Fe,Ni)_3P$	tetragonal with prismatic, platy habit Unknown as a terrestrial mineral.
Schreibersite	$(Fe,Ni)_3P$	tetragonal Unknown as a terrestrial mineral.
Sphalerite	ZnS	cubic
Taenite	γ-Fe(Ni), Ni >25%	face-centered cubic Unknown as a terrestrial mineral.

APPENDIX 7 (continued)

Mineral	Formula	Structure and Remarks
Tridymite	SiO_2	monoclinic, transforms at 400°C to hexagonal
Troilite	FeS	hexagonal Rare terrestrial pyrrhotites with similar stoichiometric composition reported.

APPENDIX 8: Solar System abundances based on analyses of C1 (undifferentiated) chondrites--from Anders and Grevesse, 1989

Element	Abundance ($^{Atoms}/_{10^6\ Si}$)	Ratio $^{\%Ni}/_{Element}$
Ni	4.93×10^4	---
Ga	37.8	0.130
Ge	119	0.414
Ru	1.86	2.65
Os	0.675	7.30
Ir	0.661	7.46
Rh	0.344	14.3
Pd	1.39	3.55
Pt	1.34	3.68
Au	0.187	26.4
As	6.56	0.752