PGE Anion Production from the Sputtering of Natural Insulating Samples:

“Lessons in Ion Sourcery”

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Geology
University of Toronto

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Abstract

The goal of this research was to devise a new analytical technique, using Accelerator Mass Spectrometry (AMS), to measure Platinum Group Element (PGE) concentrations to the sup-ppb levels in natural, insulating, samples.

The challenges were threefold. First, a method of sputtering an insulating sample to successfully produce a stable beam of anions needed to be devised. Second, a suitable standard of known PGE concentrations had to be found and third, spectral analysis of the beam had to verify any claims of PGE abundance.

The first challenge was met by employing a modified high intensity negative ion source flooded with neutral caesium that successfully sputtered insulators to produce a beam of negative ions.

The second challenge, that of finding a suitable standard, was fraught with difficulties, as no synthesized standards available were found to be appropriate for this work. As a result, direction is provided for future production of standards by ion implantation.

The third challenge, successful spectral analysis, was accomplished using a newly designed gas ionization detector which allowed for resolution of the interfering molecular fragment from the PGE ions. Coupled with the use of the SRIM computer
programme, positive identification of all peaks in the spectra of the analyzed samples was accomplished.

The success of the first and third challenges lead to the qualitative analyses of geological samples for sub-ppb levels of PGE by AMS. Quantitative analyses await only for the appropriate standards and with those will come a whole new range of research possibilities for measuring sub-ppb levels of PGE in insulating samples by AMS.
Dedication

I dedicate this thesis to my family.

To my boys, Liam and Sasha, from whom I continually learn.

To Chris, for staying by my side and helping me through the valleys.

To Kate, for allowing me to stay, so very often.

To both my parents, for their endless patience.

and

To my Mum. Especially to my Mum, for babysitting

above and beyond the call of duty.

Thank you all. Very, very much!
Acknowledgements

I would like to acknowledge the invaluable help and advise of my co-supervisors, Prof. A.E. Litherland and Prof. M. Gorton, and my former co-supervisor, Prof. J.C. Rucklidge. You’ve seen me through 13 years, 10 months and 23 three days of this Ph.D. and without your patience and persistence, this never would have happened. Thank you!

I would also like the thank the other researchers at the IsoTrace Laboratory, without whom this work would not have been possible: Especially Dr. W.E. Kieser and Dr. G.C. Wilson as well as Dr. I. Tomski and Dr. J. Doupe.

In addition, the AMS experiments could not have been accomplished without the assistance of Dr. Xiaolei Zhao. As the heavy element researcher at IsoTrace, he was present for and assisted with the tandem runs, and has my unending gratitude.

Special thanks to Mr. Y. Imahori and Dr. K. Purser for donated equipment and Mr. X-M. Fang and Mr. J. Zlicic for help in getting that equipment up and running.
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<td>$^{196}$Pt spectrum, Winter 2003</td>
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<td>E.15</td>
<td>$^{197}$Au spectrum, Winter 2003</td>
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Chapter 1

Introduction

1.1 The Platinum Group Elements

The Platinum Group Elements (PGE): Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum, are significant both economically and geologically. Found in very low levels in the earth’s crust, (see table 1.1) these precious metals, renowned for their inertness, conductivity and durability, are used in industry, medicine, jewellery and commemorative coins (Young, 1983; St. John, 1984; platinum.matthey.com).

Geologically, the analyses of PGE support a number of applications. The rhenium-
osmium (Re-Os) method of dating, has been used successfully to determine the ages of iron meteorites, sulphide ores of Mo and Cu, and Os-rich minerals. This system has also been used to confirm the extraterrestrial origin of the East Clearwater crater in Quebec (Fehn et al., 1986). In addition, the Re-Os system, has been used in conjunction with the Hf-W, Lu-Hf, Rb-Sr, U-Pb and Sm-Nd methods of dating to study the differentiation of the early earth and the evolution of the crust (Faure, 1986; Walter, 1997; Shearer & Righter, 2003). The state of the mantle is also being studied using PGE, particularly osmium. The Re-Os data indicate that the mantle is now heterogeneous on a scale of approximately 100 km, possibly as a result of meteoritic bombardment after core separation (Pattou et al., 1996). In addition, measurements from the Cretaceous-Tertiary boundary show an unusually high concentration of iridium and other PGE. This anomaly has been interpreted by some as the result of an asteroidal impact that occurred sixty-five million years ago (Alvarez et al., 1980; Kerr, 1983; Faure, 1986).

Other geological applications for PGE analysis include using Os isotopes to study volcanoes (Krähenbühl et al., 1992; Jamais et al., 2008) and exploring the Re-Os systematics of hydrothermal molybdenites (Suzuki et al., 1993). However, a more widely used PGE application, and one which is of interest to economic geologists, is the study of layered mafic intrusions (Naldrett, 2004), such as the Proterozoic Fox River Sill in Manitoba and the Paleocene Eastern Layered Series on the island of Rhum, Scotland.

1.2 Layered Intrusions

Of the many types of deposits that contain PGE, layered intrusions are of particular interest for their primary PGE mineralization, which may occur in disseminated,
marginal and discordant (pipe-like) forms. Within layered intrusions, the platinum group elements are found primarily in sulphide concentrations and in oxide (generally chromite; more rarely magnetite) reefs which often contain minute, discrete inclusions of PGE-bearing minerals (PGM). Only very low concentrations of the PGE are found in the silicate host rocks. This is due to the siderophile and chalcophile tendencies of the PGE, which preferentially enter the sulphide phase of the magma, leaving the silicate phase depleted. The partition coefficients of the PGE (the ratios of the concentrations of the PGE in sulphides as compared to silicates) are not well established, but range, experimentally, from 20 000 to 130 000 (Tredoux et al., 1995).

While some layered intrusions may have a complicated history with many pulses of new, PGE-bearing magma, others have a simpler origin.

These simple layered intrusions may be studied in order to characterize the PGE mineralization signature. In an ideal case of magma mixing and gravitational differentiation, this signature should show enrichment of PGE in the sulphide layer and low levels in the silicate host rocks both above and below this layer. The concentrations of the PGE in the two silicate horizons will be dissimilar, however. The upper layer will be depleted since the PGE were scavenged by the sulphide droplets as they settled out through it. The lower layer, not stripped of PGE in this manner, will reflect the PGE levels of the undifferentiated magma. A study of the PGE concentrations in core samples taken from various depths of a simple layered intrusion should then point to where the PGM rich reef might be located. A boon for prospectors.

Two well known layered intrusions, the Fox River Sill in northeastern Manitoba, and the intrusion on the island of Rhum, Scotland (see sections 1.3 and 1.4), have been analyzed for PGE in sulphide bearing, and sulphide poor rocks, respectively (Naldrett et al., 1994; Scoates & Eckstrand, 1986; Gijbels et al., 1976). So far, however, efforts to measure the PGE in the silicate phases have not proved reliable (Perry et al., 1995;
Hall, 1997). More rigorous evidence of PGE distributions would be welcome. The problem in gathering this evidence lies less in the measurement of PGE in sulphides, and largely in the difficulties of measuring the PGE concentrations in the rock-forming silicate minerals. While conventional techniques can provide data from bulk analysis of mineral separates, these results could easily be invalidated by the existence of minute quantities of sulphides interstitial to the silicates (Butcher et al., 1999). In situ methods of analysis, where it can be ascertained which mineral is being probed, provide the only reliable strategy for measuring the PGE concentrations in silicates (Naldrett, 1993). Unfortunately, none of the existing techniques (see section 2.2) routinely used for such in situ trace element work are adequate, primarily because their minimum detection limits (MDL) are higher than the expected concentrations.

Table 1.2: PGE Concentrations in Select Minerals in parts per billion (ppb), adapted from Wilson et al. (1995); Gijbels et al. (1976); Cabri et al. (2003). Note that the sulphide data are largely from samples collected from PGE deposits, such as Stillwater, Montana and Lac Des Iles, Ontario, and so represent PGE-rich mineral assemblages, as opposed to more typical “barren” rock.

<table>
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<th>Pyrrhotite</th>
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<td></td>
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<td>5</td>
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<td>1</td>
<td>5</td>
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<td>&lt;2</td>
<td>$10^8$</td>
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<tr>
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<td>770</td>
<td>1</td>
<td>4</td>
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<tr>
<td>Pt</td>
<td>7</td>
<td>3</td>
<td>2500</td>
<td>&lt;1</td>
<td>&lt;1</td>
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</table>

Of the analytical methods available, only one is suitable for such low level determinations, Accelerator Mass Spectrometry (AMS). AMS is an extremely sensitive technique, with published detection limits, in favourable cases, as low as 1 in $10^{12}$ (parts per trillion—ppt) for trace elements (Wilson et al., 1995), to 1 in $10^{15}$ (parts per
quadrillion—ppq) or below for some radionuclides (Litherland, 1980). PGE concentrations in sulphides have been measured successfully by AMS (Wilson et al., 1990, 1991, 1995; Wilson, 1998), the results of which are given in table 1.2, but in situ qualitative AMS analysis of PGE in silicates has only recently been realized, and is described fully here and also in Krestow et al. (2007).

1.3 Layered Intrusion: The Fox River Sill

The Fox River Sill (FRS) is an ultramafic, layered intrusion bordering the northern edge of the Superior Belt in northeastern Manitoba (Figure 1.1). The sill, dated by Heaman et al. (1986) at $1882.9^{\pm1.5}_{-1.4}$ Ma, consists of two lobes, each approximately 70 km in length and 2 km in thickness, separated by a 10 km gap (Peck et al., 2002). The intrusion, within the Fox River Belt, is divided into three series. The upper, hybrid roof and the lower, marginal series sandwich the main layered series, as shown in figure 1.2.

The hybrid roof zone (HRZ) is characterized by a heterogeneous suite of rocks that separates the top of the main layered series from the sedimentary country rock. It is primarily granophyric gabbro with quartz and feldspar, and contains inclusions of partially melted host rock. The HRZ holds little interest, economically.

The marginal zone (MZ) consists of two cyclic units, each divided into an upper, leuco-gabbroic sub-unit and a lower, ultramafic sub-unit. Between these two main units lies a horizon known as the KO zone. While typically several meters thick (Desharnais et al., 2004), the KO zone is currently recognized as the most economically interesting PGE occurrence in the FRS: analysis of grab samples from the base of the KO zone returned values of 4.1 parts per million (ppm) Pd, 0.44 ppm Pt and 0.65 ppm Au (Peck et al., 2002).
Figure 1.1: Geology of Manitoba showing the Fox River Sill, from the Manitoba Science, Technology, Energy and Mines website (http://www.gov.mb.ca/stem/mrd/geo/pges/index.html, accessed January 4th, 2010).
Sandwiched between the HRZ and MZ is the main layered series, which comprises the bulk of the FRS. Some 1500 m thick, the main layered series is divided into cyclic units, based on the disappearance and reappearance of olivine cumulates. The lower central layered zone (LCLZ), comprised of at least nine cyclic units, consists primarily of olivine-rich adcumulates with little sulphide and no significant PGE enrichment. The overlying, upper central layered zone (UCLZ), with over nineteen cyclic units, is comprised mainly of orthocumulates which contain occasional PGE-bearing sulphides, particularly near the base of the zone (Scoates & Eckstrand, 1986; Peck et al., 2002).

Precisely because the Fox River Sill has been so well described, it is an ideal intrusion from which to obtain silicate samples for AMS analysis. Accordingly, five
samples were received from the Geological Survey of Canada (see section A.3, page 88, for details of these samples) and have been studied during the course of the present work. The low energy mass spectra for three of these samples were obtained and are presented in section D.3.2 (page 162).

1.4 Layered Intrusion: Isle of Rhum

The Isle of Rhum, roughly 14 by 10 km in size, is part the Inner Hebridean islands, off the northwest coast of Scotland. The layered intrusion which forms the mountainous southeast quadrant is the subject of classic studies of igneous layering and cumulate formation.

Described in great detail by Wager & Brown (1967), the intrusion is dated at approximately 60.53 ± 0.08 Ma (Hamilton et al., 1998), and is divided by the Long Loch fault. East of this fault, the layered series, some 750 m thick, is divided into 15 rhythmic units. Each unit essentially consists of plagioclase-rich rock at the top, grading downward to olivine-rich rock at the base, a result of gravitational settling of the first-formed olivine crystals in the magma chamber. An interesting result of this gradation is the terraced features that result where numerous units of the intrusion are exposed. Since the partly serpentinized olivine rock weathers more easily than the feldspathic rock, the upper parts of each unit stand out in relief, as shown in Figure 1.3. Within the Eastern Layered Series, the PGM are located in thin layers at the inter-cyclic contacts, 6-7, 7-8 and 11-12 (Butcher et al., 1999)

The western part of the series is approximately 1350 m thick and is divided into only 4 units. As in the eastern part, each unit is characterized by the high concentration of olivine, relative to feldspar, at the base. The PGM in this series are located within very thin (millimeter), discontinuous chromite layers, primarily in the Ard
Figure 1.3: Terraced Features of the eastern series of the Rhum Layered Intrusion, with units 7 through 14 labeled. From Wager & Brown, 1967, page 252.

Mheall unit (Butcher et al., 1999).

Unlike in the FRS, no cryptic variation is seen in the layers (Brown, 1956), implying regular replenishment, by magma of constant composition, of the magma chamber. Consequently, the Rhum Layered Intrusion (RLI) has a more complicated origin than the FRS, and is perhaps not an obvious choice for inclusion in this project. However, because the RLI has been so well studied, because PGE analyses have been done on the RLI in the past (Ir values range from 1.72, down to 0.007 ppb (Gijbels et al., 1976) and are $0.34 \pm 0.04$ ppb for sample 118-134c used in this work), and because precisely located samples were readily available, some Rhum material was included in this project (see Appendix A.3, page 88 for details of these samples).
Chapter 2

Current Methods of PGE Analysis

To appreciate the significance of the AMS results detailed in this work, an understanding of the available techniques used for trace element analysis is necessary. For analysis at sub-ppm levels, there are three methods available for bulk and in situ analysis. All are isotope specific, and all have limitations. These limitations include, but are not limited to, matrix effects, nugget effects, memory problems, minimum detection limit (MDL) and spatial resolution. Problems can also arise due to differences in the electronegativity, the work function, and the chemical or nuclear properties of the specific element or isotope under investigation. Please note that while bulk analysis techniques are described here, only in situ analyses were carried out during the course of this research.

2.1 Bulk Analysis

Bulk analyses predominate in mineral exploration for two main reasons. Firstly, the larger samples (typically $\geq 30g$) minimize the “nugget effect”\(^1\) providing representat-
tive results for well chosen samples, and allowing lower detection limits. Secondly, \textit{in situ} analyses tend to be more expensive and require more expertise in interpretation. Currently, three techniques are used for bulk analysis of PGE; Neutron Activation Analysis (NAA), Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) and Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) of pre-concentrated samples.

\subsection*{2.1.1 Neutron Activation Analysis}

The best established of these three bulk techniques is NAA. The elements of interest are concentrated from the rock samples using the nickel sulphide (NiS) fire-assay pre-concentration technique, and then irradiated with neutrons in a nuclear reactor (see Hoffman et al. (1978) for a summary of this technique). The resultant radioisotopes, identified by their characteristic $\gamma$-rays, are then quantified by comparison with a similarly irradiated, known standard. Each element behaves uniquely, based on the nuclear properties of the isotopes of that element. Some elements, which have large cross-sections for neutron capture such as iridium\footnote{Iridium has in its nucleus an odd number of protons and an even number of neutrons (There are two stable isotopes of Iridium: $^{191}Ir$ has 77 protons and 114 neutrons and $^{193}Ir$ has 77 protons and 116 neutrons). Neutrons are captured through resonances, and a neutron creating an “odd-odd” nucleus has a greater chance of hitting such resonances. This is due to the fact that “odd-odd” nuclei have a great level density at the thermal neutron excitation energy. Ergo, an “odd-even” nucleus has a great chance, or cross-section, of capturing a neutron.}, are more easily activated by irradiation. The MDL of Ir, consequently, is very low, less than 0.1 \textit{ppb}. Other elements, such as platinum, lead or sulphur, have very poor detection limits, and are not so well suited for analysis by NAA (Vander Voet & Riddle, 1993).

Unfortunately, there are other factors which can adversely effect the MDL of elements analyzed by NAA. The chemical composition of the sample (the matrix) can contribute to poor detection limits. For analyses of NiS beads, the $\gamma$-ray induced
Compton scattering background that may result from residual Ni can interfere with and obscure much smaller (e.g. PGE) peaks. Unfortunately this scattering background is not flat, and therefore not easily accounted for. Delay times are sometimes employed if the isotope of interest has a long half-life compared to that of the interfering isotope. In the case of NAA of Ir in the Rhum anorthosite analyzed here (sample 118-134c), the wait time of four months revealed a concentration of $0.34 \pm 0.04$ ppb.

When analyses cannot proceed, even with an extended wait time, these matrix effects can be reduced by chemically isolating the radioisotopes after neutron activation (Radiochemical Neutron Activation Analysis, RNAA). However, this is a difficult and specialized procedure, and is performed in relatively few laboratories.

NAA itself is not a technique which many have “in-house.” The requirement of a nuclear reactor necessitates sending the samples out for analysis. In-house methods are significantly more convenient for obvious reasons, and ICP-MS is fast becoming the analytical technique of choice for many commercial assay laboratories.

### 2.1.2 Inductively Coupled Plasma Mass Spectrometry

ICP-MS, like NAA, also analyses samples that have been preconcentrated from bulk rock. Although NiS fire assay with tellurium co-precipitation is traditionally employed (Hoffman & Dunn, 2002), microwave digestion (Perry et al., 1995) and separation by solvent extraction and anion-exchange resins (Yang et al., 2001) have been investigated as methods for pre-concentrating PGE.

Once processed, the sample is then dissolved. This solution is then introduced to the inductively coupled, argon plasma by way of a fine aerosol spray. Heated to 5000–7000$K$, the sample is first atomized, then ionized, by the plasma. Unfortunately, the PGE do not experience 100% ionization, but range from a high of 96% for Ru to a
low of only 62% for Pt (Perkins & Pearce, 1995). Once ionized, the sample beam is focused by means of electrostatic lenses, and mass analyzed by a compact quadrupole. Finally, the selected ions are detected by an electron multiplier and a mass spectrum is produced.

While boasting theoretical MDL of less than 1 ppb (Vander Voet & Riddle, 1993), ICP-MS analysis sensitivity is hindered by limitations associated with sample preparation. These include the degree to which the NiS can scavenge all the PGE from the sample (these efficiencies range from 86 – 98% for most PGE), and the ability of the acid to dissolve all the PGE from the bead (See Jackson et al. (1990) for details of this method). In addition, while matrix effects are minimized in a dilute solution, there is a risk of memory effects from earlier samples enriched in the analyte. The dark current associated with the detection of eV ions also poses a problem for ICP-MS analysis, as stray electrons and photons can be detected as well as the ions of interest, and can affect results.

Nevertheless, ICP-MS has become a popular method of trace element analysis, dispensing with the need for a nuclear reactor, and commercial instrumentation is increasingly available.

### 2.1.3 Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Although conceived and generally used as an *in situ* technique, LA-ICP-MS is also used for bulk analysis of preconcentrated samples. Used initially for those samples that do not lend themselves to dissolution, this technique is now gaining in popularity because it allows for ICP-MS analysis without the need for wet chemistry dissolutions.

Instead of the analyte being introduced to the plasma via the aerosol, a laser is used to ablate material from the solid sample. The sample is enclosed in a silica
case, and mounted on an X-Y stage. A Nd:YAG or ArF laser, frequency multiplied up to ultraviolet ($\approx 200\text{nm}$) fires a pulsed beam at the sample, ablating material and creating a “crater” with each pulse. This vapourized material is carried into the plasma by helium gas that flows through the silica case, and is analyzed, as described above.

While preconcentration is employed to increase detection limits, polyatomic groupings (of, for example, the siderophile PGE) may still form. This produces a submicroscopic nugget effect, which can bias results, as the assumed homogeneity of the sample is compromised. In fact, studies have shown that while Ru, Rh, Os and Ir are distributed homogeneously through a NiS fire assay bead, Pt and Pd are distributed rather more unevenly (Shibuya et al., 1998).

In addition, standardization of the laser spot size and sampling volume, while greatly improved, remains difficult. In fact, this is one of the major drawbacks to LA-ICP-MS. The laser produces a larger area of analysis than the beam size, which while not less important for preconcentrated samples, is important during \textit{in situ} analysis. Finally, isotopic fractionation can be complex. Os, for example, is very volatile and easily forms oxides, so scanning for such compounds, while not initially obvious, is essential for thorough analysis of the sample.

\subsection{2.2 \textit{In situ} Analysis}

\textit{In situ} techniques can, in principle, reveal more facets of a sample than bulk analysis. Not only can the concentrations of the target elements be determined, but their distributions among minerals can be estimated. This is imperative for determining partition coefficients of the PGE. While Electron Microprobe Analysis (EMA),favoured by mineralogists since the late 1960s, has excellent spatial resolution, it lacks the sensitivity for PGE analysis as it has MDL typically of only hundreds of
ppm. The proton microprobe, also a well known technique, offers a complementary approach to the electron probe but with MDL ranging typically from several ppm to several tens of ppm. This too is inadequate for measuring PGE concentrations in most minerals, other than discrete PGM such as sperrylite ($PtAs_2$). These two methods, while adequate for PGE-enriched experimental run products, are not suitable for PGE determinations in natural ore minerals, let alone direct estimates of sulphide:silicate partitioning coefficients.

LA-ICP-MS, Secondary Ion Mass Spectrometry (SIMS) and AMS are three techniques which are suitable, and are employed for in situ analyses of PGE. Of the three, only AMS has the ability to analyze ions of varying charge states. LA-ICP-MS and SIMS can only produce, and thus analyze, ions of charge state +1. This flexibility with AMS is one of the aspects of the technique which make it ideal for measuring PGE in sub-ppb levels, as varying the charge state of the ions of analysis allows for the removal of numerous interfering isobars. Indeed it is this ability to choose the charge state of the ions to be analyzed that gives AMS an advantage over the other techniques as interferences can be practically eliminated.

As with all in situ techniques, LA-ICP-MS is plagued with nugget and matrix effects. While these are unavoidable, given the nature of the method, the former can be often minimized with better resolution. Also of concern with all the in situ techniques listed here, is the lack of reproducibility. However, as in situ techniques are destructive techniques, and no two grains are ever identical, reproducibility is not strictly applicable.

### 2.2.1 Laser Ablation Inductively Coupled Plasma Mass Spectrometry

LA-ICP-MS is a relatively new method for in situ trace element analysis. The
method employed is nearly identical to that described in section 2.1.2, except that the mineral sample is placed in the silica case, instead of the preconcentrated sample. While LA-ICP-MS is now the preferred method of some researchers for \textit{in situ} PGE analysis, it has limitations (see below).

Nevertheless, LA-ICP-MS has advanced rapidly in the last few years. Reaction cells (RC) have enabled reduction of isobaric interferences, such as the hafnium oxides that interfere with platinum analysis (Kan & Tanner, 2004) and recent refinements have reduced the size of the ablation craters from 150 $\mu m$ down to $\approx 7 \mu m$, which significantly increases the spatial resolution of this technique, but also increases nugget effects.\textsuperscript{3}

Problems can also arise with memory effects, where an analysis can be contaminated, because there is a memory of past (more analyte rich) sample left in the machine. This can be remedied, in part, by flushing the system between samples.

Since the laser imparts a significant quantity of heat to a small volume, over a short period of time, melting of the sample material is virtually unavoidable. While this effect is more extensive with sulphides, it has also been noticed with silicates. This melting can be so extensive during the ablation that partitioning of elements between the solid, melt and vapour phases may result in the material injected into the plasma not being representative of the sample from which it originated (Sylvester, 2001), which naturally can bias the analysis towards those elements that are most easily volatilized.

Also of concern with this melting phenomenon is the deposition of melt droplets which form an ejecta blanket around the ablation crater. This material falls on neighbouring grains, and is then the first material to be hit with the laser when analysis

\textsuperscript{3}As nuggets can be on the order of several hundred to several thousand atoms, a 7 $\mu m$ ablation crater is too large to resolve that nugget. Instead it would completely remove that nugget and effectively skew the overall concentration levels determined for the sample.
of that adjacent grain commences. This foreign material can then contaminate the sample, which can subsequently affect the analysis of that neighbouring grain. However, steps have been taken to reduce this melt effect. Since higher laser energies have been observed to produce larger rubble blankets, tuning the laser to lower energies has significantly reduced this effect. In addition, ablation in a helium atmosphere has also been found to reduce the size, and thus effect, of the ejecta blanket (Sylvester, 2001).

2.2.2 Secondary Ion Mass Spectrometry

SIMS, available in the form of various ion microprobes, is a wonderful method for the *in situ* microanalysis of minerals. It can measure virtually all elements, major, minor and trace, down to the ppm levels–ppb in favourable cases, such as lithium–in polished samples. It is truly a work horse in the analysis of geological samples, but is not ideal for *in situ* PGE analysis in the sub-ppb range.

SIMS uses a high energy, focused primary beam of $Cs^+$, $O^-$ or $O_2^+$ to sputter a target. Sample atoms, displaced by the incoming ions, are ejected from the surface. While many ejected atoms are neutrally charged, some are ejected as ions. These can be accelerated and focused by electrostatic lenses and selected for mass using an electromagnet. While the ion yield is low, less than 1% for the desired element, it is usually sufficient for analysis. SIMS can also analyze the three dimensional nature of a mineral. This “depth profiling” capability can be used to characterize interfaces, and quantify differences between phases.

Difficulties with SIMS analysis arise when the element under investigation is present in only trace amounts. Isobaric interferences, negligible when the element was more abundant, become obvious. These can be in the form of isobaric elements (which can be reduced if a reaction cell is available), or molecular isobars. $^{65}Cu_3$, 
for example, can masquerade as $^{195}$Pt. Nevertheless, while $^{65}\text{Cu}_3$ and $^{195}\text{Pt}$ do have the same number of nucleons, they can theoretically be differentiated by electric and magnetic analyzers (EA and MA) with high enough resolution because of their differing mass defects. Unfortunately, the resolutions required would necessitate apparatus with radii on the orders of tens, if not hundreds of meters, which is unrealistic for the average mass spectrometry laboratory.

### 2.2.3 Accelerator Mass Spectrometry

AMS is essentially SIMS with a tandem electrostatic accelerator and an additional mass spectrometry system (Litherland, 1980; Fifield, 1999). A powerful negative ion source produces a beam of high energy negative ions$^4$ that are mass and energy analyzed in the first of two spectrometry systems before being accelerated towards the accelerator’s high voltage (typically $0.5-10\text{MV}$) terminal. Stripped of outer electrons by argon gas at the terminal, most molecules present in the beam disintegrate. The remaining positively charged atomic ions$^5$ are mass and energy analyzed in the second spectrometry system prior to arrival in the gas ionization detector. In this manner, AMS helps to reduce and even eliminate the molecular interferences that can plague SIMS, and provides atomic ions with a variety of charge states from which differing analysis strategies can be chosen.

A range of charge states of ions are produced in the accelerator, with the selection of the charge state of interest being determined by an electric analyzer following the accelerator. Further reduction of isobaric interferences can be accomplished by the prudent selection of charge state. While interfering molecular fragments with the

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$^4$ This high voltage ($-25\text{to} -30\text{kV}$) is required to produce the higher currents ($\approx \mu\text{A}$) necessary to observe very rare isotopes.

$^5$ As well as some stable positively charged molecules, such as $XYZ^{+3}$ (possibly $Ti_2^{+3}$) or $XYZ^{+4}$ (which has not been observed, but is also possible).
same \( \frac{m}{q} \) and \( \frac{\varepsilon}{q} \) as the atomic ions of interest \( \left( \frac{M}{Q}, \frac{E}{q} \right) \) will reach the detector regardless of the combination of magnetic and electric analyzers, those molecular fragments can be distinguished from the ions of interest by an ion detector with sufficient energy resolution.\(^7\) This stems from the fact that while \( \frac{M}{Q} \& \frac{m}{q} \) and \( \frac{E}{q} \& \frac{\varepsilon}{q} \) are identical, the energy of the interfering ions is different than that of the ions of interest. Accordingly, the amount of energy lost \( (\frac{dE}{dx} \text{ and } \frac{de}{dx}) \) to the entrance window of the gas ionization detector will differ. A detector with adequate energy resolution will separate these peaks, enabling identification of the ions of interest, providing the count rate is not excessive. This interference and subsequent resolution is observed in the analysis of \(^{195}\text{Pt}^{+6}\) (See figure 5.2, page 60). \(^{65}\text{Cu}^{+2}\) has the same \( \frac{m}{q} \) and \( \frac{\varepsilon}{q} \) as does \(^{195}\text{Pt}^{+6}\), and so will travel through the electric and magnetic analyzers unhindered. Fortunately, as the current of the copper was sufficiently low, the detector can resolve the various add-ups of the \(^{65}\text{Cu}\) from the \(^{195}\text{Pt}\).

Most isobaric molecular interferences do not have identical \( \frac{m}{q} \) and \( \frac{\varepsilon}{q} \) ratios to the ions of interest. When \( \frac{m}{q} \) and \( \frac{M}{Q} \) are different, the difference can be measured by \( n = mQ - Mq \) (for convenience, \( n \) is expressed in numerical form only: units are not used).\(^8\) For most ions of \( Q \leq 10 \), \( n \) is a useful quantity which provides a convenient means to assess the severity of interference (Kilius et al., 1997).\(^9\) Precisely because these \( n \) values are so useful in helping determine the severity of the interferences, they are used extensively in this work.\(^10\) For \( n \approx \pm 1 \), the interference is sufficient to require an increase in resolution capabilities. This is due to the Coulomb explosion.

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\(^6\) Where \( M \) and \( m \) are the mass numbers of the ion of interest and the interfering molecular fragment respectively, \( E \) and \( e \) are the respective energies and \( Q \) and \( q \) are the respective charges.

\(^7\) Resolution refers to the degree of spreading out, or dispersion, measured in \( mm \), of the constituents of the beam after passage through the analyser.

\(^8\) For fragments where \( \frac{m}{q} \) equals \( \frac{M}{Q} \), \( n \approx 0 \)

\(^9\) The severity of the interference decreases with increasing \( n \).

\(^10\) Discussions of the \( n \) values of the interfering molecular fragments are found throughout Chapter 5, particularly on page 70.
of the molecular beams that increase the energy spread of the resultant fragments, which require a higher resolution by the high energy analyzers. In addition, as the mass defect is asymmetric between \( n = 2 \) and \( n = -2 \), the more simple \( n = mQ - Mq \) equation must be expanded to \( n = (mQ - Mq) + (\Delta mQ - \Delta Mq) \) \(^{11}\) for interferences in that \( n \) range. With the analysis of \(^{194}Pt^+6\), for example, \(^{65}Cu^+2\) is an obvious interference (see figure 5.3, page 63) with \( n = 2 \). With electric analyzers of insufficient resolution, even \( n = 14 \) creates interference, as seen in figure 5.5, page 67, where \(^{133}Cs^+4\) is seen.

Fortunately, AMS (and only AMS among the in situ techniques described here) allows for analysis of ions of other charge states (\( Pt^+4 \) or \( Pt^+5 \), for instance). This requires only retuning the magnetic and electric analyzers following the accelerator, and allows much greater flexibility in the reduction of interferences.

Use of charge state +6, however, is standard for PGE AMS analyses at IsoTrace. Chosen long ago, when the large tandem at the University of Rochester was used for PGE analyses,\(^ {12}\) charge state +6 allowed for the \(^{65}Cu^+2\) beam to be used for tuning. Charge state +6 was used by rote in the work described here, but future PGE determinations would benefit by more prudent choices. As each ion is unique, care must be taken when choosing the charge state in order to minimize interferences for each ion. While charge state +5 would be a suitable choice for \(^{194}Pt\), for example, it would be a less than ideal choice for \(^{195}Pt\) analyses. Since 195 is evenly divisible by 5, there would be interferences by any and all of the \(^{39}K\), \(^{78}Se\), \(^{117}Sn\) and \(^{156}Gd\) present in the sample. These choices assume, however, that a 2 MV tandem is used. If a larger accelerator, such as the MP tandem (University of Rochester) is used,\(^ {11}\) where \( \Delta m \) and \( \Delta M \) are the mass defects of the ion of interest and the molecular fragment, respectively.

\(^ {11}\) The Rochester AMS PGE work of the early 1980s gave detection limits of 0.1 – 03 ppb for \( Pt \) from powdered rock samples.
higher charge states become available as larger magnets can bend these high energy ions more easily. Regardless of the AMS system used, careful calculations involving the composition of the sample as well as the ions of interest, will make for analyses where the interference by molecular fragments can be minimized.

2.3 Standards

2.3.1 External Standards

The results generated by the aforementioned techniques are only as good as the calibrated standards to which the samples are compared.\textsuperscript{13} Typically these standards, known as external standards, are produced from large aliquots of natural materials and elements for which that material will become a standard are quantified by a variety of techniques. However, as ion yields from a given material depend on the sample matrix, the sputtering species and the analyte element, different standards are necessary for different types of samples. Numerous standards are commercially available for the trace element work typical of SIMS, for example, but no standards are readily available for the sub-ppb work done here.

The two standards which were used in this project are AX 90 and the NIST 612 glass. Unfortunately, neither was ideal, as the matrix of each was dissimilar to the samples. However, financial and time constraints stipulated their use.

AX 90 was made by Prof. Sarah-Jane Barnes and contains a, “transitional PGE composition”—elevated PGE concentrations with respect to normal crustal concentrations, yet with subeconomic levels—\textsuperscript{(Wilson \textit{et al.}, 1991)}, which is midway between the well-known Bushveld standard (the enriched, bulk rock) SARM 7, and the PGE levels

\textsuperscript{13} For without standards, only a qualitative appreciation of a sample’s constituents can be made.
in unmineralized ultramafic rocks. The PGE composition of AX 90 is approximately one tenth that of SARM 7, and thus reflects more realistically PGE concentrations found in non-conducting minerals. AX 90 was prepared from 30 kg of material (komatiite with olivine and ≈7% sulphide — primarily pyrrhotite) collected from the old Alexo nickel mine in northeastern Ontario in 1987. It has been well characterized at four different laboratories, by a variety of techniques, and the composition of our fire assay bead aliquot of this reference material has precious metal compositions as shown in table 2.1 (Wilson et al., 1990), page 23.

The NIST (U.S. National Institute of Standards and Technology) 612 glass certified reference material is a 3 mm thick wafer, approximately 12 mm in diameter. The glass rod, from which the wafers were cut, was spiked with trace elements, and synthesized as a standard.\(^\text{14}\) While not intended as a standard for, nor intentionally spiked with, PGE, the NIST 612 glass nevertheless contains sufficient concentrations of Rh, Pd, Pt and Au to be used as a standard (Sylvester & Eggins, 1997). In fact, these concentrations (see table 2.1) in the ppm range are too high for this work, as no beam attenuator was used.\(^\text{15}\) Yet this standard is non-conducting, and used in conjunction with the less enriched AX 90 standard, it was initially believed to offer valuable insight for the analyses of PGE in insulating samples.

For use in this study, the standards were drilled carefully with diamond bit corers, as the material (particularly the AX 90) was brittle. Once drilled, the standards were washed with methyl alcohol, then dried and mounted in a copper holder. As the standards were very thin, the usual mounting method of crimping the smaller back section was often ineffective, so alumina cement was placed in the sample holders and


\(^{15}\) A beam attenuator is a device, such as a mesh, which reduces the intensity of the beam by a known amount, when inserted in the beam line.
Table 2.1: PGE, Ag and Au Concentrations, in ppb, in Standard Reference Materials, from Wilson et al. (1991) and (Sylvester & Eggins, 1997). Please note that while these concentrations in AX 90 Bead 13, AX 90 Bead 14 and SARM 7 are certified, those in the NIST 612 glass are not.

<table>
<thead>
<tr>
<th>Element</th>
<th>AX 90 Bead 13</th>
<th>AX 90 Bead 14</th>
<th>SARM 7</th>
<th>NIST 612</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>41.3</td>
<td>39.0</td>
<td>430</td>
<td>n.a.</td>
</tr>
<tr>
<td>Rh</td>
<td>26.7</td>
<td>25.2</td>
<td>240</td>
<td>896</td>
</tr>
<tr>
<td>Pd</td>
<td>751</td>
<td>709</td>
<td>1530</td>
<td>1090</td>
</tr>
<tr>
<td>Ag</td>
<td>750</td>
<td>750</td>
<td>420</td>
<td>n.a.</td>
</tr>
<tr>
<td>Os</td>
<td>5.1</td>
<td>4.8</td>
<td>63</td>
<td>n.a.</td>
</tr>
<tr>
<td>Ir</td>
<td>6.0</td>
<td>5.7</td>
<td>74</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pt</td>
<td>267</td>
<td>252</td>
<td>3740</td>
<td>2590</td>
</tr>
<tr>
<td>Au</td>
<td>11.3</td>
<td>10.7</td>
<td>310</td>
<td>4580</td>
</tr>
</tbody>
</table>

the standards were pressed into the cement. The cemented standards were then dried at 60°C.

Neither of the two standards available for use in this research is ideal. The AX 90 has concentrations more appropriate for comparison with the expected concentration of the geological samples, but is conducting. The NIST glass, while non-conducting, is so highly enriched in the elements expected from the geological samples, that any calibration could therefore prove inaccurate. A more appropriate standard could be manufactured however, using ion implantation of a given PGE isotope, say $^{192}Pt$, in the sample under study. The feasibility of manufacturing such as standard/sample is described below.

### 2.3.2 Internal Standards–Ion Implantation

Internal standards are natural samples of unknown composition, to which isotopes of the element of interest have been added in known concentrations. Widely used in LA-ICP-MS, internal standards allow for quantitative analysis, as the introduced
standard experiences the same matrix effect as the isotope under investigation. Ion implantation is one possibility to introduce an internal standard for AMS analysis.

Ion implantation, as the name implies, is the process of embedding, or implanting, ions into a solid. Such ions are introduced to the solid by means of an accelerator facility. While most ion implantation facilities operate within the $10 - 500kV$ range, some, such as the (General Ionex 1.7 MV, high current) Tandem accelerator at the University of Western Ontario, implant using greater energies. While equipment at Western would be sufficient for the purpose of implanting a silicate with PGE, doping at $6 MeV$ would deliver $10^{15}$ ions of charge state +3 in $1 cm^2$, only to a depth of $\approx 6 \mu m$ (Wilson, 1994a). This is inadequate for any sample destined for AMS analysis, as $6 \mu m$ of material would be sputtered away very quickly.

The Oak Ridge National Laboratory in Tennessee is a facility which would be much better suited for fabricating a standard for trace element PGE work. Special techniques, however, would need to be employed to allow for implantation to the necessary depth. While initially believed to be sufficient for PGE standard fabrication for AMS analysis, $200 MeV \ ^{198}Pt$ is, in fact, inadequate. Even $1 GeV$ platinum is inappropriate. SRIM calculations show that $1 GeV \ ^{198}Pt$ would be implanted to a mere $0.5 mm$. However, techniques first described in 1964 (Moak, 1964) provide the necessary clues that would allow for standard production of the type required for in situ trace element PGE analysis by AMS. The strategy, called “up-stripping,” lies in operating the accelerator with additional stripping gas (above $2 \times 10^{-5} Torr$) in the high energy accelerator tubes, which allows for (rather an impressive number of ions of) charge states up to +20 to be produced. These high charge state ions

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16 The necessary depth to which ions must be implanted in insulating materials is less than that for conducting materials, as the sputtering rate of insulators is lower than that for conductors. A implantation depth up to $3mm$ is likely sufficient for insulating materials to be analyzed by AMS.

17 The SRIM (Stopping and Range of Ions in Matter) computer programme is available at www.SRIM.org
would then leave the accelerator with extremely high energies. However, as these ions of higher charge also have higher energies, the magnetic analyzer following the accelerator allows for the simultaneous passage of many of these ions (of a given \( \frac{M E}{q^2} \)). In this manner, \(^{192}\text{Pt}\) could be implanted into a solid at a variety of depths at energies greatly exceeding those usually expected of even large tandem accelerators. Using such a technique, the details of which are left to future generations of graduate students, standards appropriate for \textit{in situ}, trace element AMS analyses might be synthesized.
Chapter 3

The Sputtering of Insulators

Most research conducted on the sputtering of non-conductive materials has focused on the sputtering of insulators for ion implantation and semiconductor interfaces (Ishikawa, 1994), with emphasis on radio-frequency sputtering and sputter deposition of dopants on silicon chips. Work relating to the sputtering of insulators for trace element analyses has focused primarily on a variety of ways to neutralize the charge buildup on the sample face.

When a positive beam impinges on an electrically insulating sample, the charge cannot be immediately dissipated, so the sample face charges up. While charging up in a uniform and constant manner would allow for analysis, this rarely happens. More frequently, the sample charges in an inconsistent and variable manner, and often discharges erratically to the nearest conducting surface. Such behaviour results in an secondary ion beam that fluctuates in energy. As the analyzing devices (the magnetic and electric analyzers) are tuned for ions of a specific energy, these fluctuations prevent much of the beam from reaching the detector. Since the current varies irregularly, a thorough analysis of a sample for trace elements is virtually impossible.
3.1 Methods of Surface Charge Neutralization under Ion Bombardment

There are a number of methods that can help minimize the buildup of charge during the sputtering of insulating materials. The first is the choice of a thin (≤ 1mm thick) layer. Since the potential on the surface (ΔU) is equal to the current density (j) times the specific resistivity of the sample (ρ) multiplied by the thickness of the sample layer (l), (ΔU = jρl), reducing the thickness of the sample has the effect of lowering the potential on the surface (Werner & Warmoltz, 1984). While this may be advantageous in some situations, a very thin sample is impractical for AMS analysis, as there would be insufficient material to provide measurable numbers of the scarce PGE atoms.

Neutralization of sample charging by a pulsed extraction field (50 – 500 Hz, up to 500 V) after bombardment by a negative primary beam has had some success (Appelhans et al., 1990). However, the conditions necessary for this success—static-SIMS conditions with primary currents less than ≈ 20 pA, and exposure times of minutes—limit this technique. In fact, the scope of this technique is so limited that the authors admit that its application to dynamic-SIMS (high primary beam flux) requires power supplies with pulse rates that are faster than those that are commercially available. Clearly this option is also not relevant for use with AMS.

A third option to minimize charge buildup involves the use of a conducting layer over the sample face. Grids of conducting material pressed onto the sample face, as well as thin layers (≈ 500 Å) of carbon or gold can act as electrical conduits in this manner. However, these layers, deemed necessary in order to provide the extraction field for secondary ions in SIMS (Inoue & Isogai, 1986), would soon be destroyed under the heavy bombardment of Cs⁺ in an AMS source. Electron flood guns have
also been used in order to compensate for charge buildup. Used successfully though, these guns often require careful and time-consuming tuning for each analysis (see p. 104 in Hauri et al. (2002) for complete tuning details).

A fourth, successful method of minimizing the charge buildup on the sample face when sputtering insulators involves bombardment with a negatively charged primary beam. Although the physics of this phenomenon are still being investigated, this minimization of charge buildup is likely due to the fact that the negative beam arrives at the sample face with two more electrons than a similar positively charged primary beam. These electrons no doubt help sustain the charge neutrality of the sample, and so avoid the situation where the sample face charges up (Groenewold et al., 1997).

Although use of a negatively charged primary beam of ions and electrons generally gives a high yield of positively charged secondary ions (Andersen, 1969)–up to three to five times the yield when sputtered with a positive primary beam (Groenewold et al., 1997) –a secondary beam of this nature needs to be charge changed for AMS analysis. Unfortunately, the process of charge changing the positive ion beam to negative results in both a significant reduction in current and in multiple scattering. As platinum currents from insulators are already weak, a reduction in current of up to 99% would not be acceptable. Thus, while a viable technique, this method is not necessarily appropriate for the AMS analysis of PGE in insulators at IsoTrace.

3.2 Neutralization Using the 860 Negative Ion - Sputter Source

At the onset of this particular project, sputtering with a negative primary beam and charge changing the resultant positive secondary beam, as described above, was the anticipated method for the analysis the PGE in insulating samples. However, the
magnitude of the project and early experiments with an older style ion source, the 860\textsuperscript{1} negative ion sputter source ("the 860"), revealed that a stable secondary beam of negative ions could, in fact, be produced as a result of sputtering an insulator with a positive primary beam. Further measurements both confirmed this discovery and showed that the pyrophyllite sample used in these experiments was in fact non-conducting (see table 3.1, page 29). This unexpected success was likely due to the manner in which the 860 operates. The 860 ionizes caesium vapour to form the $Cs^+$ beam. Under certain conditions however, sufficient $Cs^-$ remains to allow for the dissipation of charge, as hypothesized by Naldrett (1993). Exactly how this dissipation occurs is still under investigation, but recent work by Dr. Xiao-Lei Zhao at IsoTrace and similar studies by Abramov et al. (2005) suggest that the sample face may exhibit properties of solid electrolytes.

Table 3.1: Results from sputtering graphite and pyrophyllite with the AMS machine ion source. The lack of stability of the beam from Pyrophyllite confirm the non-conductive properties of the sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beam</th>
<th>Current</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>$^{12}C^-$</td>
<td>4.45 $\mu A$</td>
</tr>
<tr>
<td></td>
<td>$^{16}O^-$</td>
<td>13.5 nA</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>$^{12}C^-$</td>
<td>No $^{12}C^-$ seen</td>
</tr>
<tr>
<td></td>
<td>$^{16}O^-$</td>
<td>Very unstable, varying from 20 – 80 nA</td>
</tr>
</tbody>
</table>

The 860 is shown schematically in figure 3.1 (page 30), and is presently understood to operate as follows. The neutral caesium enters the body of the 860 (that part of the ion source vacuum housing isolated by the polycarbonate insulator) through the caesium reservoir tube, and floats freely through the cavity. Any caesium vapour which comes into contact with a surface adheres to that surface. This includes the

\textsuperscript{1} “860” refers to the manufacturer’s model number of the source
Figure 3.1: Schematic of the interior of the 860 negative ion sputter source.

The caesium that contacts the ionization coil is thermally ionized. Thus stripped of an electron, this $Cs^+$ is accelerated towards the negatively-charged sample face. The $Cs^+$ sputters the sample face, which mechanically erodes the surface. Neutral atoms and molecules ejected from the surface have a probability of capturing electrons that is proportional to the velocity at which they move away from the sample. The faster a neutral recedes from the sample, the greater its chance to retain the electron that was captured. So the production of heavy negative ions, such as the PGE, which necessarily move more slowly for a given energy, has a lower efficiency than the production of lighter ions. These negative ions, produced in the sputtering process, are accelerated away from the sample
and towards and along the axes of the more positively charged focusing cones.

For conducting samples, this process is fairly well understood. For non-conducting samples, however, the mechanism for the production of a negative beam as a result of the sputtering process is not well known. What is known is that without the presence of the neutral caesium, the sample face builds up positive charge and this accumulation is released only when a pathway is created to nearby conducting surfaces. Since no direct path is available, buildup continues until arcing occurs. This arcing is erratic and precludes the production of a stable ion beam.

When sufficient neutral caesium vapour is present however, passivation\(^2\) of most insulating samples is observed. This passivation is assumed to result from the presence of caesium in and below the sample face. The mechanics of this process, known as caesiation, are subtle, but it is believed that the widespread neutral caesium diffuses into and out of the sample. It is this caesiation of the sample face that is thought to act as both a conduit for dispersing the positive charge—via the metals of the sample holder to the surrounding structures—and as a means to lower the work function of the sample thereby allowing more ions to leave the sample face. The degree of caesiation of a sample is controlled by the amount of neutral caesium available, and by the nature of the sample itself. While complete saturation of the sample would theoretically reduce the work function to that of caesium, the constant sputtering and intense temperatures continually evaporate the caesium that is present and such an extreme state has yet to be observed. Work functions, intermediate to those of the sample itself and of caesium, would be achieved by this caesium saturation hypothesis. Some samples, such as quartz (\(SiO_2\)), which are more insulating in nature and have high work functions, seem to require more neutral caesium in order to be passivated.

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\(^2\) Defined here as the result achieved when an insulating sample face is sufficiently caesiated so as to assure the production of a negative ion beam.
Likely a higher density of caesium in and below the surface is required for a stable secondary beam to form. So, while the exact nature of the caesiation is unknown, it has been observed that if left for a sufficient amount of time (up to 48 hours based on empirical evidence) even a pure quartz sample can achieve passivation and produce a steady beam of negative ions.

The disparity between the strength of the negative ion beams resulting from the sputtering of conductors and insulators was explored when both silicon metal ($Si$), and quartz ($SiO_2$) were sputtered under identical 860 conditions (see Figures D.33 and D.35, pages 142 and 144). While the production rate of $Si$ from quartz was only $\frac{1}{16}$ that of $Si$ from the silicon metal, the one half dilution factor (silicon metal is 100% $Si$, while quartz is only 46.6% $Si$ by mass), as well as the higher binding energy of the $Si$ in the quartz may be enough to explain the discrepancy.

With the discovery that the 860 negative ion source could form a stable negative ion beam from insulating samples, a new method for neutralizing the charge buildup on the surface of insulators when sputtered with positive primary beams was confirmed. This method was subsequently used to start the analytical research of PGE in non-conducting geological samples by AMS, the results of which are presented in chapter 5.

### 3.3 Sputtering of PGE

One realization made during the course of this research concerns the nature of the negative PGE ions formed during the sputtering process. Initially thought to form only as negative ions, it has become apparent that some PGE likely form molecular anions as well, due to the complex sample chemistry. Since both elemental and molecular anions are undoubtedly produced as a result of the sputtering process, discussions
of both follow.

### 3.3.1 Electron Configuration

While the formation of the platinum, ruthenium and rhodium negative ions that result from the sputtering of insulating samples is as described above, the production of negatively charged ions of palladium, osmium and iridium is more complicated. These elements do not allow for the simple addition of an electron to the ground state for the production of the negative ion.\(^3\) An electron must be acquired by an excited state of the isotope in order to form a negative ion (See table 3.2, page 34, for the electron configurations of the PGE). However, these excited states are achieved with a probability of \(e^{\frac{-E}{kT}}\),\(^4\) where \(E\) is the energy of the excited state. The greater this energy \((E)\), the less likely and more complicated the scattering that is needed to make the negative ion.

In the case of palladium, the ground state has the electron configuration \(4d^{10}\). As the d shell has a capacity of 10 electrons, another electron must be added to the s shell. Pd\(^-\) does not have the configuration of \(4d^{10}5s^1\) however, but rather \(4d^95s^2\) which fills the s shell. Simply adding an electron to Pd\(^0\) will not produce Pd\(^-\). In order to create Pd\(^-\) from the ground state of Pd\(^0\), an electron must first be removed from the 4d shell and then two electrons added to the 5s shell. This removal and addition is not a process likely to occur during the sputtering of the sample in the ion source. While Pd\(^-\) has been observed from the siliceous samples used here, it likely results from the tunneling of an electron to the sputtered excited state, \(4d^95s^1\) \((E = 0.814eV)\) of palladium.

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\(^3\) Platinum, ruthenium and rhodium have ground states of \(5d^96s^1\), \(4d^75s^1\) and \(4d^85s^1\) respectively. Addition of an electron to these states would fill the s shell, providing stability to the negative ion.

\(^4\) \(k\) is Boltzmann’s constant \((1.3807 \times 10^{23}\) Joule/Kelvin\) and \(T \approx 10000K\) at \(68\frac{meV}{K}\) or \(0.68eV\).
Likewise, the Os\textsuperscript{−} does not form from the addition of an electron to Os\textsuperscript{o}. The ground state of osmium is 5d\textsuperscript{6}6s\textsuperscript{2}. To add an electron to the d shell would require a substantial amount of angular momentum. While not impossible, this process is likely not as probable as the addition of an electron to the excited state. The excited state of osmium is 5d\textsuperscript{7}6s\textsuperscript{1} (E = 0.638 eV), and like the palladium, once this excited state is formed as a result of the sputtering process, it will readily accept an electron to form the negative ion.

Iridium is very similar in electron configuration to osmium. Its ground state (Ir\textsuperscript{o}) is 5d\textsuperscript{7}6s\textsuperscript{2}, and its excited state is 5d\textsuperscript{8}6s\textsuperscript{1} (E = 0.351 eV). Adding an electron to the excited state is how Ir\textsuperscript{−} (5d\textsuperscript{8}6s\textsuperscript{2}) is likely produced.

Table 3.2: Electron affinities and the ground state and negative ion electron configurations of the PGE, silver and gold.

<table>
<thead>
<tr>
<th>Element</th>
<th>Electron Affinity (eV)</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ground State</td>
</tr>
<tr>
<td>Ru</td>
<td>1.1</td>
<td>4d\textsuperscript{7}5s\textsuperscript{1}</td>
</tr>
<tr>
<td>Rh</td>
<td>1.14</td>
<td>4d\textsuperscript{8}5s\textsuperscript{1}</td>
</tr>
<tr>
<td>Pd</td>
<td>0.56</td>
<td>4d\textsuperscript{10}</td>
</tr>
<tr>
<td>Ag</td>
<td>1.30</td>
<td>4d\textsuperscript{10}5s\textsuperscript{1}</td>
</tr>
<tr>
<td>Os</td>
<td>1.40</td>
<td>5d\textsuperscript{9}6s\textsuperscript{2}</td>
</tr>
<tr>
<td>Ir</td>
<td>1.57</td>
<td>5d\textsuperscript{9}6s\textsuperscript{2}</td>
</tr>
<tr>
<td>Pt</td>
<td>2.123</td>
<td>5d\textsuperscript{10}6s\textsuperscript{4}</td>
</tr>
<tr>
<td>Au</td>
<td>2.308</td>
<td>5d\textsuperscript{10}6s\textsuperscript{4}</td>
</tr>
</tbody>
</table>

### 3.3.2 Complex Chemistry: Sputtered Species

The formation of negatively charged ions of the PGE is complicated, not only due to their electron configuration as shown above, but also because of the chemistry associated with these ions.
As shown in table 3.2 above, the electron affinities and configurations of platinum and gold are similar, at 2.123 and 2.308 eV respectively. As the ground state of platinum can acquire an electron, it could be assumed, given the similar electron affinities, that platinum and gold would form at approximately the same rate. While this is true when platinum and gold metals are sputtered, this has not been observed when natural samples are sputtered. This disparate production rate is noted in table 5.5, page 72, where the sensitivity of gold is shown to be three orders of magnitude greater than that of platinum (where the intrinsic concentration of platinum is more than twenty times that of gold). While no definitive explanation can be offered for the apparent deficiency in the production of negative ions of platinum, the hypothesis is that the platinum could leave the sample surface as negative oxides or carbides, in addition to negative ions (Zhai et al., 2002). For whereas gold has a closed 5d shell and one loose electron in the 6s shell, platinum has a hole in the d shell, and as such can form compounds with oxygen. While $PtO_n^-$ was only observed in low levels from sample 118-134c (see table 5.6, page 76), it and other similar molecules have been studied (Ramond et al., 2002; Middleton, 1989) previously. Middleton showed that iridium powder, for example, sputtered in a high intensity negative source reveals “strong peaks corresponding to $IrO^-$ and $IrO_2^-$. ” While these peaks did fall rapidly with time, this was undoubtedly due to the lack of available oxygen to which the iridium could bind. A natural sample, like the Rhum anorthosite, whose major constituents are $SiO_2$, $Al_2O_3$ and $CaO$ has ample oxygen for platinum to combine with, thus making $PtO_n^-$ ions. In fact, once the nature and complexities of sputtered species, in particular the molecular ions from the 860, were realised, detailed reviews of the preliminary research revealed the extent and strength of oxides and sulphides from natural samples. Of note are the $NiS_n^-$ peaks in the mass spectrum of AX 90, Bead 13 on page 162, the strong $AlO_n^-$ and $CrO_n^-$ peaks in the spectrum of sample
27, page 163 and the numerous $FeO_n^-$ peaks in the mass spectrum of sample 1055, page 164. Therefore, all future studies of PGE sputtered from insulators should aim to measure not only the atomic ions from the samples, but also the molecular ions.
Chapter 4

Method

When initially conceived, AMS analysis of PGE in silicate minerals was to be achieved using a positive ion source with subsequent charge changing of the resulting beam, as described in section 3.1 above. The arrival of several 860 sources from AECL Chalk River however, changed the direction of the research to involve sputtering with a negative primary beam and charge changing the resultant positive secondary ion to negative for injection into the accelerator (Naldrett, 1995; Krestow, 1997). While this still remains a valid method, and one which may be advanced in the future, the magnitude of the project was such that when another technique for sputtering insulators was discovered, it was pursued instead.

In May 1999, it was realized that a stable beam could in fact be produced from an insulator, using an 860 $Cs^+$ sputter source, if the right conditions are met. Following this finding, the nature of the thesis work changed direction, although the need to build an apparatus with basic analytical capability remained.

To this end, three separate systems were built and/or used to carry out the experimental work. The “yellow testbed” is the most simple in configuration and is where the discovery that a stable negative ion beam could be sputtered from an insulating
sample was made. Further tests to verify this finding, and to both qualify and quantify the nature of the negative beam, were carried out on the second, “blue testbed.” The third apparatus, the “red testbed” was used to inject this negative beam through the accelerator for final analysis. All three of these systems utilized the 860 sputter source to generate negative ions, and a combination of other components to steer, focus and analyze the beam.

4.1 The 860 Source

4.1.1 Physical Description

The 860, shown schematically in figure 3.1, on page 30 and pictured in figure 4.1 below, is fundamental to this research, and so is described here in some detail. It is a roughly cylindrical piece of equipment, approximately 40 cm long, and 20 cm in diameter. Made of aluminium and water-cooled, the exterior houses strong permanent magnets near the sputter target which deflect electrons from the beamline. A large, polycarbonate insulator, situated at the exit port for the secondary ions, provides electrical isolation for the source from ground. At the target entry port of the 860, a single sample, affixed to the end of the cooled stainless steel sample rod, is inserted concentric with the beamline. Atop the 860, towards the exit port, is a feed-through that allows variable voltages to be applied to an internal, focusing electrode. Beneath the body, the caesium reservoir is encased in a copper sheath, in which resistive heaters are embedded.

The internal structure of the 860, made almost entirely of stainless steel, is depicted in Figure 4.2, page 40.

The sample, sample rod and sample extraction cone with support structures, are
Figure 4.1: The 860 Negative Ion Sputter Source, mounted behind its power supplies within the Plexiglas housing. It is attached to the red testbed at the upper right hand side. Shown beneath and attached to the 860 body (above the foil capped cylinder) is the caesium reservoir, surrounded by the copper heater.

isolated from the rest of the 860 internal structure by Macor\textsuperscript{1} standoffs. The ionization coil, a four turn, tantalum sheathed helix, is positioned immediately adjacent to, and concentric with, the extraction cone. 15 mm below\textsuperscript{2} the ionization coil is an opening through which the caesium vapour is introduced via the reservoir tube. 20 mm beyond the ionization coil, coaxial with the beam line, is the first focusing cone. With an 8 mm diameter aperture, this cone is oriented to face the ionization coil. A second focusing cone, with a 10 mm aperture also facing the coil, is 18 mm farther along the

\textsuperscript{1} A machinable ceramic.
\textsuperscript{2} when assembled and positioned for use
Figure 4.2: The photos above show the interior of the 860. The upper photo shows the assembled components, the lower, the internal structure. The Macor standoffs labeled “A” isolate the sample assembly from the body of the 860. Those labeled “B” isolate the second focusing cone. In the lower photo, the ionization coil is visible within the left hand column, as is the opening through which the caesium is introduced (just above, and to the back of, the coil). The first focusing cone sits atop the right hand column, which houses the second focusing cone.
beamline. It is this second cone that is connected to the external feed-through, as described above. Since varying voltages can be applied to this electrode, this second cone is isolated from the rest of the 860 internal structure by Macor standoffs.

4.1.2 Operational Parameters

The production of the negative beam from the 860 requires voltages to be applied to both the 860 body, and the sample. Typically, the body is held at a voltage of $-21$ to $-22$ kV. This voltage is supplied from a power supply referenced to ground potential. A well shielded line from the power supply output to the aluminium body of the 860 brings the body up to the required voltage. This cable is also connected to the insulated “deck” upon which all the other 860 power supplies are mounted, and to which their grounds are referenced. This configuration is necessary since these other power supplies run components within the 860 that are held at voltages, referenced to the body or “deck voltage”. The sample is held at an additional potential of $-3.5$ to $-4.5$ kV by attaching a cable from a second power supply, referenced to the deck voltage, to the end of the sample rod. Likewise, the second cone’s power supply is mounted on the deck, and is tuned to between $+2$ kV and $+5$ kV, to focus the resulting negative beam.

In addition to the components held at voltage, production of the negative beam also requires that the caesium reservoir and the ionization coil be heated. The reservoir’s resistive heaters, embedded in its copper sheath, are controlled by a variable transformer which steps down alternating current from line voltage. The calibration of this transformer is approximate, but an operational temperature of $154\pm2^\circ$C is reached at $30\pm1$ V. It should be noted here that while the theoretical calculations, given in Appendix B (page 91), point to an adequate operational temperature of less
than 50°C, the higher temperature is necessary to produce good beams.

The power supply controlling the ionization coil is typically operated with an output of $19 - 20.5\,A$ in order to produce the $\approx 1200°C$ needed to ionize the caesium vapour.\(^3\) The coil is comprised of a central resistive wire surrounded by a magnesium oxide, $MgO$, insulating layer, within a thin tantalum tube. When current is passed through the wire, the $MgO$ gradually heats up and warms the tube. It is this tube that the caesium vapour comes into contact with, and which ionizes the alkali-metal atoms.\(^4\) Not all the caesium vapour in the 860 is ionized however. This neutral caesium, which collects near the sample face, is the very thing that allows for stable negative beam production from an insulating sample (see section 3.2).

In summary, typical operation of the 860 involves sputtering the target with $\leq 5\,keV$ $^{133}Cs^+$ ions, with the secondary ions emerging from the source with $\approx 26\,keV$. A summary of the operational parameters is listed below, in table 4.1.

Table 4.1: Summary of the operational parameters of the 860 negative ion source

<table>
<thead>
<tr>
<th>Power Supply</th>
<th>Ranges used to sputter Targets</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Insulating Targets</td>
</tr>
<tr>
<td>Deck</td>
<td>$-21$ to $-22kV$</td>
</tr>
<tr>
<td>Sample</td>
<td>$-2.5$ to $-4.5kV$</td>
</tr>
<tr>
<td>Focusing Cone</td>
<td>$+2$ to $+5kV$</td>
</tr>
<tr>
<td>Caesium Boiler heater</td>
<td>$30 \pm 1V$ ($\approx 154\pm2°C$)</td>
</tr>
<tr>
<td>Ionization coil</td>
<td>$19$ to $20.5A$</td>
</tr>
</tbody>
</table>

\(^3\) Towards the end of its life, the ionization coil’s resistivity goes up. To avoid a runaway effect (described fully in section C.1, page 92) in the ion source, the current to the coil is reduced so that the total output is constant at approximately $135\,W$.

\(^4\) The tantalum ionization coil, like the copper holders used in the experiments described in this work, has an unknown concentration of the PGE. While Pt itself is not volatile, Os is, and any Os present may be emitted from the ionizer during heating. In addition, sputtering of the coil by the ions emitted from the sample may provide a mechanism by which any PGE in the ionization coil could contaminate results. While the extent of this contamination is unknown and has not been taken into account here, it should not be ignored in future.
4.2 Focusing, Steering and Detecting Components

Once a stable ion beam has been produced by the 860, this beam must be manipulated in order to ensure that the desired species reaches the detector. There are numerous devices that facilitate this journey. These can be categorized by functionality as analyzing devices (with focusing properties), focusing devices, steering devices, location defining elements or recording devices. The analyzers include the magnetic analyzer (MA) and the electric analyzer (EA). The focusing elements include the slot lens and the triplet quadrupole. The steerers compensate for minor misalignments and stray electric and magnetic fields in the system while location defining elements include slits and apertures. Finally, the Faraday cups and the gas ionization detector are categorized as recording devices.

The magnet is one device used for analyzing ions in a mass spectrometry system. The magnet selects ions by the combination of mass (M) times energy (E), divided by the square of the charge (q); $\frac{ME}{q^2}$. By varying the current through the electromagnet’s coils, the magnetic field between the poles is tuned to the strength needed to allow for the ions (of a given charge) under investigation to pass through the exit slits. The magnetic field strength, $B_1$, necessary to analyze an ion of mass, $M_1$, can be calculated from the known $B_2$ and $M_2$ of another species, by $(\frac{B_1}{B_2})^2 = \frac{M_1}{M_2}$.

The quality of a magnet is given by its mass resolution capability. Mass resolution is defined as $\frac{M}{\delta M}$, where $\delta M$ is the difference in mass between two peaks of similar mass $M$, separated by a valley, 10% of the peak height (Long, 1995). For example, to resolve the $^{65}Cu_3$ trimer from $^{195}Pt$ a magnet with a resolution of at least 1074 is required. A good magnet can measure a mass resolution of $\frac{M}{\delta M} = 1000 - 10000$, but with transmission losses proportional to $\frac{M}{\delta M}$. The mass resolution is measured by

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5 Measured by a Hall probe or, more precisely, by an NMR probe.
\[
\frac{M}{\delta M} = k \frac{R}{s},
\]
where \( R \) is the radius of the magnet poles, \( s \) is the width of the entrance slits and \( k \) is a constant. The larger the magnet radius of curvature (\( R \)) the better its resolution. Narrowing the magnet entrance slits, while increasing mass resolution, decreases the intensity of the beam. For strong beams, this is not too detrimental, but for low intensity beams the need for resolution must be weighed against the requirement for high count rates.

To calibrate the magnet, a strong beam is located (e.g., \(^{12}\text{C}^-\), from carbon), then the mass of that ion, as well as the magnetic field strength to which the magnet is tuned, are used to determine the species of other, lesser beams that are observed. Calibration of the large, 90° magnet of the red testbed was done using multimers of carbon, which can be seen in figure D.49, on page 160.

An electric analyzer (EA) is another analyzing device in mass spectrometry. Two plates are positioned vertically and effectively deflect the beam in a horizontal manner. These plates are held at voltages of the same strength, but opposite polarity. The EA analyses ions by energy (\( E \)) divided by charge (\( q \)), \( \frac{E}{q} \), and can thus direct all ions of a given \( \frac{E}{q} \) ratio in the beam, regardless of mass. The high energy analyzer immediately following the accelerator in an AMS system, is the device used to select the final charge state of the ions to be analyzed.

The quality of an electric analyzer, like that of the magnet, rests on its resolution capability. As with the magnet, increased resolution is achieved by decreasing the width of the entrance slits, and/or increasing the radius of curvature of the analyzer.

The einzel lens is one of the focusing devices in a mass spectrometry system. The particular model used here is typical of einzel lenses and has a set of three, coaxial cylindrical apertures, the central of which is held at voltage. The einzel lens accelerates or retards the beam within the confines of the lens, as dictated by the polarity of that voltage. It provides radially focusing of the beam.
A slot lens also provides focusing. It is a series of three pairs of plates. The outer pairs are grounded and the inner pair is held at voltage in order to focus the beam vertically (see figure 4.3). It acts in one dimension only.

![Figure 4.3: The slot lens](image)

The triplet quadrupole, shown in figure 4.4, is a series of three sets of four poles that focus the beam. For each set of four poles, the adjacent poles have opposite polarity. By combining these three sets of poles in series, a net focusing effect can be obtained in both planes.

Steerers, as their name implies, steer the ion beam, compensating for minor misalignments and stray electric and magnetic fields. Steerers are pairs of flat stainless steel plates, positioned horizontally or vertically on either side of the ion beam trajectory, to steer the ion beam vertically or horizontally, respectively. The plates are usually held at voltages equal in strength, but opposite in polarity. Steerers provide only weak steering capabilities, and can only really “tweak” the beam.

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6 A description of the wiring of these poles is given in the latter part of section C.3, page 98.
Slits are simply flat rectangular plates of stainless steel or tantalum, which are inserted and retracted in an incremental manner, into and from the beamline, in order to define the beam for mass or energy. Horizontal and vertical slits are often used in combination to trim the beam as symmetrically as possible and to define the location of waists for focusing the ion beam.

An aperture is simply a round, knife-edged opening that limits the beam. It cuts off the concentric tails of the beam, much like the slits. Like slits, an aperture can be retracted from the beam line, but unlike slits, an aperture’s diameter is not easily changeable.

Two types of detectors have been used in the experiments of this thesis work; the Faraday cup and the gas ionization detector. The detector used most often is the Faraday cup. The cup used in this work is a solid copper cup, 25.4 mm in diameter, with a graphite cone positioned at its base. Often used in an intermediate location along the beam line, it can be retracted, to allow the ion beam to pass beyond it.

Figure 4.4: The triplet quadrupole
When used to measure the current, it is placed in the path of the ion beam. When this beam hits the carbon cone, the electrical current deposited travels along the wire connected at the back to a picoammeter. A current of 1.6 picoampere (1.6 pA) of singly charged ions represents $10^7$ particles hitting the carbon cone, per second. Faraday cups (FC) can be of any size, although the ones used in these experiments can accept high currents, and have water cooling. Often there is a negative bias voltage applied to a plate immediately before the cup which provides a retarding field strong enough to deflect electrons and keep them from entering or leaving the cup and affecting results.

The gas ionization detector is used when a very low current\(^7\) is expected. Two gas ionization detectors were used during the course of this work, the second, designed and built by Dr. Xiao-Lei Zhao having markedly better resolution than the first. Both detectors involve a cylindrical chamber filled with isobutane gas ($C_4H_{10}$) to a pressure of 20 Torr (Zhao, 1992). A very thin ($\leq 120 \mu g/cm^2$ in the case of the newer detector, thicker for the older version), polypropylene window confines the gas within the chamber. While the older detector had the window situated farther forward along the beamline, the newer detector placed the window immediately adjacent to the anode and cathode, thereby reducing the dead space, and effectively increasing the detector’s resolution. This increase in resolution is in fact sufficient to allow for the separation of the $^{195}Pt^{+6}$ peak from the peaks due to the $^{65}Cu^{+2}$ interferences (See Figure 5.2, page 60). This is significant, as such resolution has never before been reported, and critical to this work.

The incoming beam passes through the window and ionizes the gas molecules. The positive ions produced from these interactions are then attracted to a cathode, as shown in figure 4.5. The electrons that result from the interactions are attracted

\(^7\) less than 5000 cps (counts per second).
to a grid (oriented opposite the cathode from the beam line) which is held at +200 V. The electrons pass through the grid and continue to move towards an anode\(^8\) which is held at +350 V. The signal produced when the electrons hit the anode is sent through both a preamplifier and an amplifier. The resultant spectrum produces peaks according to the energy of these electrons (channel) and by the number of incoming electrons (height of the peak).

Figure 4.5: A schematic of the new gas ionization detector, used for the Spring 2004 and June 2009 runs.

Due to this method of detecting the energy lost by the ions (the pulse height is related to ion energy once the ions have passed through the window), the gas ionization detector makes it possible to separate fragments of molecular isobars of the isotope under study with the same \( \frac{M}{Q} = \frac{m}{q} \) and \( \frac{E}{Q} = \frac{\varepsilon}{q} \) (in this case the PGE ions) (Kilius et al., 1997). This is because the total energy lost by the fragments (the combined energy lost by the three \( ^{65}Cu \) in the case of the \( ^{195}Pt \) spectrum) is greater

---

\(^8\) Only the first of the two anodes–the one on the left in figure 4.5–was used in this work, as all ions were stopped before reaching the second anode.
than the energy lost by the PGE ion (which arrived at the window with three times the energy). This loss of energy is apparent in the spectrum, where the fragment peaks show up at lower energies than the PGE peak (Examples are shown in chapter 5).

4.3 The Yellow, the Blue & the Red Testbeds

The yellow, blue and red testbed were a series of increasingly complex systems on which the preliminary experiments were accomplished. All were used extensively, and more detailed descriptions of each can be found in the appropriate sections of Appendices C and D. The yellow testbed was important primarily because it provided a platform where the operation of the 860, with respect to sputtering insulating materials, was first achieved. Once the 860 was transferred to the blue testbed, the beams produced could be analyzed more precisely. The red testbed, later the injection line to the spectrometer, facilitated AMS analysis of the negative ions from these insulating materials.

While certainly important, use of the testbeds was primarily to aid in the understanding of the operations of the 860. Once fully commissioned, the 860 was then used to inject the stable beams of PGE ions into the spectrometer for identification, free of molecular interferences.

4.4 The Red Injection Line and The Tandem

The tandem experiments were completed in three series. The “winter runs” were in November and December 2003, and the “spring runs” were in May and June, 2004 and the “final run” was in June 2009. The AMS system at IsoTrace, like all AMS systems,
is essentially two mass spectrometry systems, with a tandem accelerator between. In the case of these PGE experiments, the red injection line, shown schematically in figure 4.6, bypasses the usual low energy apparatus, and so is considered the first mass spectrometry system.

While a detailed description of the set up and operation of the red injection line is given in appendix C (beginning on page 98), the excellent resolution of the red line’s $90^\circ$ MA must be noted here. Figure 4.7 shows the resolved copper trimers, and demonstrates that when tuned for one mass, little else is observed. This is especially important during the analysis of the spectra from the spring runs, as mass resolution is critical for the interpretation of results (see section 5.2.2). Also of note is the virtual lack of electric analysis in the red line. The existing $7^\circ$ EA unfortunately does not provide the necessary resolution, but as no other EA was available, these PGE experiments went ahead.

Figure 4.6: Schematic of the Red Injection Line. The photo referred to can be found in appendix C.3, page 99 (figure C.2).
Figure 4.7: The copper multimers, measured at the low energy FC, after the installation of the “red line remote.” The area under the curves of the isotopes have ratios reasonably consistent with those expected for the isotopes, and so confirm the excellent resolution of the red testbed magnet.

The red injection line links to the AMS system (as shown in Figure 4.8) through the straight through port of the system’s low energy MA. The beam then continues, through slits, to the tandem accelerator. The negative ions accelerate towards the positive terminal voltage, where they are stripped of their outer electrons by the argon gas contained within the stripping canal. Coloumb explosions destroy virtually all molecules at this stage, and the resultant fragments, as well as positively charged ions, are accelerated towards ground. The beam then passes through a 15° EA, another 90° MA, then a 45° EA before ending in the gas ionization detector. The settings
associated with the accelerator and with various focusing and steering components are listed below, in tables 4.2 and 4.3.

Figure 4.8: The system’s low energy MA is labeled “M2”; the stripping canal, “SC”; the 15° EA, “E2”; the 90° MA, “M5”; the 45° EA, “E3” and the gas ionization detector, the “Heavy Element Detector.”
Table 4.2: The settings for the machine components, for the light PGE (charge state, +4) and heavy PGE (charge state, +6) of AX 90, as set for the runs of December 9th and 10th, 2003. The dial settings are reproduced here merely for the purpose of reference, for IsoTrace researchers.

<table>
<thead>
<tr>
<th>Component</th>
<th>Light PGE (Pd, Ru, Rh) settings</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dial settings</td>
<td></td>
</tr>
<tr>
<td>Accelerator</td>
<td></td>
<td>1.9266MV</td>
</tr>
<tr>
<td>HE steerers</td>
<td>693 667 358 448</td>
<td></td>
</tr>
<tr>
<td>15° EAS/quad</td>
<td>941 504 593 632 940</td>
<td>33.65 kV</td>
</tr>
<tr>
<td>Matching lens</td>
<td>--</td>
<td>−17.5 kV</td>
</tr>
<tr>
<td>45° EA/quad</td>
<td>562 482 727 757 910</td>
<td>44.46 kV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Component</th>
<th>Heavy PGE (Os, Ir, Pt) settings</th>
<th>Voltages</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dial settings</td>
<td></td>
</tr>
<tr>
<td>Accelerator</td>
<td></td>
<td>1.9266MV</td>
</tr>
<tr>
<td>HE steerers</td>
<td>595.5 558 371 326</td>
<td></td>
</tr>
<tr>
<td>15° EAS/quad</td>
<td>878 503 581 636 940</td>
<td>31.40 kV</td>
</tr>
<tr>
<td>Matching lens</td>
<td>--</td>
<td>−17.7 kV</td>
</tr>
<tr>
<td>45° EA/quad</td>
<td>516 497 776 777 910</td>
<td>41.51 kV</td>
</tr>
</tbody>
</table>

Table 4.3: Four sets of slits were used for the tandem runs. The four sets of slits in the beam line are set differently for tuning and measuring. For tuning, the slits are narrowed in order to tune for the ions of interest, and not any adjacent beam. For measurements, the slits are opened up, in order to accommodate more of the beam profile. SL1 and SL2 are situated before the low energy MA of the carbon beam line, and are not used, as they are not in the beam line for this research. “Left” and “right” are the slits, as seen by the approaching ions. All units are in millimeters.

<table>
<thead>
<tr>
<th>Slit</th>
<th>Tuning</th>
<th>Measuring</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left</td>
<td>Right</td>
</tr>
<tr>
<td>SL3</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>SL4</td>
<td>3</td>
<td>-1.5</td>
</tr>
<tr>
<td>SL5</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>SL6</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Chapter 5

Results & Discussion

5.1 Preliminary Work

As so much preliminary work was accomplished on the yellow, blue and red testbeds, it would be remiss to exclude that work. While one spectrum is shown here, the results of the earlier work are included in Appendix D, starting on page 106.

The one spectrum included here, low energy mass spectrum of the Rhum anorthosite, sample 118-134c, is shown below in figure 5.1. 118-134c is the sample most frequently and successfully analyzed by AMS for PGE, and careful analysis of the low energy spectra helps resolve ambiguities noticed in the PGE results.

5.2 AMS Results

Seven samples were eventually analyzed by AMS. The first sample, gold embedded in copper, was run in June 2003. Following the success of this injection from the red testbed, the standard AX 90 bead 13 and three geological samples: 27, the Stillwater chromite; 118-134c the anorthosite from the Rhum Intrusion; and FR5 from the Fox
Figure 5.1: The red testbed’s 860 settings for this anorthosite spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -4.0kV \\
HV_{\text{deck}} &= -21.3kV \\
HV_{\text{cone}} &= +1.5kV \\
\text{i}_{\text{coil}} &= 20.0A \\
\text{i}_{\text{sample}} &= 2.65mA
\end{align*}
\]

River Sill, were run in November and December 2003. Both the light and heavy PGE were measured during these winter runs. The standards AX 90 bead 14 and NIST 612, as well as the geological samples 118-133 and 118-134c, both from the Rhum Intrusion, were run in May and June 2004. However, due to time constraints, only the platinum isotopes and gold were analyzed during the spring. The Rhum
anorthosite, 118-134c was run a final time in June of 2009 to explore the possibility that platinum sputters as molecular anions.

While data were obtained from all runs, only the spring 2004 data, taken with the modified gas ionization detector\textsuperscript{1} from 118-134c, AX 90 bead 14, and the NIST 612 glass, as well as the June 2009 data are presented here. The data for the winter runs are presented in Appendix E, starting on page 171.

The analysis of these AMS results ideally takes two forms. The first aspect involves verification that a given peak seen by the gas ionization detector is the PGE species in question and not merely a fragment add-up peak. The second aspect involves an estimate of the intrinsic PGE concentration in the sample. The PGE concentrations determined could then be checked against any NAA results obtained. While the PGE peaks for the three samples of the spring runs have been verified, and are presented in the following section, estimations of the intrinsic PGE concentrations would only be possible with appropriate standards. As none are available\textsuperscript{2} PGE concentrations have not been determined.

\subsection{5.2.1 Spectral Analysis}

There are three aspects to be considered when analyzing a spectrum. The first involves identifying and distinguishing the PGE peaks from those of the interfering molecular fragments. While this is accomplished with the help of the SRIM (Stopping and Range of Ions in Matter) computer programme, this identification is only possible because the gas ionization detector provides sufficient resolution to separate the peaks. Without this remarkable resolution, analyses would not be possible. The sec-

\textsuperscript{1} The detector was modified after the winter runs by Dr. Xiao-Lei Zhao, producing spectra with much higher resolution.

\textsuperscript{2} See section 2.3.2, page 23, for details on the possible synthesis of standards appropriate for use with this work.
ond involves determining the relative strengths of the molecular add-up peaks using the negative binomial formula. The final consideration involves those spectra with high counts and concerns the accidental add-ups that constitute the PGE background in those spectra.

**Analysis using SRIM**

The spectra provided by the gas ionization detector show the channel, or energy, of the incoming ions on the x-axis and the number of ions counted on the y-axis. The analysis of a spectrum can become complicated by molecular fragments that pass through the electric and magnetic analyzers along with the PGE ions of interest. An PGE ion of mass $M$ and final charge state $Q$, will travel through the EA and MA which are tuned appropriately. So too, however, will fragments (of mass $m$ and final charge state $q$) of a molecule of mass $M$, if $Mq = mQ$, as discussed in section 2.2.3, page 18. The fragment energy, in such a case, would be $(q + \frac{m}{N})V$, where $V$ is the terminal voltage (in $keV$), and $N$ is the mass of the two molecular ions. The atomic ion energy would be $(Q + \frac{M}{N})V$. Clearly then, if $\frac{M}{Q} = \frac{m}{q}$ and $\frac{E}{Q} = \frac{E}{q}$, both the PGE ions and the molecular fragments will reach the final detector (Kilius et al., 1997).

Fortunately, these molecular fragments arrive at the gas ionization detector with different energies than the ions of interest and so can be separated by the detector.\(^3\) This separation of fragments and ions of interest is apparent in some spectra, as in the spring 2004 spectrum of $^{195}Pt$ in the Rhum anorthosite 118-134c (see figure 5.2, page 60), but is not so obvious in others. A quantitative analysis, used to calibrate the spectra, is achieved with the help of the SRIM programme (Ziegler & Biersack, 2003), which calculates the energy loss of the incoming ions to the polypropylene window. The energy losses of $Pt$ and the interfering molecular fragments, from the

---

\(^3\) As these energies are below the Brag peak, these ions can be resolved.
spring 2004 run were determined using SRIM and are presented in table 5.1. Incom-
ing ions lose increasingly less energy as they decelerate through the window. A series of ten calculations was carried out to determine the energy of the ions as they exit the window. This exiting energy is the measurement used to calibrate the energy spectrum and thus verify the separation of fragment add-ups from the PGE peak.

In the May 2004, AX 90 Bead 14 $^{195}Pt$ spectrum, for example, the exiting ener-
gies of the $^{65}Cu$, $^{133}Cs$ and $^{195}Pt$ were used to calibrate the spectrum. This was accomplished by plotting the final energies of the $^{65}Cu$, $^{133}Cs$ and the $^{195}Pt$ peaks versus the observed channels of those peaks. The calibration was determined to be 15.72 keV per channel: the slope of this linear plot. Each spectrum was calibrated in a similar manner and the details of these calculations are given in Table 5.2.

In a perfect world, there would be no variation in the calibrations, as they all calibrate the same detector. Differences occur however, given the stopping power averaging, the non-uniformity of the window thickness, as well as the uncertainty in the window thickness. Nevertheless the calibrations are precise within 5% and are used with confidence.

**Binomial Theorem**

In order to identify the molecular fragment add-up peaks in complex spectra, some quantitative analysis is necessary to positively identify those peaks. Using the binomial theorem, with the incidence of triple add-up defined as $p^3$, the double add-up is $3(1 - p)p^2$ and the single is $3(1 - p)^2p$. While this analysis is not required to describe every spectrum, those with high counts and/or add-up peaks from multiple

---

4 where each calculation corresponds to a thickness of one tenth the actual thickness

5 Where $p$ is the detection probability of a particular ion after the stripping canal.
ions benefit from this type of analysis. One such spectrum is that of $^{195}$Pt in the Rhum anorthosite, sample 118-134c, on page 60. In this spectrum, not

Table 5.1: Calculations used in the Calibration of Spectra: Ion energy losses in the window, were calculated using Ziegler & Biersack’s SRIM programme, using a window thickness of 120 $\mu g/cm^2$.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Ion</th>
<th>Final Charge State</th>
<th>Initial Energy (keV)</th>
<th>Energy loss to the window (keV)</th>
<th>Final Energy (keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass 194</td>
<td>$^{193}$Pt</td>
<td>+6</td>
<td>13511</td>
<td>3888</td>
<td>9623</td>
</tr>
<tr>
<td></td>
<td>$^{97}$Mo</td>
<td>+3</td>
<td>6755</td>
<td>2219</td>
<td>4536</td>
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<tr>
<td></td>
<td>$^{65}$Cu</td>
<td>+2</td>
<td>4507</td>
<td>1659</td>
<td>2848</td>
</tr>
<tr>
<td>Mass 195</td>
<td>$^{193}$Pt</td>
<td>+6</td>
<td>13511</td>
<td>3884</td>
<td>9627</td>
</tr>
<tr>
<td></td>
<td>$^{133}$Cs</td>
<td>+4</td>
<td>9036</td>
<td>2482</td>
<td>6554</td>
</tr>
<tr>
<td></td>
<td>$^{65}$Cu</td>
<td>+2</td>
<td>4503</td>
<td>1660</td>
<td>2843</td>
</tr>
<tr>
<td>Mass 196</td>
<td>$^{193}$Pt</td>
<td>+6</td>
<td>13511</td>
<td>3881</td>
<td>9630</td>
</tr>
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<td></td>
<td>$^{133}$Cs</td>
<td>+4</td>
<td>9030</td>
<td>2481</td>
<td>6549</td>
</tr>
<tr>
<td></td>
<td>$^{98}$Mo</td>
<td>+3</td>
<td>6755</td>
<td>2207</td>
<td>4548</td>
</tr>
<tr>
<td></td>
<td>$^{65}$Cu</td>
<td>+2</td>
<td>4500</td>
<td>1657</td>
<td>2843</td>
</tr>
<tr>
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<td>9638</td>
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<td>8029</td>
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<td>$^{66}$Zn</td>
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<td>1870</td>
<td>2633</td>
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<td></td>
<td>$^{33}$S</td>
<td>+1</td>
<td>2252</td>
<td>1270</td>
<td>982</td>
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Table 5.2: Calibration of Spectra

<table>
<thead>
<tr>
<th>Spectra</th>
<th>Calibration in $keV$ per channel</th>
<th>Energy at channel 0 ($keV$)</th>
<th>$R^2$ value for linear plot</th>
<th>Peaks used for Calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass 194</td>
<td>15.85</td>
<td>979.1</td>
<td>0.9937</td>
<td>$Cu, Mo, Pt$</td>
</tr>
<tr>
<td>Mass 195</td>
<td>15.72</td>
<td>967.9</td>
<td>0.9946</td>
<td>$Cu, Cs, Pt$</td>
</tr>
<tr>
<td>Mass 196</td>
<td>15.30</td>
<td>1080</td>
<td>0.997</td>
<td>$Cu, Mo, Cs, Pt$</td>
</tr>
<tr>
<td>Mass 198</td>
<td>15.97</td>
<td>706</td>
<td>0.9996</td>
<td>$S, Zn, Ho, Pt$</td>
</tr>
</tbody>
</table>

only are the double and triple add-up peaks of $^{65}Cu$ observed, but so too is the
quadruple add-up.\(^6\) The calculated values for the triple and quadruple add-up (using those observed counts of the single and double add-ups) are 591 and 4.7 respectively.

\[
\text{\textbf{Figure 5.2: This 118-134c spectrum shows the separation of the }^{195}\text{Pt peak, from the }^{65}\text{Cu add-ups. The run time for this spectrum was 1000 seconds, and the fragment peaks are labeled with the channel of the peak noted in brackets. The probability of a triple add-up of }^{65}\text{Cu ions, calculated using the negative binomial function (see section 5.2.1, page 58) from the single events and double add-up events is }3.1x10^{-2}, \text{ or 591 counts. This correlates well to the number of counts observed (446), and so supports the fragment add-up analysis of the spectrum. So too does the quadruple add-up, which is calculated at 4.7 counts, and observed at 4 counts. The counts between the peaks are accidental add-ups (see section 5.2.1, page 61) and are observed roughly as calculated (2016 counts between the first two copper fragment add-up peaks).}
\]

This correlates nicely with the observed count rates of 446 and 4 for the triple and

\(^6\) In this case, the incidence of a quadruple add-up is defined as \(p^4\), the triple add-up is \(4(1-p)p^3\), the double add-up is \(6(1-p)^2p^2\) and the single is \(4(1-p)^3p\).
quadruple add-ups.

**Accidental Add-ups**

The final aspect of the quantitative analysis of the PGE spectra concerns the accidental add-up of counts that comprise the PGE background. For $n$ counts per second, the accidental add-up would be $2n^2\tau$ where $\tau$ is the width of the square pulse ($\approx 3\,\mu$s). For spectra with a high number of molecular add-up counts (again, see the spectrum of $^{195}Pt$ from sample 118-134c, Figure 5.2, page 60) this explains the region between the peaks which have some counts (for example at channels 200 and 375 in Figure 5.2). Again, this analysis is not necessary for all spectra.

### 5.2.2 Spring 2004 Spectra

The gas ionization detector was modified between the winter 2003 and spring 2004 runs producing markedly better results. Consequently, only the results from the spring 2004 are presented here. Results from the June 2009 runs are presented in the following section.

The platinum and gold isotopes were observed in the spring 2004 runs. The discussions and spectra of $^{194}Pt$, $^{195}Pt$, $^{196}Pt$, $^{198}Pt$ and $^{197}Au$ from the Rhum anorthosite 118-134c, the standard AX 90 Bead 14 and the standard NIST 612 follow (figures 5.3 through 5.7), with the three samples differentiated in the spectra by colour.

**The $^{194}Pt$ spectrum**

The $^{194}Pt$ spectrum (figure 5.3, page 63) shows five prominent peaks and two lesser peaks. The $^{194}Pt$ itself, the rightmost peak, is obvious at channel 566. The three

---

7 The increased resolution, and shift in spectral peaks are obvious when compared with those spectra taken during the winter 2003 runs (see section E.1, starting on page 171).
copper fragment add-up peaks (\(^{65}\text{Cu}\)) are well resolved, appropriately proportioned (see the section on the negative binomial formula, page 58) and so are labeled accordingly. While not as strong an interference as in the \(^{195}\text{Pt}\) spectrum (the count rate of the single \(^{65}\text{Cu}\) fragment peak from the AX 90 Bead 14 are 0.23 cps and 50 cps from the \(^{194}\text{Pt}\) and \(^{195}\text{Pt}\) spectra, respectively), where \(n = 0\), the \(mQ - Mq\) value for \(^{65}\text{Cu}\) in the \(^{194}\text{Pt}\) spectrum is 2 and thus a fairly prominent feature of this spectrum (see section 2.2.3 for a discussion of the use of \(n\) as a tool to determine the severity of an interference).

A fifth peak, at channel 222 is \(^{97}\text{Mo}^{+3}\) (\(^{97}\text{Mo}\) is 9.55\% of all Molybdenum). This is not surprising as \(n = 0\) for \(^{97}\text{Mo}^{+3}\) in this spectrum. While there was some discussion as to whether this peak might be \(^{48}\text{Ti}^{49}\text{Ti}^{+3}\), a metastable triply charged, diatomic molecule, recent SRIM calculations suggest that peak would appear at channel 172.

The sixth peak, a small one observed only in the NIST 612 sample at channel 350, might be \(^{133}\text{Cs}^{+4}\). Though very unlikely, given \(n = 22\), as \(^{133}\text{Cs}^{+4}\) is seen in all the other spectra, and is known to exit the ion source in large quantities, it is a possibility that the peak at channel 350 is the Caesium. It could also be \(^{130}\text{Ba}\), with \(n = 4\), but the Barium peak is calculated to be at channel 330. \(^{129}\text{Xe}\), with \(n = 2\) is also likely not the source, as the Xenon peak is expected at channel 308.

The final, small peak is at channel 16. This peak is likely Sulphur. \(^{32}\text{S}^{+}\) has \(n = 2\) in this spectrum, and so could likely make it through to the detector. As \(^{33}\text{S}^{+}\) is seen prominently in the \(^{198}\text{Pt}\) spectrum, a Sulphur peak in this spectrum, from a more common isotope\(^8\) is not unlikely.

\(^8\) \(^{32}\text{S}\) is 95.02\% of all Sulphur, while \(^{33}\text{S}\) is only 0.75\%. 62
Figure 5.3: The $^{194}Pt$ peak from 118-134c, AX 90 bead 14 and NIST 612 is labeled, as are the copper fragment peaks. The peak at channel 222 is $^{97}Mo$ and the peak at channel 351 may be $^{133}Cs$. The run times for these spectra are 1000 seconds for 118-134c and NIST 612 and 300 seconds AX 90 Bead 14.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Final Charge State</th>
<th>Initial Energy to the window (keV)</th>
<th>Energy loss to the window (keV)</th>
<th>Expected Position (channel)</th>
<th>Severity of Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{65}Cu$</td>
<td>+2</td>
<td>4507</td>
<td>1659</td>
<td>126</td>
<td>2</td>
</tr>
<tr>
<td>$^{48}Ti^{19}Ti$</td>
<td>+3</td>
<td>6755</td>
<td>1729+1857</td>
<td>172</td>
<td>0</td>
</tr>
<tr>
<td>$^{97}Mo$</td>
<td>+3</td>
<td>6755</td>
<td>2219</td>
<td>222</td>
<td>0</td>
</tr>
<tr>
<td>2x $^{65}Cu$</td>
<td>+4</td>
<td>–</td>
<td>–</td>
<td>291</td>
<td>–</td>
</tr>
<tr>
<td>$^{129}Xe$</td>
<td>+4</td>
<td>9003</td>
<td>3139</td>
<td>308</td>
<td>2</td>
</tr>
<tr>
<td>$^{130}Ba$</td>
<td>+4</td>
<td>9013</td>
<td>2794</td>
<td>330</td>
<td>4</td>
</tr>
<tr>
<td>$^{133}Cs$</td>
<td>+4</td>
<td>9044</td>
<td>2495</td>
<td>351</td>
<td>22</td>
</tr>
<tr>
<td>3x $^{65}Cu$</td>
<td>+6</td>
<td>–</td>
<td>–</td>
<td>456</td>
<td>–</td>
</tr>
<tr>
<td>$^{194}Pt$</td>
<td>+6</td>
<td>13511</td>
<td>3889</td>
<td>564</td>
<td>–</td>
</tr>
</tbody>
</table>
The $^{195}\text{Pt}$ spectrum

The $^{195}\text{Pt}$ spectrum is shown in figure 5.4. Only those results from 118-134c and AX 90 Bead 14 are shown here, as the copper fragment flux from the NIST 612 was too high. Like the $^{194}\text{Pt}$ spectrum, the $^{195}\text{Pt}$ spectrum is well resolved showing the copper fragment add-up peaks. The add-ups are again appropriately proportioned and distinct from the platinum peak and are labeled accordingly (see figure 5.4, page 65). In this instance however, the $mQ - Mq$ value for $^{65}\text{Cu}$ is 0, and so the interference from these add-ups is much stronger than was seen in the $^{194}\text{Pt}$ spectrum. Strong enough, in fact, to catch a glimpse of the quadruple add-up in the anorthosite sample, to the right of the platinum peak.

Being so abundant, the $^{65}\text{Cu}_3$ fragments also produce accidental add-up counts, which are those seen, especially in 118-134c, between the $^{65}\text{Cu}$ fragment peaks.

While it is unlikely, as is glimpsed in the $^{194}\text{Pt}$ spectrum, the peak near channel 350 of the AX 90 Bead 14 might be that of $^{133}\text{Cs}^{+4}$. In this case, $n = 18$, an extremely large value and one that might lead to the assumption that it could not be an interference. However other interferences with smaller $n$ values are less likely, and the possibility that this peak might be $^{133}\text{Cs}^{+4}$ should not be ruled out, given the abundance of caesium in the ion source and the fact that there is only one stable isotope of caesium. In fact, a look back at the low energy mass spectrum of 118-134c, figure 5.1, page 55, shows a peak that could be $^{133}\text{Cs}^{16}\text{O}_4$. If the peak is in fact the caesium oxide, than such an intense interference could easily overwhelm high $n$ values and $^{133}\text{Cs}$ could in fact be observed in the platinum spectra.

The $^{196}\text{Pt}$ spectrum

The $^{196}\text{Pt}$ spectrum, seen in figure 5.5, page 67 shows four obvious peaks. The largest
Figure 5.4: The only definitely identified peaks here are those of the copper fragment add-ups and \(^{195}\text{Pt}\). The run times for these spectra are 1000 and 300 seconds for 118-134c and AX 90 Bead 14, respectively. The “calculated counts” for the copper fragments are those calculated using the binomial theorem for sample 118-134c. The observed counts are also those of sample 118-134c. It should be noted, the accidental add-ups for platinum are \(10^{-5}\), and so do not contribute to the observed counts.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Final Charge State</th>
<th>Initial Energy (keV)</th>
<th>Energy loss to the window (keV)</th>
<th>Expected Position (channel)</th>
<th>Severity of Interference (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{65}\text{Cu})</td>
<td>+2</td>
<td>4503</td>
<td>1660</td>
<td>126</td>
<td>0</td>
</tr>
<tr>
<td>2x (^{65}\text{Cu})</td>
<td>+4</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(^{133}\text{Cs})</td>
<td>+4</td>
<td>9036</td>
<td>2483</td>
<td>354</td>
<td>18</td>
</tr>
<tr>
<td>3x (^{65}\text{Cu})</td>
<td>+6</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(^{195}\text{Pt})</td>
<td>+6</td>
<td>13511</td>
<td>3884</td>
<td>564</td>
<td>–</td>
</tr>
<tr>
<td>4x (^{65}\text{Cu})</td>
<td>+8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
peak seen from all three samples, at channel 566 is $^{196}\text{Pt}$. Unlike those spectra of the lighter platinum isotopes, there is little interference from the copper, with only the single fragment from the copper trimer being present, in the NIST 612, at channel 125.

The peak at channel 222, similar to that seen in the $^{194}\text{Pt}$ spectrum, is likely Molybdenum. In this case however, it is $^{98}\text{Mo}^{+3}$, which at 24.13% of all Molybdenum, shows a strong peak, given $n = 0$. This peak might also have some Ruthenium, as $^{98}\text{Ru}^{+3}$, also with $n = 0$ would make it through to the detector. Resolving the $^{98}\text{Mo}^{+3}$ and $^{98}\text{Ru}^{+3}$ peaks is difficult, as the $^{98}\text{Ru}^{+3}$ is calculated to be at channel 237. While this is improbable, the right hand side of the $^{98}\text{Mo}^{+3}$ peak does not fall off as quickly as expected, suggesting some Ruthenium might be present in the sample. Indeed, $^{99}\text{Ru}^{+4}$ is believed to have been identified (see figure E.1 on page 172) during the Winter runs, so some Ruthenium is likely in the sample and might be seen in this spectrum.

The smallest peak, at channel 345, is (again) likely $^{133}\text{Cs}^{+4}$, a molecular fragment from $^{133}\text{Cs}^{16}\text{O}_4^-$. While $n = 14$, the final energy of $^{133}\text{Cs}^{+4}$ positions the peak at 345, right where it is seen. So, though it might seem unlikely the interference would be from that fragment due to the high $mQ - Mq$ value, because $^{133}\text{Cs}$ is the only stable isotope of caesium and because $^{133}\text{Cs}^{16}\text{O}_4$ was noticed in the low energy spectrum (see figure 5.1, page 55) the peak may very well be $^{133}\text{Cs}^{+4}$.

**The $^{198}\text{Pt}$ spectrum**

The $^{198}\text{Pt}$ spectrum is shown in figure 5.6, page 69 and is the most complex of all the spectra presented here. All three sample show four peaks. The AX 90 Bead 14 shows an additional three peaks and the NIST 612 shows another one peak.

All three samples show the $^{198}\text{Pt}$ at channel 569. Likewise, the $^{33}\text{S}^+$ peak at
$^{196}$Pt$^{6+}$ in 118-134c, AX 90 Bead 14 and NIST 612

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Figure 5.5: The $^{196}$Pt peak is labeled, as is the $^{65}$Cu peak. The peak at 222 is $^{98}$Mo and that at 345 may be $^{133}$Cs. The run times for these spectra are 20000, 300 and 1000 seconds for 118-134c, AX 90 Bead 14 and NIST 612, respectively.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Final Charge State</th>
<th>Initial Energy (keV)</th>
<th>Energy loss to the window (keV)</th>
<th>Expected Position (channel)</th>
<th>Severity of Interference (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{65}$Cu</td>
<td>+2</td>
<td>4500</td>
<td>1657</td>
<td>125</td>
<td>2</td>
</tr>
<tr>
<td>$^{48}$Ti$^{50}$Ti</td>
<td>+3</td>
<td>6755</td>
<td>1768 + 1897</td>
<td>169</td>
<td>0</td>
</tr>
<tr>
<td>$^{98}$Mo</td>
<td>+3</td>
<td>6755</td>
<td>2207</td>
<td>222</td>
<td>0</td>
</tr>
<tr>
<td>$^{98}$Ru</td>
<td>+3</td>
<td>6755</td>
<td>2045</td>
<td>237</td>
<td>0</td>
</tr>
<tr>
<td>$^{133}$Cs</td>
<td>+4</td>
<td>9030</td>
<td>2481</td>
<td>345</td>
<td>14</td>
</tr>
<tr>
<td>$^{196}$Pt</td>
<td>+6</td>
<td>13511</td>
<td>3881</td>
<td>566</td>
<td>–</td>
</tr>
</tbody>
</table>

channel 17 and the $^{66}$Zn$^{+2}$ at channel 124 are observed in all three samples, as $n = 0$
for both these isotopes. The double add-ups of those isotopes are also observed, mostly clearly in the AX 90 Bead 14, at channels 76 and 288. Additionally, in the AX 90 Bead 14, there is the clear peak at 176, which is the add-up of the Sulphur and Zinc isotopes. The peak observed in the NIST 612 at channel 455 is most certainly $^{165}Ho^{+5}$, as $n = 0$. The peak at channel 349 is more challenging to determine. Initially it was believed to be $^{132}Ba$, which has a $mQ - Mq$ value of 0. As Barium is present at 41 ppm in the NIST 612 glass, it would not surprising to observe, even though $^{132}Ba$ is only 0.101% of all barium. However, the barium peak is calculated at 369. While less likely, this peak is believed to be $^{133}Cs^{+4} (mQ - Mq = 6)$, as is observed in the other spectra, as it has a calculated value precisely where a peak is observed, at channel 349.

The $^{197}Au$ Spectrum

The spring 2004 $^{197}Au$ spectrum shows little background, which is a marked improvement over the Winter 2003 $^{197}Au$ spectrum (see figure E.15, page 186) which was taken prior to the installation of the new detector. The prominent peak visible in the spectrum is the $^{197}Au$ peak, with a much smaller peak present in the NIST 612 spectrum at channel 456. This is $^{164}Dy$, which is a strong interference as the $mQ - Mq$ value is $-1$. Dysprosium is one of those elements for which the NIST 612 is an international standard, having a known concentration of 35ppm, seven times that of gold. Also present in the AX 90 Bead 14 are the Sulphur and Zinc peaks. The fragment peaks are not as prominent in this Gold spectrum as in the $^{198}Pt$ spectrum, as the count time was shorter (100 seconds here versus 959 seconds for the $^{198}Pt$ spectrum) and severity of interference is less, with $n = 1$ for the Sulphur and $n = 2$ for the Zinc.
Figure 5.6: This spectrum, more complicated than the others, has the peaks identified on the plot. The run times for these spectra are 8000, 959 and 1000 seconds for 118-134c, AX 90 Bead 14 and NIST 612, respectively.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Final Charge State</th>
<th>Initial Energy (keV)</th>
<th>Energy loss to the window (keV)</th>
<th>Expected Position (channel)</th>
<th>Severity of Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{33}\text{S}$</td>
<td>+1</td>
<td>2252</td>
<td>1270</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>2x $^{33}\text{S}$</td>
<td>+2</td>
<td>–</td>
<td>–</td>
<td>76</td>
<td>–</td>
</tr>
<tr>
<td>$^{66}\text{Zn}$</td>
<td>+2</td>
<td>4503</td>
<td>1870</td>
<td>124</td>
<td>0</td>
</tr>
<tr>
<td>$^{33}\text{S}+^{66}\text{Zn}$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>180</td>
<td>–</td>
</tr>
<tr>
<td>2x $^{66}\text{Zn}$</td>
<td>+4</td>
<td>–</td>
<td>–</td>
<td>288</td>
<td>–</td>
</tr>
<tr>
<td>$^{132}\text{Ba}$</td>
<td>+4</td>
<td>9007</td>
<td>2448</td>
<td>369</td>
<td>0</td>
</tr>
<tr>
<td>$^{133}\text{Cs}$</td>
<td>+4</td>
<td>9030</td>
<td>2481</td>
<td>349</td>
<td>6</td>
</tr>
<tr>
<td>$^{165}\text{Ho}$</td>
<td>+5</td>
<td>11259</td>
<td>3230</td>
<td>455</td>
<td>0</td>
</tr>
<tr>
<td>$^{198}\text{Pt}$</td>
<td>+6</td>
<td>13511</td>
<td>3873</td>
<td>569</td>
<td>–</td>
</tr>
</tbody>
</table>
The most prominent peaks in these spectra are $^{197}\text{Au}$. The peak at channel 456 in the NIST 612 spectrum is $^{164}\text{Dy}$. The run times for all three samples are 100 seconds.

### Table: Fragment Interferences

<table>
<thead>
<tr>
<th>Ion</th>
<th>Charge State</th>
<th>Initial Energy (keV)</th>
<th>Energy loss to the window (keV)</th>
<th>Expected Position (channel)</th>
<th>Severity of Interference (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{33}\text{S}$</td>
<td>+1</td>
<td>2243</td>
<td>1270</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>$^{66}\text{Zn}$</td>
<td>+2</td>
<td>4503</td>
<td>1870</td>
<td>124</td>
<td>2</td>
</tr>
<tr>
<td>$^{164}\text{Dy}$</td>
<td>+5</td>
<td>11257</td>
<td>2990</td>
<td>456</td>
<td>-1</td>
</tr>
<tr>
<td>$^{197}\text{Au}$</td>
<td>+6</td>
<td>13511</td>
<td>3169</td>
<td>569</td>
<td>–</td>
</tr>
</tbody>
</table>

### Discussion of the Spring 2004 Spectra: Fragment Interferences

The severity of interference of the molecular fragments is related to $n$, where
\( n = mQ - Mq \) (or more precisely, \( n = (mQ - Mq) + (\Delta mQ - \Delta Mq) \)) as introduced within section 2.2.3, on page 19. The larger the value of \( n \), the less severe the interference. This is noticeable when a given interfering molecular fragment is compared in different spectra. For example, \(^{33}\text{S}\) is an interference in both the \(^{198}\text{Pt}\) and \(^{197}\text{Au}\) spectra, with \( n \) values, using the more precise formula, of \(-0.28\) and \(0.72\) respectively. The sulphur is more of an interference in the platinum spectra of all three samples than in the gold spectra. In fact, for all four interfering molecular fragments for which these calculations were done, the trend of higher \( n \) value and lower count rates is obvious, as shown in Table 5.3, below. For this reason the \( n = (mQ - Mq) \) values are used here (as elsewhere in the literature–see Kilius et al. (1997)) with confidence.

Table 5.3: Interfering molecular fragments and their calculated \( n \) values for a given spectrum are listed with the counts in that spectrum. Note that as the \( n \) value increases in magnitude, the number of counts decrease. All counts are per 100 seconds. No \(^{195}\text{Pt}\) spectrum is available for the NIST 612 sample, as the count rate was too high for the detector.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spectrum</th>
<th>( n )</th>
<th>Number of counts in 118-134c</th>
<th>Number of counts in AX 90 Bead 14</th>
<th>Number of counts in NIST 612</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{33}\text{S})</td>
<td>(^{198}\text{Pt})</td>
<td>-0.28</td>
<td>1405</td>
<td>75737</td>
<td>52</td>
</tr>
<tr>
<td>(^{197}\text{Au})</td>
<td>0.72</td>
<td>3</td>
<td>7</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>(^{65}\text{Cu})</td>
<td>(^{195}\text{Pt})</td>
<td>-0.73</td>
<td>57917</td>
<td>55275</td>
<td>no spectrum</td>
</tr>
<tr>
<td>(^{194}\text{Pt})</td>
<td>1.28</td>
<td>279</td>
<td>229</td>
<td>4378</td>
<td></td>
</tr>
<tr>
<td>(^{196}\text{Pt})</td>
<td>-2.73</td>
<td>0.004</td>
<td>0.67</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>(^{66}\text{Zn})</td>
<td>(^{198}\text{Pt})</td>
<td>-0.76</td>
<td>5.16</td>
<td>7123</td>
<td>0.7</td>
</tr>
<tr>
<td>(^{197}\text{Au})</td>
<td>1.25</td>
<td>0</td>
<td>5</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>(^{133}\text{Cs})</td>
<td>(^{198}\text{Pt})</td>
<td>6.26</td>
<td>6.76</td>
<td>3.65</td>
<td>351</td>
</tr>
<tr>
<td>(^{197}\text{Au})</td>
<td>10.27</td>
<td>1</td>
<td>in noise</td>
<td>in noise</td>
<td></td>
</tr>
<tr>
<td>(^{196}\text{Pt})</td>
<td>14.28</td>
<td>0.0015</td>
<td>0</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>(^{195}\text{Pt})</td>
<td>18.28</td>
<td>in noise</td>
<td>8.7</td>
<td>no spectrum</td>
<td></td>
</tr>
<tr>
<td>(^{194}\text{Pt})</td>
<td>22.30</td>
<td>0</td>
<td>0</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>
Discussion of Spring 2004 Spectra: Sensitivity

The AMS sensitivity for the platinum is somewhat complex, as four isotopes were observed. The $^{196}\text{Pt}$ counts for 118-134c seems unusually high, for example, while the number of $^{198}\text{Pt}$ counts from the NIST 612 seems somewhat low. Because these two values are aberrant, they were excluded from the total counts calculations. A summary of the counts of the platinum isotopes observed for the three samples is given in table 5.4, while the AMS sensitivity for platinum in the samples is given, along with the gold values, in table 5.5. It should be noted here that gas ionization detector used in this research does not have a “dark current.” If no beam is put through the AMS system, there are no counts (no signal) detected by the gas ionization detector, and as such, there is no such interference under the platinum peaks.

Table 5.4: A summary of the platinum isotope counts of the spring 2004 runs: All counts are per 100 seconds.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance</th>
<th>118-134c</th>
<th>AX 90 Bead 14</th>
<th>NIST 612</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{194}\text{Pt}$</td>
<td>32.9%</td>
<td>3.1</td>
<td>61.7</td>
<td>58.4</td>
</tr>
<tr>
<td>$^{195}\text{Pt}$</td>
<td>33.8%</td>
<td>4.2</td>
<td>55.7</td>
<td>–</td>
</tr>
<tr>
<td>$^{196}\text{Pt}$</td>
<td>25.3%</td>
<td>8.5</td>
<td>43</td>
<td>46.2</td>
</tr>
<tr>
<td>$^{198}\text{Pt}$</td>
<td>7.2%</td>
<td>0.88</td>
<td>12.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Platinum</td>
<td>100%</td>
<td>11.3</td>
<td>174</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 5.5: The AMS sensitivity of platinum and gold in 118-134c, AX 90 Bead 14 and NIST 612 for the spring 2004 runs. The AX 90 Bead 14 and NIST 612 sensitivity are in $\text{counts/s/ppb}$. While the 118-134c sensitivity are in $\text{counts/s}$, as the intrinsic concentration previously determined by NAA was found to result from contamination.

<table>
<thead>
<tr>
<th>Element</th>
<th>118-134c</th>
<th>AX 90 Bead 14</th>
<th>NIST 612</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>0.113</td>
<td>0.0069</td>
<td>0.00069</td>
</tr>
<tr>
<td>Gold</td>
<td>148</td>
<td>32.2</td>
<td>0.0225</td>
</tr>
</tbody>
</table>
Discussion of Spring 2004 Spectra: Estimate of Minimum Detection Limit

While it is true that only the AMS sensitivity of the platinum can be calculated, an estimate of the minimum detection limit of platinum by AMS can be determined. This can be accomplished by comparing the observed data with the known platinum concentrations in the standards.

Take the case of the AX 90 Bead 14, which has a known concentration of 252 ppb of platinum (85 ppb of $^{195}Pt$—as $^{195}Pt$ is 33.8% of all platinum, 83 ppb of $^{194}Pt$ (32.9%), 64 ppb of $^{196}Pt$ (25.3%) and 28 ppb of $^{198}Pt$ (7.2%)). The platinum isotope which would give the highest MDL is $^{195}Pt$, as there is the $^{65}Cu$ interference ($n = 0$) to contend with. The 178 counts of $^{195}Pt$ that were observed from the AX 90 Bead 14 (see figure 5.4, page 65) during the 300 second spectrum were well resolved from, and well above, the copper add-up peaks. Clearly, AMS can easily measure 250 ppb platinum, but so too can other methods. Had the concentration of platinum in fact been only one one hundredth its real value, 0.85 ppb of $^{195}Pt$, only 1.78 counts would have been observed in 300 seconds, or 5.93 counts in 1000 seconds. These 5.93 counts are hardly more than the 4 counts of the quadruple $^{65}Cu$ add-up observed in 1000 second. Therefore, AMS could see 2.5 ppb of platinum (if $^{195}Pt$ were used as a basis), in a sample, but only barely. A minimum detection limit of 2.5 ppb is high, and not noteworthy.

A lower MDL is possible, however, if a different type of sample holder was used. This is because the copper interference in the $^{195}Pt$ spectra is from the sample holder, not the sample itself: both the Rhum anorthosite (118-134c) and the AX 90 Bead 14 spectra have the same number of $^{65}Cu$ counts per unit time ($\approx 570 \text{ cps}$). Had an aluminium sample holder been used instead, a lower MDL would have been achievable. The desire to reduce the copper interference in the $^{195}Pt$ spectra needs to be weighed
against the usefulness of the copper signal however, as it is that copper signal that is used as a pilot beam to tune the high energy end of the AMS system for the final analyses.

A more prudent way to estimate a lower MDL of platinum by AMS would be to look at the spectra of other platinum isotopes. The second most abundant isotope of platinum, after $^{195}Pt$, is $^{194}Pt$. The $^{194}Pt$ spectra, shown in figure 5.3, on page 63, shows 177 counts of $^{194}Pt$ from the AX 90 Bead 13, in 300 seconds (590 counts in 1000 seconds). However, the copper interference in this spectra is much less significant, as $n = 2$ for $^{65}Cu$. In fact, in 1000 seconds, only 3700 single $^{65}Cu$ counts, 83 double add-up counts and no triple or quadruple add-ups are seen. With no other interferences noticed in the spectrum of the AX 90 Bead 14 (not a single count between channels 302 and 488), it would only be when the copper interference increases as a result of longer analysis times that a detection limit would be reached. In fact even with an analysis time of 30 000 seconds (the longest analysis time of this research), only 19 triple copper add-up counts and no quadruple add-up counts would be expected. With such an long analysis time, 17 700 $^{194}Pt$ counts would be expected from AX 90 Bead 14, with a platinum concentration of 252 ppb. Should there have been only a thousandth of the platinum in the sample, there would still be 17.7 counts of $^{194}Pt$. Given the isolation of the platinum peak in this sample, this type of analysis would allow for a detection limit of 0.2 ppb.

This MDL however, is for this isotope, this sample, and using charge state +6. Other samples (118-134c, for example) that have $^{97}Mo$, would have great interference and would likely have a higher MDL. Nevertheless, with judicious choices, MDL of tens of ppt are not impossible, given long enough analysis times, and sufficient sample volumes.

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9 Calculated using the binomial theorem, see section 5.2.1, page 58, for details.
5.2.3 June 2009 Results

The June 2009 experiments were carried out to determine if in fact platinum was sputtered from a natural, insulating sample as a molecular anion. This was surmised as the count rate from the spring runs was much lower than expected. Review of the literature confirms that platinum sputters as oxides (Ramond et al., 2002) and recent research at IsoTrace has shown that fluoride anions are sputtered very strongly. While much discussion about the likelihood of the platinum sputtering as oxides from the anorthosite took place over the year preceding the runs, the June 2009 runs did not support this hypothesis.

Three tests were carried out on June 16th and 17th, 2009. The first involved sputtering ZnO in the usual AMS sputter source (the “834”), the second involved sputtering a ZnO plus Pt powder sample in the same manner and the third was a repeat of the spring 2004 runs, where platinum was measured in the Rhum anorthosite, sputtered in the 860.

Cross contamination with platinum of all the samples in the 834 yielded less detailed data than hoped for, but platinum oxides were observed. When the ZnO plus Pt was analyzed, the $^{194}Pt^-$ to $^{194}Pt^{+5}$ current was 1216.27 counts per second. The $^{194}Pt^{+5}$ beams from the oxides, listed in table 5.6, show fewer counts, indicating that platinum is in fact not preferentially leaving the sample face as oxides. While these results were intriguing, they were inconclusive as ZnO plus Pt is hardly a similar matrix to anorthosite.

AMS Analysis of the Rhum anorthosite (118-134c), sputtered in the 860 operating under identical conditions to those of the spring 2004 runs gave a $^{194}Pt^{+5}$ count rate of 0.116 per second. As observed in the ZnO plus Pt sample, the oxides were also sputtered, but the $^{194}Pt^{+5}$ seen from those oxide beams (see table 5.6) was less than
that from the atomic ion beam.

The June 2009 count rate for the $^{194}\text{Pt}$ is almost four times that of the spring 2004 runs. While certainly ions of lower charge state are more common after the sputtering canal, no definitive explanation can be given for this discrepancy at this time. However, it must be remembered that the June 2009 run was to explore the possibility of platinum sputtering as molecular ions. In this respect, these runs were very successful, as they showed, conclusively, that while platinum is sputtered as oxides, it is not those oxide fragment ions that show the strongest peaks.

Table 5.6: The results from June 2009 runs are listed below. Note the $^{194}\text{Pt}^{+5}$ is strongest from the $^{194}\text{Pt}^-$ beam in both samples. All counts are per 100 seconds

<table>
<thead>
<tr>
<th>Sputtered Anion</th>
<th>$^{194}\text{Pt}^{+5}$ from ZnO plus Pt powder sample</th>
<th>$^{194}\text{Pt}^{+5}$ from 118-134c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{194}\text{Pt}^-$</td>
<td>121627</td>
<td>11.6</td>
</tr>
<tr>
<td>$^{194}\text{Pt}^{16}O^-$</td>
<td>33707</td>
<td>0.4</td>
</tr>
<tr>
<td>$^{194}\text{Pt}^{16}O_2$</td>
<td>15191</td>
<td>0</td>
</tr>
<tr>
<td>$^{194}\text{Pt}^{16}O_3^-$</td>
<td>1229</td>
<td>–</td>
</tr>
<tr>
<td>$^{194}\text{Pt}^{16}O_4^-$</td>
<td>1719</td>
<td>–</td>
</tr>
</tbody>
</table>
Chapter 6

Conclusions & Recommendations

The experimental work outlined here has shown that it is possible to sputter natural insulating samples for AMS analysis, provided the ion source used supplies a constantly replenishing layer of neutral caesium to the sample face to dissipate the charge buildup that is characteristic of bombardment with positive ions. This work has also shown that with adequate detectors, PGE ions from these insulating samples can be resolved from interfering molecular fragments. This remarkable ability, to resolve the PGE peak from the interferences in the spectra, has not been observed before and cannot be overemphasized. For it is only with such resolution that quantitative analyses can be given with confidence. While no PGE concentrations could be calculated for the Rhum anorthosite, sample 118-134c, the AMS sensitivity of the PGE was calculated for the two standards, AX 90 and NIST 612. The values determined for the AX 90 Bead 14 are 0.0069 counts/s/ppb for platinum and 32.2 counts/s/ppb for gold. The values determined for the NIST 612 are 0.00069 counts/s/ppb for platinum and 0.0225 counts/s/ppb for gold. With an estimated minimum detection limit of tens of ppt, this AMS technique has an MDL below the detection limits of other methods and will undoubtedly be of interest to economic geologists.
In addition, the relative ease of detecting the PGE (in one hour) in these samples, versus NAA, makes this technique worthy of development. This development though, should incorporate three major (and a few minor) aspects where modifications to the analytical regime would lead to significant improvement in experimental results.

The first of these three major recommendations can easily be incorporated into future studies. This is the analysis of not only sputtered atomic ions but molecular ions from the sample. Since the PGE from a sputtered sample produces negative oxides, as well as atomic ions, tuning the low energy portion of the (existing) equipment to enable the analysis of these species is not only advisable, but necessary, given the uncertainty of the strength of the molecular ion beam which will necessarily vary from sample to sample. Measuring both atomic and molecular PGE ions would allow for greater flexibility during analysis, and a more complete picture of the PGE levels within the sample.

A second recommendation for future work can again be incorporated easily. While a charge state of +6 was used throughout most of the work described here, differing charge states, chosen to reduce interferences, as was used in the June 2009 runs, should be used in the future for the detection of the various ions of interest. The careful consideration of both sample composition and the PGE isotope to be analyzed would allow more judicious choices of charge state for AMS analysis. This in turn would reduce the amount of interference giving rise to less background and thus lower detection limits.

The third recommendation for improvement of PGE analysis by AMS is more difficult, time consuming and costly. This work involves obtaining adequate standards. In order to quantify the observed PGE data, standards must be synthesized. Ion implantation of some of the less abundant, stable PGE isotopes into the sample itself is the most appropriate avenue to pursue is this regard. While such a standard is
theoretically possible to manufacture, the details and reality of such an endeavour will likely prove enormously challenging.

Along with the three major recommendations, two minor modifications, both involving changes to the existing equipment, could also enhance AMS analyses of PGE in insulating samples.

A $45^\circ$ electric analyzer, to replace the $7^\circ$ electric analyzer in the low energy section of the beam line, would be sufficient to eliminate fragmenting molecules which previously plagued the system. While this would require reconstruction of the beam line, it would certainly further the development of the analysis of PGE in insulating samples and should be considered.

The present ion source holds only one sample and changing samples requires breaking the vacuum. This is not an efficient method for the analysis of multiple samples, especially when long caesiumation times are considered. Modifications to the ion source to allow for the use of a multiple target holder which could expose all samples to the neutral caesium vapour should be considered. Such an ion source could dramatically reduce the amount of time necessary to ready a new sample for AMS analysis, making the technique more attractive to potential customers, as the expense of an analysis is necessarily correlated with operating time.

Should these modifications be undertaken, successful \textit{in situ} sub-ppb AMS analyses of PGE, sputtered from natural insulating samples, may become routine.
# Glossary

## Glossary of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMS</td>
<td>Accelerator Mass Spectrometry</td>
</tr>
<tr>
<td>ELS</td>
<td>Eastern Layered Series of the Rhum Layered Intrusion, island of Rhum (or Rum), Scotland</td>
</tr>
<tr>
<td>EA</td>
<td>Electric Analyser</td>
</tr>
<tr>
<td>FRS</td>
<td>Fox River Sill, Manitoba</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>LA-ICP-MS</td>
<td>Laser Ablation Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>MA</td>
<td>Magnetic Analyzer</td>
</tr>
<tr>
<td>MDL</td>
<td>Minimum Detection Limit. 3 counts in 100 seconds in the region of interest with no background (Wilson et al., 1991).</td>
</tr>
<tr>
<td>NAA</td>
<td>Neutron Activation Analysis</td>
</tr>
<tr>
<td>PGE</td>
<td>Platinum Group Element(s)</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum Group Mineral(s)</td>
</tr>
<tr>
<td>RC</td>
<td>Reaction Cell</td>
</tr>
<tr>
<td>RLI</td>
<td>Rhum Layered Intrusion, including the Eastern Layered Series of the Rhum Intrusive Complex, plus other lesser intrusions.</td>
</tr>
<tr>
<td>RNAA</td>
<td>Radiochemical Neutron Activation Analysis</td>
</tr>
</tbody>
</table>
**Glossary of terms**

**Angstrom (Å)**  
$10^{-10}$ meters.

**anorthosite**  
If unqualified, an intrusive igneous rock composed almost entirely of plagioclase feldspar (> 90 volume percent).

**bleb**  
Irregular speck, generally of sulphide, in silicate host.

**chalcopyrite**  
A sulphide mineral, $CuFeS_2$.

**chromite**  
An oxide mineral, $FeCr_2O_4$.

**cumulates**  
Rocks formed from the gravitational settling of crystals. This term has been shortened from “accumulated rocks.” (Wager & Brown, 1967).

**cryptic layering**  
Within a layered intrusion, systematic variation of the composition of the minerals due to the progressive change in chemistry of the melt caused by the crystallization and settling of early-formed grains.

**cyclic unit**  
A unit, or layer, within a layered intrusion characterized by the disappearance and reappearance of certain minerals.

**electron affinity**  
The energy change occurring when an atom, or molecule, gains an electron. It is the energy released due to the electron’s attachment reaction.

**electronegativity**  
The ability of an atom within a molecule to attract electrons. Electronegativity is equivalent to the electron affinity of a free atom.

**feldspar**  
An abundant group of rock-forming minerals–feldspars constitute 60% of the earth’s crust–of the general formula, $XAl(AlSi)_3O_8$ where $X$ can be any of $K$, $Na$, $Ca$ or less often, $Ba$, $Rb$, $Sr$ or $Fe$. 

**ROI**  
Range of Interest

**SIMS**  
Secondary Ion Mass Spectrometry

**860**  
The high intensity negative ion source used in this work.
felsic
A light-coloured igneous rock, generally rich in feldspars and silica.

gabbro
Dark-coloured, intrusive igneous rock, which is essentially clinopyroxene plus plagioclase feldspar.

ionization potential
The energy required to completely remove a single electron from a neutral atom, or molecule.

mafic
A dark coloured igneous rock, comprised of minerals rich in magnesium and/or iron.

magnetite
A cubic oxide mineral, with spinel structure, Fe$_3$O$_4$.

matrix effect
In the context of AMS and SIMS, the effect of the sample’s chemical composition (matrix) on the formation of secondary ions, when bombarded by a primary ion beam.

olivine
A silicate solid solution series most especially, the complete solid solution between fayalite (Fe$_2$SiO$_4$) and forsterite (Mg$_2$SiO$_4$). One of the first minerals to crystallize from a cooling mafic magma.

nugget effect
Submicroscopic inclusions of certain elements within a sample that can skew the final determination of concentration of those elements in that sample.

partition coefficients
In the present context, the ratio of the concentrations of two particular elements in a sulphide phase as compared to a silicate phase.

passivation
The result achieved when an insulating sample face is sufficiently caesiumated so as to assure the production of a negative ion beam.

pentlandite
A sulphide mineral, (Fe, Ni)$_9$S$_8$.

pyroxene
A group of silicate minerals, including orthopyroxenes such as enstatite, MgSiO$_3$, and clinopyroxenes, such as diopside, CaMgSi$_2$O$_6$, augite, Ca(Mg, Fe)Si$_2$O$_6$ and pigeonite, (Mg, Fe, Ca)(Mg, Fe)Si$_2$O$_6$.

pyrrhotite
A sulphide mineral, Fe$_{(1−x)}$S, where 0 ≤ x ≤ 0.2.

reaction cell
An instrument added to a beam line to reduce isobaric interferences by ion-ion or ion-molecule collisions and reactions.
| **reef** | Stratiform and generally thin layers (cm to m scale) of economically important components (chromite, sulphides, precious metals) within the host, silicate-dominated stratigraphy of a layered intrusion. |
| **resolution** | Dispersion, in mm after the analyzer when a point object is used. |
| **rhythmic layering** | Believed to result from repeated injections of magma into a chamber. |
| **silicates** | Those minerals based on a wide range of crystal structures of silicon and oxygen, usually with a range of incorporated cations ± anions. Among them: quartz, pyroxenes, olivine, and feldspars. |
| **sill** | A concordant intrusion, wider than it is thick, usually forming within a few kilometers of the earth’s surface, generally less than one to a few hundred meters thick. |
| **sulphides** | Minerals containing essential sulphur. Among them: pyrrhotite, chalcopyrite, and pentlandite. |
| **ultramafic** | An igneous rock composed primarily (≥ 90 volume percent) of mafic minerals, such as olivine, pyroxenes, and chromite. |
| **uralitization** | Alteration of pyroxene to the secondary amphibole, actinolite. |
| **work function** | The quantity that determines the extent to which the photoelectric emission will occur. The work function of an element can be increased or decreased when sputtered with ions with greater or lesser work functions, respectively. Caesium has a work function of only 1.81 eV and so is often used for sputtering. |
Appendix A

Samples

A selection of samples used in the 860 sputter source is shown in Figure A.1. The

Figure A.1: A selection of samples used in the 860. They are, from left to right, a copper blank, aluminium, gold in copper, silver in copper, Macor, silica glass, pyrophyllite, a copper blank, milled to hold geological samples, and anorthosite: 118-134c.

most common sample type, using the Chalk River copper blanks, measure 9mm in
diameter, and 12mm long. While most samples are embedded or pressed into copper,
a few were tapped or otherwise mounted directly onto the 8-32 set screw by which
they are affixed to the sample rod.

Those samples that were embedded into milled copper blanks were first sawn into slabs approximately 7\,mm think. The slab was then drilled using two JKM Lamage, diamond bit hollow core drill bits, while submerged in water. This both cooled the sample and provided lubrication for the drilling process. The larger of the two drill bits ($ID = 9\,mm$) was used first to drill completely through the slab. Next, the smaller drill bit ($ID = 7\,mm$) was carefully centred on the cylindrical sample and while the sample was held steady by the bottom, the top portion was drilled again to achieve the stepped, cylindrical sample necessary to crimp into the milled copper blanks. These blanks were milled to accept the narrower end of the geological samples, the wider end exposed to the primary caesium ion beam.

The powdered samples that were used during the preliminary experiments and on the yellow test were pressed into pre-drilled copper blanks. Stainless steel presses were fashioned by the physics workshop for this purpose and a small hydraulic press were used to ensure the powder was sufficiently packed so as to not fall out when held horizontally.

All samples used are listed below, categorized as either conducting, insulating or geological.

### A.1 Conducting Samples

The following is a list of the conducting samples analyzed, with details concerning the origin and type.
Table A.1: Catalogue of the Conducting Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Description</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper</td>
<td>solid copper</td>
<td>rod of oxygen free, high purity solid copper, 9mm in diameter, 12mm long, tapped at one end for an 8-32 screw, counter sunk at the other end, 6mm in diameter by 2mm deep.</td>
<td>Chalk River Laboratories. Received in 1998.</td>
</tr>
<tr>
<td>silicon</td>
<td>metal</td>
<td>brittle, dark gray, shiny. metal in sheet form.</td>
<td>IsoTrace stock</td>
</tr>
<tr>
<td>rhodium</td>
<td>rhodium wire in copper</td>
<td>rhodium wire, 1mm in diameter, 99.8% pure. The rhodium wire was pressed into three holes, drilled into a copper blank.</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>gold</td>
<td>gold rod in copper</td>
<td>gold metal</td>
<td>J. C. Rucklidge</td>
</tr>
<tr>
<td>AuI</td>
<td>AuI powder in copper</td>
<td>Gold powder, mixed with iodine and niobium, pressed into a copper blank.</td>
<td>IsoTrace stock</td>
</tr>
<tr>
<td>silver</td>
<td>silver rod in copper</td>
<td>silver metal</td>
<td>J. C. Rucklidge</td>
</tr>
<tr>
<td>AgI</td>
<td>AgI powder, in copper</td>
<td>Silver powder, mixed with iodine and niobium, pressed into a copper blank.</td>
<td>IsoTrace stock</td>
</tr>
<tr>
<td>carbon</td>
<td>graphite in copper</td>
<td>spectroscopic graphite</td>
<td>J. C. Rucklidge</td>
</tr>
<tr>
<td>silver solder</td>
<td>silver solder</td>
<td>XRF analysis on 20-4-99 revealed major constituents: 38.7% Ag, 22% Cu, 19.5% Cd and 17.5% Zn.</td>
<td>Physics workshop</td>
</tr>
<tr>
<td>AX 90</td>
<td>NiS fire assay bead</td>
<td>friable, medium grayish brown, shiny material. XRF Analysis of Bead 13, in October 2004 revealed major constituents: 58.8% Ni, 29.7% S and 7.8% Na₂B₄O₇. See section 2.3 for a more complete analysis of trace elements.</td>
<td>Dr. Sarah-Jane Barnes, Université Du Québec à Chicoutimi</td>
</tr>
</tbody>
</table>
A.2 Insulating Samples

The following is a list of the synthetic, insulating samples analyzed, with particular details, including the origin and type.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Description</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrophyllite</td>
<td>$Al_2Si_4O_{10}(OH)_2$</td>
<td>pale gray massive, synthetic, but from natural sources. XRF analysis on 1-6-99 revealed major constituents: 62.4% $SiO_2$ and 30.0% $Al_2O_3$.</td>
<td>Department of Geology stock</td>
</tr>
<tr>
<td>NIST 612</td>
<td>Glass</td>
<td>SRM silicate glass; 72.3% $SiO_2$, 14.2% $Na_2O$, 11.8% $CaO$.</td>
<td>US National Institute of Standards and Technology.</td>
</tr>
<tr>
<td>silica glass</td>
<td>Pure $SiO_2$</td>
<td>silica tube, sealed at both ends. 8-32 set screw glued to one end. Other end roughened by a diamond grit grinding head.</td>
<td>Department of Chemistry, glass blowing shop</td>
</tr>
<tr>
<td>Macor</td>
<td>Glass &amp; mica</td>
<td>white machinable ceramic, of glass and mica. Composed of micron-scale, randomly oriented phlogopite mica flakes in a boro-luminosilicate matrix.</td>
<td>Corning</td>
</tr>
<tr>
<td>Otolith</td>
<td>organic calcium carbonate</td>
<td>carbonate structure, with growth bands, from the inner ear of a fish</td>
<td>Department of Fisheries and Oceans</td>
</tr>
</tbody>
</table>
## A.3 Geological Samples

The following is a list of the mineralogical samples analyzed, including details of the sample and its origin and type.

**Table A.3: Catalogue of the Geological Samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Description</th>
<th>Source/Locality</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>chromitite</td>
<td><em>FeCr₂O₄</em>, XRF analysis on 5-10-04 revealed major constituents: 40.5% <em>Cr₂O₃</em>, 21% <em>FeO</em>, 16.9% <em>MgO</em>, 9.8% <em>SiO₂</em> and 8.6% <em>Al₂O₃</em>. NAA analysis in October 2004 revealed 20 ppb Au and 6 ppm U in a 125 g sample, although these values may not be reproducible.</td>
<td>Stillwater, Montana, USA</td>
</tr>
<tr>
<td>917</td>
<td>vein quartz, <em>SiO₂</em></td>
<td>Vein quartz, parent sample is 98% coarse quartz, with many fluid inclusions, minor muscovite and carbonate and trace tourmaline, pyrite and magnetite.</td>
<td>3300' level, McIntyre gold mine, Timmins, Ontario.</td>
</tr>
<tr>
<td>1055</td>
<td>pyroxene, magnetite pegmatite</td>
<td>Magnetite pegmatite, pyroxene grains to <em>7x4 cm</em>. Dark, coarse-grained pyroxene, altered to amphibole (chain silicates) in granular magnetite matrix (Wilson, 1994b).</td>
<td>Grenville province, southeastern Ontario: West margin of Bedford Township against Hinchinbrooke Township, west side of Highway 38 opposite site of samples 1053 – 1054, adjacent to the known mag-ap showing.</td>
</tr>
</tbody>
</table>
Table A.3 continued . . .

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type</th>
<th>Description</th>
<th>Source/Locality</th>
</tr>
</thead>
<tbody>
<tr>
<td>1099</td>
<td>norite</td>
<td>brown orthopyroxene (28%), in blue-grey plagioclase (60%), plus 8% amphibole, 2% clinopyroxene, 1% biotite and 1% Fe Ti oxides with trace sulphide (Wilson, 1994b).</td>
<td>Grenville province, southeastern Ontario: south west side of High Rock Island in Caribou Lake, from the west-facing shore, 2 m above lake level.</td>
</tr>
<tr>
<td>118-133</td>
<td>Anorthosite</td>
<td>extreme plagioclase adcumulate. Monomineralic cumulate. Grayish-white, granular, massive.</td>
<td>Island of Rhum, northwest Scotland. (See 118-134c)</td>
</tr>
<tr>
<td>118-134c</td>
<td>Anorthosite</td>
<td>extreme plagioclase adcumulate. Monomineralic cumulate. Greenish-white, granular, massive. XRF analysis on 5-10-04 revealed major constituents: 47% SiO₂, 33% Al₂O₃ and 17% CaO.</td>
<td>Island of Rhum, northwest Scotland. Top 2 m of unit 14 of the eastern layered series, 25 m north of the summit Hallival. Grid reference NM396962.</td>
</tr>
<tr>
<td>118-138</td>
<td>Ultrabasic breccia</td>
<td>Predominantly dark brown, granular olivine with irregular intercumulus bluish white plagioclase.</td>
<td>Island of Rhum, northwest Scotland. Just west of the track to Harris, which is by the southwest shore of Rhum. Ard Mheall series, unit B of the western layered series of the ultrabasic complex. Grid reference NM345965.</td>
</tr>
<tr>
<td>W053</td>
<td>quartz-sericite schist (porphyry): 56% quartz and 40% mica</td>
<td>Barren felsic porphyry, 3% coarse quartz phenocrysts, 3% feldspars and 1% pyrite.</td>
<td>9660 level, 28 stope: Williams gold mine, Hemlo, Ontario.</td>
</tr>
</tbody>
</table>
For more information or more precise collection localities, contact, Dr. Graham C. Wilson (www.turnstone.ca) and/or Dr. R. F. J. Scoates (Geological Survey of Canada).
Appendix B

Caesium Reservoir Calculations

Production of the caesium vapour requires a higher reservoir temperature than theoretically calculated. The reason for this is not fully understood, although the inefficiency of the design of the apparatus is, in large part, to blame. The caesium reservoir tube is 116.5 mm long, and has an internal diameter of 4.4 mm. Therefore, the molecular conductance of this tube is $0.55 l/s$. At the operating temperature of $\approx 155^\circ C$, the vapour pressure of caesium is $10 mT$, with a mean free path of approximately 5 mm. This equates to $3.6 \times 10^{17}$ atoms of caesium per litre, so at $0.55 l/s$, $43 \mu g$ of caesium flows per second, or 5 g in a day and a half. As the 5 g supply usually lasts several months, this calculation is obviously not representative of actual events. If the surface of the caesium is oxidized, high temperatures are needed to “break the skin” and produce a metallic surface, from which atoms can be vapourized. Accordingly, once the skin is broken, high temperatures should no longer be needed. However, empirical evidence shows that turning the temperature down reduces the strength of the negative beam. Clearly, the temperature must remain high to produce a strong stable beam. Typically, the caesium boiler temperature is kept at $\approx 155^\circ C$ for the duration of an experiment.
Appendix C

Method

C.1 The Yellow Testbed

The yellow testbed, shown in figure C.1, was received from the Chalk River Laboratories in February of 1998. Named for the colour of the support stand, it is a simple system that consisted of an 860 ion source, an einzel lens, a removable Faraday cup, a small, 30° magnet, slits after the magnet, and a final Faraday cup.

In Chalk River, the yellow testbed was primarily used to assess the health of a particular 860 source before that source was transferred to another system. The vacuum was generated by a 160l liquid nitrogen (LN) cooled, oil diffusion pump backed by a rotary pump, which provided an operating vacuum of approximately 7x10^{-7} Torr.

Unfortunately, the magnet resolution was very poor and as there were no entrance slits, no possibility of increasing that resolution. Thus the peaks observed were very broad and isotope separation (e.g.. $^{63}Cu$ and $^{65}Cu$) was not possible. However, the resolution was sufficient to distinguish carbon from oxygen, and the system as a whole could determine the general operational parameters and capabilities of the 860.
Figure C.1: The Yellow Testbed. The 860 is behind the deck power supplies, on the right, its aluminium safety cage opened forward. The diffusion pump, painted white, is situated behind the liquid nitrogen tank, which is partially hidden by the “do not ice” sign. The magnet sits atop two aluminium slabs, above the main power rack.
Two recommendations involving the operation of the 860 were noted when using the yellow testbed. The first involved the need to determine the placement of the sample face while the 860 is disassembled. This procedure ensures that the sample rod is adjusted so that the sample face is held just shy of the sample cone, when seen in profile. Such a positioning allows for the most effective space charge field around the sample, and cannot easily be determined when the 860 is operational.

The second recommendation involved the startup procedure of the 860. The order in which the power supplies are turned up is significant. Flooding the 860 cavity with caesium is inadvisable, as it can lead to a “runaway”\(^1\), due to the caesiation of all internal surfaces and the subsequent failure of the insulating standoffs. The sample and deck voltages and the ionization coil must be turned on before the caesium boiler. In fact, the ionization coil should be hot enough to ionize before neutral caesium starts to enter the chamber. Empirically, it has been determined that the other supplies should be on for at least twenty minutes before the caesium boiler is turned on. Ergo, once the sample is in place, the sample and deck voltages are ramped to \(-4.0\) \(kV\) and \(-21.0\) \(kV\) respectively and the ionizer is ramped to 20.0 A.

Once the source is hot, the sample surface has to become caesiated before a strong current is observed. Caesiating is the process by which caesium atoms are embedded in the matrix of the sample surface, thus lowering the work function of the surface and allowing for ejection of atoms from the surface. This usually takes between twenty minutes to two hours for conducting samples like copper, and up to 24 hours for insulating materials like quartz. This caesiation can be assessed by watching the current output of the sample power supply. Immediately after startup, the current reads zero, but after warm-up, an extraction current of 2.0 mA and higher is recorded.

\(^1\) So named since the current readout of the \(HV_{deck}\) increases rapidly to 10mA and beyond. Normally the readout shows currents of \(\leq 2.0mA\).
The stability of the source can be monitored by watching the current output of both the sample and the deck power supplies. If the readings remain steady, as is the case with all conducting samples, the source is not arcing. If, however, spikes are observed, the sample needs more time to stabilize.

The overall condition of the 860 was found to be effectively monitored by noting the current of the deck power supply. If the current remains at or below 2.0 mA, the source is behaving well and not leaking current to ground. If, however, the current climbs beyond 4.0 mA, it can be assumed that the internal surfaces of the 860, especially the second cone’s standoffs, are dirty—most likely having been caesiated by the flooding of the source with caesium—and leakage to ground is occurring. The only way to rectify this “runaway” source is to turn off all supplies, isolate the 860 from the system, and disassemble and thoroughly clean the 860.

The discovery of the stable beam, sputtered from non-conducting samples in the 860, was fortuitous. A pyrophyllite (synthetic, insulating, machinable aluminium silicate, $Al_2Si_4O_{10}(OH)_2$) target was made and inserted into the 860 on May 20th, 1999. There was no expectation for this sample, only that the characteristic arcing would be observed. The sample was inserted in the morning and the 860 was tuned to low, “gentle” settings. No beam was observed immediately, but after several hours, a stable beam was observed. This discovery was greeted with guarded excitement, since the result was not understood, and had not been reproduced. However, the ensuing experiments proved the 860 could produce a stable beam from a non-conducting sample. The necessary environment involved turning the boiler temperature up slightly, to 40V—to produce more caesium vapour, and the ionization coil down slightly, to 19.0 A—to ionize less of that vapour. In addition, it was discovered that patience is

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2 Placing the various components in the lathe and buffing with fine sand paper, followed by an alcohol rinse, is the best method for cleaning the 860 thoroughly.
vital. The 860 needs time to stabilize and caesiate the sample, in order to produce
the desired negative beam, in extreme cases, (e.g. quartz, and silica glass) for upward
of 24 hours.

C.1.1 860 Operational Difficulties

Numerous problems have been discovered and overcome in the effort to operate the
860 in a efficient and effective manner. While this list is by no means complete, a
sampling of these difficulties is offered in table C.1.

C.2 The Blue Testbed

The blue testbed was built in large part by Dr. Ilia Tomski, and used by him for
his doctoral work. It was named for the colour of the magnet, which has a bright
blue yoke. It has since evolved, but at that time, the blue testbed consisted of, in
order; the 860, an einzel lens, a first Faraday cup, vertical and horizontal steerers,
a mini tandem accelerator, a second Faraday cup, a high resolution 90° magnet, a
aperture, and a third and final Faraday cup. The blue testbed was used to provide
more detailed analyses of samples previously studied on the yellow testbed, as well
as analysis of new samples.

The two main differences between the yellow testbed and the blue testbed were
the inclusion of the mini tandem accelerator in the latter setup and the magnet.
The tandem accelerator was used for charge changing the beam from the 860, from
negative to positive, with an efficiency of approximately 10%. While critical to Dr.
Tomski’s work, such charge changing was not necessary for reanalysis of the yellow
testbed samples. However, as most samples produced a beam of sufficient magnitude,
### Table C.1: Summary of Operational Difficulties and Solutions

<table>
<thead>
<tr>
<th>Problem</th>
<th>Cause</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unusual beam spots and atypical focusing</td>
<td>Second focusing cone not aligned symmetrically with the beam</td>
<td>New Macor standoffs, of correct diameter, located and installed</td>
</tr>
<tr>
<td></td>
<td>First focusing cone missing</td>
<td>Installed first focusing cone</td>
</tr>
<tr>
<td></td>
<td>Ionizer backplate reversed</td>
<td>Position ionizer backplate correctly (screws to be visible on ionizer side)</td>
</tr>
<tr>
<td>Current lower than expected</td>
<td>Running out of caesium</td>
<td>Refill caesium reservoir</td>
</tr>
<tr>
<td></td>
<td>Ionization coil touching backplate, thus dissipating heat too quickly to vapourize caesium</td>
<td>Mount backplate in opposite configuration</td>
</tr>
<tr>
<td></td>
<td>Beam poorly focused</td>
<td>Rewire second focusing cone, using a positive power supply, mounted on the deck</td>
</tr>
<tr>
<td></td>
<td>Sample improperly positioned</td>
<td>Adjust sample position to maximize current</td>
</tr>
<tr>
<td>Excessive sample current</td>
<td>Small gate valve partially closed, grounding the sample rod</td>
<td>Prop gate valve open</td>
</tr>
<tr>
<td>Excessive deck current: Source “Runaway”</td>
<td>Dirty insulators, particularly the large, Teflon insulator, allowing leakage to ground</td>
<td>Remove 860 from system, disassemble, and clean thoroughly, or replace insulators as needed</td>
</tr>
<tr>
<td>Deposition and buildup of vacuum varnish on 860 components, especially the insulators, causing leakage to ground</td>
<td>Too much caesium flooding the 860 cavity</td>
<td>Leave the ionizer and voltages on long after the caesium boiler is turned off in order to remove caesium from source</td>
</tr>
<tr>
<td>Little beam current and unusual isotopic ratios</td>
<td>Poisoned ionizer caused when the ionizer was heated while two standards were positioned atop the coils</td>
<td>Replaced ionizer with a new one</td>
</tr>
</tbody>
</table>
the polarity of the magnet power supply was not usually reversed. The tandem was thus used for most of the blue testbed experiments.

The magnet on the blue testbed was very well characterized and has excellent resolution. Because of this, the blue testbed could therefore provide more detailed mass spectra than could the yellow testbed. Of significance, a stable beam from silica glass was observed, which had not been seen on the yellow testbed.

The results of those experiments carried out on the blue testbed are summarized in section D.2.

C.3 The Red Testbed

The design of the red testbed was finalized in the spring of 1999, during the yellow testbed experiments. Unfortunately, the construction was delayed by the demise of the tandem’s accelerator tubes in late June of that year. It was not until October, 2000 that the positioning and aligning of the 90° magnet was accomplished. Some months later, in July 2001, the red testbed produced its first results. Almost two years and many experiments later, in June 2003, the first beam, $^{194}Pt$, from gold in copper, was run through the tandem, injected from the red testbed. The final configuration of the red testbed is pictured in figure C.2.

The red testbed, named for the red stands upon which most of the components rest, has the 860 attached to the turbo pump column, which fronts the 90° magnet. Beyond the magnet are two boxes, though for the low energy experiments, only the first box (equipped with a slot lens, vertical and horizontal slits and a $FC$) was in place.

After tuning difficulties were diagnosed and solved (see table C.2, page 102), the
Figure C.2: The Red Testbed. The cryo power supply and second, right hand power supply rack visible in this photo are not shown in the schematic on figure 4.6, page 50.
second box was aligned. The second box contains the Faraday cup ($FC1$) relocated from in the first box, the $7^\circ$ electric analyzer, vertical steerers and the triplet quadrupole.

The negative ion beam from the 860 is first defined by a 14 mm aperture before injection into the $90^\circ$ magnet. Once through the magnet, the beam is steered slightly by a slot lens\textsuperscript{5} before passing through a set of horizontal and vertical slits.

Passing into the second box, the beam is either measured by $FC1$, or if the Faraday cup is raised, manipulated by the $7^\circ$ EA, vertical steerers and the triplet quadrupole to pass through the LE magnet, the LE slits and into $FC2$, immediately prior to the accelerator.

The settings for the devices that facilitate this journey are detailed here:

Initially, the voltages on the inner plates of the slot lens were identical, but differing voltages were used once it was determined that the magnet had settled, and even after adjustments to the magnet stand, vertical steering was required. The slot lens’ power supplies were wired so that one control can operate the overall strength of the lens, and another can increase the difference between the voltages. The optimal setting for the slot lens differ when the beam is focused through to the different $FC$. For focusing the beam into the $FC1$, the slot lens is optimized at $-1.7 \, kV$ on the top plate and $-1.62 \, kV$ on the bottom plate. When focused through the low energy (LE) magnet of the tandem and into the low energy $FC$ ($FC2$ for this work) the settings are $-2.9 \, kV$ and $-2.75 \, kV$, respectively. For focusing through the accelerator, into the high energy $FC$ ($FC3$ for this work), the slot lens settings are $-4.65 \, kV$ and $-4.2 \, kV$, respectively. Empirical results have determined that the vertical slits can remain wide open. The horizontal slits are usually held at 6 mm for tuning to the

\textsuperscript{5} While technically a vertical steerer, the first component in the first box continues to be called the “slot lens” when discussing the testbed.
first $FC1$, but are brought in to $4\,mm$ for the machine measurements.

The $7^\circ$ EA is a set of two plates, one angled and one straight. Both plates have voltages applied to them, equal in strength, but opposite in polarity. These voltages are $\pm 0.77\,kV$ respectively. The curved plate, the one to which the negative ions are attracted, necessarily has the positive voltage. The vertical steerers need very little voltage to maximize the current, as the beam is virtually centred at this point. The top plate has a mere $+20\,V$ while the bottom is (permanently) grounded. The triplet quadrupole focuses the beam axially and is the final component of the red testbed. The quad is wired such that all four inner electrodes are equal in voltage, with the vertical pair supplied with a positive voltage and the horizontal pair, negative. The eight outer electrodes are also equal in voltage, though this voltage differs from the inner electrodes. The outer, vertical electrodes are supplied with a negative voltage and the outer horizontal, positive. The optimal voltages for focusing the beam are $\pm 0.95\,kV$ for the inner pairs and $\pm 1.4\,kV$ for the outer pairs. Beyond the triplet quadrupole is the gate valve which separates the red testbed from the low energy (LE) magnet of the tandem. Once the gate valve is opened, the beam passes through the straight-through port of the LE magnet, the LE slits and impinges $FC2$. The leads from the power supply to this magnet must be reversed, to facilitate analysis, since the poles have been magnetized in one direction for so long to have picked up a permanent field. A reverse field of $17\,G$ is sufficient to steer the beam through the LE slits and to $FC2$. It is into this Faraday cup that the $7^\circ$ EA, the vertical steerer and the triplet quadrupole focus the beam.

Typically, the transmission from $FC1$ to $FC2$ is approximately $20\%$. While this is decidedly low, it is not unexpected, as the configuration of the red testbed was designed using only those components that were available at the time, and so is less than ideal.
The controls for these components, from the slot lens through to the triplet quadrupole, are adjusted with a remote control panel\(^6\). This remote was designed in order to assure that the equal but opposite voltages required for a given component were controlled simultaneously.

C.3.1 Red Testbed Difficulties and Subsequent Modifications

The red testbed has been, and remains, a work in progress. While it is considered complete and operational, minor changes continue to enhance the ease of use of the red testbed. Major changes and improvements which have been carried out are detailed in table C.2.

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Change</th>
<th>Explanation/Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>13-9-2001</td>
<td>First focusing cone</td>
<td>Installed missing part</td>
<td>For better focusing</td>
</tr>
<tr>
<td></td>
<td>Second focusing cone</td>
<td>Metal standoffs installed, replacing insulating ones</td>
<td>To duplicate internal structure of the 860 used on the yellow and blue testbeds</td>
</tr>
<tr>
<td></td>
<td>Sample cone</td>
<td>New one has sample stop</td>
<td>To avoid sample protruding too far</td>
</tr>
<tr>
<td></td>
<td>Deionized water supply for 860</td>
<td>Hooked up to main deionized water supply</td>
<td>To free the portable deionized water unit for other purposes</td>
</tr>
<tr>
<td>17-9-2001</td>
<td>Ionizing coil backplate</td>
<td>Reversed</td>
<td>To duplicate the original 860</td>
</tr>
<tr>
<td></td>
<td>Vacuum gauges</td>
<td>Additional units added</td>
<td>To better assess the vacuum of the system</td>
</tr>
<tr>
<td>18-9-2001</td>
<td>Main 860 insulator</td>
<td>Polycarbonate replaced with Teflon</td>
<td>Small cracks in polycarbonate insulator may be the source of small leaks</td>
</tr>
</tbody>
</table>

\(^6\) This remote is attached to the power supplies by a 20m cable in order to facilitate movement around the room so that focusing can proceed wherever the appropriate readout is positioned.
Table C.2 continued ...

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Change</th>
<th>Explanation/Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-9-2001</td>
<td>Faraday cup slits</td>
<td>5 mm vertical slits inst-</td>
<td>To better distinguish peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>alled on front of FC1</td>
<td></td>
</tr>
<tr>
<td>21-9-2001</td>
<td>Hall probe</td>
<td>New unit installed</td>
<td>To better determine the resolution capabilities of the magnet</td>
</tr>
<tr>
<td>29-10-2001</td>
<td>Faraday cup slits</td>
<td>5 mm slits were re-</td>
<td>To better distinguish the two silver peaks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>placed with 1 mm slits</td>
<td></td>
</tr>
<tr>
<td>31-10-2001</td>
<td>Suppression for FC</td>
<td>Magnet added before the FC</td>
<td>To direct electrons away from entering the cup</td>
</tr>
<tr>
<td>2-11-2001</td>
<td>Suppression for FC</td>
<td>Power supply hooked up to</td>
<td>To direct electrons away from entering the cup</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FC suppressor plate</td>
<td></td>
</tr>
<tr>
<td>27-11-2001</td>
<td>FC moved</td>
<td>FC placed at end of first</td>
<td>To place the FC farther from the magnet for $2\rho$ focusing</td>
</tr>
<tr>
<td></td>
<td></td>
<td>box, in six way cross</td>
<td></td>
</tr>
<tr>
<td>12-12-2001</td>
<td>Baffle for FC slits</td>
<td>Installed</td>
<td>To mask the beam, or electrons, from getting around the slits and into the FC</td>
</tr>
<tr>
<td>7-1-2002</td>
<td>Aperture</td>
<td>14 mm aperture inst-</td>
<td>To better define the beam</td>
</tr>
<tr>
<td></td>
<td></td>
<td>alled, 21.05 cm before the</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>einzel lens</td>
<td></td>
</tr>
<tr>
<td>15-2-2002</td>
<td>Slot lens</td>
<td>Made and installed</td>
<td>To help steer the beam</td>
</tr>
<tr>
<td>2-4-2002</td>
<td>Second cone</td>
<td>Metal standoffs re-</td>
<td>To better focus the beam. (The grounding was not successful.)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>placed with insulators,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>and feed through made</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>and installed to allow</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>second cone to be</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>grounded</td>
<td></td>
</tr>
<tr>
<td>5-4-2002</td>
<td>Caesium boiler thermo-couple</td>
<td>Added</td>
<td>To better determine the temperature of the Caesium</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Air cooling for the Caesium boiler</td>
<td>Added</td>
<td>To allow quenching of the boiler</td>
</tr>
</tbody>
</table>
Table C.2 continued . . .

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Change</th>
<th>Explanation/Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>23-4-2002</td>
<td>Caesium boiler</td>
<td>The boiler from the blue testbed was installed</td>
<td>To determine if the low current observed resulted from boiler malfunction</td>
</tr>
<tr>
<td>16-5-2002</td>
<td>Additional $FC$</td>
<td>Installed through magnet box pumping port</td>
<td>To better determine magnitude of the current immediately after the 860</td>
</tr>
<tr>
<td>27-6-2002</td>
<td>Vertical and horizontal slits</td>
<td>Installed and tested</td>
<td>To better define the beam</td>
</tr>
<tr>
<td>13-2-2003</td>
<td>Ionizing coil backplate</td>
<td>Reversed</td>
<td>As per Mr. Y. Imahori’s instructions</td>
</tr>
<tr>
<td>3-2003</td>
<td>Second box alignment brackets</td>
<td>Made and installed</td>
<td>To facilitate alignment of second box</td>
</tr>
<tr>
<td>4-2003 &amp; 5-2003</td>
<td>Second box</td>
<td>Installed and connected</td>
<td>Required to inject beam through the accelerator</td>
</tr>
<tr>
<td>7-2003</td>
<td>Remote for red line</td>
<td>Made and installed</td>
<td>All second box power supplies wired to remote for convenience</td>
</tr>
<tr>
<td>12-8-2003</td>
<td>Hall probe</td>
<td>Re-anchored</td>
<td>Probe more appropriately placed and fastened more securely in that position</td>
</tr>
<tr>
<td>7-10-2003</td>
<td>Main 860 insulator</td>
<td>Teflon replaced with polycarbonate</td>
<td>Teflon was dirty and was a possible outgassing source</td>
</tr>
<tr>
<td>8-10-2003</td>
<td>Second cone</td>
<td>Feed through connected to a $-25, keV$ power supply, sitting at ground</td>
<td>To increase focusing</td>
</tr>
<tr>
<td></td>
<td>Second cone</td>
<td>Insulating standoffs replaced</td>
<td>Dirty and likely cracked, allowing current to pass along</td>
</tr>
<tr>
<td>9-10-2003</td>
<td>Second cone</td>
<td>Some structural components changed</td>
<td>Changes required in order to mask insulators from beam</td>
</tr>
</tbody>
</table>
Table C.2 continued . . .

<table>
<thead>
<tr>
<th>Date</th>
<th>Component</th>
<th>Change</th>
<th>Explanation/Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>15-10-2003</td>
<td>Feed through for second cone</td>
<td>Changed to a smaller version, so now connected to a +5\text{kV} power supply, sitting on the deck</td>
<td>New 860 body piece required did not accommodate high voltage feed through</td>
</tr>
<tr>
<td></td>
<td>140 MΩ resistor</td>
<td>Installed, linking second cone fee through to deck</td>
<td>To provide a current path in order to eliminate the tracking of the power supply of the cone with the power supply of the deck</td>
</tr>
<tr>
<td>15-10-2003</td>
<td>Caesium boiler tube</td>
<td>Changed to one with a copper liner</td>
<td>In order to allow Cs to heat more quickly</td>
</tr>
<tr>
<td>16-10-2003</td>
<td>Caesium boiler tube</td>
<td>Changed back to the stainless steel version</td>
<td>No Cs observed when copper version used</td>
</tr>
<tr>
<td>2-6-2004</td>
<td>Ionizer</td>
<td>Changed to a spiral ion-izer</td>
<td>Helical ionizer likely poisoned due to heating while the AX 90 and NIST 612 were resting on it</td>
</tr>
</tbody>
</table>
Appendix D

Testbed Results

D.1 Yellow Testbed Results

Seventeen different samples were run on the yellow testbed. These included elemental samples, synthetic materials, pressed powders and geological specimens. The elemental samples included copper, aluminium, carbon, gold, silver and rhodium. The carbon (graphite), gold, silver and rhodium were all solid targets, mounted into copper blanks. The synthesized samples included silver solder, silica glass ($SiO_2$), fluorite ($CaF_2$), silver iodide (AgI), silver chloride (AgCl) and sodium chloride (NaCl). The latter four samples in this group were pressed powders. They were mixed with niobium powder to increase the conductivity, and pressed into holders of either copper or aluminium. The geological samples included pyrophyllite, 1055, W053, W188, and W192. Details of all samples are provided in Appendix A, tables A.1, A.2 and A.3.

Highlights of these yellow testbed experiments are given below, in table D.1 with the full details in the spectra following.
Table D.1: Summary of all results from the Yellow Testbed. All voltages are in kilovolts (kV), all $i_{\text{sample}}$ currents are in milliamperes (mA), and all $i_{\text{FC}}$ currents are in microamps ($\mu$A), unless otherwise noted. Currents are quoted for elements rather than discrete isotopes because of the low mass resolution of the analyzing magnet.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beam</th>
<th>$HV_{\text{sample}}$</th>
<th>$HV_{\text{deck}}$</th>
<th>$i_s$</th>
<th>$i_{\text{FC}1}$</th>
<th>$i_{\text{FC}2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>$Cu^-$</td>
<td>−5.5</td>
<td>−21.5</td>
<td>5.8</td>
<td>107</td>
<td>54</td>
</tr>
<tr>
<td>Aluminium</td>
<td>$Al^-$</td>
<td>−4</td>
<td>−18.1</td>
<td>2.5</td>
<td>52</td>
<td>7.0</td>
</tr>
<tr>
<td>Carbon, in copper</td>
<td>$C^-$</td>
<td>−4</td>
<td>−15.5</td>
<td>4.0</td>
<td>420</td>
<td>135</td>
</tr>
<tr>
<td>Gold, in copper</td>
<td>$Au^-$</td>
<td>−3</td>
<td>−13.3</td>
<td>1.5</td>
<td>36.5</td>
<td>14</td>
</tr>
<tr>
<td>Silver, in copper</td>
<td>$Ag^-$</td>
<td>−4</td>
<td>−12.8</td>
<td>−</td>
<td>40</td>
<td>0.48</td>
</tr>
<tr>
<td>Rhodium wire, in copper</td>
<td>$Rh^-$</td>
<td>−4</td>
<td>−15.8</td>
<td>1.7</td>
<td>6.4</td>
<td>170 nA</td>
</tr>
<tr>
<td>Silver Solder</td>
<td>$Ag^-$</td>
<td>−5.5</td>
<td>−15.1</td>
<td>2.1</td>
<td>5.6</td>
<td>0.47</td>
</tr>
<tr>
<td>$SiO_2$</td>
<td></td>
<td>−2</td>
<td>−10</td>
<td>No</td>
<td>stability</td>
<td>achieved</td>
</tr>
<tr>
<td>$CaF_2$, in copper</td>
<td>$F^-$</td>
<td>−2</td>
<td>−8.3</td>
<td>0.5</td>
<td>56</td>
<td>38</td>
</tr>
<tr>
<td>$AgI$, in copper</td>
<td>$Ag^-$</td>
<td>−2</td>
<td>−7.4</td>
<td>0.4</td>
<td>15.5</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>$I^-$</td>
<td>−2</td>
<td>no resolution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>between the $I$ and</td>
<td></td>
<td>$Cu_2$</td>
<td></td>
</tr>
<tr>
<td>$AgI$, in aluminium</td>
<td>$I^-$</td>
<td>−4</td>
<td>−18</td>
<td>2.9</td>
<td>50</td>
<td>41</td>
</tr>
<tr>
<td>$AgCl$, in copper</td>
<td>$Ag^-$</td>
<td>−2</td>
<td>−7.2</td>
<td>0.4</td>
<td>38</td>
<td>110 nA</td>
</tr>
<tr>
<td></td>
<td>$Cl^-$</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>$NaCl$, in copper</td>
<td>$Na^-$</td>
<td>−1.4</td>
<td>−5.8</td>
<td>0.75</td>
<td>17.5</td>
<td>no Na$^-$ seen</td>
</tr>
<tr>
<td></td>
<td>$Cl^-$</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>$O^-$</td>
<td>−5</td>
<td>−18.5</td>
<td>0.25</td>
<td>12</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td>$Si^-$</td>
<td></td>
<td></td>
<td>190 nA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1055</td>
<td>$O^-$</td>
<td>−3</td>
<td>−14</td>
<td>0.35</td>
<td>32</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>$Si^-$</td>
<td></td>
<td></td>
<td></td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>W053</td>
<td>$O^-$</td>
<td>−4</td>
<td>−15</td>
<td>0.25</td>
<td>6.1</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>$Si^-$</td>
<td></td>
<td></td>
<td></td>
<td>105 nA</td>
<td></td>
</tr>
<tr>
<td>W188</td>
<td>$O^-$</td>
<td>−4</td>
<td>−13</td>
<td>−</td>
<td>24</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>$Si^-$</td>
<td></td>
<td></td>
<td></td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>W192</td>
<td>$O^-$</td>
<td>−4</td>
<td>−15.8</td>
<td>−</td>
<td>1.1</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>$Si^-$</td>
<td></td>
<td></td>
<td></td>
<td>17 nA</td>
<td></td>
</tr>
</tbody>
</table>
The following mass spectra are presented by sample type. For samples that have more than one mass spectrum, the data are presented in chronological order.

### D.1.1 Elemental Samples

#### Mass Spectrum from Copper, 1-3-99

![Mass Spectrum from Copper, 1-3-99](image)

Figure D.1: The yellow testbed's 860 settings for this first spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -3kV \\
HV_{\text{deck}} &= -10kV \\
i_{\text{sample}} &= 1.5mA \\
i_{\text{FC1}} &= 27.5\mu A
\end{align*}
\]
Figure D.2: The yellow testbed’s 860 settings for this copper spectrum were as follows:

- $HV_{sample} = -5.5kV$
- $HV_{deck} = -21.2kV$
- $i_{sample} = 3.5mA$
- $i_{FC1} = 107\mu A$
Figure D.3: The yellow testbed’s 860 settings for this aluminium spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & \quad -4\text{kV} \\
HV_{\text{deck}} & \quad -17\text{kV} \\
i_{\text{sample}} & \quad \text{not noted} \\
i_{\text{FC1}} & \quad 4.8\mu\text{A}
\end{align*}
\]
Figure D.4: The yellow testbed’s 860 settings for this aluminium spectrum were as follows:

- $HV_{\text{sample}} = -4kV$
- $HV_{\text{deck}} = -18.1kV$
- $i_{\text{sample}} = 2.6mA$
- $i_{F\text{C1}} = 52\mu A$
Mass Spectrum from Aluminium, with a 2mm wide depression, 13-4-99
second scan, after source warm up

Figure D.5: The yellow testbed’s 860 settings for this aluminium spectrum were as follows:

\[ HV_{sample} = -4\text{kV} \]
\[ HV_{deck} = -18.1\text{kV} \]
\[ i_{sample} = 2.5\text{mA} \]
\[ i_{FC1} = 52\text{µA} \]
Figure D.6: The yellow testbed’s 860 settings for this aluminium spectrum were as follows:

\[HV_{\text{sample}} = -34kV\]
\[HV_{\text{deck}} = -18.6kV\]
\[i_{\text{sample}} = 1.7mA\]
\[i_{\text{FC1}} = 28.3\mu A\]
Figure D.7: The yellow testbed’s 860 settings for this first carbon spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -1.5kV \\
HV_{\text{deck}} & = -5.5kV \\
I_{\text{sample}} & = 3.25mA \\
I_{FC1} & = \text{not noted}
\end{align*}
\]
Figure D.8: The yellow testbed’s 860 settings for this silver spectrum were as follows:

\[
\begin{align*}
HV_{sample} &= -4kV \\
HV_{deck} &= -12.8kV \\
i_{sample} &= \text{not noted} \\
i_{FC1} &= 40\mu A
\end{align*}
\]
Mass Spectrum from Rhodium, in copper, 18-5-99

Figure D.9: The yellow testbed’s 860 settings for this rhodium spectrum were as follows:

\[
\begin{align*}
HV_{sample} & = -5.5kV \\
HV_{deck} & = -15.8kV \\
i_{sample} & = 5.5mA \\
i_{FC1} & = 6.4\mu A
\end{align*}
\]
D.1.2 Synthetic Samples

Mass Spectrum from Silver Solder, in copper, 19-3-99

Figure D.10: The XRF analysis of this silver solder sample revealed the major constituents to be, 38.7% Ag, 22% Cu, 19.5% Cd and 17.5% Zn. The yellow testbed’s 860 settings for this silver solder spectrum were as follows:

\[
\begin{align*}
HV_{sample} & = -5.5kV \\
HV_{deck} & = -17.8kV \\
\ i_{sample} & = 1.5mA \\
\ i_{FC1} & = 3.2\mu A
\end{align*}
\]
Figure D.11: The yellow testbed’s 860 settings for this silver solder spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -5.5kV \\
HV_{\text{deck}} & = -15.1kV \\
I_{\text{sample}} & = 2.1mA \\
I_{FC1} & = 5.6\mu A
\end{align*}
\]
Figure D.12: This second spectrum from the silver solder sample was taken several hours after that in figure D.11. The settings remained as follows:

\[
\begin{align*}
HV_{sample} & = -5.5kV \\
HV_{deck} & = -15.1kV \\
i_{sample} & = 2.1mA \\
i_{FC1} & = 5.6\mu A
\end{align*}
\]
Figure D.13: The yellow testbed’s 860 settings for this fluorite spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -2kV \\
HV_{\text{deck}} &= -8.3kV \\
i_{\text{sample}} &= 0.2mA \\
i_{\text{FC1}} &= 56\mu A
\end{align*}
\]
Figure D.14: This second spectrum from fluorite was taken several hours after that in figure D.13. The yellow testbed’s 860 settings remained as follows:

\[
\begin{align*}
HV_{sample} & = -2kV \\
HV_{deck} & = -8.3kV \\
i_{sample} & = 0.2mA \\
i_{FC1} & = 56\mu A
\end{align*}
\]
Figure D.15: The yellow testbed’s 860 settings for this fluorite spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -2kV \\
HV_{\text{deck}} & = -8.2kV \\
i_{\text{sample}} & = \text{not noted} \\
i_{FC1} & = 25\mu A
\end{align*}
\]
Figure D.16: The yellow testbed’s 860 settings for this fluorite spectrum were as follows:

\[
\begin{align*}
HV_{sample} &= -2kV \\
HV_{deck} &= -7.4kV \\
\dot{i}_{sample} &= 0.1mA \\
\dot{i}_{FC1} &= 11.5\mu A
\end{align*}
\]
Figure D.17: The yellow testbed’s 860 settings for this silver iodide spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -3\text{kV} \\
HV_{\text{deck}} &= -13.8\text{kV} \\
i_{\text{sample}} &= 1.5\text{mA} \\
i_{\text{FC1}} &= 47\mu\text{A}
\end{align*}
\]
Figure D.18: The yellow testbed’s 860 settings for this silver iodide spectrum were as follows:

\begin{align*}
    HV_{\text{sample}} & = -2kV \\
    HV_{\text{deck}} & = -7.2kV \\
    i_{\text{sample}} & = 0.4mA \\
    i_{FC1} & = 15.5\mu A
\end{align*}
Figure D.19: Since the copper dimer swamped the iodine monomer peak when silver iodide was pressed into a copper target, an aluminium target was fashioned. While silver was both anticipated and sought in this spectrum, silver was neither looked for nor observed. The yellow testbed’s 860 settings for this resulting spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -4kV \\
HV_{\text{deck}} & = -18kV \\
i_{\text{sample}} & = 2.0mA \\
i_{\text{FC1}} & = 50\mu A
\end{align*}
\]
Figure D.20: This second spectrum of silver iodide in aluminium was taken with the entrance slits of the magnet wide open. The yellow testbed’s 860 settings for this second spectrum were increased, as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -5.5\,kV \\
HV_{\text{deck}} &= -20\,kV \\
i_{\text{sample}} &= 0.7\,mA \\
i_{FC1} &= 81\,\mu A
\end{align*}
\]
Figure D.21: The yellow testbed’s 860 settings for this silver chloride spectrum were as follows:

\[HV_{sample} = -2kV\]
\[HV_{deck} = -7.4kV\]
\[i_{sample} = 0.5mA\]
\[i_{FC1} = 38\mu A\]
Figure D.22: As the magnitude of the chloride peak from the run of May 10, 1999 (see figure D.21) was not as great as expected, a second sample of silver chloride was prepared, using significantly more $\text{AgCl}$ powder. The spectrum from this second sample is shown here. The yellow testbed’s 860 settings for this silver chloride spectrum were as follows:

$HV_{\text{sample}} = -2\text{kV}$
$HV_{\text{deck}} = -8.5\text{kV}$
$i_{\text{sample}} = 0.4\text{mA}$
$i_{\text{FC1}} = 6.8\mu\text{A}$
Figure D.23: The yellow testbed’s 860 settings for this silver chloride spectrum were as follows:

\[
\begin{align*}
HV_{sample} & = -2kV \\
HV_{deck} & = -7.2kV \\
i_{sample} & = 0.4mA \\
i_{FC1} & = 34\mu A
\end{align*}
\]
Figure D.24: The yellow testbed’s 860 settings for this sodium chloride spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -1.4kV \\
HV_{\text{deck}} & = -5.8kV \\
i_{\text{sample}} & = 0.75mA \\
i_{FC1} & = 17.5\mu A
\end{align*}
\]
D.1.3 Geological Samples

Mass Spectrum from Pyrophyllite, 20-5-99

When negative ions from an insulator were first observed

Figure D.25: Undoubtedly the most significant sample run on the yellow testbed was the pyrophyllite \((Al_2Si_4O_{10}(OH)_2)\). While the oxygen, silicon and silicon dioxide peaks were observed, aluminium was neither sought, nor observed in this spectrum. The 860 settings for this first pyrophyllite run were set very low initially. They were gradually increased over the course of the day as the 860 was found to remain stable. The yellow testbed’s 860 settings associated with this pyrophyllite mass spectrum were as follows:

- \(HV_{\text{sample}}\) = \(-5kV\)
- \(HV_{\text{deck}}\) = \(-17.8kV\)
- \(i_{\text{sample}}\) = 0.25\(mA\)
- \(i_{FC1}\) = 12\(\mu A\)
Figure D.26: To confirm the results of the previous day, the pyrophyllite sample was run again. Once again, the oxygen, silicon and silicon dioxide peaks were observed, but the aluminium was neither sought, nor observed in this spectrum. The yellow testbed’s 860 settings for this pyrophyllite spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -4kV \\
HV_{\text{deck}} &= -16.5kV \\
i_{\text{sample}} &= 0.4mA \\
i_{\text{FC1}} &= 9.4\mu A
\end{align*}
\]
Figure D.27: The yellow testbed’s 860 settings for this pyrophyllite spectrum were as follows (as before, the oxygen, silicon and silicon dioxide peaks were observed, but the aluminium was neither sought, nor observed in this spectrum):

\[\begin{align*}
HV_{sample} & = -4kV \\
HV_{deck} & = -15.5kV \\
 i_{sample} & = 1.1mA \\
 i_{FC1} & = 10\mu A 
\end{align*}\]
Figure D.28: This mass spectrum was taken the same day, but two hours after the spectrum shown in figure D.27, after the sample had caesiated further. This quick scan shows the advantage of caesiation of insulating samples, as the currents of both O and Si (the only elements looked for) increased. The yellow testbed’s 860 settings were not changed from the previous scan, but the $i_{\text{sample}}$ and $i_{FC1}$ increased as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -4kV \\
HV_{\text{deck}} & = -15.5kV \\
i_{\text{sample}} & = 1.8mA \\
i_{FC1} & = 20.5\mu A
\end{align*}
\]
Figure D.29: The yellow testbed’s 860 settings for this coarse-grained pyroxene are as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -3kV \\
HV_{\text{deck}} & = -14kV \\
i_{\text{sample}} & = 0.35mA \\
i_{FC1} & = 34\mu A
\end{align*}
\]
Figure D.30: The yellow testbed’s 860 settings for this quartz-sericite schist sample were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -5kV \\
HV_{\text{deck}} &= -17.8kV \\
\bar{i}_{\text{sample}} &= 0.25mA \\
\bar{i}_{\text{FC1}} &= 12\mu A
\end{align*}
\]
Figure D.31: The yellow testbed’s 860 settings for this quartz-sericite schist sample were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -4kV \\
HV_{\text{deck}} &= -13kV \\
i_{\text{sample}} &= \text{not noted} \\
i_{\text{FC1}} &= 24\mu A
\end{align*}
\]
Figure D.32: The yellow testbed’s 860 settings for this feldsparic porphyry sample were as follows:

\[
\begin{align*}
HV_{sample} &= -4kV \\
HV_{deck} &= -15.8kV \\
i_{sample} &= \text{negligible} \\
i_{FC1} &= 1.1\mu A
\end{align*}
\]
D.2 Blue Testbed Results

Ten samples were run on the blue testbed, using the 860 negative ion source transferred from the yellow testbed. The only element that was run on the blue testbed was silicon metal. The two synthetic samples tested were Macor and silica glass ($\text{SiO}_2$), the latter of which produced a lovely stable beam. The samples from the natural sources included pyrophyllite, a piece of otolith (carbonate), 917, 1055, FR1, W053, and W192.

The most significant results of the blue testbed experiments include a reanalysis of the pyrophyllite, verifying the initial yellow testbed findings, and the production of a stable beam from the silica glass sample, which had not previously been observed.

Highlights of the blue testbed experiments are shown below, in table D.2, with the full details following.
Table D.2: Summary of Results from the Blue Testbed. All voltages are in kilovolts, all $i_{\text{sample}}$ currents are in milliamps, and all $i_{\text{FC}}$ currents are in microamps, unless otherwise noted. The beams are negative at FC1 and positive at FC2 and FC3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beam</th>
<th>$HV_{\text{sample}}$</th>
<th>$HV_{\text{deck}}$</th>
<th>$i_{\text{sample}}$</th>
<th>$i_{\text{FC1}}$</th>
<th>$i_{\text{FC2}}$</th>
<th>$i_{\text{FC3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon metal</td>
<td>$^{28}\text{Si}$</td>
<td>-6.0</td>
<td>-25</td>
<td>not noted</td>
<td>121</td>
<td>11.4</td>
<td>1.44</td>
</tr>
<tr>
<td>Macor</td>
<td>$^{16}\text{O}$</td>
<td>-5.0</td>
<td>-21</td>
<td>0.8</td>
<td>29</td>
<td>1.5</td>
<td>0.46nA</td>
</tr>
<tr>
<td>$\text{SiO}_2$</td>
<td>$^{16}\text{O}$</td>
<td>-2.5</td>
<td>-17</td>
<td>6.4</td>
<td>0.75</td>
<td>5.9nA</td>
<td>105pA</td>
</tr>
<tr>
<td></td>
<td>$^{28}\text{Si}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>27.2pA</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>$^{16}\text{O}$</td>
<td>-4.0</td>
<td>-15</td>
<td>0.4</td>
<td>33</td>
<td>5</td>
<td>2.89nA</td>
</tr>
<tr>
<td>Otolith</td>
<td>-</td>
<td>-7.5</td>
<td>-11</td>
<td>0.55</td>
<td>2.96</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>917</td>
<td>-</td>
<td>-1.75</td>
<td>-16</td>
<td>9.4</td>
<td>2.63</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1055</td>
<td>$^{16}\text{O}$</td>
<td>-1.0</td>
<td>-5.0</td>
<td>0.75</td>
<td>36</td>
<td>4.3</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>$^{28}\text{Si}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.1nA</td>
</tr>
<tr>
<td>FR1</td>
<td>$^{16}\text{O}$</td>
<td>-5.0</td>
<td>-13.5</td>
<td>1.0</td>
<td>2.4</td>
<td>-</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>$^{28}\text{Si}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21.5nA</td>
</tr>
<tr>
<td>W053</td>
<td>$^{16}\text{O}$</td>
<td>-2.5</td>
<td>-17.3</td>
<td>8.8</td>
<td>2.0</td>
<td>0.48</td>
<td>16.5nA</td>
</tr>
<tr>
<td></td>
<td>$^{28}\text{Si}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0nA</td>
</tr>
<tr>
<td>W192</td>
<td>$^{16}\text{O}$</td>
<td>-2.5</td>
<td>-14</td>
<td>5.4</td>
<td>4.1</td>
<td>8nA</td>
<td>2.25nA</td>
</tr>
<tr>
<td></td>
<td>$^{28}\text{Si}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>21pA</td>
</tr>
</tbody>
</table>
The following mass spectra are presented by sample type. For samples that have more than one mass spectrum, the data are presented in chronological order.

D.2.1 Elemental Samples

Mass Spectrum from Silicon Metal, 8-9-99

Figure D.33: The 860 and blue testbed settings for this spectrum of positively charged isotopes were identical to those set for the SiO$_2$ sample, shown below in figure D.35. The settings were as follows:

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HV_{sample}$</td>
<td>$-2.5kV$</td>
</tr>
<tr>
<td>$HV_{deck}$</td>
<td>$-17kV$</td>
</tr>
<tr>
<td>$i_{sample}$</td>
<td>$4.9mA$</td>
</tr>
<tr>
<td>$i_{FC1}$</td>
<td>$44.5\mu A$</td>
</tr>
<tr>
<td>$HV_{einzel}$</td>
<td>$-8.4kV$</td>
</tr>
<tr>
<td>$HV_{tandem}$</td>
<td>$+20kV$</td>
</tr>
<tr>
<td>$VS$</td>
<td>506</td>
</tr>
<tr>
<td>$HS$</td>
<td>584</td>
</tr>
<tr>
<td>$i_{FC2}$</td>
<td>$+0.63\mu A$</td>
</tr>
</tbody>
</table>
D.2.2 Synthetic Samples

Figure D.34: The mass spectrum profiling the $O^+$ peak from pyrophyllite as measured at the third Faraday cup on the blue testbed. The current of negative ions at $FC_1$ and $FC_2$ were 33 $\mu$A and 5 $\mu$A respectively. The tandem was used to charge change for this spectrum were as follows:

$$
\begin{array}{|c|c|c|}
\hline
HV_{sample} & -4kV & HV_{tandem} & +40kV \\
HV_{deck} & -15kV & VS & 506 \\
i_{sample} & 0.4mA & HS & 584 \\
i_{FC1} & 33\mu A & i_{FC2} & -5\mu A \\
HV_{einzel} & -10.4kV & & +0.42\mu A \\
\hline
\end{array}
$$
Figure D.35: The 860 and blue testbed settings for this spectrum of positively charged isotopes (note the Cu isotopes from the sample holder) were as follows:

- $HV_{sample} = -2.5kV$
- $HV_{deck} = -17kV$
- $i_{sample} = 6.4mA$
- $i_{FC1} = 0.75\mu A$
- $HV_{einzel} = -8.4kV$
- $HV_{tandem} = +20kV$
- $VS = 506$
- $HS = 584$
- $i_{FC2} = +5.9nA$
Mass Spectrum from Macor, 21-9-99

Figure D.36: The blue testbed’s settings for this spectrum of negatively charged isotopes, from Macor, were as follows:

\[
\begin{align*}
HV_{sample} & = -5kV \\
HV_{deck} & = -21kV \\
i_{sample} & = 0.8mA \\
i_{FC1} & = 29\mu A \\
HV_{einzell} & = -13.3kV \\
HV_{tandem} & = +15kV \\
VS & = 414 \\
HS & = 666 \\
i_{FC2(-)} & = 1.5\mu A
\end{align*}
\]
Figure D.37: While no mass spectra were taken from the Otolith sample, the current at the first Faraday cup was strong and stable. That current, the sum of all negative ions from the 860, observed with a $HV_{deck} = -11kV$, at varying $HV_{sample}$ is shown above.
Figure D.38: The current at the first Faraday cup from the Otolith sample was recorded with the \( HV_{sample} = -7.5kV \), at varying \( HV_{deck} \). The results are shown above.
Figure D.39: While no mass spectra were taken from this quartz sample, 917, the current at the first Faraday cup was relatively strong and stable. That current, observed with a $HV_{deck} = -10kV$, at varying $HV_{sample}$ is shown above.
Figure D.40: The current at the first Faraday cup from the quartz sample, 917, was recorded with the $HV_{\text{sample}} = -1.75\text{kV}$, at varying $HV_{\text{deck}}$. The results are shown above. Further increases of the $HV_{\text{deck}}$ were not attempted as the $i_{\text{sample}}$ was getting dangerously high (9.4mA).
Figure D.41: The blue testbed’s settings for this spectrum of negatively charged isotopes, from this coarse-grained pyroxene, were as follows:

- $HV_{sample} = -3.0kV$
- $HV_{deck} = -14.5kV$
- $i_{sample}$ not noted
- $i_{FC1} = 17\mu A$
- $HV_{einzl} = -9.2kV$
- $HV_{tandem}$ not used
- $VS = 352$
- $HS = 734$
- $i_{FC2}(-) = 1.0\mu A$
Figure D.42: The blue testbed’s settings for this profile of the oxygen peak from this coarse-grained amphibole, were as follows:

- $HV_{sample} = -6.0kV$
- $HV_{deck} = -22.5kV$
- $i_{sample} = 1.85mA$
- $i_{FC1} = 36\mu A$
- $HV_{einzel} = -13.6kV$
- $HV_{tandem} = +9.0kV$
- $VS = 136$
- $HS = 706$
- $i_{FC2(-)} = 4.3\mu A$
- $i_{FC2(+)} = 0.5\mu A$
Figure D.43: The blue testbed’s settings for this spectrum of negatively charged isotopes, from this coarse-grained pyroxene, were as follows (note that mangesium does not make negative ions):

\[
\begin{align*}
HV_{\text{sample}} & = -6.0kV \\
HV_{\text{deck}} & = -22.5kV \\
i_{\text{sample}} & = 1.85mA \\
i_{\text{FC1}} & = 24\mu A \\
HV_{\text{einzel}} & = -13.6kV \\
HV_{\text{tandem}} & = \text{not used} \\
VS & = 212 \\
HS & = 806 \\
i_{\text{FC2}}(-) & = 3.0\mu A
\end{align*}
\]
Mass Spectrum from Fox River #1, 15-2-00

Figure D.44: The blue testbed’s settings for this spectrum of positively charged isotopes, from Fox River #1, were as follows:

- $HV_{sample}$ = $-5.0kV$
- $HV_{deck}$ = $-12kV$
- $i_{sample}$ = $1.0mA$
- $i_{FC1}$ = $2.4\mu A$
- $HV_{einzell}$ = $-6.5kV$
- $HV_{tandem}$ = $+15kV$
- $VS$ not noted
- $HS$ not noted
- $i_{FC2}(+)$ = $1.0\mu A$
Figure D.45: The blue testbed’s settings for this spectrum of positively charged isotopes, from this quartz-sericite schist, were as follows:

- $HV_{\text{sample}} = -2.5kV$
- $HV_{\text{deck}} = -17.3kV$
- $i_{\text{sample}} = 8.8mA$
- $i_{FC1} = 3.5\mu A$
- $HV_{\text{einzl}} = -10.6kV$
- $HV_{\text{tandem}} = +15kV$
- $VS = 614$
- $HS = 634$
- $i_{FC2}(+) = 0.48\mu A$
Figure D.46: The blue testbed’s settings for this spectrum of the $O^+$ peak, from this quartz-sericite schist, were the same as those of its whole mass spectrum, as seen in figure D.45, and remained as follows:

- $HV_{sample} = -2.5kV$
- $HV_{deck} = -17.3kV$
- $i_{sample} = 8.8mA$
- $i_{FC1} = 3.5\mu A$
- $HV_{einzel} = -10.6kV$
- $HV_{tandem} = +15kV$
- $VS = 614$
- $HS = 634$
- $i_{FC2}(+) = 0.48\mu A$
Figure D.47: The blue testbed’s settings for this spectrum of positively charged isotopes, from this quartz and feldspar sample, were as follows:

\[
\begin{align*}
HV_{\text{sample}} &= -2.5\text{kV} \\
HV_{\text{deck}} &= -14\text{kV} \\
 i_{\text{sample}} &= 9.0\text{mA} \\
 i_{\text{FC1}} &= 4.1\mu\text{A} \\
HV_{\text{einzel}} &= -8.9\text{kV} \\
HV_{\text{tandem}} &= +20\text{kV} \\
VS &= 640 \\
HS &= 574 \\
 i_{\text{FC2}(+)} &= 8\text{nA}
\end{align*}
\]
D.3 Red Testbed Results

Once the red testbed was commissioned and some early troubles resolved, the red testbed was used to run many of the sample samples analyzed on the yellow and blue testbeds. Seventeen samples were run through the red testbed. The elemental samples analyzed include copper, carbon, silver, gold and silicon metal. The geological samples run include 27, 917, 1055, 1099, 118-133, 118-134c, 118-138, FR2, FR3, FR5 and W192. The sulphide standard, AX 90 bead 13, was also analyzed on the red testbed.

Highlights of these sample runs are given below, in table D.3, with full details following.

Table D.3: Summary of Results from the Red Testbed. All voltages are in kilovolts (kV), all $i_{sample}$ currents are in milliamps (mA), and all $i_{FC}$ currents are in nanoamps (nA), unless otherwise noted.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beam</th>
<th>$HV_{sample}$</th>
<th>$HV_{deck}$</th>
<th>$HV_{cone}$</th>
<th>$i_{s}$</th>
<th>$i_{FC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>$^{12}C$</td>
<td>−4.05</td>
<td>−21.2</td>
<td>+1.7</td>
<td>1.0</td>
<td>5800</td>
</tr>
<tr>
<td></td>
<td>$^{13}C$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125</td>
</tr>
<tr>
<td>Silver, in copper</td>
<td>$^{107}Ag$</td>
<td>−5.0</td>
<td>−20</td>
<td>−</td>
<td>0.63</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>$^{109}Ag$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>Gold, in copper</td>
<td>$^{63}Cu$</td>
<td>−3.0</td>
<td>−17</td>
<td>−</td>
<td>1.4</td>
<td>3400</td>
</tr>
<tr>
<td></td>
<td>$^{197}Au$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13500</td>
</tr>
<tr>
<td>Silicon Metal</td>
<td>$^{28}Si$</td>
<td>−3.4</td>
<td>−21.8</td>
<td>+2.0</td>
<td>1.1</td>
<td>5800</td>
</tr>
<tr>
<td></td>
<td>$^{29}Si + ^{28}SiH$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>275</td>
</tr>
<tr>
<td></td>
<td>$^{30}Si + ^{28}SiH_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>170</td>
</tr>
<tr>
<td>AX 90</td>
<td>$^{32}S$</td>
<td>−4.0</td>
<td>−21.5</td>
<td>+1.5</td>
<td>0.2</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>$^{58}Ni$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.4</td>
</tr>
<tr>
<td>27</td>
<td>$^{16}O$</td>
<td>−3.5</td>
<td>−21.8</td>
<td>+2.0</td>
<td>1.1</td>
<td>14000</td>
</tr>
<tr>
<td></td>
<td>$^{32}C + ^{16}O$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>125</td>
</tr>
<tr>
<td>917</td>
<td>$^{16}O$</td>
<td>−4.0</td>
<td>−21.5</td>
<td>+1.5</td>
<td>2.0</td>
<td>2900</td>
</tr>
<tr>
<td></td>
<td>$^{28}Si$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>105</td>
</tr>
<tr>
<td>1055</td>
<td>$^{16}O$</td>
<td>−4.3</td>
<td>−21.5</td>
<td>+1.4</td>
<td>0.1</td>
<td>16000</td>
</tr>
<tr>
<td></td>
<td>$^{56}Fe + ^{16}O$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1200</td>
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</table>
Table D.3 continued...

<table>
<thead>
<tr>
<th>Sample</th>
<th>Beam</th>
<th>$HV_{sample}$</th>
<th>$HV_{deck}$</th>
<th>$HV_{cone}$</th>
<th>$i_s$</th>
<th>$i_{FC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1099</td>
<td>$^{16}O$</td>
<td>-3.95</td>
<td>-21.4</td>
<td>+2.2</td>
<td>2.1</td>
<td>3200</td>
</tr>
<tr>
<td></td>
<td>$^{28}Si$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>82</td>
</tr>
<tr>
<td>118-134c</td>
<td>$^{16}O$</td>
<td>-4.0</td>
<td>-21.3</td>
<td>+1.0</td>
<td>0.2</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>$^{28}Si$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.6</td>
</tr>
<tr>
<td>118-138</td>
<td>$^{16}O$</td>
<td>-4.0</td>
<td>-21.3</td>
<td>+1.6</td>
<td>0.2</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>$^{24}Mg^{16}O$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.8</td>
</tr>
<tr>
<td>FR2</td>
<td>$^{16}O$</td>
<td>-3.8</td>
<td>-21.6</td>
<td>+2.0</td>
<td>0.5</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>$^{28}Si$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.4</td>
</tr>
<tr>
<td>FR3</td>
<td>$^{16}O$</td>
<td>-3.8</td>
<td>-21.6</td>
<td>-</td>
<td>1.0</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>$^{35}Cl$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.8</td>
</tr>
<tr>
<td>FR5</td>
<td>$^{16}O$</td>
<td>-3.8</td>
<td>-21.6</td>
<td>+2.3</td>
<td>0.4</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>$^{28}Si$</td>
<td></td>
<td></td>
<td>+3.1</td>
<td></td>
<td>2.2</td>
</tr>
<tr>
<td>W192</td>
<td>$^{16}O$</td>
<td>-3.0</td>
<td>-15</td>
<td>-</td>
<td>0.1</td>
<td>275</td>
</tr>
<tr>
<td></td>
<td>$^{28}Si$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

The following mass spectra are presented by sample type. For samples that have more than one mass spectrum, the data are presented in chronological order. Those spectra taken prior to the installation of the second focusing cone’s power supply, on October 15th 2003, necessarily have no value for $HV_{cone}$. 
D.3.1 Elemental Samples

90° Magnet Characterization using Carbon, 15-9-2003

Figure D.48: The red testbed’s settings for this carbon spectrum were as follows:

\[ HV_{\text{sample}} = -3.0kV \]

\[ HV_{\text{deck}} = -15kV \]

\[ i_{\text{coil}} = 20.0A \]

\[ i_{\text{sample}} = 1.6mA \]
Figure D.49: This mass spectrum was taken immediately following the installation of the power supply for the second focusing cone. The red testbed’s settings for this spectrum were as follows:

\[ \begin{align*}
\text{HV}_{\text{sample}} & = -4.0\,\text{kV} \\
\text{HV}_{\text{deck}} & = -21.3\,\text{kV} \\
\text{HV}_{\text{cone}} & = +1.7\,\text{kV} \\
i_{\text{coil}} & = 21.0\,\text{A} \\
i_{\text{sample}} & = 1.1\,\text{mA}
\end{align*} \]
Figure D.50: The red testbed’s settings for this silicon metal (note the $CsSi$ molecules, an example of things to come) spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -3.4kV \\
HV_{\text{deck}} & = -21.8kV \\
HV_{\text{cone}} & = +2.0kV \\
i_{\text{coil}} & = 19.5A \\
i_{\text{sample}} & = 1.1mA
\end{align*}
\]
D.3.2 Geological Samples

The mass spectrum of the Rhum anorthosite, sample 118-134c, is presented within the text, in section 5.1, on page 55.

Figure D.51: The red testbed’s settings for this AX 90 bead 13 (again, note the Cs molecules, spectrum were as follows:

\[ HV_{\text{sample}} = -4.0kV \]
\[ HV_{\text{deck}} = -21.5kV \]
\[ HV_{\text{cone}} = +2.0kV \]
\[ i_{\text{coil}} = 20.5A \]
\[ i_{\text{sample}} = 0.4mA \]
Figure D.52: The red testbed’s 860 settings for this chromitite spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} &\quad -3.5kV \\
HV_{\text{deck}} &\quad -21.8kV \\
HV_{\text{cone}} &\quad +2.0kV \\
i_{\text{coil}} &\quad 19.0A \\
i_{\text{sample}} &\quad 1.1mA
\end{align*}
\]

While not obvious from the spectrum above, there was no beam at mass 103 (indicating no high currents of $^{103}$Rh). The beams in that region correspond to masses 100, 102, 104, 108 and 112.
Figure D.53: The red testbed’s settings for this spectrum, from this coarse-grained pyroxene, were as follows:

\[HV_{\text{sample}} = -4.3kV\]
\[HV_{\text{deck}} = -21.5kV\]
\[HV_{\text{cone}} = +1.4kV\]
\[i_{\text{coil}} = 19.0A\]
\[i_{\text{sample}} = 0.1mA\]
Figure D.54: The red testbed’s settings for this orthopyroxene spectrum were as follows:

\[
\begin{align*}
HV_{sample} & = -3.95kV \\
HV_{deck} & = -21.4kV \\
HV_{cone} & = +2.2kV \\
i_{coil} & = 20.0A \\
i_{sample} & = 0.2mA
\end{align*}
\]
Mass Spectrum of 118-138, 22-10-2003

Figure D.55: The red testbed’s settings for this olivine (ultramafic breccia) spectrum were as follows:

\[
\begin{align*}
HV_{\text{sample}} & = -4.0 \text{kV} \\
HV_{\text{deck}} & = -21.3 \text{kV} \\
HV_{\text{cone}} & = +1.6 \text{kV} \\
\dot{i}_{\text{coil}} & = 20.5 \text{A} \\
\dot{i}_{\text{sample}} & = 0.75 \text{mA}
\end{align*}
\]
Figure D.56: The red testbed’s settings for this Fox River spectrum were as follows:

- $HV_{sample} = -3.8kV$
- $HV_{deck} = -21.6kV$
- $HV_{cone} = +2.0kV$
- $i_{coil} = 19.0A$
- $i_{sample} = 0.5mA$
Figure D.57: The red testbed’s settings for this Fox River spectrum were identical to those of the FR2 spectrum, as shown in figure D.56. They remained as follows:

\[\begin{align*}
HV_{sample} &= -3.8kV \\
HV_{deck} &= -21.6kV \\
HV_{cone} &= +2.0kV \\
i_{coil} &= 19.0A \\
i_{sample} &= 0.5mA
\end{align*}\]
Figure D.58: The red testbed’s 860 settings for this spectrum were as follows:

- \( HV_{\text{sample}} = -3.8kV \)
- \( HV_{\text{deck}} = -21.6kV \)
- \( HV_{\text{cone}} = +2.0kV \)
- \( i_{\text{coil}} = 19.0\text{A} \)
- \( i_{\text{sample}} = 1.4mA \)
Figure D.59: The red testbed’s settings for this spectrum, from this quartz and feldspar sample, were as follows:

\[
\begin{align*}
HV_{sample} &= -3.0kV \\
HV_{deck} &= -15kV \\
i_{coil} &= 19.0 A \\
i_{sample} &= 0.1mA
\end{align*}
\]
Appendix E

AMS Results

While the spring 2004 data are well resolved and easily calibrated, the data from the Winter 2003 used an older detector and the separation of peaks is more challenging. Nevertheless, the spectra are worthy of inclusion here, and the PGE, silver and gold spectra of these winter runs is presented by isotope. While considerable effort was made to identify the peaks in the spring 2004 spectra, the lack of resolution precluded accurate determination of the peaks in the winter 2003 runs, and as such only the obvious peaks are identified.

E.1 Winter 2003 Spectra

In all, fifteen isotopes were analyzed during the winter 2003 runs, $^{99}Ru$, $^{101}Ru$, $^{103}Rh$, $^{102}Pd$, $^{105}Pd$, $^{106}Pd$, $^{108}Pd$, $^{107}Ag$, $^{109}Ag$, $^{188}Os$, $^{191}Ir$, $^{193}Ir$, $^{194}Pt$, $^{196}Pt$ and $^{197}Au$.

The four samples analyzed during the winter 2003 runs were, 27, the Stillwater chromite, FR5, a Fox River clinopyroxenite, 118-134c, the Rhum Anorthosite, and the standard AX 90, Bead 13. Note that only 118-134c and the AX 90 Bead 13 were analyzed for both light PGE (Pd, Ru, Rh) and heavy PGE (Os, Ir Pt), as well as
silver and gold. Samples 27 and FR5 were only analyzed for the light PGE and silver. As in chapter 5, each isotope is showcased in a separate spectrum, with the samples differentiated by colour.

Figure E.1: The run times for these spectra were 61701 seconds (over 17 hours) for the 118-134c, 16000 seconds for the AX 90 Bead 13, 200 seconds for 27 and 600 seconds for the FR5
Figure E.2: The run times for these spectra were 19203 seconds for the 118-134c, 2000 seconds for the AX 90 Bead 13, 200 seconds for 27 and 600 seconds for the FR5.
Figure E.3: The run times for these spectra were 100 seconds for the 118-134c, 100 seconds for the AX 90 Bead 13, 2003 seconds for 27 and 600 seconds for the FR5
$^{102}$Pd$^{4+}$ in 27, the Stillwater Chromite

Winter 2003

Figure E.4: The run time for the spectrum for this Stillwater Chromite was 200 seconds.
$^{105}\text{Pd}^{4+}$ in 118-134c, AX 90 Bead 13, 27 and FR5

Winter 2003

Figure E.5: The run times for these spectra were 13600 seconds for the 118-134c, 503 seconds for the AX 90 Bead 13, 200 seconds for 27 and 35001 seconds for the FR5
$^{106}\text{Pd}^{4+}$ in AX 90 Bead 13 and FR5

Winter 2003

Figure E.6: The run times for these spectra were 100 seconds for the AX 90 Bead 13 and 600 seconds for the FR5
Figure E.7: The run time for the spectrum for this Fox River Sill sample was 600 seconds.
\[ ^{107} \text{Ag}^{4+} \text{ in 118-134c, AX 90 Bead 13, 27 and FR5} \]

Winter 2003

Figure E.8: The run times for these spectra were 100 seconds for the 118-134c, 10 seconds for the AX 90 Bead 13, 20 seconds for 27 and 100 seconds for the FR5
Figure E.9: The run times for these spectra were 100 seconds for the 118-134c, 10 seconds for the AX 90 Bead 13, 20 seconds for 27 and 100 seconds for the FR5
Figure E.10: The $^{188}\text{Os}^{6+}$ peak from 118-134c and AX 90 bead 13 is small. The run times for these spectra were 30000 seconds for the 118-134c and 600 seconds for the AX 90 Bead 13.

Winter 2003
$^{191}\text{Ir}^{6+}$ in 118-134c and AX 90 Bead 13

Winter 2003

Figure E.11: The $^{191}\text{Ir}$ peak from 118-134c and AX 90 bead 13. The run times for these spectra were 3600 and 300 seconds for 118-134c and AX 90 Bead 13, respectively.
Figure E.12: The $^{193}\text{Ir}^{6+}$ peak from 118-134c and AX 90 bead 13. The run times for these spectra are 5400 and 100 seconds for 118-134c and AX 90 Bead 13, respectively.
Figure E.13: The $^{194}$Pt peak from 118-134c and AX 90 bead 13. The run times for these spectra are 3600 and 100 seconds for 118-134c and AX 90 Bead 13, respectively.
Figure E.14: The $^{196}\text{Pt}^{6+}$ peak from 118-134c and AX 90 bead 13. The run times for these spectra are 3600 and 100 seconds for 118-134c and AX 90 Bead 13, respectively.
The only peaks in these spectra are $^{197}\text{Au}$. The run times for these spectra are 3600 and 100 seconds for 118-134c and AX 90 Bead 13, respectively.
A summary of the AMS sensitivity for the heavy PGE is given below, in table E.1.

Table E.1: The AMS sensitivity of osmium, iridium, platinum and gold of the AX 90 Bead 13 and 118-134c for the Winter 2003 runs. Each AX 90 Bead sensitivity is in counts/ppb/100 seconds (c/ppb/100s), as is the iridium sensitivity for 118-134c. The platinum and gold sensitivities for 118-134c are in counts/100 seconds (c/100s), as no intrinsic concentration is known. No counts were recorded for osmium in 118-134c.

<table>
<thead>
<tr>
<th>Element</th>
<th>AX 90 Bead 13</th>
<th>118-134c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Osmium</td>
<td>0.49 c/ppb/100s</td>
<td>–</td>
</tr>
<tr>
<td>Iridium</td>
<td>12.9 c/ppb/100s</td>
<td>0.22 c/ppb/100s</td>
</tr>
<tr>
<td>Platinum</td>
<td>50.3 c/ppb/100s</td>
<td>0.25 c/100s</td>
</tr>
<tr>
<td>Gold</td>
<td>$18.3 \times 10^2$ c/ppb/100s</td>
<td>218 c/100s</td>
</tr>
</tbody>
</table>
Table E.2: The relative abundances of the stable PGE, silver and gold isotopes, as well as interfering isobars and molecular fragments, are tabulated below. Those isotopes that are commonly measured by AMS are noted with an asterisk.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Relative Abundance</th>
<th>Interferences</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Isobars</td>
</tr>
<tr>
<td>$^{96}$Ru</td>
<td>5.54%</td>
<td>$^{96}Mo$, $^{96}Zr$</td>
</tr>
<tr>
<td>$^{98}$Ru</td>
<td>1.86%</td>
<td>$^{98}Mo$</td>
</tr>
<tr>
<td>* $^{99}$Ru</td>
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</tr>
<tr>
<td>$^{100}$Ru</td>
<td>12.6%</td>
<td>$^{100}Mo$</td>
</tr>
<tr>
<td>* $^{101}$Ru</td>
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</tr>
<tr>
<td>$^{102}$Ru</td>
<td>31.6%</td>
<td>$^{102}Pd$</td>
</tr>
<tr>
<td>$^{103}$Ru</td>
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<td>$^{103}Pd$</td>
</tr>
<tr>
<td>* $^{103}$Rh</td>
<td>100%</td>
<td>none</td>
</tr>
<tr>
<td>$^{104}$Pd</td>
<td>1.02%</td>
<td>$^{102}Ru$</td>
</tr>
<tr>
<td>$^{106}$Pd</td>
<td>11.14%</td>
<td>$^{104}Ru$</td>
</tr>
<tr>
<td>* $^{107}$Pd</td>
<td>22.33%</td>
<td>none</td>
</tr>
<tr>
<td>* $^{106}$Pd</td>
<td>27.33%</td>
<td>none</td>
</tr>
<tr>
<td>* $^{108}$Pd</td>
<td>26.46%</td>
<td>$^{108}Cd^{1}$</td>
</tr>
<tr>
<td>* $^{110}$Pd</td>
<td>11.72%</td>
<td>$^{110}Cd^{1}$</td>
</tr>
<tr>
<td>$^{184}$Os</td>
<td>0.02%</td>
<td>$^{184}W$</td>
</tr>
<tr>
<td>$^{185}$Os</td>
<td>1.58%</td>
<td>$^{186}W$</td>
</tr>
<tr>
<td>$^{187}$Os</td>
<td>1.6%</td>
<td>$^{187}Re$</td>
</tr>
<tr>
<td>* $^{188}$Os</td>
<td>13.3%</td>
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<tr>
<td>* $^{189}$Os</td>
<td>16.1%</td>
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</tr>
<tr>
<td>$^{190}$Os</td>
<td>26.4%</td>
<td>$^{190}Pt$</td>
</tr>
<tr>
<td>$^{194}$Os</td>
<td>41.0%</td>
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</tr>
<tr>
<td>* $^{191}$Ir</td>
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<tr>
<td>* $^{193}$Ir</td>
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</tr>
<tr>
<td>$^{197}$Pt</td>
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<td>$^{197}Os$</td>
</tr>
<tr>
<td>$^{192}$Pt</td>
<td>0.79%</td>
<td>$^{192}Os$</td>
</tr>
<tr>
<td>* $^{194}$Pt</td>
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</tr>
<tr>
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<td>33.8%</td>
<td>$^{195}Pt$</td>
</tr>
<tr>
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<td>25.3%</td>
<td>$^{196}Hg$</td>
</tr>
<tr>
<td>* $^{198}$Pt</td>
<td>7.2%</td>
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</tr>
<tr>
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<tr>
<td>* $^{109}$Ag</td>
<td>48.161%</td>
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</tr>
<tr>
<td>* $^{197}$Au</td>
<td>100%</td>
<td>none</td>
</tr>
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</table>

1Cadmium does not readily make negative ions, & so is not considered an isobaric interference.
Bibliography


