

**Micro PIXE analyses of Furnace and Converter Mattes for the
Determination of Trace Element Distribution and
Concentrations**

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A dissertation submitted in partial fulfillment of the requirements for the
degree of Master of Science in Physics at the University of Zululand

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**December
2006**

Declaration:

I hereby declare that the work contained in this dissertation is my own and has not been submitted for a degree or other qualification in any other university or institution

.....
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04/04/2007
.....
Date

Acknowledgements

I would like to thank the following people for their input in making this study a success.

Dr J Nell for giving me a chance to work on this project and for supplying all the literature that I needed to write up my thesis.

Dr W. Przybylowicz for his guidance and support during the time I spent at iThemba LABS, he has been my mentor.

Prof O.M Ndwandwe for arranging this project for me, and for assisting me with the write up of the thesis.

I would like to thank all the staff at Mintek who assisted me with this project.

I would like to thank the staff at the Material Research Group, Dr C Theron, Miss Lisa Gordan, Mr P Sechogela and Mr Springhorn.

The iThemba LABS research institute as well as Mintek for all the funds and equipment I needed to carry out this study.

And finally I would like to thank all my friends who supported and assisted me with my study.

Abstract

Analyses of the constituent matte phases by Particle Induced X-ray emission (PIXE) were performed to investigate the distribution and concentration of trace elements. These levels of sensitivity are beyond that of the electron microprobe. The objective of these analyses was to examine low level concentrations (ppm or ppb) in phases such as alloys, oxides and sulphides. The analyses were done at the nuclear microprobe chamber of Material Research Group in iThemba LABS. Samples consisted of slow cooled furnace and converter mattes which were prepared at Mintek. The samples were first analysed using SEM/EDX techniques to characterise the phases present, XRD was also performed to characterise the sample but due to the complexity of the samples it was unsuccessful. The SEM images were used to position the samples during experiments in the nuclear microprobe. Each phase was analysed to determine the distribution and concentration of the major and trace elements. The proton beam can be scanned in the same way as the electron microprobe, generating a map; this map indicates concentration as a function of position, the map includes a distance bar and concentration bar which is in weight percent. Also included are tables which contain the results of all the phases which were analysed. To confirm the presence of low level trace elements, inductively coupled plasma mass spectrometry (ICP-MS) was performed on the samples at the University of Stellenbosch, this technique was also unsuccessful. Interesting information about PGEs and Au was obtained, as well as information about other elements such as Mo, W, Se, As, Bi, Pb, Sn, Sb and many more. Information such as their distribution and concentration in the phases, and the association they have with each other.

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Chapter 1

1.1 Introduction

South Africa is the world's foremost primary producer of platinum. The Platinum Group Elements (PGE) is almost exclusively extracted from three mineralized horizons within the Bushveld Complex (BC) which is the repository for in the order of 75% to 80% of the world's reserves of PGE (Jones, 1999; Cawthorn and Hochreiter, 2000). PGEs consist of platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). In the earth's crust, the PGEs have an abundance of the order of 10^{-6} % to 10^{-7} % (Cotton and Wilkinson, 1980). Despite these extremely low abundance, geological processes have in places, concentrated them into particular horizons of rock from which they can be extracted and processed. The Bushveld Complex is divided into three regions, Eastern and Western limbs and the Potgietersrus or Northern limb.

Platinum group minerals (PGMs) mineralisations in the Eastern and Western limbs are concentrated in the Merensky Reef and the Upper Group 2 (UG2) chromites layer. The Merensky reef in the Bushveld complex is an example of Stratiform sulfide bearing horizons in layered intrusions which are the most important repositories of platinum group elements in the world. Average ore grades of the Merensky reef are about 8 ppm (Naldrett et al., 1987). In the Merensky ore, the PGEs occur to a large extent as discrete PGEs phases, mostly as sulfides, arsenides, bismuthotellurides, and alloys with Fe (Vermaak and Hendriks, 1976; Kinloch, 1982; Kinloch and Peyerl, 1990).

The uses of PGEs prior to the Industrial Revolution were limited to jewellery and decorating personal possessions. In the 18 century they were being used in fabricating laboratory apparatus and temperature measuring instruments. In the 19 century they were being used in the manufacturing of various chemicals, sulfuric acid in particular. Since the Second World War, these elements have rapidly become metals of the technological era with a wide range of applications ranging from auto catalysts through to dental alloys, and include applications in the petroleum, electronics, glass and chemical industries (Lindsay, 1988).

1.2 A brief review of the chemistry of PGEs

Platinum group elements (PGEs) together with Fe, Ni, and Co form group VIII of the periodic table and Cu falls into group IB. These elements are all part of the transition element series and therefore display all the properties of transition elements. In each of the three periods in which they occur, these elements have the tendency to successively add electrons to the *d* atomic orbitals. In the fourth period, elements with atomic numbers 21 to 29 (scandium to copper) have a partially filled *d* subshell. Transition elements tend to have high tensile strength, density, melting and boiling points. Ions of the transition elements may have multiple stable oxidation states, since they can lose *d* electrons without a high energetic penalty. They have variable coloured ions and compounds in one or all oxide states, and they are metallic with all the properties of metals (Cotton and Wilkinson, 1980).

1.3 Platinum group minerals (Group 1)

PGEs fall into two categories, the first groups known as the Platinum group minerals (PGMs), here the PGEs occur as impurities within other minerals, and the second group are those minerals which the PGEs occur as trace elements. A variety of PGMs have been discovered in the last 40 years due to the help of the Electron microprobe. One third of the PGMs can be grouped as metals, alloys and intermetallic compounds of PGEs with Sn, Fe, Pb, Hg, Cu and Ni and the remaining PGMs are PGEs compounds formed with S, As, Te, Bi, and Sb (Cabri, 1976; 1981b). The most common PGMs found are Sulphides,

Tellurides, Arsenides and alloys (Cabri, 1981b). The PGMs tend to be fairly distinctive, they exhibit high reflectivity and are hard, the duller but the hardest PGMs tend to be the sulphides and the brightest PGMs tend to be alloys (Lindsay, 1988).

1.4 Trace PGEs (Group 2)

The second group refers to those minerals in which PGEs are hosted as trace elements and the PGEs are not determinative to the definition of the mineral, pentlandite being an example ((Fe, Ni)₉S₈) (Lindsay, 1988).

a) PGEs hosted in Sulphides found in the Merensky Reef.

Many publications have shown that sulphides are a major repository of PGEs, listed below is a list of some of the sulphides which can host some traces of PGEs.

- i. **Pentlandite** ((Fe, Ni)₉S₈) , it is an iron-nickel sulphide, which is an important PGE bearing mineral. In the Merensky Reef pentlandite has a concentration of 140-500 ppm Pd and 20-75 ppm Ru, bulk analysis of mineral concentrates indicate values of Pt less than 36 ppm (Kinloch, 1982; Peyerl 1983). Rh and Ru are found in concentrations less than 110 ppm (Kinloch, 1982). Experimental results have shown that pentlandite can dissolve up to 12.5% Pd, 12.4% Rh and 12.9% Ru but no detectable dissolved Pt was found (Makovicky et al. 1986).
- ii. **Pyrrhotite** (Fe_{1-x}S) is a brownish iron sulphide mineral. Merensky Reef sulphide concentrations are around 11 ppm Pt, 3 ppm Rh and Pd was not

detected (Kinloch, 1982; Peyerl, 1983). Experimental work done by Distler (1980) indicated that pyrrhotite can dissolve up to 8% Pd at 1000°C and 40% Rh at 750°C.

- iii. **Pyrite** (FeS_2) is a common mineral composed of iron disulphide with a pale brass-yellow colour, it is called fools gold. Bulk techniques were used to analyse pyrite that was found in the Merensky Reef, the results produced indicated 15 ppm Pt, 34 ppm Pd and 9 ppm Rh in these sulphides (Kinloch, 1982; Peyerl, 1983).
- iv. **Chalcopyrite** (CuFeS_2) it has not been found to contain any detectable PGEs, even by proton microprobe (Cabri et al., 1984).

b) PGEs found in Oxides

Neutron activation analyses was performed on oxides separates and, the outcome was that their Pt and Pd content were up to 500 ppb each, (Parry, 1984). Analysis of mixtures of magnetite (Fe_3O_4) - ilmenite (FeTiO_4) gave PGE values of up to 5 ppm Pt and less than 250 ppb Pd (Lindsay, 1988).

1.5 Platinum Group Mineral Deposits of the Bushveld Complex

The bushveld is the largest stratiform body known and it exists in South Africa (Vermaak, 1985). The PGM mineralization in the Bushveld Complex was discovered by Merensky and Lombard in 1924 on a farm in Mooihoek on the Eastern Limb. It is 7-9km

thick and comprises three major units, the Eastern and Western limbs and the Potgietersrus or Northern limb (Cawthorn and Hochreiter, 2000). Platinum group minerals (PGM) mineralization in the Eastern and Western limb are concentrated in the Merensky Reef and Upper Group 2 (UG2) chromite layer.

The Merensky Reef is 'pyroxenitic' rocks containing a few percent sulphide minerals (Van der Merwe, 1976; Vermaak and Hendriks, 1976; Mostert, 1982). The Pt/Pd ratio in the Merensky Reef can vary on a mine scale from 1.8 (Viljoen et al., 1986) to 2.4 (Viljoen and Hieber, 1986), while some samples can reach a ratio of 1 (Von Gruenewaldt et al., 1990). According to Keller (1986) the average PGE value is 5.31 ppm and Pt/Pd ratio approximately 2.4. A significant proportion of the PGEs is accounted for by PGMs (45%), although (50%) is hosted as trace elements in base metal sulphides (Peyerl, 1982). On average, the base metal sulphide assemblage in the Merensky Reef is dominated by pyrrhotite with decreasing amounts of pentlandite, chalcopyrite and pyrite (Brynard et al., 1976; Mostert et al., 1982; Jones, 1999). The base metal sulphide content of the Merensky Reef is variable and it falls in the range 2.5-2.9 vol%. The relative abundance of the principle base metal sulphides are, pyrrhotite 43.6%, pentlandite 34.3%, chalcopyrite 16.9% and pyrite 4.4% (Lindsay, 1988). The grain size of the PGM in the Merensky Reef is highly variable with most grains falling in the size regions around 10 to 200µm size (Kinloch, 1982). The PGMs are sometimes found in association with the sulphides as inclusions or along the sulphide/silicate grain boundaries, they also occur as inclusions in the silicate and in close association with chromite. The dominant PGMs are cooperite (PtS) and braggite((Pt, Ni, Pd) S). Some amounts of sperrylite (PtAs₂) and

tellurides (Pt-Pd) are present (Lindsay, 1988). The UG2 is considered to be a better ore which is due to its density (4.3g/cm^3) compared to the Merensky Reef (3.2g/cm^3) (Von Gruenewaldt, 1977). It is slightly richer in the total PGE content and it is denser, therefore it's cheaper to mine. The UG2 also contains a greater Rh content and the concentrates have a higher PGE content (Merkle and McKenzie, 2001). The UG2 chromitite is a layer of well packed cumulate chromites which is found below the Merensky Reef. The PGE values of this horizon is relatively high around 5.97 ppm and the Pt/Pd ratio is 1.2 (Keller, 1986). The base metal sulphides are small in size and quantity; they include pentlandite, pyrrhotite, chalcopyrite and pyrite (Lindsay, 1988). The UG2 is dominated by chromite with 10 to 40 vol % silicate (McLaren and De Villers, 1982; Vermaak, 1995; Penberthy and Merkle, 1999). The most characteristic of the PGMs are Os and Ir bearing laurites (Lindsay, 1988). The grain size of the PGM in the UG2 is significantly smaller than for the Merensky Reef, it is around 2 to $4\mu\text{m}$ (Kinloch, 1982; Penberthy et al., 2000).

1.6 Trace PGEs and their distribution

Tentative analysis has shown that pyrrhotite and pentlandite are important PGE repositories. Both pyrrhotite and pentlandite host platinum, Au and Pd are favoured more by pentlandite (Lindsay, 1988). Kinloch (1982) and Peyerl (1983) used X-ray emission spectrographic to analyse pure base metal sulphide concentrations from various localities (Rustenburg, Union and Amandebult sections of RPM) and the results showed that pyrrhotite contains 11-47 ppm Pt and 3 ppm Rh; pentlandite contains 11-13 ppm Pt, 142-

415 ppm Pd and 23-74 ppm Rh; pyrite contains 15 ppm Pt, <34 ppm Pd and <9ppm Rh; and no PGEs were detected in chalcopyrite. It is clear from these and other publications that base metal sulphides host PGEs, and pyrrhotite is the main repository for Pt and pentlandite for Pd.

1.7 The concentration process

A degree of oxidation occurs in the furnace matte resulting in the removal of sulphur as SO₂. This results in the creation of a matte that is sulphur deficient which results in the early formation of metallic phases such as Ni-Fe alloy. This alloy collects most of the precious metals. The matte composition corresponds to monosulphide solid-solution which on cooling forms, pyrrhotite and pentlandite, bornite exsolves out of the Cu rich pentlandite into the grain boundaries along with a significant amount of PGEs (Lindsay, 1988). Converting of the furnace matte causes more of the sulphur to be removed, Fe is also oxidized and removed, this results in a metal excess Ni-Cu matte to be formed. The converter matte is allowed to crystallise to form a coarse grained product consisting of dendroidal chalcocite and Ni-Cu-Fe alloy set in the heazlewoodite matrix, the PGEs occur predominately in the Ni-Cu-Fe alloy (Lindsay, 1988).

1.8 General process description of the metallurgical extraction of the Platinum Group Elements

The smelting operation processes wet concentrate to produce a crushed, sulphur deficient Ni-Cu matte which is rich in PGMs, gold and Base metal sulphide which are dispatched to the base metal refinery (Jones, 2006). The wet concentrate is dried and then melted in an electric furnace, the excess Fe and sulphides are removed in the converter process. The slag is removed and treated for any lost PGMs. The treatment of the ore requires four processes, beneficiation, smelting and converting, base metal extraction and PGE refining. Figure 1.1 shows the general process flowchart for processing PGE ores. Smelting and converting is a pyrometallurgical concentration process which produces a PGE enriched Ni-Cu sulphide matte. Base metals can be extracted by a hydrometallurgical or gravity concentration method. In this process we will concentrate on the hydrometallurgical method. In the PGE refining process individual Platinum group metals are produced.

1.8.1 Mining

Mining in the Bushveld Complex ranges from small tonnage opencast operations to the development of large high tonnage mechanised underground operations (Merkle and McKenzie, 2001). Historical mining consisted of a series of shallow depth inclined shafts along the strike of the mineralised horizon. When depth renders opencast mining difficult, sub surface mining commences, first via inclined and later via vertical shafts.

1.8.2 Mineral beneficiation

The beneficiation process consists of two processes, comminution (crushing and milling) and floatation which concentrates the PGMs. The greatest losses of PGMs occur during these processes. The main reason for this is the diversity in the PGM mineralization. Beneficiation is the improvement of the grade of the ore by liberating the ore minerals and separating them from the silicate gangue. The process results in the production of a concentrate of ore minerals and a barren tailing. During beneficiation most of the PGMs are recovered by gravity separation or flotation and the trace PGEs are recovered by flotation only (Lindsay, 1988). Milling is performed until the milled product forms a mixture of liberated particles of valuable components in a barren mix. In most operations jaw or cone crushers are used for the primary crushing. The milling operation is highly variable with some using standard rods or ball mills and others use semi-autogenous mills and autogenous mills. Dense media separation has been introduced between primary crushing and milling; it is used to remove the lighter silicate from the denser chromite and PGM prior to milling (Merkle and McKenzie, 2001). Some operations use gravity concentration methods that are capable of removing some of the PGMs prior to milling and flotation. Efficient milling, effective liberation and the production of closely sized product is essential for the success of flotation, losses due to tailings comprise of slimes ($<38\mu\text{m}$) and coarse matte ($>106\mu\text{m}$) (Lindsay, 1988). Under grinding results in losses due to the liberation of sulphides as well as the presence of coarse sulphides, which do not always float well (Lindsay, 1988). Particles which are very fine (slime) result from over grinding, these fine particles are liberated but are difficult to float.

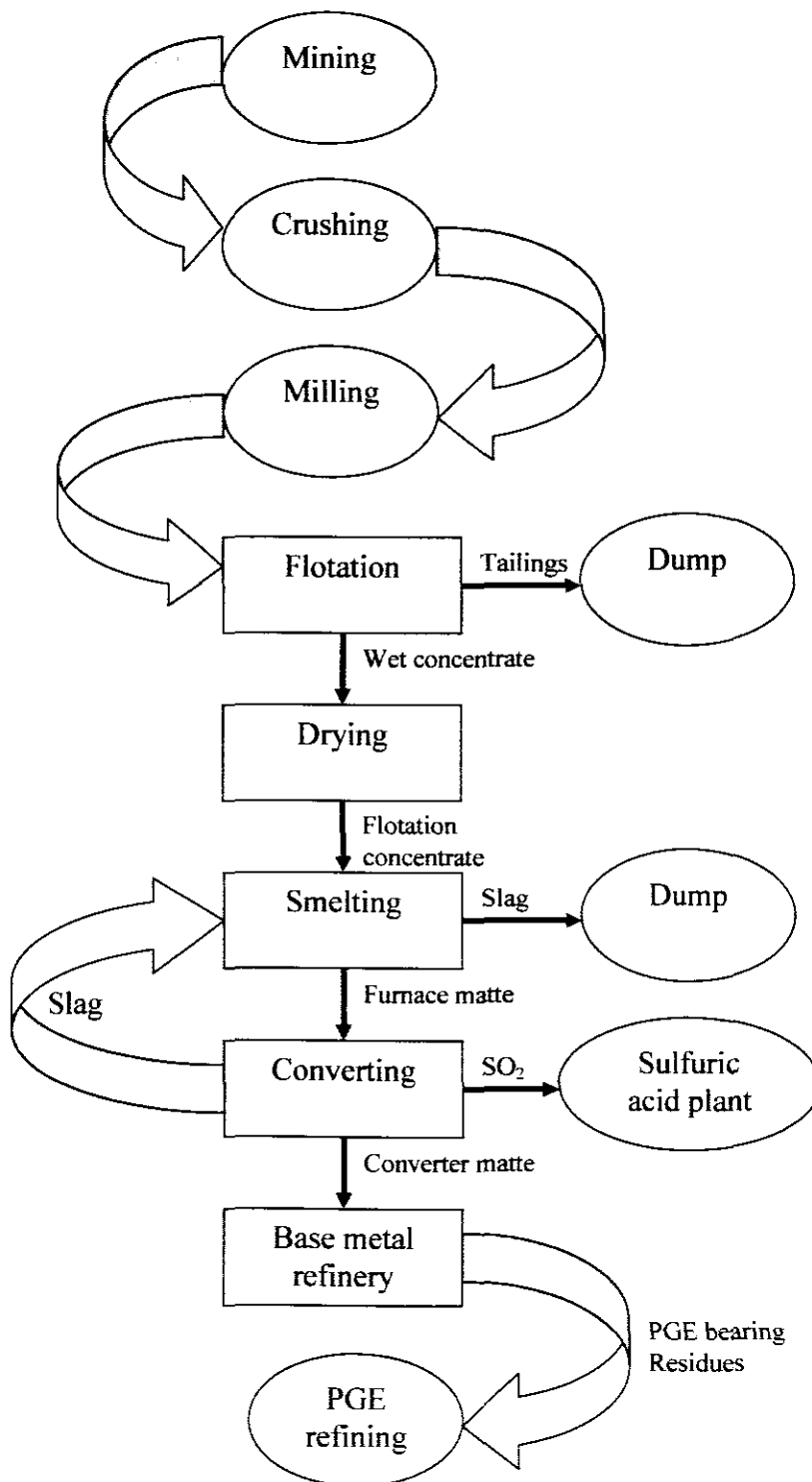


Figure 1.1 General process flowchart for the processing of PGE ore

Following the comminution process the milled mine ore is concentrated by froth flotation. A mixture of milled ore and water is chemically treated to create conditions that will allow certain mineral particles to be attached to air bubbles. These bubbles carry the selected minerals to the surface of the pulp and form a stabilised froth which is then skimmed off. Flotation is designed to separate ore minerals from gangue through differences in surface chemistry. The presence of gangue minerals in flotation concentrations is unwanted because it affects both concentration grade and recovery, to ensure that gangue those not float and dilute in the concentrate, depressants are added (Lindsay, 1988). Complete depression is unwanted because it can lead to BMS and PGE losses. Flotation occurs in cells which are arranged in a series of banks which are also arranged in a particular configuration, usually a rougher, cleaner and recleaner in each cell (Merkle and Mckenzie, 2001). The feed from the mills or previous cell enters as slurry which is agitated by a rising stream of bubbles which passes through the pulp to create froth at the surface. This froth overflows to channels where it is collected. The remaining particles, which are called tailings, settle and are passed to the next cell. The froth is known as the concentrate, which moves to the next bank for cleaning (Lindsay, 1988). This process continues through the bank of cells until the pulp is depleted in ore minerals. The tailings are reprocessed until all the ore minerals are removed. The tailings is dewatered and sent to the tailings dam. The concentrate is passed through the recleaner until it is rendered suitable for smelting. Following the flotation process, the final concentrate is dried using flash or spray driers. The wet concentrate goes through the flash drying process where most of the moisture is removed from it. The dry concentrate is then

transferred to silos where it is mixed with lime stone and the final blend is transferred to the feed bins at the electric furnaces.

1.8.3 General smelting processes

Following the beneficiation process the dried flotation concentrate undergoes two pyrometallurgical processes, which consists of smelting and converting. During these processes the PGE values are upgraded and the PGEs concentrate in the sulphide matte.

a) Matte smelting

During the smelting process sulphides combine to form a molten matte while the silicates and oxides melt and form a slag phase. These two liquids separate from each other due to the differences in densities. The furnace feed consist of dried flotation concentrate mixed with limestone, the flotation concentrate consist of base metal sulphides, diluted by gangue with trace elements (Lindsay, 1988). In addition molted converter slag is recycled back through the furnace. The sulphide content of the UG2 is low which prevents the sulphide matte from forming; therefore it is blended with the Merensky Reef concentrate prior to smelting. Most of the valuable metals concentrate in the matte phase, Ni, Cu, Co, and the PGEs have high partitioning coefficients therefore they concentrate in the sulphide matte phase (Fleet et al., 1991; Peach and Mathez., 1996; Crocket et al., 1997). The limestone that is added to the mixture assists to minimize the liquids temperature of the smelting and to optimise slag viscosity (Merkle and Mckenzie, 2001). Because the

sulphide matte has a higher density it settles at the bottom of the furnace, small amounts of matte droplets can remain in the slag resulting in PGE losses. During production the mean matte temperature is around 1180°C and slag at $\pm 1350^{\circ}\text{C}$ (Lindsay, 1988). The solid feed is fed through the roof and as it enters the furnace it spreads out as unsmelted material, which is about 15 cm thick and forms the top of the molten slag (Boldt and Queneau, 1967; Newman, 1973). As it heats up, it gradually melts and separates into the two immiscible silicate and sulphide phases. The silicate forms the upper slag layer which is about 130 cm thick and the sulphide forms the matte layer which is about 75 cm thick (Lindsay, 1988). The silicate is processed again for any lost sulphides that were trapped in it; the furnace matte which is also known as green matte is tapped and transferred to the converters.

b) Converting

The furnace matte is poured into the converter where air is blown into the matte over a period of a few hours, this leads to the removal of iron and sulphur from the matte by oxidation. Silica is added to the converter to react with the oxidized iron to form a fayalite slag (Lindsay, 1988). The sulphur that leaves the system is captured and processed to produce sulfuric acid. A Cu-Ni alloy is formed in the converter matte and most of the precious metals tend to concentrate in the alloy. The alloy phase first forms in the smelting process, but the Fe component is oxidized and replaced by Ni and Cu in the converter process (Lindsay, 1988). The converter matte consists of copper and nickel sulphides (Cu_2S , Ni_3S_2) and small amounts of Ni-Cu alloy, and some Fe-sulphide, cobalt

and PGEs (Merkle and McKenzie, 2001). Some impurities such as selenium, tellurium, arsenic, lead, tin and antimony may concentrate in the matte (Merkle and McKenzie, 2001). The matte which is also known as white matte is cast into ingots or granulated prior treatment in the base metal refinery. Slow cooling of the white matte promotes the crystallization of magnetic copper nickel alloys, and because of the high siderophile nature of PGEs they concentrate in the alloy (Merkle and McKenzie, 2001).

1.9 Refining

The white matte is transferred to the base metal refineries where the base metals are removed and refined prior to sale. The PGE bearing residue from the base metal refineries is transferred to the precious metals refinery where the PGEs can be separated and purified.

1.10 Scope of this work

This thesis examines the concentration and behaviour of trace/minor elements in the different phases which are produced during the pyrometallurgical concentration processes. In base metal smelting the behaviour of the minor elements can be of as much importance as that of the major. Minor elements are those elements which are found in concentrations of less than 500 ppm. The minor elements can significantly influence product quality and impact substantially on the environmental and economic sustainability of an operation. Optimal removal, followed by recovery and safe disposal

of minor elements from the appropriate process stages can benefit the operation of most plants.

The initial part of the study involved the identification of phases which were produced during the processing stages, and this was carried out at Mintek, Randberg, South Africa. Scanning Electron Microscopy and Optical Microscopy were used for the phase identification. The majority of the experiments were done at Materials Research Group, iThemba Labs, Faure, South Africa. The measurements at iThemba Labs included Particle Induced X-Ray Emission (PIXE), this technique was used to determine the trace elements concentrations and distribution in the different phases.

Chapter 2

Experimental techniques and equipment

2.1 Ion beam analysis

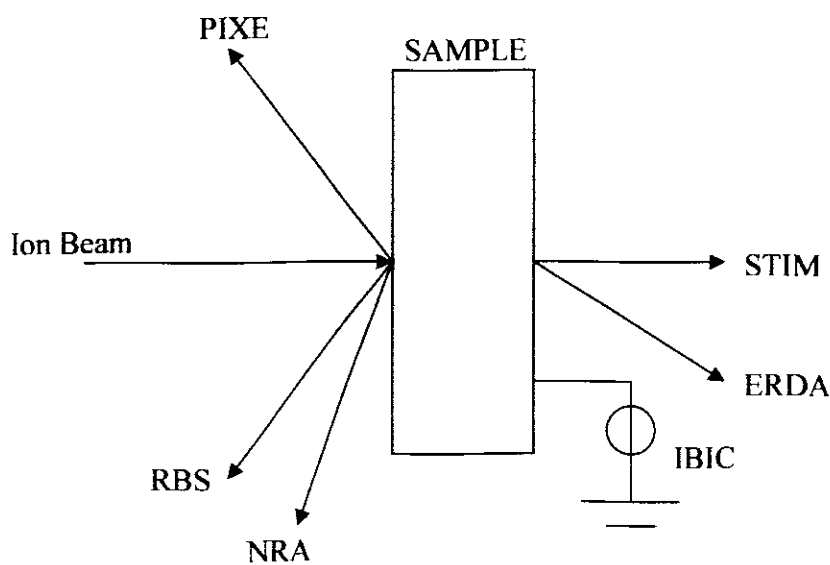


Figure 2.1 Types of ion beam techniques (www 1)

Ion Beam Analysis (IBA) is based on the interaction, at both the atomic and the nuclear level, between accelerated charged particles and the material being bombarded. When a charged particle moving at a high speed strikes a material, it interacts with the electrons and nuclei of the atoms in the material, slowing down and possibly deviating from its initial trajectory (www 2). This can lead to the emission of particles or radiation whose

energy is characteristic of the elements from which they come from. The techniques that are offered at iThemba include PIXE, RBS, NRA and STIM. A common occurrence in all the analysis techniques is that during the ion beam interaction, most of the individual particles penetrate the specimen in roughly their incident direction and gradually lose energy until they stop in the matrix of the sample. Only certain types of particles will get close to the nucleus of the target, normally neutrons (Mookodi, 2006).

2.1.1 Details about the techniques

a) PIXE: (Particle Induced X-Ray emission) When a fast moving charged particle collides with an atom there is a high probability that an electron will be ejected from an inner atomic shell. When the electrons in the outer shells re-arrange themselves, there is an emission of a quantum of energy (X-ray), the energy of which is characteristic of the atom from which it came from. The measurement of these characteristic X-rays enables the chemical composition of a sample to be determined with high quantitative accuracy and sensitivity.

b) RBS: (Rutherford Backscattering) As the ion traverses the sample, there is a small probability that a direct elastic nuclear collision will also occur causing the ion to recoil out of the sample. By measuring the energy of recoiling ions, information can be obtained on the concentration and depth distribution of major constituents of the sample, such as the light element matrix C, N and O (www 1).

c) NRA: (Nuclear Reaction Analysis) It is the Measurement of reaction products, such as gamma rays, alpha particles and protons which follow nuclear reactions between the incident ion and the target atoms.

d) STIM: (Scanning Transmission Ion Microscopy) It is mostly used for biological samples (tissue sections, isolated cells), where a high energy particle beam passes through the sample, energy is lost due to the electron collision with the sample. By measuring the energy loss of individual particles in the transmitted beam, information on the density or thickness of the specimen can be obtained.

e) ERDA: (Elastic Recoil Detection Analysis) it is used for the measurement of recoiling atoms following elastic nuclear collisions at a glancing angle. Used mainly for profiles of very light ions such as hydrogen or deuterium (www 1).

2.2 Optical Microscopy

A microscope is an instrument which is used for viewing objects that are too small to be seen by the naked or unaided eye. The science of investigating small objects using such an instrument is called microscopy, and the term microscopic means minute or very small. Microscopes give us a large image of a tiny object. The most common type of microscope and the first to be invented was the optical microscope. This is an optical instrument containing one or more lenses that produce an enlarged image of an object placed in the focal plane of the lenses; most optical microscopes can operate in either transmission or reflection (www 3). Depending on the type of microscope that is used

images can be viewed in the eyepieces or digitally captured on the computer. A general setup of the optical microscope is shown in figure 2.2. Lens qualities in early microscopes were often poor so the images were not very clear. Optical microscopes use refractive lenses, typically of glass and occasionally of plastic, to focus light into the eye or another light detector. Typical magnification of an optical microscope is up to 1500x with a resolution of around 2 micrometers (www 4).

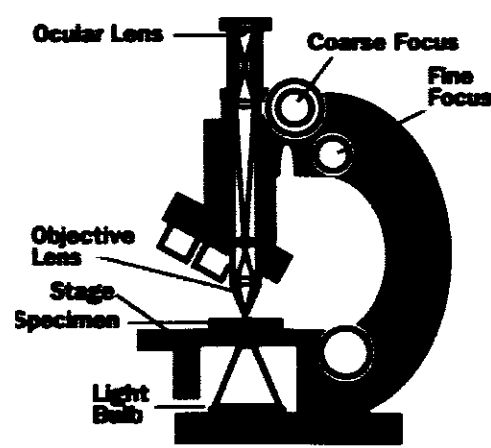


Figure 2.2 General setup for an optical microscope

2.3 Scanning electron microscope

The development of the Scanning Electron Microscope in the early 1950's brought with it new areas of study in the medical and physical sciences because it allowed examination of a great variety of specimens. An optical microscope uses lenses to bend the light waves and the lenses are adjusted for focus. In the SEM, electromagnets are used to bend the electron beam which is used to produce the image on a screen. By using electromagnets the user has more control in how much magnification he/she obtains. The

electron beam also provides greater clarity in the image produced. The SEM is designed for direct studying of the surfaces of solid objects. By scanning the surface with an electron beam that has been generated and focused, an image is formed. The SEM allows for a greater depth of focus than the optical microscope. For this reason the SEM can produce an image that is a good representation of the three-dimensional sample (www 11). Chemical analysis in the SEM is performed by measuring the energy or wave length and the intensity distribution of X-Ray signals which are generated by focusing electron beams on the specimen. With the attachment of the energy dispersive spectrometer (EDS) or wavelength dispersive spectrometer (WDS) the elemental composition of the material being analysed can be obtained, these two concepts will be discussed in section 2.3.3.

2.3.1 General SEM operations

A beam of electrons is generated in the electron gun, which is located at the top of the column; it is generated by heating a metallic filament which is found inside the electron gun. Figure 2.3 a and b show the SEM operation and the location of the detectors. The stream of electrons is condensed by the first condenser lens. This lens is used to form the beam and limit the amount of current in the beam. It works together with the condenser aperture to eliminate the high-angle electrons from the beam. The beam is then constricted by the condenser aperture eliminating some high-angle electrons. The second condenser lens forms the electrons into a thin, tight, coherent beam. An objective aperture further eliminates high-angle electrons from the beam. A set of coils then scan the beam in a grid fashion on the sample (www 6).

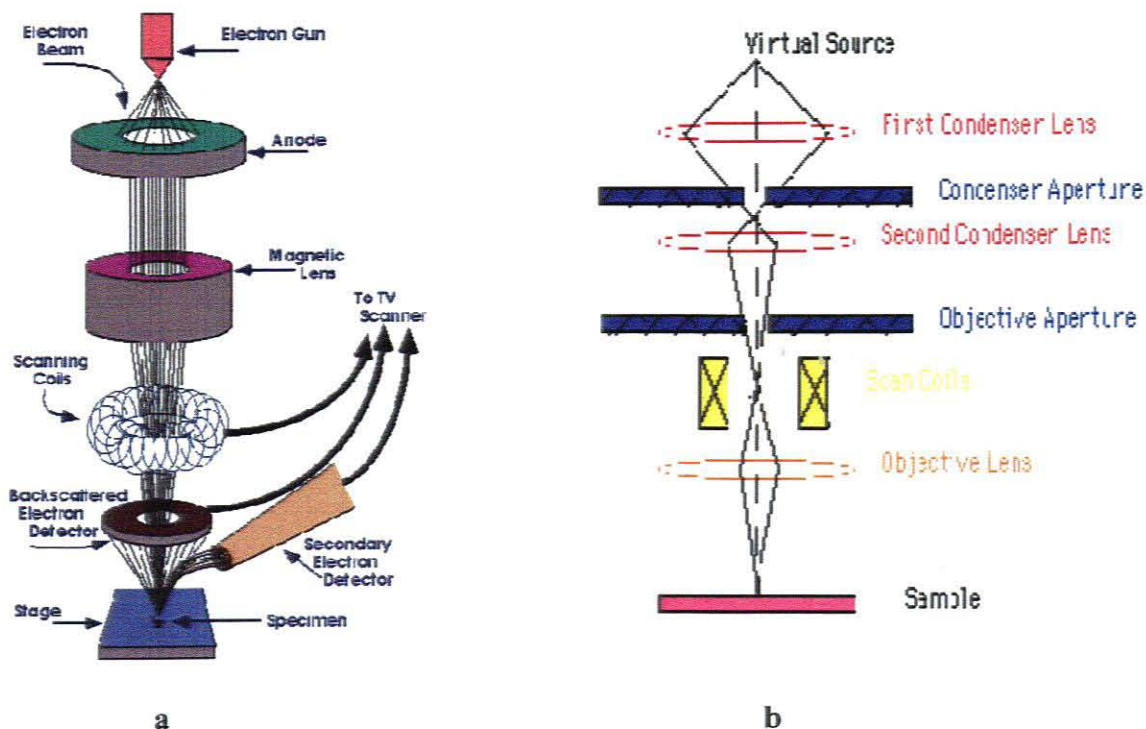


Figure 2.3 General SEM operations

(www 5 and www 6)

The Objective lens focuses the scanning beam onto the part of the specimen desired. When the beam strikes the sample interactions occur inside the sample and are detected with various instruments (www 6). After the interaction the detected electrons are converted into signals that are then sent to a viewing screen whereby an image is produced. All of this is done under vacuum where air is removed from the chamber to avoid any beam instabilities caused by the interaction between the beam and air molecules before bombarding the sample. Other problems maybe, the burning of the electron source, ionizing of the beam molecules and defocusing of the beam (Mookodi, 2006). During the interaction, the following types of signals are produced, secondary

electrons, backscattered electrons, auger electrons, characteristic X-rays and other photons of various energies.

2.3.2 Electron/Specimen interactions

The energetic electrons in the microscope strike the sample and various reactions can occur as shown below.

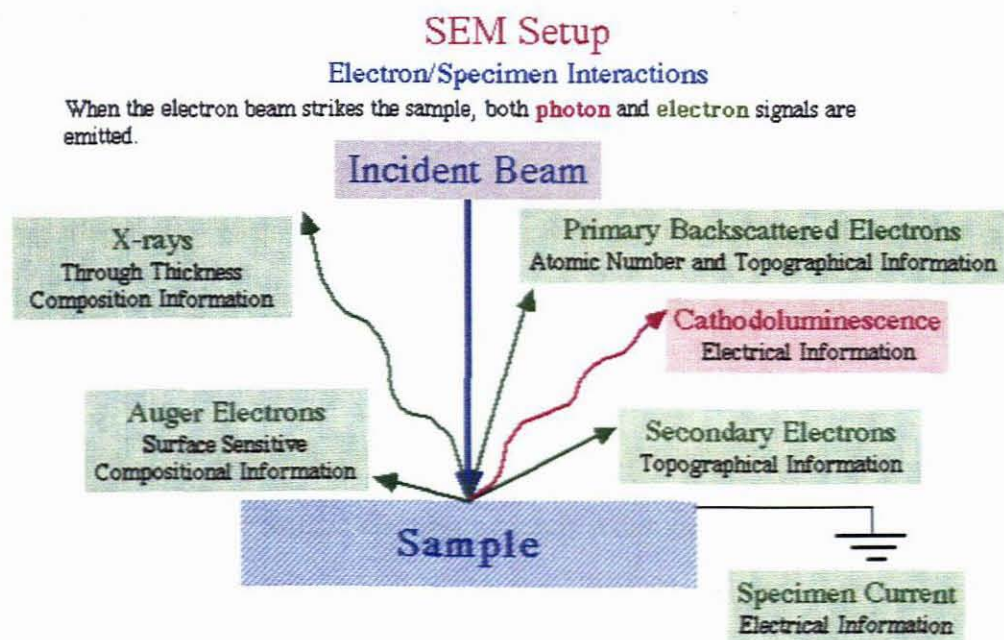


Figure 2.4 Electron/Specimen Interactions

a) **Secondary electrons:** They are caused when the incident electrons knocks loosely bound conduction electrons out of the sample. If the weak electrons are released within about 10nm of the specimen's surface, they may escape as low energy secondary electrons (Lawes, 1987). This also causes a slight energy loss and path change in the

incident electron. Each incident electron can produce several secondary electrons. Production of secondary electrons is very topography related. Due to their low energy only secondary electrons that are near the surface can exit the sample and be examined.

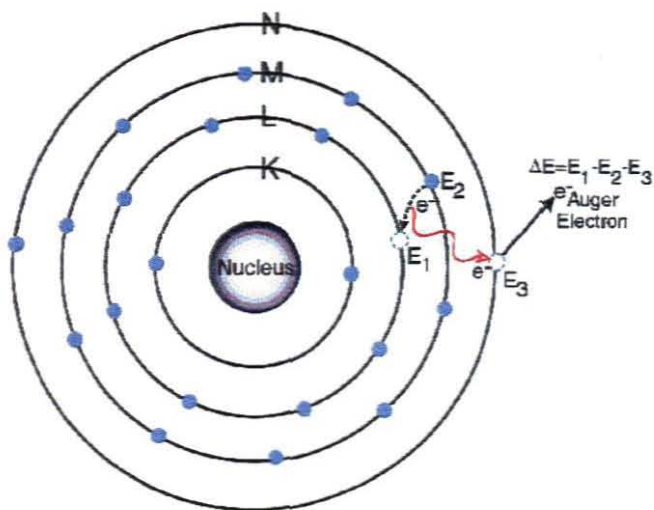
b) Backscattered Electrons: It is caused when an incident electron is scattered backward (180 degrees) after its collision with an atom which is almost normal to the plain. The production of backscattered electrons varies with the specimen's atomic number. This differing production rates causes higher atomic number elements to appear brighter than lower atomic number elements. This interaction is utilized to differentiate parts of the specimen that have different average atomic number (www 6).

c) Auger electrons: When an inner shell electron is knocked out of its orbit by the incident beam, the atoms reacts by trying to rearrange its outer shell electrons. If the electron drops down from the outer shell into the vacancy that was created, the atom becomes excited or ionized and has excess energy. One way for the atom to lose this energy is for it to transfer it to an electron which is found in the outer shell. This electron gains enough energy and is emitted from the atom (Lawes, 1987). These are known as Auger electrons. Figure 2.5 illustrates the whole process of how an auger electron is formed.

d) X-rays: Another way of filling the vacancy which was created by the incident beam is for a high energy electron from the outer shell to fall into the lower energy shell, filling the vacancy. As the electron falls it emits energy, usually X-rays to balance the total

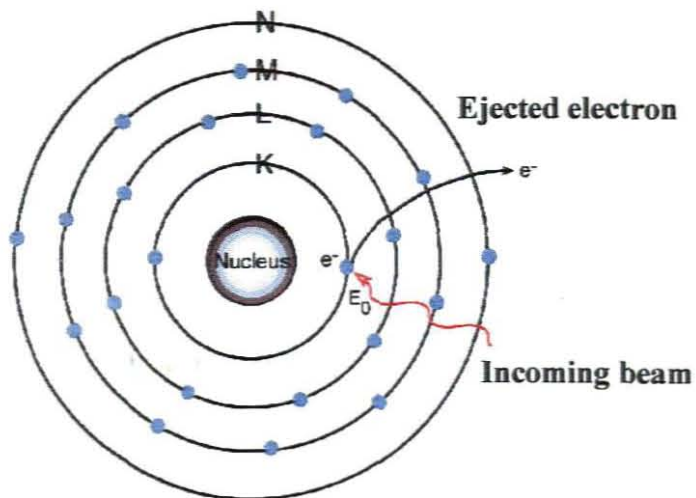
energy of the atom (www 6). Generation of different X-ray lines is caused by de-excitation of electrons from different shell levels; this process is shown in figure 2.5. For example, a vacancy in the K shell results in a K_{α} X-ray being emitted if an L shell electron fills the vacancy and a K_{β} X-ray is emitted if an M shell electron fills the vacancy (Breese, 1996). L_{α} , L_{β} and L_{γ} X-rays emissions are caused by an L shell vacancy which was filled by electron transitions from higher shells. Using this information the chemical composition of the specimen can be identified. There are two forms of X-rays that are produced during the interaction, characteristic X-rays and the X-ray continuum or Bremsstrahlung.

- **Characteristic X-rays:** When a vacancy is created, an electron from the outer shell falls into the lower shell filling the vacancy, as it falls it releases energy in the form of X-rays. The X-rays emitted from the atom will have characteristic energies which is unique to the element from which it originated. This is known as characteristic radiation.
- **X-ray continuum or Bremsstrahlung:** The Bremsstrahlung process produces the most photons. Bremsstrahlung is a German word for "braking radiation" and is a good description of the process. Electrons that penetrate sample and pass close to a nucleus are deflected and slowed down by the attractive force from the nucleus. The energy lost by the electron during this encounter appears in the form of a ray photon (www 8). Some beam electrons may be unaffected, whilst others are slowed dramatically. Figure 2.6 illustrates this process.



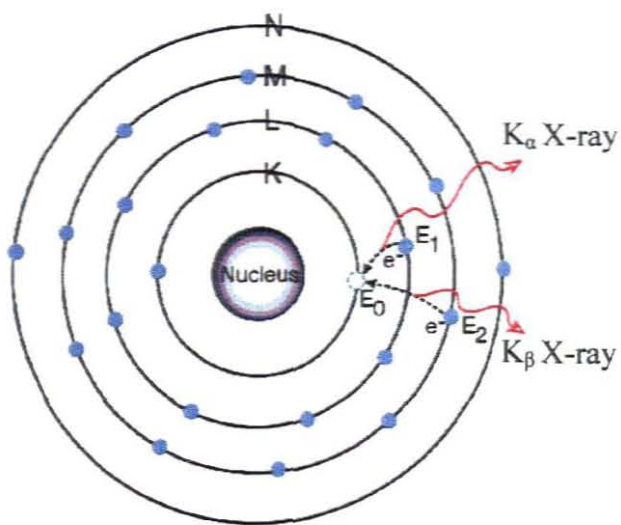
"Auger" Electron

The excitation energy from the inner atom is transferred to one of the outer electrons causing it to be ejected from the atom.



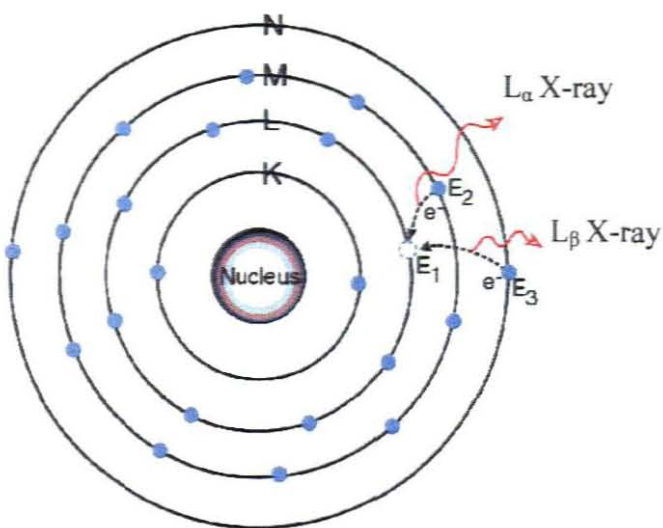
X rays production process

An electron in the K shell is ejected from the atom, creating a vacancy.



The K Lines

An electron from the L or M shell "jumps in" to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the L or M shell.



The L Lines

When a vacancy is created in the L shell, an electron from the M or N shell "jumps in" to occupy the vacancy. In this process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the M or N shell.

Figure 2.5: Schematic of inner shell vacancy creation with subsequent X-ray and Auger electron emission.

(www 7)

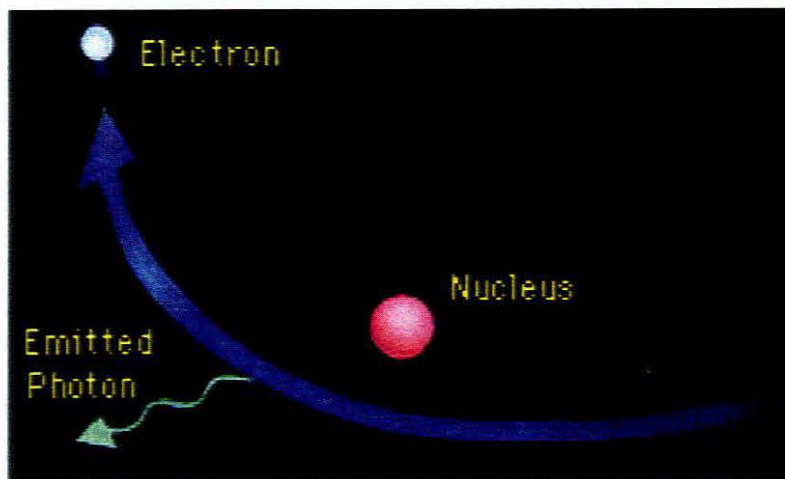


Figure 2.6 X-ray Bremsstrahlung process

(www 9)

2.3.3 Wavelength and Energy dispersive systems

Wavelength Dispersive X-ray Spectroscopy (WDS or WDX) and Energy Dispersive X-ray Spectroscopy (EDS or EDX) are X-ray microanalysis techniques. Both methods sort X-rays to identify individual elemental components in a sample, but with different approaches.

a) Wavelength Dispersive X-ray Spectroscopy: Sometimes referred to as WDS (wavelength dispersive spectrometry) or WDX (wavelength dispersive X-ray). This type of instrument determines the specimens composition by analysing the wavelength of the X-rays emitted from it. The characteristic X-ray photons which are excited by the electron beam are separated using a diffracting crystal, whose angular placement relative to the sample and photodetector is a unique measure of their wavelengths (www 12). Some advantages and disadvantages of WDS are presented below.

- When analysing for light elements it has a higher sensitivity than EDS.
- It has better resolution of spectrum peaks resulting in improved element specificity
- Lowered detection limits over the entire periodic table
- It is more accurate in quantitative analyses, the serial nature of spectrum acquisition means that qualitative analysis is slow compared to EDS.
- Considerably higher specimen currents are needed for WDS compared to EDS.
- For minor elements, WDS is fast relative to EDS (www 13)

b) Energy Dispersive X-ray Spectroscopy: It is a chemical microanalysis technique performed in conjunction with a scanning electron microscope (SEM), EDS is more commonly used due to its simplicity and speed. The technique utilises X-rays that are emitted from the sample during the electron bombardment process; the X-rays are used to characterize the elemental composition of the specimen being analysed. Features or phases as small as about 1 μ m can be analyzed. When the sample is bombarded by the electron beam, X-rays are emitted to balance the atom. The EDS X-ray detector measures the number of emitted X-rays versus their energy. The energy of the X-ray is characteristic of the element from which the X-ray was emitted. A spectrum of the energy versus relative counts of the detected X-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sample (www 14). Some disadvantages of EDS.

- The design of the equipment makes the technique incapable of detecting elements lighter than carbon.

- There is also poor sensitivity for light elements in a heavy matrix.
- Resolution of the X-ray energy levels limits the positive identification of certain elements due to overlapping energy slots.
- Quantitative analysis is usually limited to flat, polished specimens. Unusual geometries, such as fracture surfaces, individual particles, and films on substrates can be analyzed, but with considerably greater uncertainty (www 15).

2.3.4 General Sample preparation process

Remove all water, solvents, or other materials that could vaporise while in the vacuum.

When surface morphology is being examined, it is sufficient to glue the clean sample onto a brass mount, or any other conductive mount. When studying the internal structure (cross section), the samples are cut into small pieces, mounted in conductive plastic, ground and polished using the normal metallographic procedures. The sample must be conductive before viewing by the SEM, if not it will charge up when the electrons bombard it resulting in image defects. A sputter coater is used to coat non-conductive samples such as slag, ceramics or organic materials with a thin layer of gold or carbon. If the sample is conductive they can be placed in the SEM after they have been mounted (www 10).

2.4 Particle Induced X-ray Emission

Particle induced X-ray emission (PIXE) is a technique that is used for multi-elemental analysis. A beam of protons or sometimes heavier ions is accelerated to energy of a few mega volts, usually around 2 to 3 MeV, excites characteristic X-rays in the atoms of the specimen (Johansson et al., 1995). The X-rays are produced in the de-excitation process. The X-ray spectrum is recorded in energy dispersive mode by a semiconductor X-ray detector; a Si (Li) detector is commonly used. This detector has an energy resolution of 150 eV which makes it possible to resolve the K X-rays from adjacent elements; it can be placed very close to the specimen which is being analysed, subtending a large solid angle, which provides better efficiency (Johansson et al., 1995). Johansson from Lund Institute of Technology in Sweden showed that a combination of excitation with 2Mev protons and X-ray detection with a Si(Li) detector produced a very powerful method for multi-elemental analysis of trace elements (Johansson et al., 1970). Elemental analysis by PIXE can be applied in various areas, which include geology, material science, biology and botany, as well as studies of the environment.

2.4.1 a) Characteristic X-rays

These X-rays are produced during the beam-specimen interaction and their energies are unique to the element from which they originated. Section 2.3.2 d has a detailed explanation of characteristics X-rays.

2.4.1 b) Continuous background

The continuous background that underlines the characteristic X-ray peaks in a PIXE spectrum is the main determinant of the detection limit of any element. The background is due to proton bremsstrahlung, electron bremsstrahlung, and gamma rays generated in nuclear reactions. The intensity ratio between bremsstrahlung and characteristic X-ray radiation is much less for protons than it is for electron beams. The intensity of proton bremsstrahlung is negligible in comparison with that of the electron in the case of electron microprobe analysis. Secondary electrons are emitted preferentially in the forward direction and bremsstrahlung emission is maximum at 90° to the electron direction. Therefore the X-ray detector is placed preferably at an angle other than 90° to reduce the continuous background intensity, usually at an angle of 135° (Johansson et al., 1970).

2.4.1 c) Pile-up Distortion of Spectrum

At high counting rates there is a possibility of two X-rays arriving at the detector almost at the same time. When this occurs the X-rays are recorded as a single event, and this leads to pile ups (Watt and Grime, 1987). This problem can be solved by the application of an on-demand beam deflector. More details on this can be found in section 2.4.2.b.

2.4.1 d) Basic principles of PIXE

Charged particles, usually protons, are accelerated in an accelerator and enter an experimental chamber under vacuum containing the specimen to be analysed. Protons excite electrons in the innermost shell of the atoms in the specimen and X-rays are emitted. The X-ray spectrum produced contains a continuous background together with the characteristic X-ray lines of the atoms present in the specimen (Johansson et al., 1995). The X-rays are detected by means of a Si(Li) detector. The obtained PIXE spectrum is complex with many peaks; some of them tend to overlap. A computer is used for its deconvolution. The number of pulses in each peak which is a measure of the concentration of the corresponding element in the specimen is calculated. If the current is measured, it is possible to calculate the amount of various elements since parameters such as X-ray production cross section, solid angle, efficiency of the detector are known (Johansson et al., 1995). PIXE allows absolute determinations of concentrations. However, it is often convenient to obtain quantitative results by calibration against standard specimens or reference materials.

The accelerators used for PIXE analysis produce a beam of protons with energy of a few mega electron volts. An important advantage of PIXE is that any type of solid specimens can be analysed [gases and liquids are not analysed except for special cases]. PIXE is an analytical method based on X-ray emissions, the accelerated proton ejects electrons from the innermost shell of the atom creating a vacancy, when the vacancy is filled by an electron from the outermost shell an X-ray is emitted (Johansson et al., 1995). The de-

excitation can also take place by means of an Auger electron. The probability of a heavy element emitting an X-ray is around 100% but for lighter elements it's just a few percent. The X-ray spectrum is determined by the energy levels of the electrons in the atom. In a PIXE spectrum light and medium elements ($20 < Z < 50$) are analysed by K X-ray lines, giving only two resolved peaks, K_α and K_β . Heavy elements ($Z > 50$) are analyzed by L X-ray lines. In the L X-ray group of lines there are four predominant resolved components and four weaker ones (Johansson et al., 1995). The efficiency of the Si(Li) detector is fairly constant in the interval 5-25 keV but drops sharply for lower and higher energies (Johansson et al., 1995).

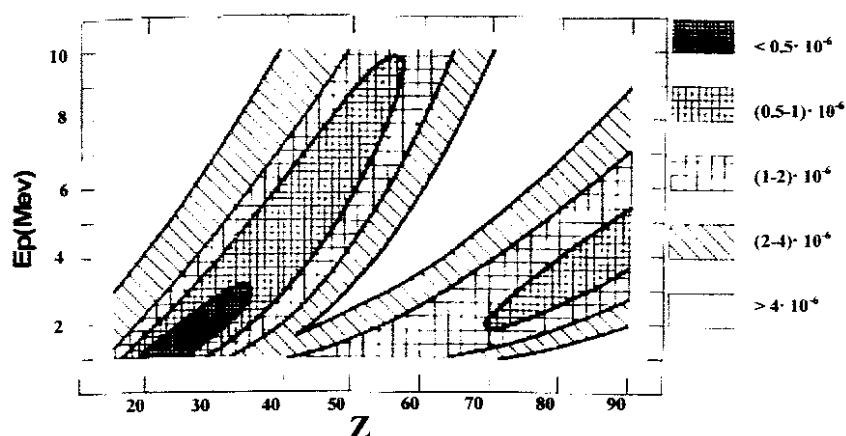


Figure 2.7 Minimum detectable concentration as function of atomic number and proton energy for organic specimens in typical PIXE arrangement (from Johansson et al., 1995).

The detection limit is the most important characteristic of any analytical method, figure 2.7 illustrates this. It gives a plot of minimum detection limits as function of the proton energy and the atomic number. Other parameters such as beam current, detector efficiency are assumed to have values that are normally used in routine analysis. In figure

2.7 we see that the highest sensitivity is obtained at low proton energies, between 2 and 3 MeV, this means that relatively small accelerators will be needed to produce this voltage. We also notice that the highest sensitivity is obtained for atomic numbers $20 < Z < 40$ as well as $Z > 70$. The best absolute sensitivity (expressed in weight units) is reached when the beam size is reduced to the micrometer region. With a spatial resolution of a few micrometers, the absolute detection limits are of the order of 10^{-15} and 10^{-16} g (Johansson et al., 1995). The opening of the object aperture can be varied, in the range of 10-100 μ m, with a demagnification of 10, the spatial resolution is of the order of 1-10 μ m (Johansson et al., 1995). This means that small parts of a larger specimen can be analysed for trace elements. The proton beam can be scanned in the same way as the electron microprobe, generating elemental map; this map indicates concentration as a function of position.

2.4.2 The iThemba nuclear microprobe facility

a) Description of the facility

The nuclear microprobe (NMP) at iThemba LABS was purchased from Oxford Instruments in 1991 and installed at the 0° line at the 6MV Van de Graaff accelerator. The areas of application include geology, materials science, biology and studies of the environment and botany. The standard Oxford triplet set of magnetic quadrupole lenses (LM150) is being used at iThemba, it offers little lens aberration and small beam size. For proton currents of 100 pA, resolutions of the order of 1 μ m beam spot can be obtained and also currents of the order of 10nA are possible for beam spot not exceeding 10 μ m. Relatively large scan sizes, up to 2.5 x 2.5mm for 3 MeV protons are possible. The target

chamber of the NMP was modified to allow fast changes of the specimen's position using a stepper motor. A built-in wheel accommodates 10 absorbers of which a selected one is inserted between the detector and specimen to reduce the intensity of the X-rays from lighter elements which are present amongst the major elements. Other features include Oxford scanning coils, object and halo slit assemblies, and lens and steering coil power supplies (Prozesky et al., 1995). The charge is collected using a sensitive electrometer that measures current simultaneously from a Faraday cup behind the sample and from the insulated specimen holder. The XSYS general purpose data acquisition system at iThemba allows for the complex use of data, with event by event storing capability, as well as the use of multi-parameter system and multiple windows. The event handling is done by the high level EVAL language code, which is complemented by the VAX computer network which facilitates full multitasking and background processing. The steering of the NMP beam is done by an IBM PC interfaced to both the steering coils and the VAX computers which are linked by the CAMAC crate (Prozesky et al., 1995).

A schematic view of the iThemba NMP is shown in figure 2.8 with all the beam optic features and distance scales indicated. The Van de Graaff accelerator accelerates ions vertically downwards, the ions bend at 90° by means of an analysing magnet and travel through a horizontal path of about 15 m to the target (Prozesky et al., 1995). After the analysing magnet, the ions travel through the energy stabilisation slits situated in front of the beam stop. The ions pass through a quadrupole doublet, then through a switching magnet, with a narrow entrance of 1.2mm in the Y direction. This magnet is used for beam lines other than the NMP line (Prozesky et al., 1995). The beam then passes through the object slits where the elimination of scattered ions takes place.

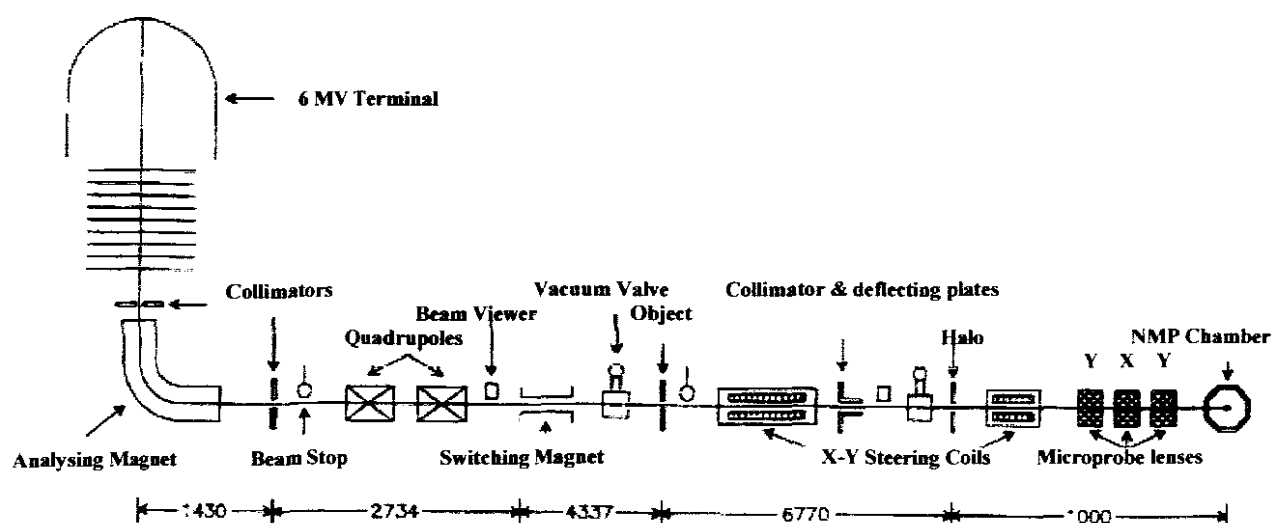


Figure 2.8 A schematic representation of the Van de Graaff accelerator and NMP layout at iThemba labs (Prozesky et al., 1995)

The path from the object slit to the target is around 7.5m, and there is a pair of halo slits situated 1m before the target chamber. The target chamber is a standard Oxford NMP chamber, with X-ray detector which is situated 25 mm away from the target at 135° to the incoming ion direction, an annular Si surface barrier (SSB) detector situated close to 180° , channeltron electron detector for secondary electron imaging, electron suppression ring in front of the target and the optical microscope at 45° with respect to the normal to the sample surface. Lighting of the chambers is done by using separate light sources in front and behind the target. The lid was custom made to allow more flexibility in sample loading. The target chamber uses a stepper motor for control of the samples in the X, Y, and Z axes. The maximum movement obtainable by the target ladder in the Z direction is 250mm, 40 mm in the X and 30 mm in the Y (focus) direction (Prozesky et al., 1995). A

permanent set of standards has been placed on the non-removable part of target ladder. This comprises one set of 44 single elements and a set of mineral standards. All the elements positions have been pre-programmed into the computer so that they can be accessed easily for calibration purposes. Signals that are accepted during the scanning mode include X-rays, Rutherford backscattering (RBS), secondary electrons and digitised current measurements.

The software used to analyse the X-Ray spectrums that are produced, is the Geo PIXE Suite of programs. It allows the analysis of thick and thin target spectrum incorporating thick target corrections for beam stopping, X-ray attenuation and secondary fluorescence. One major advantage of this software is the Dynamic Analysis capability of on-line semi-quantitative analysis of spectra and online elemental mapping. The on-line semi-quantitative analysis enhances areas of interest on the specimen when it is difficult to take an X-ray map of that localised area (Prozesky et al., 1995). If an RBS spectrum has to be analysed a software known as RUMP is used.

b) On demand beam deflection system

The beam instabilities at the NMP are relatively high. Typical causes of these variations are belt ripple and the corona stabilisation loop time (Prozesky et al., 1995). The resulting energy variations in the downward acceleration phase are transmitted as movement in the Y direction. This movement either leads to movement of the beam on the sample, or to pulsation of the beam on target. This gives occasional high counting frequencies and significant pulse pileups at relatively low average count rates. Processing of electronic

signals is severely affected. The addition of an on-demand beam deflection system for the NMP was done to reduce the dead time to low percentages and to regulate the higher count rates. This system has two plates which operate at ground potential, which allow the beam to pass through to the target. After an event has been processed in the X-ray detector, the plates are charged to equal voltages of opposite polarity which then deflects the beam from the target, allowing the slow spectroscopy amplifier to process the same event, with another signal in this time arising from the finite loop time, determined by the time taken for fast processing of the event, charging the plates and the flight time of the ions already past the plates (Prozesky et al., 1995). The design also minimised the distance between the target and deflection plates to 2 m. A collimator was inserted to protect the plates and it also acts as a beam divergence limiter.

On-demand beam deflection system solved the problem of excessive dead times due to beam variations. Another advantage is the preservation of fragile samples, by reducing the beam dose deposited on the sample.

Chapter 3

The distribution and concentration of Trace elements in Furnace and Converter mattes

Three samples were prepared at Mintek, furnace matte, converter matte and spiked converter matte samples. All samples were slow cooled, resulting in certain phases forming. The spiked converter matte (SCM) was doped with unknown concentrations of impurity elements. Samples were broken into pieces and mounted into a sample holder which is circular in shape and has a diameter of 25mm and a thickness of 15mm. The holders consist of a clear conductive resin. Samples were then ground and polished using the normal metallographic procedures. Prior to imaging and analysing samples were sputter coated with carbon, this slowed down the oxidation process and made it conductive. Samples were labeled FM for furnace matte, CM for converter matte and SCM for spiked converter matte. Samples were first analysed using the light microscope, it helped in locating certain phases that would be difficult to distinguish under the electron microscope. Several phases were observed in each of the samples, pictures were taken of these phases and circles were scribed around them with a diamond tipped tool. This made them easier to find under the electron microscope. Free hand drawings of the positions of the circles on the sample were also done, this made the location of the circles easy to find under the electron microscope, as well as when the nuclear microprobe was used.

Imaging and analyses of the phase compositions was done using a JEOL 840A scanning electron microscope (SEM) at Mintek. The operating voltage was 20 kV and a working distance of 39 mm was used. Phases were identified using backscattered electrons (BSE) and secondary electron images, whereas phase compositions were quantified by Energy Dispersive X-Ray (EDS) analysis. In the BSE mode the contrast of each phase is dependent on the average atomic number; various phases thus emerge with different contrasts, depending on their average atomic number. The EDS system used to acquire and process spectra was a Tracor Northern system, with a 7.5 μm thick beryllium windowed Tracor Northern Microtrace detector utilising an acquisition time of 50s. The spectra were processed using the ZAF (atomic number, absorption and fluorescence) algorithm. Several other phases were identified with the SEM, several spot analysis were done for each phase. Using the results that were obtained, each phase could be identified by name, eg bornite and heazlewoodite. The samples comprised of mostly sulphides with a few oxides and alloys being present. Images of the analysed regions were captured on computer and saved in Microsoft word and the areas where the spot analyses were performed were marked with numbers on the saved images.

After the SEM analyses, microanalyses were performed using a Nuclear Microprobe at the Material Research Group, iThemba LABS, South Africa. Particle induced X-Ray emission (PIXE) and proton backscattering were used simultaneously. A proton beam of 3.0 MeV energy and a current of 200-300 pA was focused to a $3 \times 3 \mu\text{m}$ spot and scanned over selected areas of interest; the areas that were scanned are the same regions that were analysed by SEM. Maps were generated this way by summing the X-Ray counts in every

pixel with no energy discrimination. These maps showed enough contrast to match the detailed optical micrographs of the same region. Due to the size of the samples only one sample could be mounted at a time. External absorbers were positioned between the PIXE Si(Li) detectors and samples, two types of absorbers were used, 102 μ m Al and a 203 μ m Al filter was used, 203 μ m Al proved to be a more suitable filter and it was used for all the samples. Samples were scanned over a varied period of time, until acceptable counting statistics has been reached.

The initial data inspection was performed using the XSYS (Indiana, 1985) system, and final data analyses was performed using GeoPIXE (Ryan, 1990). PIXE and BS spectra obtained from additional scans of smaller areas selected on the basis of elemental maps of all scanned areas were used as a refinement of the analysis. Data was collected in list mode, using square or rectangle scans with a variable number of pixels, up to (128x128) and processed using a PC version of GeoPIXE (GeoPIXE II), (Ryan, 2000, 2002). True elemental maps were generated using the Dynamic Analysis method (Ryan, 1993, 1995); this was obtained by using the matrix composition matching selected areas rather than using the average matrix composition of the whole matrix. Several new phases were identified using this method. The selected areas from scanned area are the same areas that were analysed by SEM, the new phases were also selected to be analysed using the PC version of GeoPIXE. All the PIXE maps in chapter 3 represent the scanned areas and different selected areas that were used in the Dynamic Analysis method. Each selected region of interest produced a PIXE spectrum, using the X-Ray identification tool the spectrum was fitted. After the spectrum was fitted a tool called FIT RESULTS was used

to produce quantitative and qualitative results of the selected regions, an example of the fit results is found in table 3.1.1a, the detection limits and error are also included. Different element standards were used for standardisation and verification of the analysis. This was done by analysing the standards using the fundamental parameter method, and comparing the obtained results with the corresponding predetermined results. If they did not correspond, a simple mathematical formula was used to obtain a ratio. When this ratio was multiplied to the results obtained it would match the predetermined results. The ratio is essentially a correction for occasional changes of experimental geometry and charge collection, which could take place between different measurement sessions. Two ratios were obtained for two different analyses periods, 1.25 and 0.9. Each set of PIXE results will indicate the ratio that was used. Individual elemental maps with concentration scale and distance bars were produced.

In some cases, due to high local variability of elemental matrix (composition of major elements) concentrations from maps obtained by Dynamic Analysis method showed high deviations and were clearly not correct. This problem was due to the mismatch between the assumed matrix composition and the effective composition in the mapped areas. In such cases only the results obtained from full deconvolution of PIXE spectra were taken into account. For such spectra, selected from specific parts of maps in which the composition of major elements could be assumed constant, the most accurate results were obtained.

To confirm the presence of low concentration trace elements, inductively coupled plasma mass spectrometry (ICP-MS) was performed at the University of Stellenbosch. This machine is fairly new and due to a lack of standards to calibrate the machine, the results that were produced are poor and could not be used.

3.1 Furnace matte

Furnace matte and slag are produced when flotation concentrates are melted in an electric arc furnace resulting in the formation of two immiscible layers, a slag layer which is on top and a matte layer which is formed at the bottom. The slag is tapped and removed so that it can be processed again to remove any lost PGE's. Grades in the slag are around 0.5 ppm PGE's + Au, and matte grades are up to 900 ppm PGE + Au (Lindsay, 1988).

3.1.1 Mineralogy

The crystalline furnace matte consists of base-metal sulphides, alloys and dispersed magnetite. There are two main alloys that occur in the specimen, one being the Cu-rich alloy and the other being the Ni-Fe alloy. The Ni-Fe alloys occur throughout the matte as a white, highly reflective phase varying in shape from anhedral plates occurring along the grain boundaries and intergrown with pentlandite through to euhedral cubes (Lindsay, 1988). Lindsay (1988) showed that the Ni-Fe alloy occurs in two forms. The first is the unzoned form which contains small quantities of Cu, Co, Pd, S and occasionally Sn. When it occurs, Sn takes the form of small cores included in the alloy. The second Ni-Fe

alloy is the zoned one. The cores tend to be platinum - rich relative to the rims; they may also contain small amounts of S and Co, and rare specks of Sn and Pd (Lindsay, 1988). Eleven phases were identified and analysed by Scanning Electron Microscope (SEM/EDX), results of the analysis are presented in table 3.1. Phases 1, 4 and 11 (figure 3.1.1 and 3.1.2) are Ni-Fe alloys; these alloys occur throughout the matte and appear as bright white spots which vary in shape. These phases have high concentrations of Sn, Sb, Pd as well as trace quantities of Fe, Pt and Pb. Phase 2 (figure 3.1.1) is an Fe-Ni-Cu sulphide which is interlocked by magnetite (phase 3). This phase contains some traces of Pt and Ag. Phase 3 and 10 are magnetite phases (Fe_3O_4), phase 3 (figure 3.1.1) has a skeletal shape. Phase 5 and 9 are Cu-Fe sulphide phases, the type of Cu-Fe sulphide found on this matte is bornite (Cu_5FeS_4). In the phase 5 region, (figure 3.1.1) bornite occurred around the grain boundaries of pentlandite and in the phase 9 region (figure 3.1.2) it occurred on the boundary of the pores. Results from the analyses show that traces of Pt and Ni were present in both phases, sum traces of Sn, Sb, Pb and Pd were found in phase 9. Phase 6 (figure 3.1.1) is a Fe-Ni sulphide phase, which is known as pentlandite. This is one of the dominant sulphide phases which occur throughout the matte, SEM analysis show that this phase contains minor amounts of Cu and Pt in it. Pyrrhotite (Fe_2S) was found to concentrate on the boundary of the pores, phase 7 (Figure 3.1.2). The black area on the image is just pores which have been filled up by resin. Results show that phase 7 has traces of Ni, Pt, Ag, Sb and Pb. Phase 8 is a Cu rich alloy, it is a bright distinct phase, which has a copper brown colour. The Cu-rich alloy forms on the walls of pores, figure 3.1.2. Results from SEM\EDX show that this phase contains traces of Ni, S, Fe, Ag, Pb, Pd and Sn.

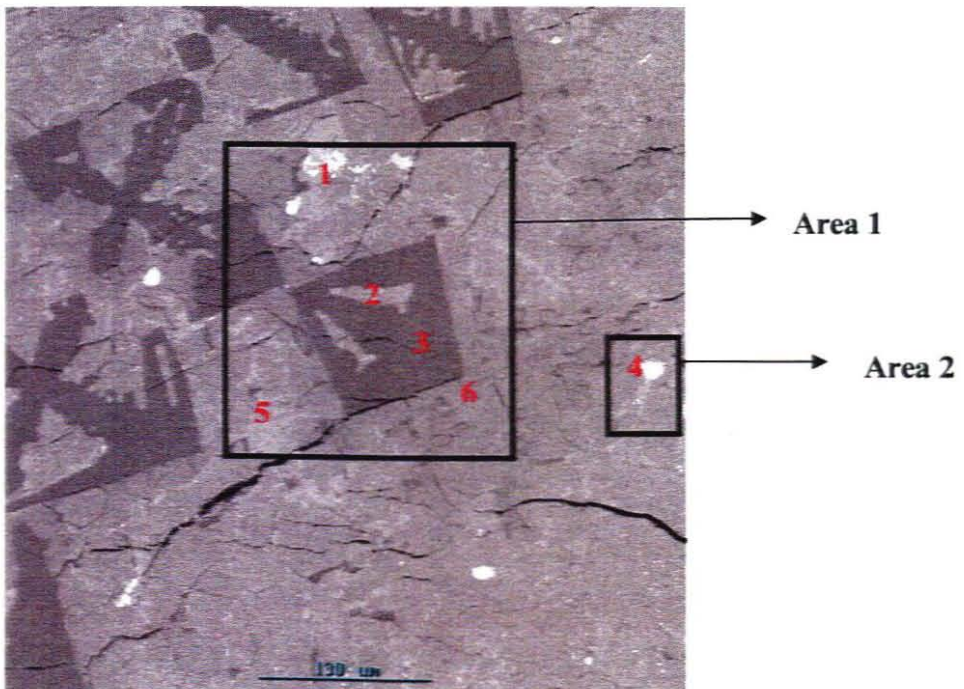


Figure 3.1.1. Photomicrograph of furnace matte showing its assemblage: [1] and [4] Ni-Fe alloys; [2] Fe-Ni-Cu Sulphide; [3] Magnetite (Fe_3O_4); [5] Bornite (Cu_5FeS_4) and [6] Pentlandite (Fe-Ni Sulphide).

TABLE 3.1

	Elements	Ni	S	Cu	Pt	Fe	Ag	Sn	Sb	Pb	Pd	Total
		Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	
Phase 1	Ni-Cu alloy	29.5	0.2	15.1	0.5	2.5	0	19.2	15.2	0.5	12.4	95.1
Phase 2	Fe-Ni-Cu Sulphide	16.8	28.9	12.0	0.2	35.0	0.3	0.0	0.0	0	0	93.2
Phase 4	Ni-Cu alloy	36.3	0	10.1	3.4	4.4	0	16.7	15.2	0.7	5.2	92.0
Phase 5	Bornite	1.7	22.8	59.1	0.4	10.2	0	0	0	0	0	94.3
Phase 6	Pentlandite	18.8	30.7	2.8	0.8	40.2	0	0	0	0	0	93.3
Phase 7	Pyrrhotite	3.4	33.6	0.8	0.9	54.8	0.1	0	0.1	1.6	0	95.4
Phase 8	Cu alloy	0.2	0.1	93.7	0	1.0	0.3	0.1	0	0.1	0.2	95.7
Phase 9	Bornite	1.1	22.9	59.4	0.7	10.2	0	0.2	0.1	1.0	0.2	95.9
Phase 11	Ni-Cu alloy	36.3	0.2	14.6	0.6	3.4	0	20.6	13.9	0.4	4.5	94.5

OXIDES

	Elements	NiO	SO ₃	CuO	Fe ₂ O ₃	Ag ₂ O	SnO ₂	Sb ₂ O ₃	PbO	Pd	Pt	Total
		Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	
Phase 3	Magnetite	0.4	0.8	0.1	97.6	0	0	0	0	0	0.1	99.0
Phase 10	Magnetite	0.0	2.0	0.6	97.6	0	0.3	0	0	0.1	0	100.6

Electron Microprobe analyses of the principal phases in Furnace Matte

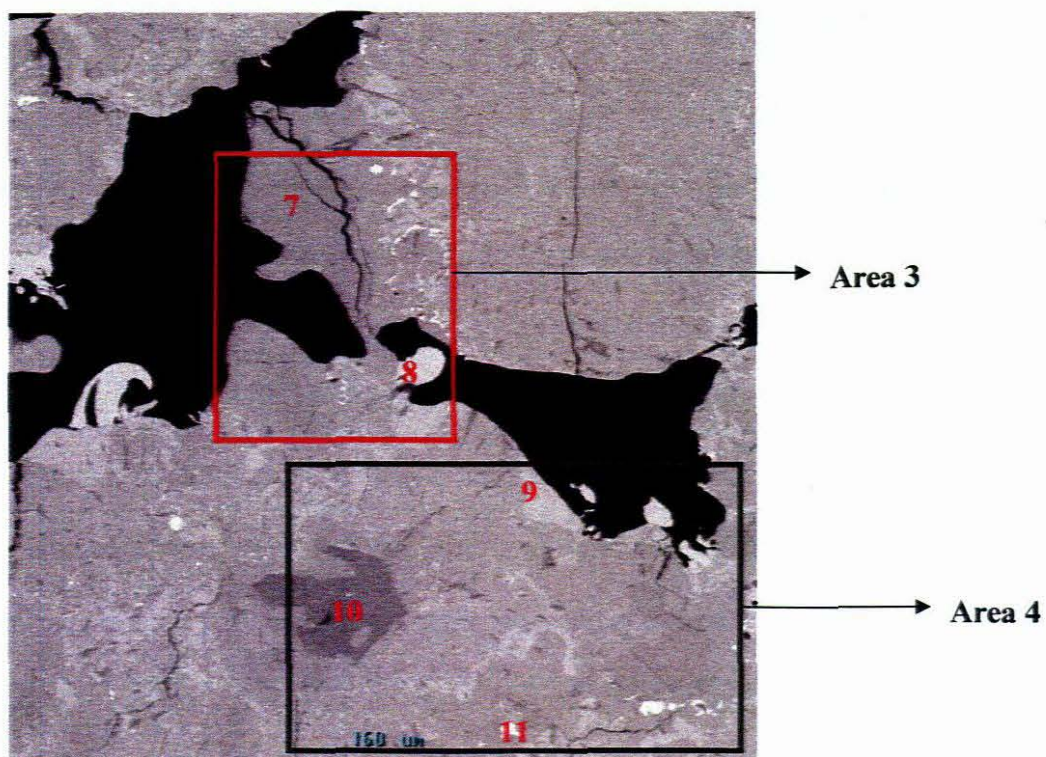


Figure 3.1.2 Photomicrograph of furnace matte showing the principal phases: [7] Pyrrhotite (Fe_2S); [8] Cu alloy; [9] Bornite (Cu_5FeS_4); [10] Magnetite (Fe_3O_4); [11] Ni-Fe alloy.

3.1.2 PIXE Microanalyses of Trace element distributions and concentration in Furnace Matte phases

Four regions on the matte were selected to be analysed by the nuclear microprobe (PIXE). In figure 3.1.1 area (1) around phase 1, 2, 3, 5 and 6 was selected and area (2) with phase 4 was also selected. The scan ran until a charge of 1211 nC was obtained for area (1) and 943 nC was obtained for area (2). In figure 3.1.2 area (3) around phase 7 and 8 and area (4) around phases 9, 10 and 11 was selected. The scan ran until a charge of 4609 nC was obtained for area (3) and 5000 nC was obtained for area (4). In the following figures are a series of images of major and trace elements distribution in Furnace matte phases.

Platinum: The highest concentration of Pt was found in phase 4 (Ni-Fe alloy phase) figure 3.1.4 f; table 3.1.3 contains the results for that phase. High concentrations of Pt were also found in phase 1 and 11 (Ni-Fe alloy phases), figure 3.1.1, results are tabulated in table 3.1.2b and 3.1.1 b. Images show that Pt tends to concentrate towards the core of the alloy (figure 3.1.3 c and figure 3.1.4f). A small trace of Pt was found in Phase 3 (magnetite phase), the result for this phase is found in table 3.1.2b.

Tin and Antimony: High concentrations were found in phases 1 and 4 and in phase 11, all of which are Ni-Fe alloy phases. In figure 3.1.3, images d and e show the distribution of Sb and Sn in phase 11. Table 3.1.1b, 3.1.2b and 3.1.3 contain the results of these phases. Analyses show that both Sn and Sb were not present in the Fe-Ni-Cu sulphide and pentlandite phases.

Ruthenium and Rhodium: Both were found in phase 4, figure 3.1.1, the highest concentrations of Ru and Rh were found in that phase followed by phase 11 figure 3.1.2. In figure 3.1.4, images d and e show that they concentrate in the core of the alloy, results of these phases are presented in table 3.1.1 a and 3.1.3. Traces of Ru were present in magnetite phase (phase 10, figure 3.1.2), results of this analysis is tabulated in 3.1.1 a.

Iridium: Ir was only found in phase 4 (Ni-Fe alloy), a good image of its distribution in the phase could not be produced because of its low concentrations. Table 3.1.3 shows the result of this phase. This Ni-Fe alloy phase is particularly rich with Pt; research done by Lindsay (1988) has shown that Ir has a tendency to concentrate in Pt-rich areas.

Chromium: Cr was only detected in 3 phases, phase 5 (Bornite phase), phase 6 (Pentlandite phase) and phase 10 (Magnetite phase). Concentrations of Cr were too low to produce a reasonable image, so the distribution of this element in these phases is not clear.

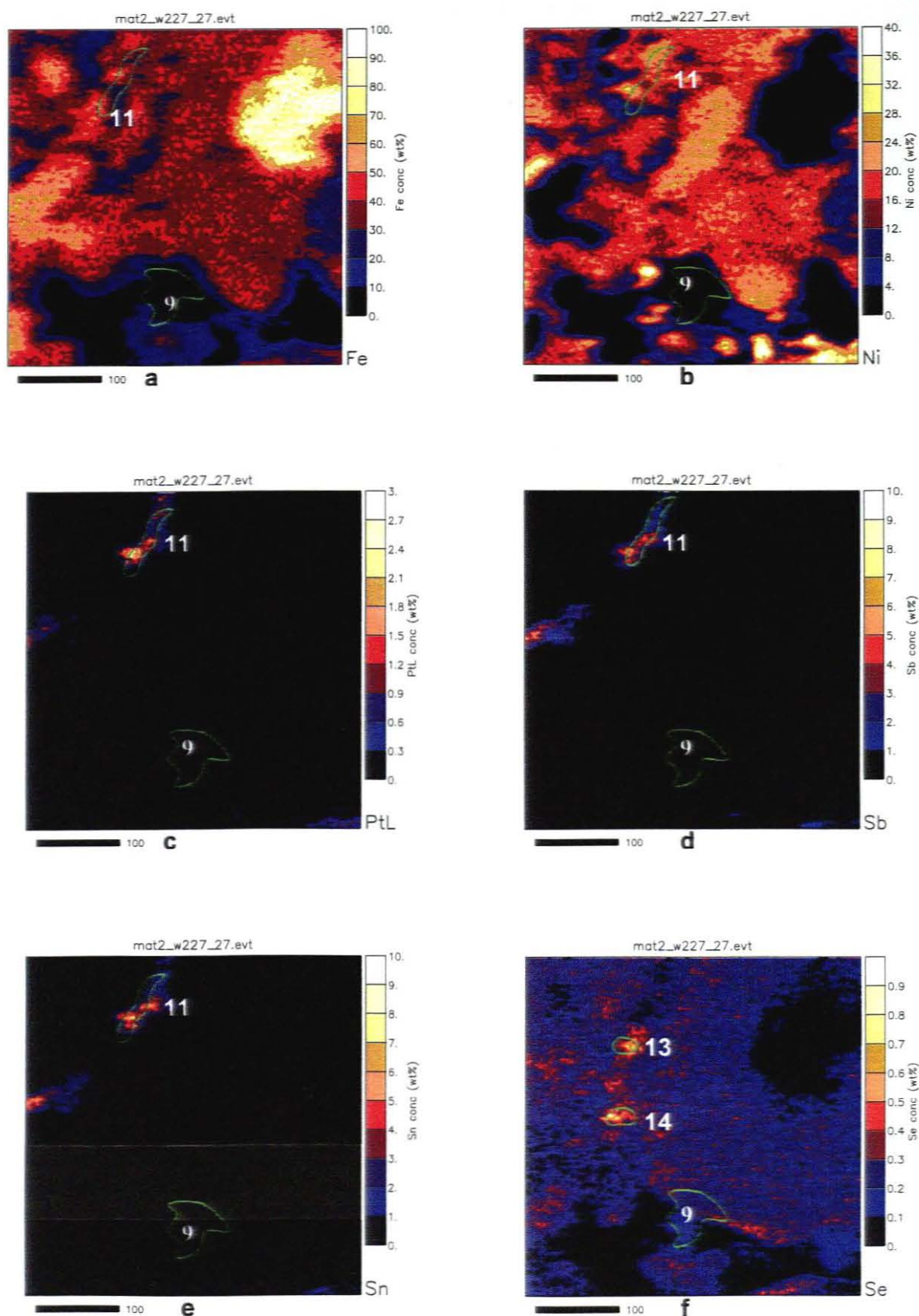


Figure 3.1.3 PIXE maps of furnace matte showing the distribution of Pt, Sb, Sn, and Se in Ni-Fe alloy and bornite

TABLE 3.1.1a

Concentration (ppm)		1	2	3	4	5	6	7	8	9	10	11	12	13				
		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Ru	Rh	Pd				
Phase 9	Bornite		980	48730	1060	10190	509620		1230	826				58				
Phase 10	Magnetite	2470	1620	612600	7340	16110	11490	251	172	267	8570	130		75				
Phase 11	Ni-Fe alloy			592700	23330	175140	51400		27540	1860		1140	1440	9350				
Phase 12	Ni-Fe alloy			564130	16110	91970	39900		993	2270		326		3510				
Phase 13	Ni-Fe alloy			510450	23860	146140	71510		2180	2270		274		5790				
Uncertainty (ppm)																		
		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Ru	Rh	Pd				
Phase 9	Bornite		316	481	315	489	2710		33	32				18				
Phase 10	Magnetite	570	318	2550	420	230	254	21	12	11	113	16		12				
Phase 11	Ni-Fe alloy			7570	1450	1040	1210		319	92		66	73	194				
Phase 12	Ni-Fe alloy			11590	1770	1010	1580		511	175		90		221				
Phase 13	Ni-Fe alloy			7650	1980	1550	1670		335	162		64		266				
Detection Limits (99% confid.)																		
		Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Mo	Ru	Rh	Pd				
Phase 9	Bornite		609	159	79	208	65		26	23				38				
Phase 10	Magnetite	640	616	82	84	112	62	35	14	13	11	16		13				
Phase 11	Ni-Fe alloy			514	439	275	190		68	64		48	53	64				
Phase 12	Ni-Fe alloy			727	662	412	281		192	146		164		199				
Phase 13	Ni-Fe alloy			707	635	417	279		176	126		125		162				

Nuclear Microprobe analyses of the principal phases present in area 4 (A ratio of 0.9 was used)

TABLE 3.1.1b

Concentration (ppm)		14	15	16	17	18	19	20	21	22	23							
		Ag	Sn	Sb	Te	W L	Os L	Pt L	Au L	Pb L	Bi L							
Phase 9	Bornite	2380		658	730				143	362	100							
Phase 10	Magnetite	159	650	233		1290				144	73							
Phase 11	Ni-Fe alloy	2740	21460	19910	1130			8090	438	3160	3473							
Phase 12	Ni-Fe alloy	53690	1320	2080	8610		1670		13050	59210	40340							
Phase 13	Ni-Fe alloy	18690	834	1270	3460		2930	500	1420	68430	36400							
Uncertainty (ppm)																		
		Ag	Sn	Sb	Te	W L	Os L	Pt L	Au L	Pb L	Bi L							
Phase 9	Bornite	100		82	105				49	50	23							
Phase 10	Magnetite	15	39	28		47				20	14							
Phase 11	Ni-Fe alloy	152	488	509	220			230	107	162	139							
Phase 12	Ni-Fe alloy	927	553	366	798		1070		385	1510	796							
Phase 13	Ni-Fe alloy	526	325	275	470		1110	270	162	1130	709							
Detection Limits (99% confid.)																		
		Ag	Sn	Sb	Te	W L	Os L	Pt L	Au L	Pb L	Bi L							
Phase 9	Bornite	46		112	163				85	63	56							
Phase 10	Magnetite	16	30	38		76				31	29							
Phase 11	Ni-Fe alloy	90	167	205	298			256	212	206	163							
Phase 12	Ni-Fe alloy	246	617	643	934		578		319	301	312							
Phase 13	Ni-Fe alloy	201	452	524	761		554	439	283	268	288							
Nuclear Microprobe analyses of the principal phases present in area 4 (A ratio of 0.9 was used)																		

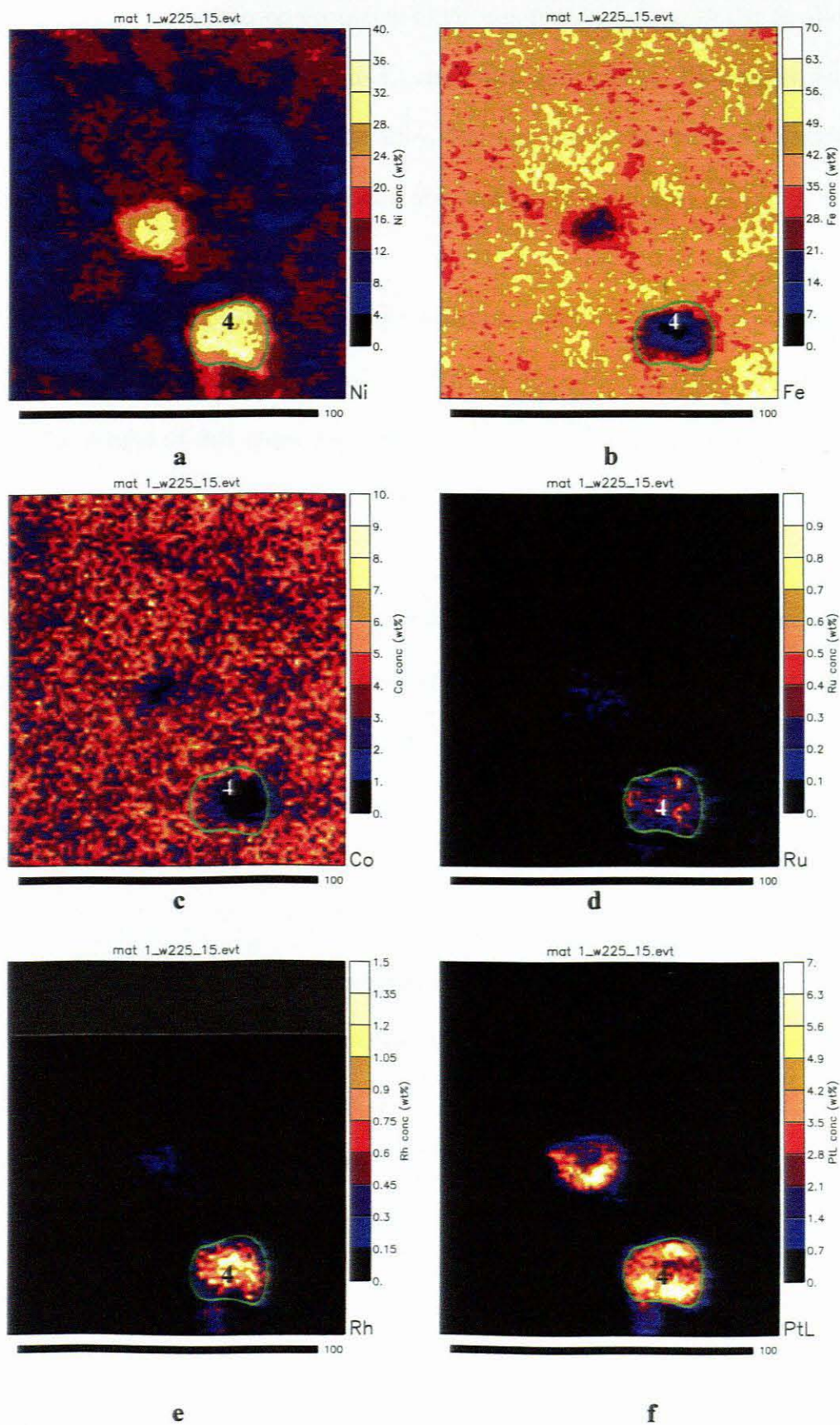


Figure 3.1.4 PIXE maps of furnace matte showing the distribution of Co, Ru, Rh, and Pt in Ni-Fe alloy

Palladium: The highest concentration of Pd was found in phase 11 (Ni-Fe alloy phase), figure 3.1.1 followed by phase 4 and 1 also Ni-Fe alloy phases. The images show that Pd also concentrates in the core of the alloy, figure 3.1.5a. Some traces of Pd were found in the magnetite phase (phase 10), results are shown in table 3.1.1a.

Arsenic: Phase 4 produced the highest concentration of Arsenic, the image shows a bright spot in the center of the alloy indicating that As concentrates at the core; figure 3.1.5b, results of this phase are present in table 3.1.3. Arsenic was present in all the phases with its lowest concentrations being found in the magnetite and pyrrhotite phases.

Cobalt: Co was found in trace quantities in all the phases but appears to be more concentrated in the Ni-Fe alloys. The highest Co concentration was found in phase 4 (Ni-Fe alloy phase) figure 3.1.4c; results are presented in table 3.1.3. The map generated for Co is incorrect; only the results from full deconvolution of PIXE spectra from table 3.1.3 should be used. Co has a higher concentration in phase 4 than in the surrounding areas.

Molybdenum: Mo was present in phase 3 and 10, both are magnetite phases, the highest concentration of Mo was found in phase 10, results of this phase are found in table 3.1.1a. Images show that it concentrates in the core of the magnetite phase, the core of the magnetite phase is Fe enriched, and figure 3.1.5c illustrates this. Figure 3.1.5d illustrates the distribution of Mo in the magnetite phase.

TABLE 3.1.2a

Concentration (ppm)		1	2	3	4	5	6	7	8	9	10	11			
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Nb			
Phase 1	Ni-Fe alloy			160010	13380	155350	168630	724		26120	2120				
Phase 2	Fe-Ni-Cu sulphide			383440	17630	107710	119290	1370		3480	1570				
Phase 3	Magnetite		2100	610260	4410	4850	4860	215	45	150	<23.	54			
Phase 5	Bornite	4560		260780	5510	25820	227040	1190		3900	1790				
Phase 6	Pentlandite	7240		529270	16660	27270	18090	212	59	337	961				
Uncertainty (ppm)															
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Nb			
Phase 1	Ni-Fe alloy			4290	1100	3500	2160	210		876	374				
Phase 2	Fe-Ni-Cu sulphide			6710	1580	2440	2170	279		307	192				
Phase 3	Magnetite		704	4590	495	267	150	42	32	23	22	20			
Phase 5	Bornite	1990		2080	381	530	1140	85		176	77				
Phase 6	Pentlandite	2150		3800	659	561	600	48	24	46	76				
Detection Limits (99% confid.)															
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Nb			
Phase 1	Ni-Fe alloy			1250	688	826	498	355		335	305				
Phase 2	Fe-Ni-Cu sulphide			1320	853	1010	543	477		253	235				
Phase 3	Magnetite		1860	203	247	250	127	70	32	24	23	47			
Phase 5	Bornite	3710		313	212	314	141	127		48	45				
Phase 6	Pentlandite	3610		386	356	291	134	81	42	38	35				

Nuclear Microprobe analyses of the principal phases present in area 1 (A ratio of 1.25 was used)

TABLE 3.1.2b

Concentration (ppm)		12	13	14	15	16	17	18	19	20	21	22	23	24	25
		Mo	Ru	Rh	Pd	Ag	Sn	Sb	Te	W L	Os L	Pt L	Au L	Pb L	Bi L
Phase 1	Ni-Fe alloy			<980.	4050	49130	5000	10500	<4530			5370	5050	14680	9970
Phase 2	Fe-Ni-Cu sulphide	1000				<1400		<3460						3430	1010
Phase 3	Magnetite	7510					483			1200		191		174	
Phase 5	Bornite		<96.	<115.	349	989	<330.	2150	897	513	482	<238.		2050	645
Phase 6	Pentlandite	325	488					<538.			511	<122.		125	108
Uncertainty (ppm)															
		Mo	Ru	Rh	Pd	Ag	Sn	Sb	Te	W L	Os L	Pt L	Au L	Pb L	Bi L
Phase 1	Ni-Fe alloy			391	683	2250	1780	1950	1960			831	721	1170	703
Phase 2	Fe-Ni-Cu sulphide	263				568		1480						473	287
Phase 3	Magnetite	213					145			115		51		47	
Phase 5	Bornite		43	48	86	125	169	274	253	232	212	118		169	73
Phase 6	Pentlandite	51	81					231			154	68		69	41
Detection Limits (99% confid.)															
		Mo	Ru	Rh	Pd	Ag	Sn	Sb	Te	W L	Os L	Pt L	Au L	Pb L	Bi L
Phase 1	Ni-Fe alloy			980	1190	1440	2910	3520	4530			1010	841	865	727
Phase 2	Fe-Ni-Cu sulphide	547				1400		3460						578	538
Phase 3	Magnetite	55					286			145		77		54	
Phase 5	Bornite		96	115	140	169	330	413	532	370	310	238		123	109
Phase 6	Pentlandite	85	121					538			166	122		89	82

Nuclear Microprobe analyses of the principal phases present in area 1 (A ratio of 1.25 was used)

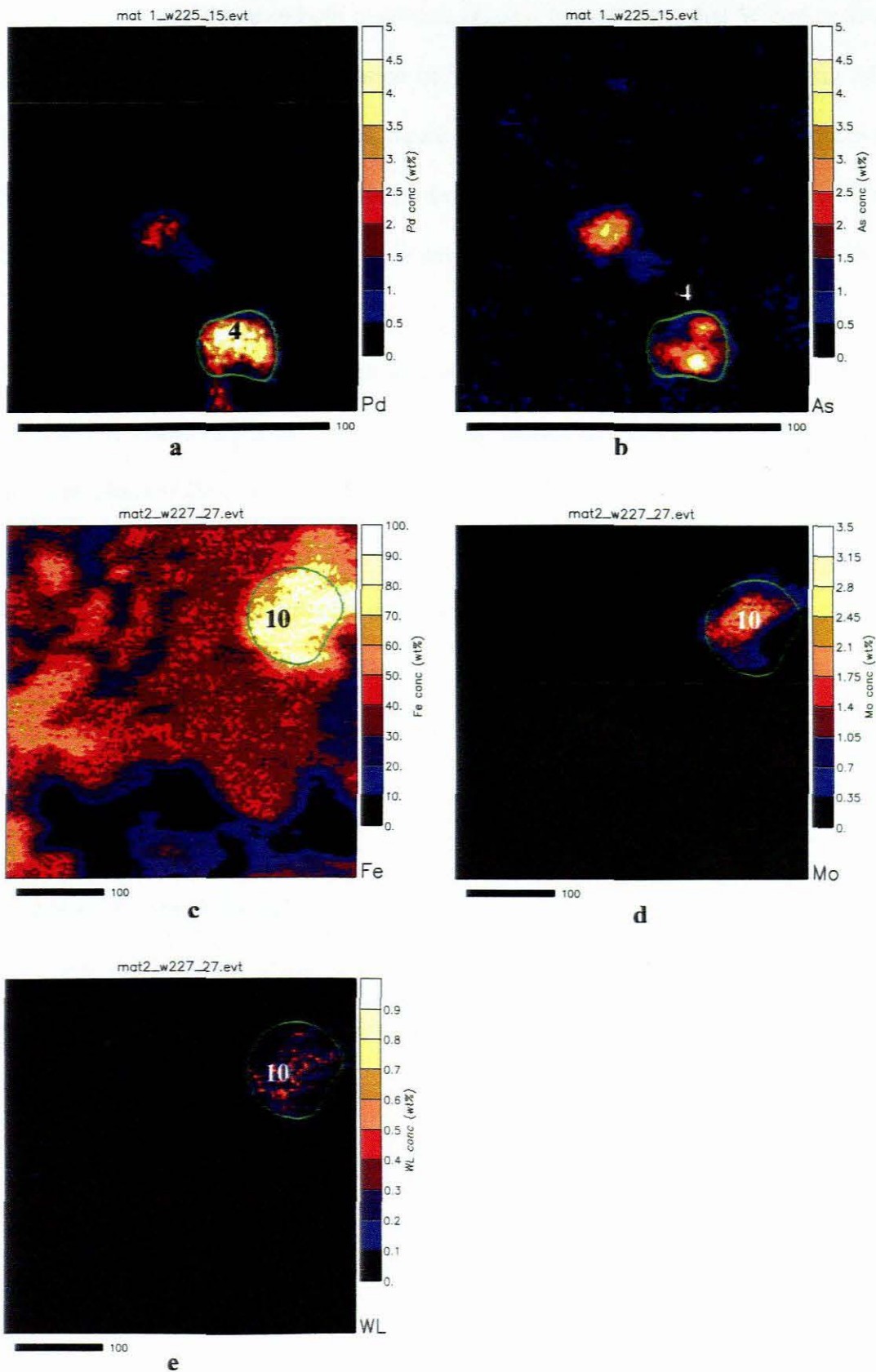


Figure 3.1.5 PIXE maps of furnace matte showing the distribution of Pd and As in Ni-Fe alloy and the distribution of Mo and W in magnetite.

Tungsten: W was found in both magnetite phases, images show that W concentrates in the Mo regions. Highest concentration of W was found in phase 10. W has an affinity towards Mo in the magnetite phases, figure 3.1.5e. The only other phase with traces of W was phase 5 (bornite Phase), results of the concentrations of these phases are in tables 3.1.1b and 3.1.2b. The distribution of W and Mo in phase 3 is shown in the appendix.

Lead: Results show that the highest concentration of Pb was present in Phase 13 followed by phase 12 (figure 3.1.6c), these two phases are Ni-Fe alloys which have high concentrations of Fe; results are shown in table 3.1.1b.

Gold and Silver: The highest concentration of Ag and Au was found in Phase 12 (Ni-Fe alloy phase), figure 3.1.6 d and f. Both Au and Ag have an affinity for the alloy phases, Ag is found in all the phases but in small amounts. Au was only present in the Ni-Fe alloy phases and phase 9 (bornite phase). Results of phase 12 are present in table 3.1.1b.

Osmium: Traces of Os was found in phase 12 and 13, figure 3.1.6e. These two phases are Ni-Fe alloy phases; Os has the tendency to concentrate in the core of the alloy as shown in figure 3.1.6 e. Minor amounts of Os were found in phase 5 (bornite) and phase 6 (pentlandite), results of these phases are tabulated in table 3.1.1b and 3.1.2b.

Tellurium: Te has an affinity for the Ni-Fe alloy phases, as shown in figure 3.1.7 e. It was present in small quantities in most of the phases but absent from the magnetite phases.

TABLE 3.1.3

[illegible]

Nuclear Microprobe analyses of the principal phases present in area 2 (A ratio of 1.25 was used)

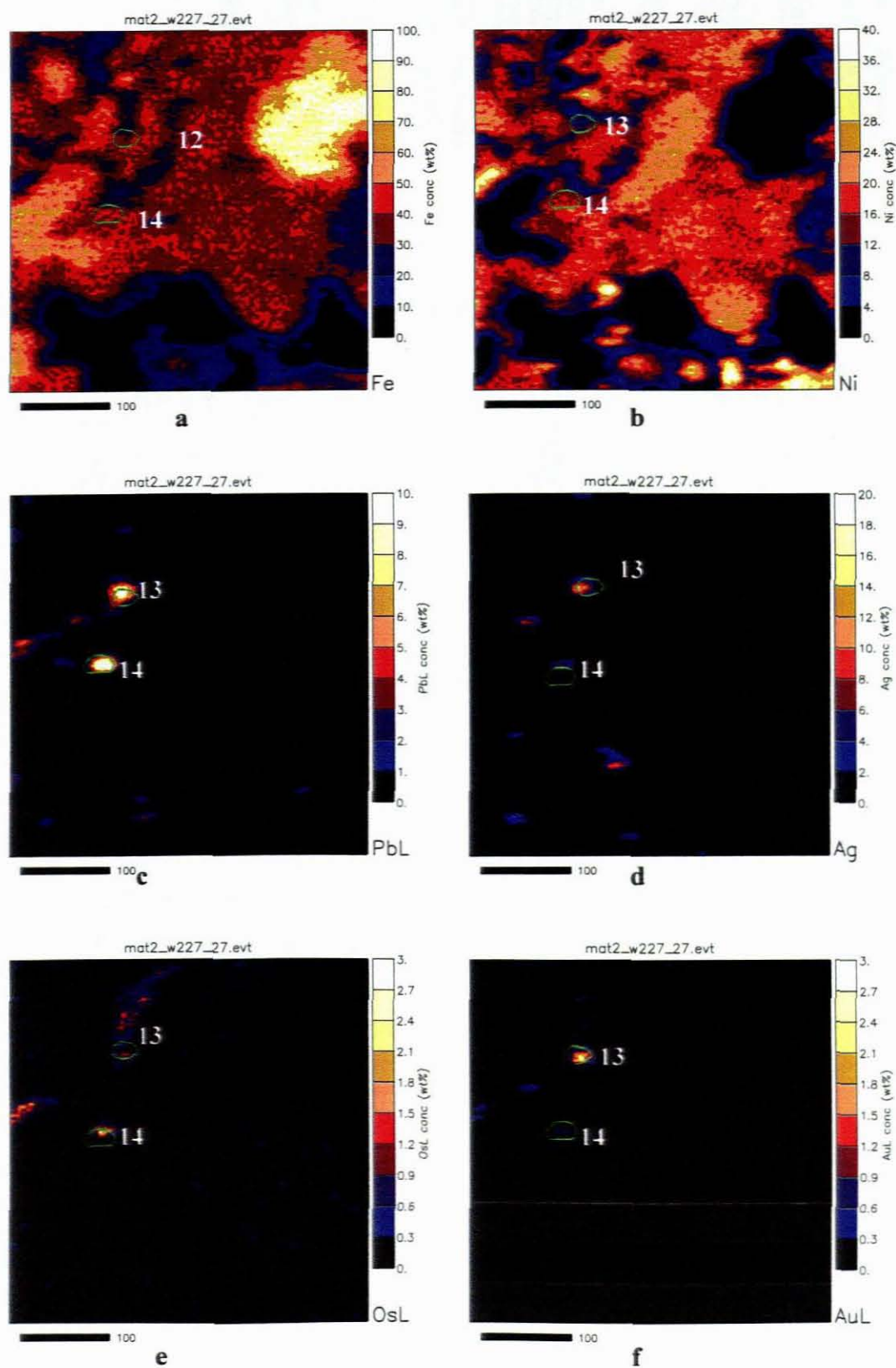


Figure 3.1.6 PIXE maps of furnace matte showing the distribution of Pb, Ag, Os and Au in Ni-Fe alloy.

TABLE 3.1.4

Concentration (ppm)		1	2	3	4	5	6	7	8	9
		Fe	Co	Ni	Cu	As	Se	Mo	Ru	Rh
Phase 7	Pyrrhotite	518200	16400	23000	9620	120	1100	133	490	38
Phase 8	Cu alloy	38730	1620	8000	456400	1500	780		29	34
Uncertainty (ppm)										
		Fe	Co	Ni	Cu	As	Se	Mo	Ru	Rh
Phase 7	Pyrrhotite	2600	621	279	203	8	19	9	15	8
Phase 8	Cu alloy	309	213	409	3160	40	44		12	11
Detection Limits (99% confid.)										
		Fe	Co	Ni	Cu	As	Se	Mo	Ru	Rh
Phase 7	Pyrrhotite	92	82	76	44	12	11	8.4	7.7	8.7
Phase 8	Cu alloy	113	51	132	44	29	25		19	23

Concentration (ppm)		10	11	12	13	14	15	16	17
		Pd	Ag	Cd	Sn	Sb	Te	Pb L	Bi L
Phase 7	Pyrrhotite	31	87	32		44	76	57	
Phase 8	Cu alloy	78	390		187	626	574	287	120
Uncertainty (ppm)									
		Pd	Ag	Cd	Sn	Sb	Te	Pb L	Bi L
Phase 7	Pyrrhotite	7	12	9		15	21	16	
Phase 8	Cu alloy	15	33		43	67	70	38	28
Detection Limits (99% confid.)									
		Pd	Ag	Cd	Sn	Sb	Te	Pb L	Bi L
Phase 7	Pyrrhotite	11	13	16		32	46	27	
Phase 8	Cu alloy	27	33		64	79	114	68	61

Nuclear Microprobe analyses of the principal phases present in area 3 (A ratio of 0.9 was used)

Te highest concentration was found in phase 12 followed by the rest of the Ni-Fe alloy phases. Pyrrhotite and the Cu alloy phases seem to produce the lowest concentrations of Te, these result are found in table 3.1.4.

Zinc: Counting statistics for Zn were low; therefore the concentrations for this element are reported with relatively high errors and detection limits. Traces of Zn were found in all the phases in area 1, figure 3.1.1. The highest Zn concentration was found in Fe-Ni-Cu sulphide phase, phase 2. Results are found in table 3.1.2a.

Selenium: Se was found in all of the phases, with its concentration varying in each phase, the highest concentration of Se was found in Phase 12 and 13, figure 3.1.3f. Figure 3.1.3f and 3.1.7d shows how Se is distributed in the Ni-Fe alloy and pentlandite regions. Traces of Se were found present in most of the phases, results from the nuclear microprobe analysis are found in tables 3.1.1a and 3.1.2a.

3.1.3 PIXE Spectra

In figure 3.1.8 two spectra are presented, one representing the bornite phase and the other the magnetite phase. The bornite spectrum shows characteristic x-ray peaks of high intensity peaks for Cu and Fe. It also clearly indicates the presence of As and Se. The magnetite spectrum is dominated by Fe peaks, indicating that this phase is predominantly composed of Fe, peaks for Mo and W were also present.

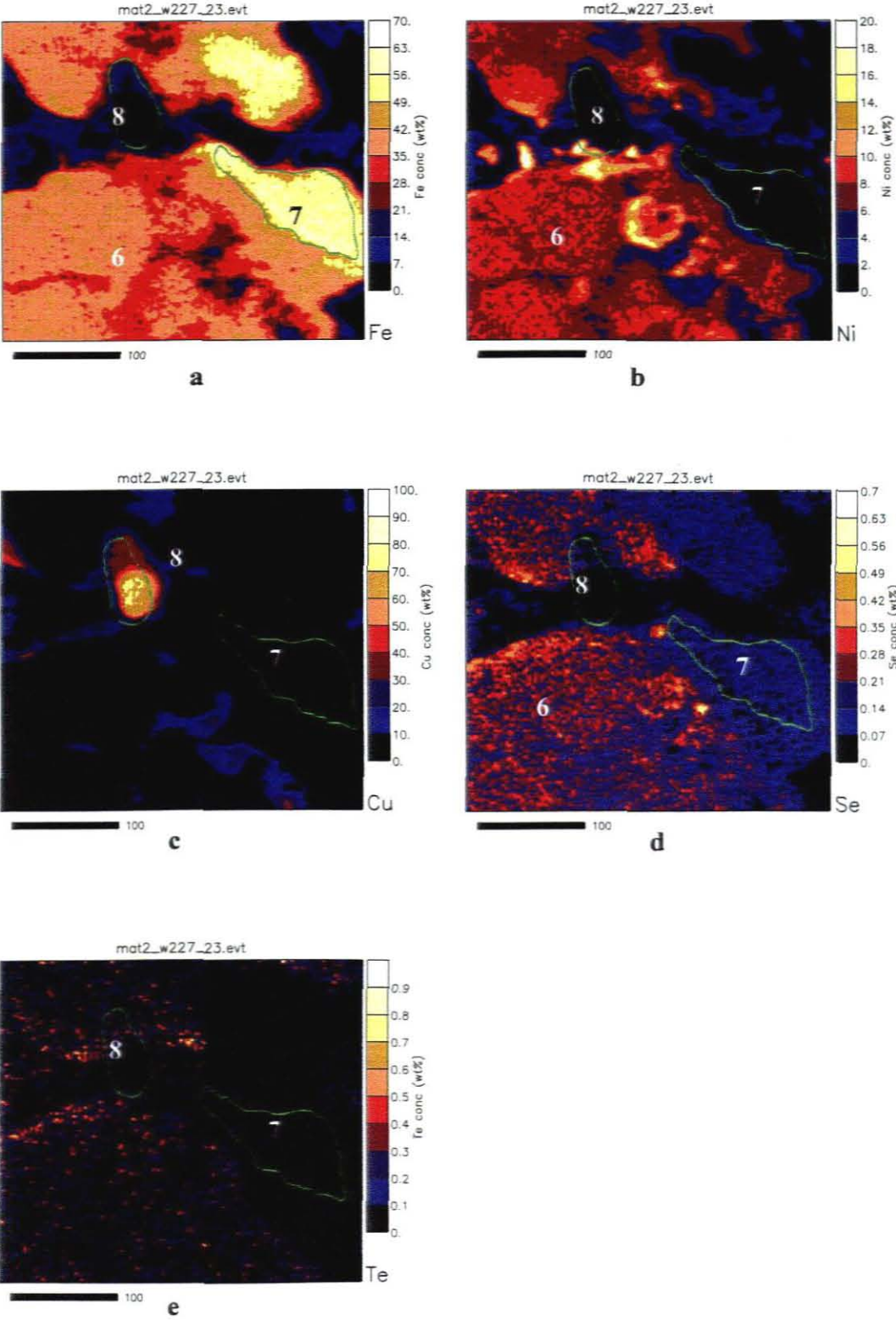
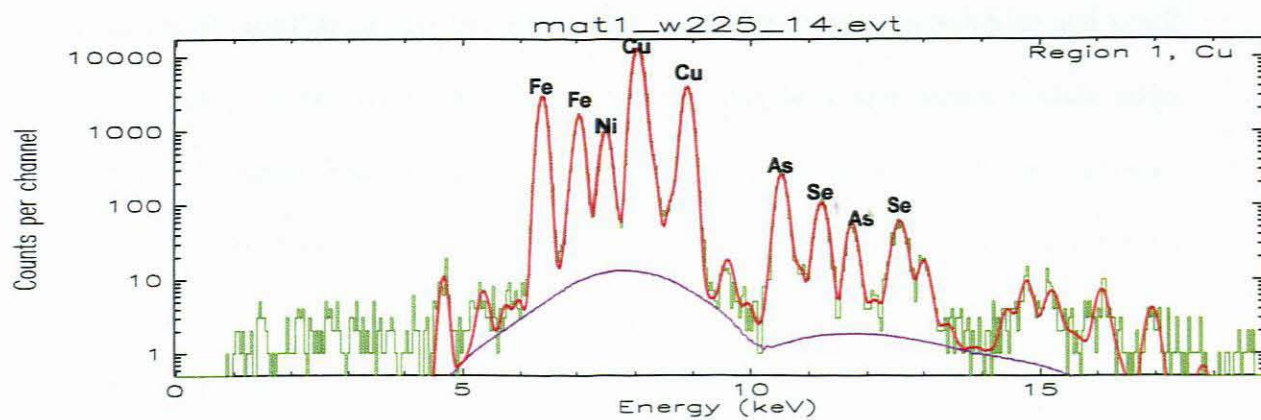
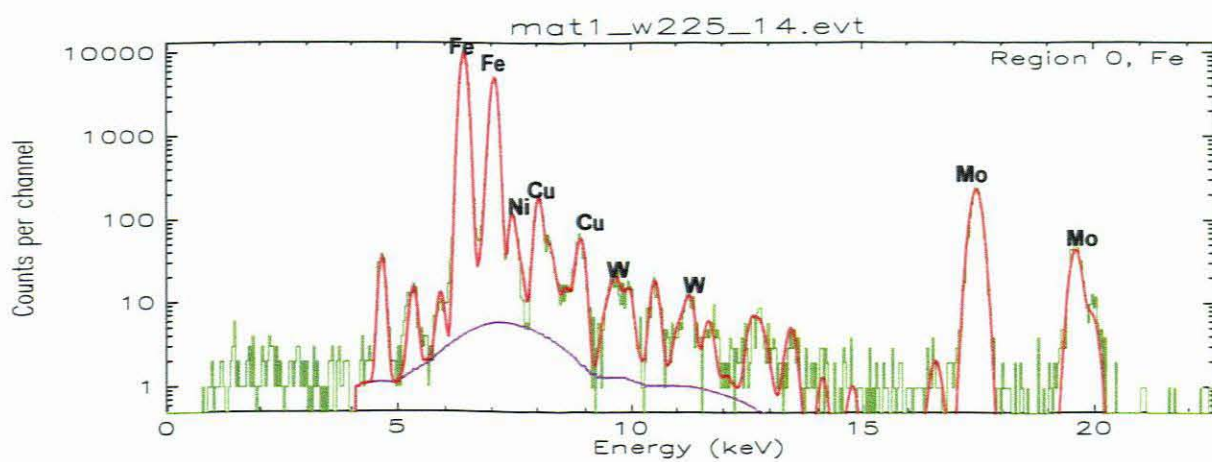


Figure 3.1.7 PIXE maps of furnace matte showing the distribution of Se, Co and Te in Ni-Fe alloy and pentlandite.



Bornite



Magnetite

Figure 3.1.8 PIXE spectra of bornite and magnetite phases

3.1.4 Summary of analytical observations

Furnace matte consists of bornite, pentlandite, pyrrhotite, Ni-Fe-Cu-Sulphide and small quantities of Cu alloy, Ni-Fe alloy and magnetite. All the major phases contain large quantities of sulphur. The correlation between Ni and Cu is positive and the correlation of Fe with both Ni and Cu is negative. Ni and Cu are closely associated. The negative association of Fe with Cu and Ni is accounted for by the fact that significant amounts of Fe are found in the Fe sulphides and this is related to the fact that Ni and Fe substitute for each other in the sulphide matte and in pyrrhotite and pentlandite (Lindsay, 1988). The PGEs show a slight positive trends with Ni and Cu, and a negative trend with Fe which explains the low concentration of precious metals in pyrrhotite. Bornite and pentlandite have some association with PGEs, small traces of some of the PGEs were found in them. The formation of the Ni-Fe alloy is related to the metallization of the furnace matte through the loss of sulphur, the alloy is an early collector of PGEs (Lindsay, 1998).

The Ni-Fe alloys tend to have the highest concentration of PGEs and Au, and the Ni-Fe-Cu-sulphide phases have no detectable traces of PGEs and Au. The most amount of trace elements was found in pyrrhotite followed by magnetite, trace elements such as Cd and Te were found in pyrrhotite and Ge, Nb, and Zn was detected in magnetite. The Ni-Fe alloys had the least amount of trace elements. Fe-Ni-Cu sulphide contains the least amount of detectable elements and the alloys contain the most. PIXE maps show that most of the elements tend to concentrate towards the core, Mo is an example, and it concentrates in the core of magnetite.

Bi, Pb, Se and As concentrations tend to decrease in the phases in which the Fe content is high and the Ni content is low eg: (pentlandite, magnetite and pyrrhotite). High concentrations of these elements were found in the Ni-Fe alloys which had an increase in the Ni and Cu content. Reasonable concentrations of these elements were also found in the Fe-Ni-Cu sulphide phases, which is mostly due to the increase in Ni and Cu and decrease in Fe. Due to the high concentration of Fe in the magnetite phases, the Ni concentration was low resulting in these elements occurring as trace elements. The same result occurred for pyrrhotite when the Fe concentration was high. The Cu alloy had low concentrations of Ni and high Cu concentrations resulting in trace quantities of Pb and Bi, As and Se were found present but in low concentrations.

Pd, Ag, Pt, Sn, Sb, and Au have an affinity for the Ni-Fe alloy phases which have Ni concentration that are high relative to the Cu. These elements were reduced to trace quantities in phases where the Cu concentrations were higher than that of Ni, eg (bornite and Cu alloy). In phases where the Fe concentration was high and Ni was low, phases such as pyrrhotite and magnetite, resulted in the concentration of the above elements to decrease to trace quantities. No traces of Pd, Sn, Pt, Au were found present in the Ni-Fe-Cu sulphide phases. No Pt or Au was detected in the Cu alloy. Ag and Au showed an increase in concentration in phase 13 which is a Ni-Fe alloy with a low concentration of Cu and Pt, but in phase 4 which is also a Ni-Fe alloy, Cu was low in concentration but the concentration of Ag and Au is also low, this is perhaps due to the fact that the Ni concentration is higher than that of the Fe or due to the large concentration of Pt.

Ru and Rh are often found presents in the Ni-Fe alloys which are high in Ni and Pt and low in Cu, phase 4 and 11 are examples. If the Ni-Fe alloy has a high concentration of Cu similar to phase 1 these elements are not present. These elements were not found present in some of the sulphide phases like Ni-Fe-Cu sulphide and bornite, only trace quantities of Ru was found in pentlandite and magnetite. Ru and Rh occur as trace elements in pyrrhotite and Cu alloy, this perhaps is due to the high Fe and Cu concentrations the respected phases. Ru is found in phases that have a high Fe concentration eg: magnetite, pentlandite, pyrrhotite, but only in trace quantities and in phases which had a high Cu content it was not detected eg bornite. Mo and W were found in the magnetite phases, with the concentration of W being several times less than that of Mo. PIXE images show that both elements concentrate towards the core of the magnetite phase, this is due to the high concentration of Fe in the core of magnetite.

3.2 Converter matte

The material studied is in a solid form, and it is produced in the second smelting stage, the converter stage. Converter matte falls within the bounds of the Cu-Ni-S ($\pm$ Fe) ternary system (Lindsay, 1988). Converter matte samples were prepared by Mintek, two samples were prepared. One of the samples was spiked with unknown concentrations of impurity elements. Both samples were slowly cooled at room temperature. Samples were labeled CM for the converter matte sample and SCM for the spiked converter matte sample. Samples were cut, mounted and prepared for examination by Scanning Electron Microscope.

3.2.1 Mineralogy

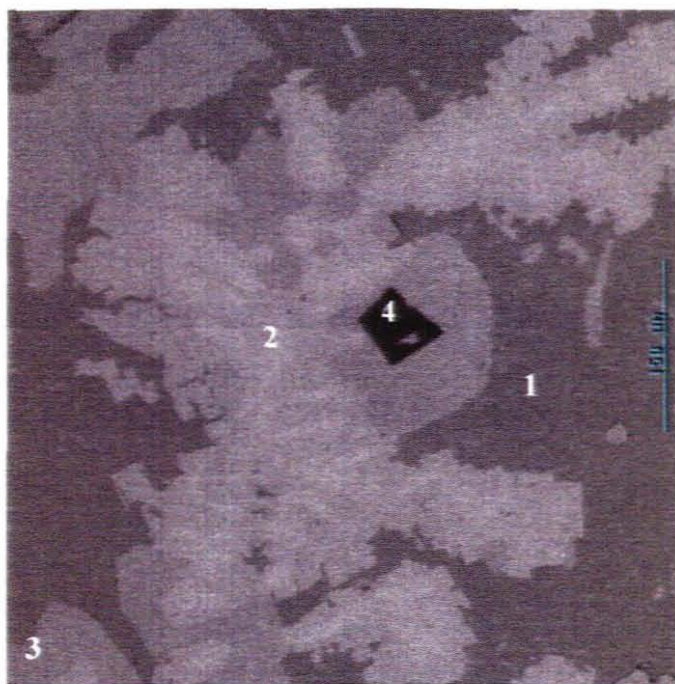
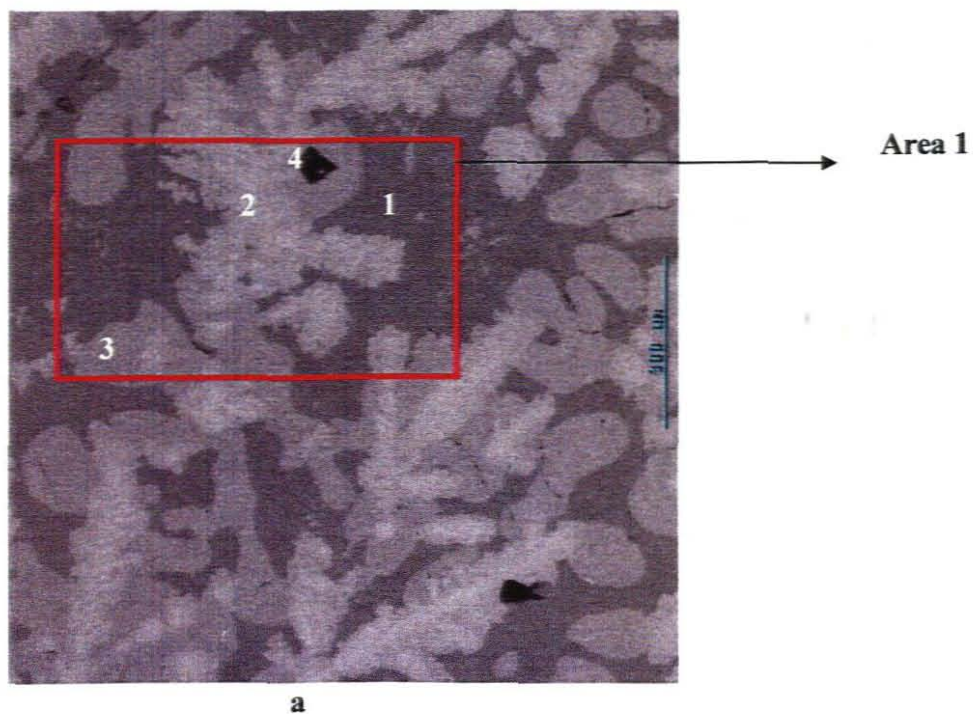
The coarsely crystalline matte sample shows vertical zoning or stratification throughout the entire sample. The converter matte sample consisted of four phases as shown in figure 3.2.1a and b. Phase 1 is commonly known as heazlewoodite (Ni_3S_2), which is a relatively monotonous phase which occurs throughout the sample, this phase has a dark grey colour. Results in table 3.2 show that this phase is pure with no detectable trace elements being found. Phase 2 is a Ni-Cu alloy with detectable trace quantities of S and Pt. The results are shown in table 3.2. This phase is found in abundance in the sample, but it seems to be inter-locked by the dendroidal Cu-Sulphide phase (phase 3). Figure 3.2.1a shows that this phase forms the core in most of the Cu-Sulphide phases, it is the brightest

phase amongst the four and it also contains the largest concentration of Pt. This phase also has a branch-like structure, which is found throughout the matte.

Phase 3 (Cu-Sulphide phase) is also found throughout the sample. Detectable trace quantities of Ni and Pt were found present in this phase. In the matte this phase was represented by Chalcocite (Cu_2S), no traces of Bornite (Cu_5FeS_2) were detected. Results of this phase are presented in table 3.2. A minor phase which was encountered includes Trevorite (NiFe_2O_4), Phase 4. Phase 4 was found to be inter-locked by the Cu-sulphide phases as shown in figure 3.2.1a, this phase is the darkest phase in figure 3.2.1a and b, but under a light microscope this phase appears to be the most distinct and noticeable phase, the quantity of this phase as compared to the rest of the phases is small.

3.2.2 PIXE Microanalyses of Trace element distributions and concentration in Converter Matte phases

Analysis of the constituent matte phases by Particle Induced X-ray emission (PIXE) was performed to investigate the distribution of trace elements. The objective of these analyses was to examine low level concentrations (ppm or ppb) in phases such as alloys and sulphides, making use of much better sensitivity of this technique in comparison with the electron microprobe. Area 1 was selected for generating a map; the scan ran until a charge 100 μC was obtained. Area 1 contains the following phases, phase 1, 2, 3, 4, and 1a. The following figures are a series of distribution maps for trace elements in the Converter Matte phases.



b

Figure 3.2.1 Photomicrograph of converter matte showing its assemblage: [1] Heazlewoodite (Ni_3S_2); [2] Ni-Cu alloy; [3] Chalcocite (Cu_2S); [4] Trevorite (NiFe_2O_4).

TABLE 3.2

[illegible]

OXIDES

	Elements	NiO	SO ₃	CuO	Fe ₂ O ₃	Ag ₂ O	SnO ₂	Sb ₂ O ₃	PbO	Pd	Pt	Total
		Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	Wt.%	
Phase 4	Trevorite	22	0	1	75	0	0	0	0	0	0	98

Electron Microprobe analysis of the principal phases in Converter Matte

Platinum: The highest concentration of platinum was found in the Ni-Cu alloy phase (phase 2), as shown in figure 3.2.2c. Traces of platinum were found in the Trevorite phase 4. These marked phases were selected for analysis. Quantitative results of these phases are presented in table 3.2.1. The results that are shown on the map show some discrepancy with the results presented in the tables. This is caused by high local variability of the composition elemental matrix for which no corrections in map were made. The results in the table represent the selected phases on the map.

Palladium: Traces of palladium were found in all phases. The image shows that palladium has the highest concentration in the Ni-Cu alloy phase 2 (figure 3.2.2d) followed by heazlewoodite. Pd was found in phase 1 a, which is a phase that contains a droplet of Au. Results from PIXE show that this phase is actually a heazlewoodite phase which is rich in Au.

Ruthenium and Rhodium: Rh is present in almost all of the phases, but it is absent from the chalcocite phase. Its highest concentration was found to be present in the Ni-Cu alloy as shown in Figure 3.2.3a followed by the heazlewoodite phase. Ru is present in almost all phases. The image shows that the highest concentration of Ru was found to be in the Ni-Cu alloy phase, figure 3.2.3 b.

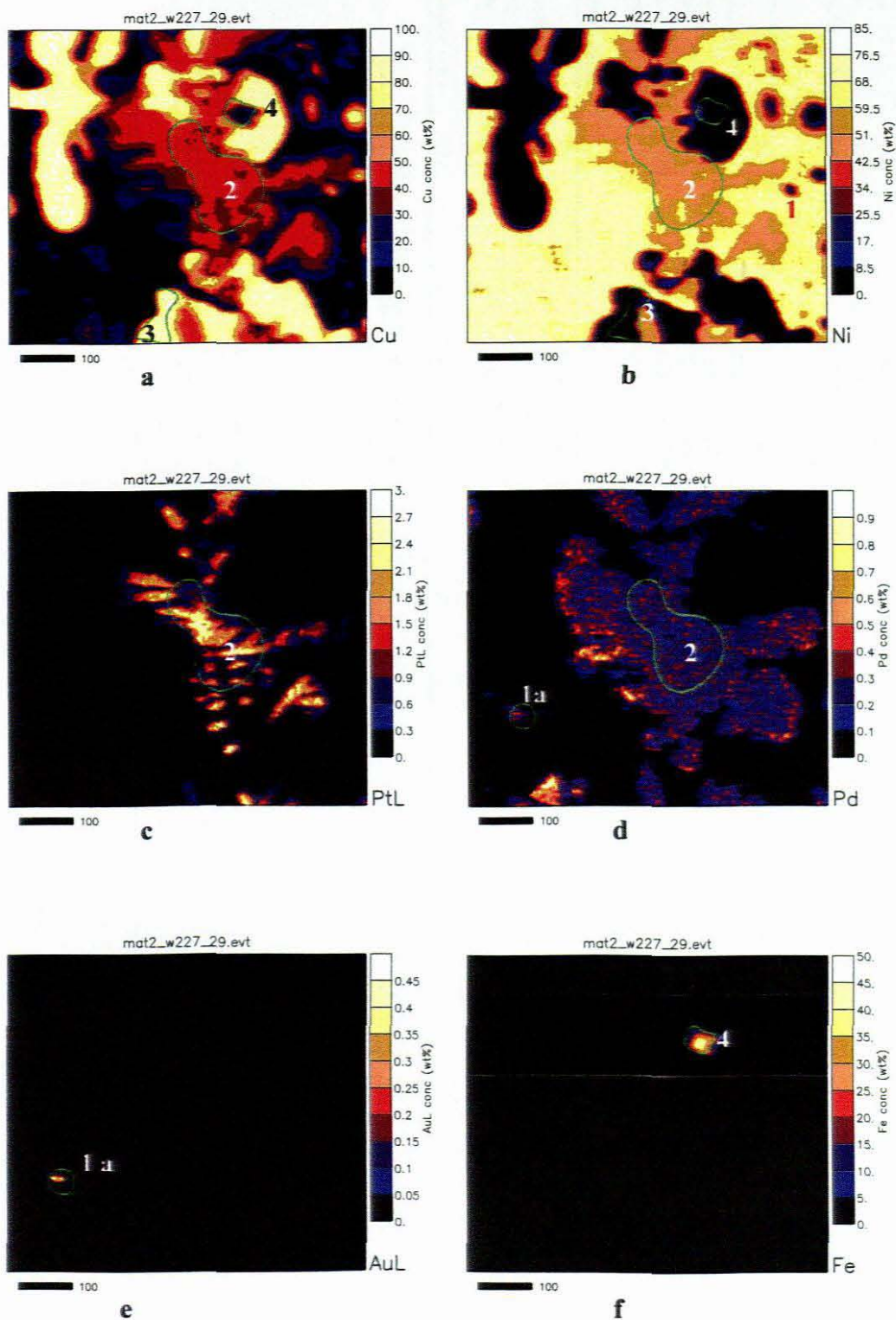


Figure 3.2.2 PIXE maps of converter matte showing the distribution of Pt and Pd in Ni-Cu alloy and Au in heazlewoodite and the distribution of Fe in trevorite.

TABLE 3.2.1

Concentration (ppm)		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
		Fe	Co	Ni	Cu	Zn	As	Se	Ru	Rh	Pd	Ag	Te	Ir L	Pt L	Au L	Pb L	Bi L
Phase 1	Heazlewoodite	730	1710	719120	87160		225	537	395	300	1020	66	255		505		121	116
Phase 2	Ni-Cu alloy	1320	2110	511160	360590	810	329	26	2130	1170	2380	65		411	11810	260		59
Phase 3	Chalcocite	540		18600	709560			1340	52		103	175					121	83
Phase 4	Trevorite	314030	10390	293650	501040		74	434	296	122	446	166			190			71
Phase 1a	Heazlewoodite + Au	640	1360	678480	52040		338	516		80	1280					852	573	267
Uncertainty (ppm)																		
		Fe	Co	Ni	Cu	Zn	As	Se	Ru	Rh	Pd	Ag	Te	Ir L	Pt L	Au L	Pb L	Bi L
Phase 1	Heazlewoodite	181	264	2220	292		17	35	24	26	56	23	60		66		31	30
Phase 2	Ni-Cu alloy	264	181	1150	1630	110	12	21	34	22	49	15		75	122	72		46
Phase 3	Chalcocite	199		701	5660			35	15		20	28					32	26
Phase 4	Trevorite	4220	309	1170	7330		15	26	39	30	57	47			70			27
Phase 1a	Heazlewoodite + Au	127	218	2270	391		36	32		24	90					84	65	47
Detection Limits (99% confid.)																		
		Fe	Co	Ni	Cu	Zn	As	Se	Ru	Rh	Pd	Ag	Te	Ir L	Pt L	Au L	Pb L	Bi L
Phase 1	Heazlewoodite	141	234	102	111		25	23	20	24	29	36	127		119		56	52
Phase 2	Ni-Cu alloy	63	75	68	47	67	17	18	15	17	19	20		115	75	61		38
Phase 3	Chalcocite	170		188	55			25	23		33	40					65	59
Phase 4	Trevorite	267	209	484	224		29	25	46	55	68	83			115			60
Phase 1a	Heazlewoodite + Au	177	256	122	149		45	40		52	63					136	100	93

Nuclear Microprobe analyses of the principal phases present in area 1 (Ratio of 0.9 was used)

Cobalt and Arsenic: Results show that both Co and As are absent from the chalcocite phase but are present in the rest of the phases, images show that the highest Co concentration was found in the trevorite phase (phase 4) followed by the Ni-Cu alloy Phase figure 3.2.3c, results of these analysis are present in table 3.2.1. As highest concentration was found in the Ni-Cu alloy and in the heazlewoodite phase which is enriched with Au phase 1a. Figure 3.2.2d shows As affinity for the Ni-Cu alloy phase.

Selenium and Bismuth: Both elements were found in all the phases, with bismuth being found in very low concentrations. Images show that the highest concentration of Se was found in the chalcocite regions followed by heazlewoodite figure 3.2.3e, when this concentration is compared to the results in table 3.2.1 they match perfectly. The lowest Se concentration was found in the Ni-Cu alloy as shown in the results in table 3.2.1. The highest Bi concentration was found in the heazlewoodite phase which is enriched with Au (phase 1a) followed by heazlewoodite figure 3.2.3(f). The image shows its affinity for the Ni-Cu alloy, in this case the image produced is false in describing the intensity Bi in the Ni-Cu alloy phase.

Zinc, Iridium and Tellurium: Zn and Ir were only found in one phase, the Ni-Cu alloy phase. These two elements were found in minor quantities, no images were produced for these elements because of their low concentrations.

Te was absent in most of the phases but present in the heazlewoodite phase.

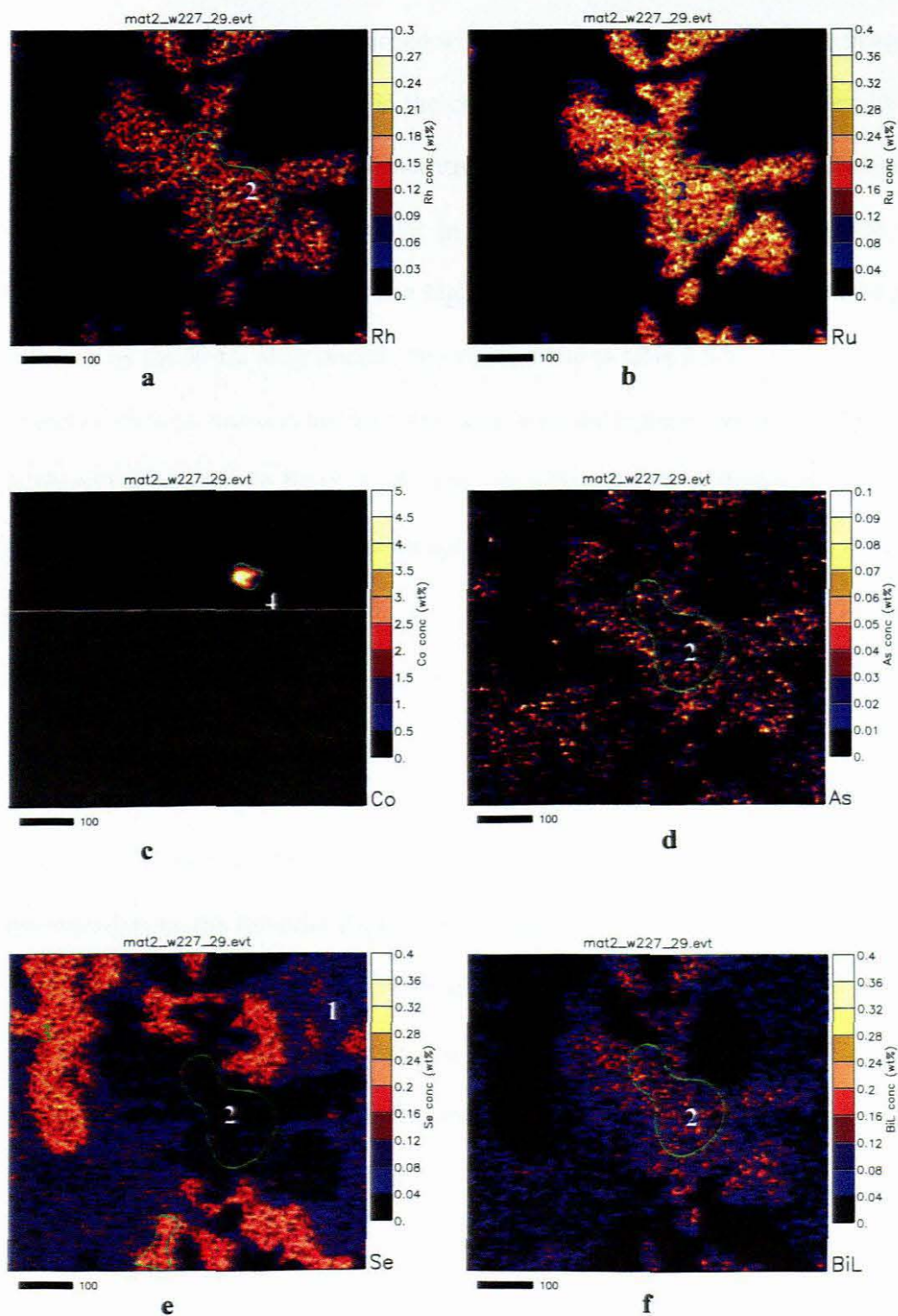


Figure 3.2.3 PIXE maps of converter matte showing the distribution of Rh, Ru, As, Se and Bi in Ni-Cu alloy, heazlewoodite and chalcocite and the distribution of Co in trevorite.

Silver, Gold and Lead: Ag is present in almost all phases. It is absent from the heazlewoodite phase which is enriched with a droplet of Au (phase 1a). The image shows that droplets of Ag were formed in the chalcocite phases, figure 3.2.4a. Results in table 3.2.1 indicate that the greatest concentration of Ag was found in the chalcocite and trevorite phases. Au is only present in two phases, the Ni-Cu alloy phase and the heazlewoodite phase (phase 1a). The highest concentration was found to be in phase 1a followed by the Ni-Cu alloy phases, results are found in table 3.2.1.

Traces of Pb were found in the heazlewoodite, with the highest concentration being found in phase 1 a. Image b in figure 3.2.4 shows an affinity of Pb in the heazlewoodite phase (phase 1) and a lack of it in the chalcocite phase (phase 3), but the results in table 3.2.1 show even amounts in both phases.

3.2.3 PIXE Spectra

In figure 3.2.5 two spectra are presented, one representing the heazlewoodite phase and one representing the trevorite phases. In the heazlewoodite spectrum an intense peak for Ni indicates its abundance in the phase, smaller peaks for Fe, Zn, As, Se, Pd and Sn were also present. The trevorite spectrum has three highly intense doublets of peaks which represent Cu, Fe and Ni. These three elements constitute the bulk of the phase, smaller peaks for Se, Ru and Pd were also present.

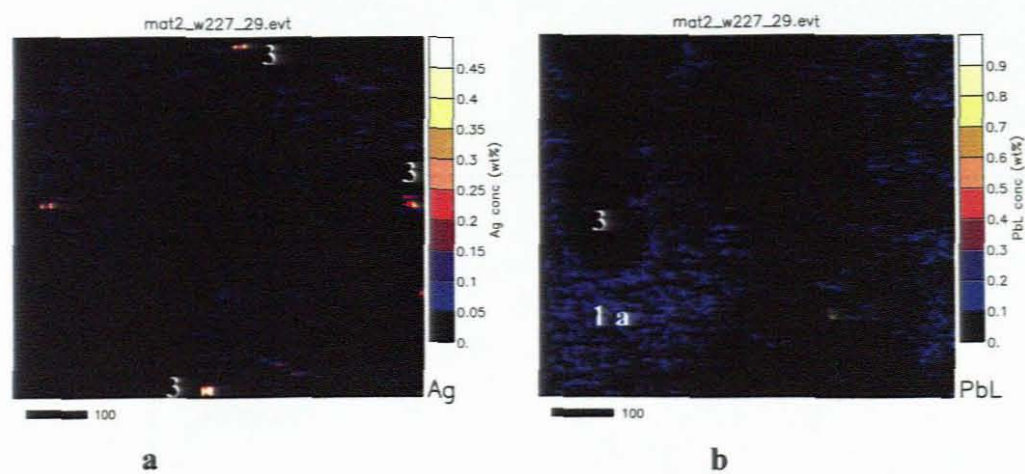


Figure 3.2.4 PIXE maps of converter matte showing the distribution of Ag and Pb in chalcocite and heazlewoodite.

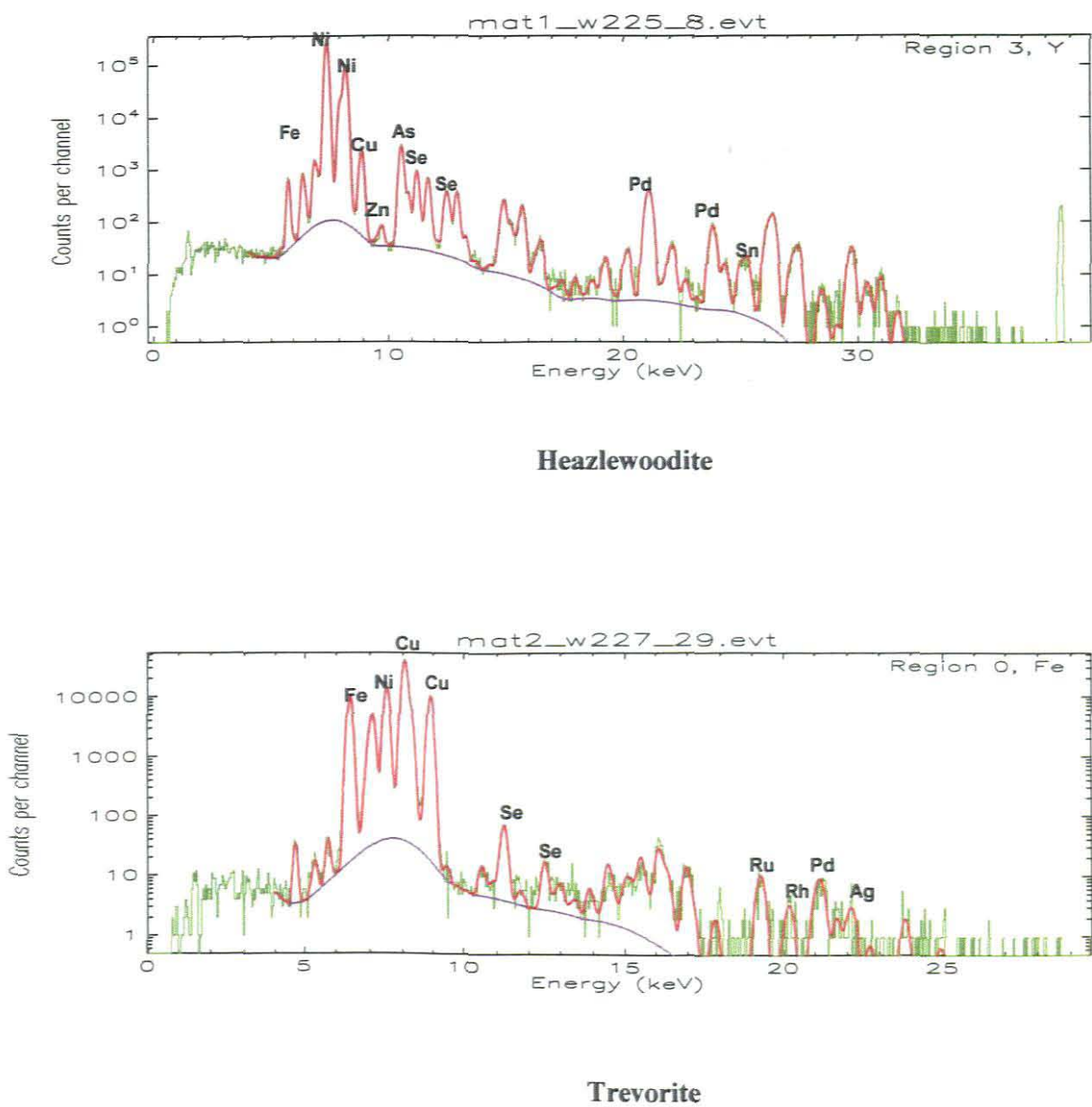


Figure 3.2.5 PIXE spectra of heazlewoodite and trevorite phase

3.2.4 Summary of analytical observations

Converter matte mostly consists of heazlewoodite, chalcocite and small quantities of Ni-Cu alloys and trevorite. A relative increase in the heazlewoodite concentration has lead to an increase in the Ni and S content, and an increase in Cu-sulphides has resulted in an increase in the Cu content. The loss of Fe from the matte by oxidation during the converting process has resulted in an increase in the PGE content in the alloy and there has been an increase in the alloy content in the matte. The enrichment of alloy phases in the matte resulted in an increase in PGE and Au concentrations. Ru, Rh, Au and Pd show a positive correlation with Ni as seen in the heazlewoodite and Ni-Cu alloy phases, but they have a negative correlation with Fe and Cu as seen in the chalcocite and trevorite phases.

The highest amounts of trace elements were found in chalcocite followed by trevorite, the alloy phases showed an increase in element concentration and had the least amount of trace elements. Trevorite and chalcocite contain the highest amounts of trace PGE's and Au and the alloys contained the highest concentration of PGE's and Au. The alloy phases contain the highest amounts of detectable elements and chalcocite and trevorite has the least. As, Se, Co, Ag, Pb and Bi concentrations have decreased to trace quantities in most of the phases, only Se has a high concentration in the chalcocite phase. The results show that Co has an affinity for Fe, with trevorite containing the highest concentration of Fe. The Co concentration decreased in regions where the Fe content was low, so the reduction of Co may be due the low Fe content or it has been oxidised along with Fe.

Ru, Rh and Pt were found in trace quantities in heazlewoodite and trevorite and they were absent from chalcocite. Ir was found only in the alloy region which had a high Pt concentration, and shows a positive association for Pt. Au was found in trace quantities in the alloy phase, droplets of it appeared on the heazlewoodite phase as well. PIXE maps show that Pt, Rh, Ru and As tend to have high concentrations in the alloy phases and concentrate towards the core, Pd on the other hand has an affinity for the alloy phase but tends to concentrate on the borders. Arsenic distributes itself evenly through the heazlewoodite phase. Maps also show Se affinity for chalcocite, it is also found in heazlewoodite and is evenly distributed in both phases. Also shown is the lack of Se in the alloy phase. Co tends to concentrate in the core of trevorite, no other elements were found in high concentrations in trevorite.

3.3 Spiked Converter Matte

The sample being analysed was a converter matte sample in a solid form which has been doped with unknown concentrations of impurity elements. The sample consisted of base metal sulphides and alloys. The most common alloy that was detected was the Ni-Cu alloy. Two sulphide phases were detected, one being the Cu-sulphide which is represented by chalcocite (Cu_2S), and the second being heazlewoodite (Ni_3S_2). These two phases occurred throughout the sample, and they were the most abundant phases.

3.3.1 Mineralogy

Five phases were chosen to be analysed by scanning electron microscope, the most common phases in the matte were the chalcocite and heazlewoodite phases. A minor phase which was also encountered was the Ni-Cu alloy phase; all these phases are shown in figure 3.3.1. Phases 1 and 4 are both Ni-Cu alloys, both have a similar triangular shape, this phase is surrounded by heazlewoodite. Both phases have traces of Fe, Pt and sulphur in them. Phase 4 has a lower Ni content than phase 1 but this is complemented by an increase in the Pt content. Both these phases show an affinity to the chalcocite phase, phase 3, they are attached to the chalcocite in some way or the other. Table 3.3 contains the results of all the phases present in Figure 3.3.1 a and b. Phase 2 is a heazlewoodite phase, it is the darkest phase on the matte and appears in large quantities. This phase has some trace quantities of Cu and Pt.

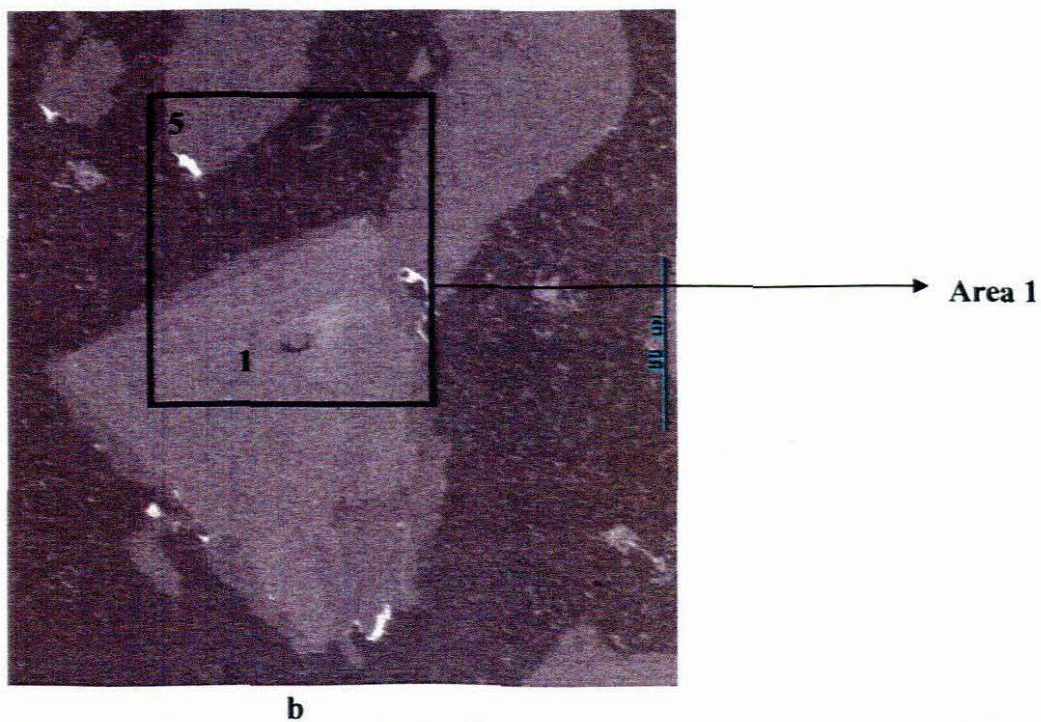
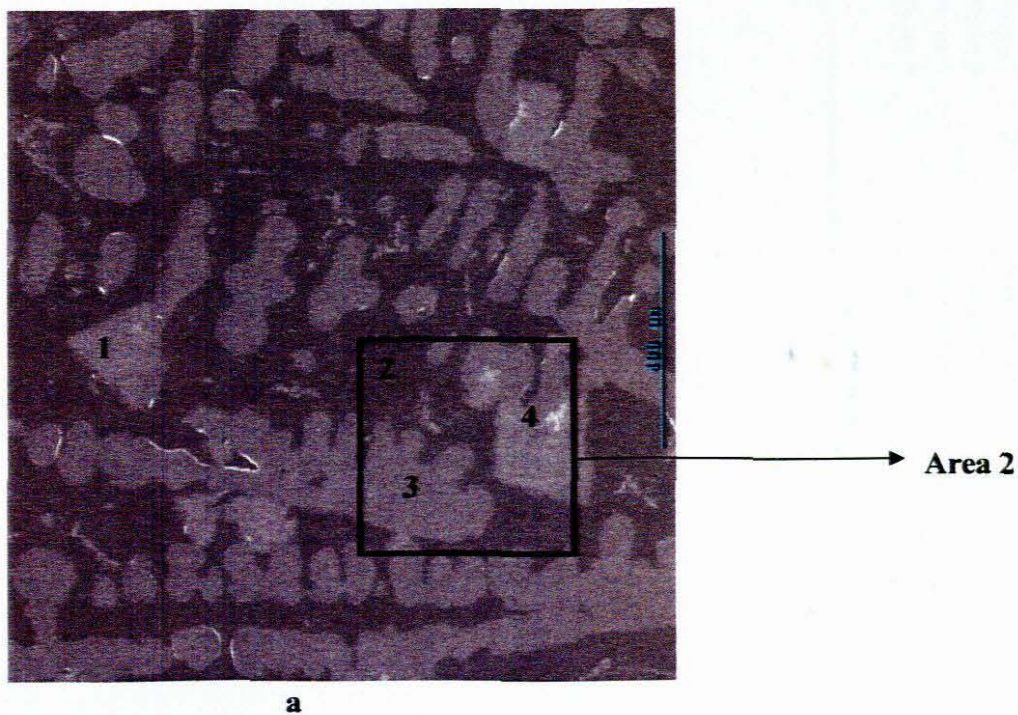


Figure 3.3.1 Photomicrograph of spiked converter matte showing its assemblage: [1] Ni-Cu alloy; [2] Heazlewoodite (Ni_3S_2); [3] Chalcocite (Cu_2S); [4] Ni-Cu alloy; [5] Ag alloy.

TABLE 3.3

	Elements	Ni	S	Cu	Pt	Fe	Ag	Sn	Sb	Pb	Pd	Total
		Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	Wt. %	
Phase 1	Ni-Cu alloy	75.3	0.3	17.2	0.2	5.0	0.0	0.0	0.0	0.0	0.0	97.9
Phase 2	Heazlewoodite	72.9	25.6	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	100.5
Phase 3	Chalcocite	0.3	19.6	74.8	0.4	1.2	0.0	0.0	0.0	0.0	0.0	96.4
Phase 4	Ni-Cu alloy	59.2	0.2	15.8	16.8	5.8	0.0	0.0	0.0	0.0	0.0	97.8
Phase 5	Ag alloy	1.0	1.8	10.3	0.3	0.5	89.7	0.0	0.0	0.0	0.0	103.5

Electron Microprobe analyses of the principal phases in Spiked Converter Matte

Phase 3 is a chalcocite (Cu_2S) phase which also appears in large quantities on the matte, it has a branch-like structure which appears throughout the matte, traces of Ni, Pt and Fe were found present in this phase. Phase 5 appeared as a bright white spot on the rim of the chalcocite phase. Many of these phases appeared on the matte as bright white spots which varied in shape and size; they also formed around the border of the chalcocite phase. Analyses from SEM\EDX show that this phase comprises mostly of Ag, followed by Cu. Traces of Ni, S, Pt and Fe were found present in this phase. Only small quantities of this phase was present in the matte.

3.3.2 PIXE Microanalyses of trace element distribution and concentration in Spiked Converter Matte phases.

Two areas in figure 3.3.1 were selected to be mapped by the Nuclear Microprobe, area 1 and area 2. Phases 1 and 5 made up area 1 and phases 2, 3 and 4 made up area 2. The scan ran until a charge of 700 nC was accumulated for area 1 and 4386 nC was accumulated for area 2. A few new phases were discovered on the maps and they were analysed for trace elements. In area 1 phase 7 and phase 1a were analysed, phase 1a is found in phase 1; this phase is clearly illustrated in the maps generated by PIXE. Phase 7 is located on the border of the Ni-Cu alloy. In area 2 three new phases were analysed, phase 4a and 4b, both were found in phase 4. Phase 6 was found on its own in the heazlewoodite phase. All these phases were selected to be analysed for trace element concentrations and distributions. Results of these phases are presented in tables 3.3.1 a and b and tables 3.3.2 a and b.

Platinum: The highest concentration of platinum was found in phase 4a, phase 4a formed in the core of the Ni-Cu alloy. In figure 3.3.2d it is clearly shown that Pt tends to concentrate in the cores of Ni-Cu alloys. No detectable trace of Pt was found in heazlewoodite. Results of this phase are presented in table 3.3.1b. In figure 3.3.4 d, it is also shown that Pt concentrates in the Ni-Cu alloy.

Selenium: Se has an affinity for the chalcocite phase (phase 3); the distribution of Se in the chalcocite is shown in figure 3.3.2 c. The image also shows a decrease in concentration of Se in the Ni-Cu alloy (phase 4). Se is evenly distributed throughout the chalcocite phase. Se is present in most of the phases with the highest concentration being found in the chalcocite phase.

Cobalt: Co was found present in all the phases, image f in figure 3.3.2 shows the affinity Co has for the Ni-Cu alloy (phase 4). The highest concentration of Co was found in phase 1 followed by phase 4. The lowest concentration of Co was in the chalcocite phases, image f clearly shows the deficiency of Co in this phase. Results of these phases are in table 3.3.1a and 3.3.2a (phase 1).

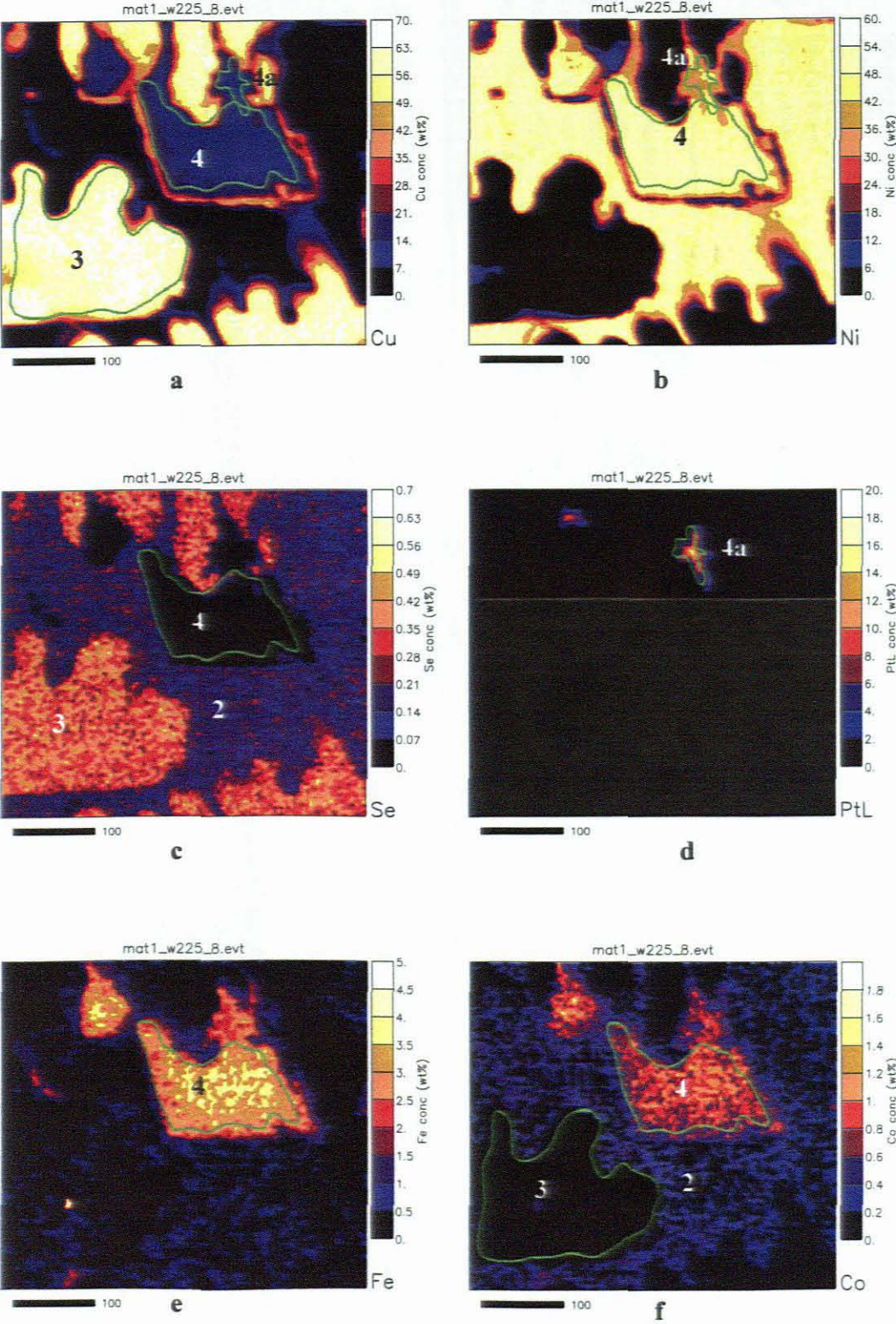


Figure 3.3.2 PIXE maps of spiked converter matte showing the distribution of Se, Pt and Co in Ni-Cu alloy, heazlewoodite and chalcocite.

TABLE 3.3.1a

Concentration (ppm)		1	2	3	4	5	6	7	8	9	10	11	12	13
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Zr	Nb	Mo
Phase 2	Heazlewoodite	1820	397	6000	5560	655070	31210	191		5090	1710		33	22
Phase 3	Chalcocite	1690		9890	275	14120	645480			57	3380			18
Phase 4	Ni-Cu alloy			44030	8700	654360	135430	203		3760	87			
Phase 4a	Ni-Cu alloy		1540	38000	8190	515370	167060	670	<183.	8540			100	
Phase 4b	Ni-Cu alloy	1850		43110	9230	579170	142390	358		11330	182	109	44	
Phase 6	Heazlewoodite		1220	14060	6260	659320	56650	250		6170	1230		90	62
Uncertainty (ppm)														
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Zr	Nb	Mo
Phase 2	Heazlewoodite	918	316	276	407	2410	694	62		76	28		14	9
Phase 3	Chalcocite	500		249	173	820	2160			9	47			6
Phase 4	Ni-Cu alloy			401	435	2120	524	83		51	18			
Phase 4a	Ni-Cu alloy		558	854	419	2200	3700	288	93	272			53	
Phase 4b	Ni-Cu alloy	896		529	376	1760	2180	118		170	111	35	24	
Phase 6	Heazlewoodite		565	519	482	2600	583	92		164	63		33	23
Detection Limits (99% confid.)														
		Cr	Mn	Fe	Co	Ni	Cu	Zn	Ge	As	Se	Zr	Nb	Mo
Phase 2	Heazlewoodite	1330	356	104	168	64	79	76		23	20		17	15
Phase 3	Chalcocite	1030		77	33	82	26			13	12			13
Phase 4	Ni-Cu alloy			91	118	82	74	89		21	19			
Phase 4a	Ni-Cu alloy		949	258	354	291	244	381	183	129			68	
Phase 4b	Ni-Cu alloy	1720		152	198	151	131	185		55	60	36	35	
Phase 6	Heazlewoodite		887	243	422	174	199	200		56	51		46	52

Nuclear Microprobe analyses of the principal phases present in Area 2 (A ratio of 1.25 was used)

TABLE 3.3.1b

Concentration (ppm)		14	15	16	17	18	19	20	21	22	23	24	25	26	27
		Ru	Rh	Pd	Ag	Sn	Sb	Te	Cs	Os L	Ir L	Pt L	Au L	Pb L	Bi L
Phase 2	Heazlewoodite	122	249	4650	491	690	6330	2220		335			321	1010	1860
Phase 3	Chalcocite	13	20	76	882	94	193	590	195						
Phase 4	Ni-Cu alloy	2130	2180	7540	487	191	1330	162				1040	192		58
Phase 4a	Ni-Cu alloy	7980	3570	3910	373		2170			2370	2230	85620	1060		
Phase 4b	Ni-Cu alloy	6410	3450	4150	274	292	2880	186		855	465	29060	517		
Phase 6	Heazlewoodite	495	1080	20700	388	2070	13930	1690					1560	1240	2030
Uncertainty (ppm)															
		Ru	Rh	Pd	Ag	Sn	Sb	Te	Cs	Os L	Ir L	Pt L	Au L	Pb L	Bi L
Phase 2	Heazlewoodite	13	18	71	31	60	141	105		246			30	69	40
Phase 3	Chalcocite	7	7	11	33	22	25	47	52						
Phase 4	Ni-Cu alloy	39	51	95	33	41	58	36				83	42		26
Phase 4a	Ni-Cu alloy	234	170	213	120		282			1630	570	1110	381		
Phase 4b	Ni-Cu alloy	138	98	118	69	63	171	68		760	253	455	180		
Phase 6	Heazlewoodite	72	88	371	78	206	542	249					114	147	95
Detection Limits (99% confid.)															
		Ru	Rh	Pd	Ag	Sn	Sb	Te	Cs	Os L	Ir L	Pt L	Au L	Pb L	Bi L
Phase 2	Heazlewoodite	21	24	30	35	51	50	64		107			62	58	49
Phase 3	Chalcocite	13	14	16	17	27	30	33	61						
Phase 4	Ni-Cu alloy	26	31	38	43	38	38	49				109	67		46
Phase 4a	Ni-Cu alloy	105	122	151	188		431			752	606	554	469		
Phase 4b	Ni-Cu alloy	48	56	66	74	95	119	152		363	265	254	194		
Phase 6	Heazlewoodite	75	86	106	130	251	315	406					156	145	122
Nuclear Microprobe analyses of the principal phases present in Area 2 (A ratio of 1.25 was used)															

Palladium: Pd was found present in all of the phases, its concentration decreased to trace quantities in the chalcocite phases (phase 3). Results can be found in table 3.3.1b and 3.3.2b. The highest concentration of Pd was found in phase 6 (heazlewoodite). This phase appears as a small bright semi-circle in image c figure 3.3.3, also clearly visible in the image is the distribution of Pd. In phase 6 Pd concentrates in the core and in phase 4 high concentrations were found on the rim of the Ni-Cu alloy. Figure 3.3.5 b (phase 1) also shows that Pd is distributed in the same way as in phase 4; it is a Ni-Cu alloy phase.

Lead and Bismuth: The highest concentrations of these elements were found in phase 6. Both Bi and Pb were absent from the Pt enriched phases (phase 4a and 4b). Minor concentrations of Pb were found in the phase 7. Results of these phases are presented in table 3.3.1b and 3.3.2b. Images d and e in figure 3.3.3 show the distribution of these two elements in the heazlewoodite phase.

Tin and Antimony: Both Sn and Sb were present in almost all of the phases only Sn was absent from the Pt rich alloys (phase 4a and phase 1a). Results in table 3.3.1b show that Sn and Sb are proportional to each other; Sn and Sb increase simultaneously. Sb was found to always have higher concentrations than Sn. The highest concentrations of these elements were found in phase 6, concentrations decreased in the chalcocite phases: these results are also shown in table 3.3.1b. Image e and f figure 3.3.4 show how these elements are distributed in the matte.

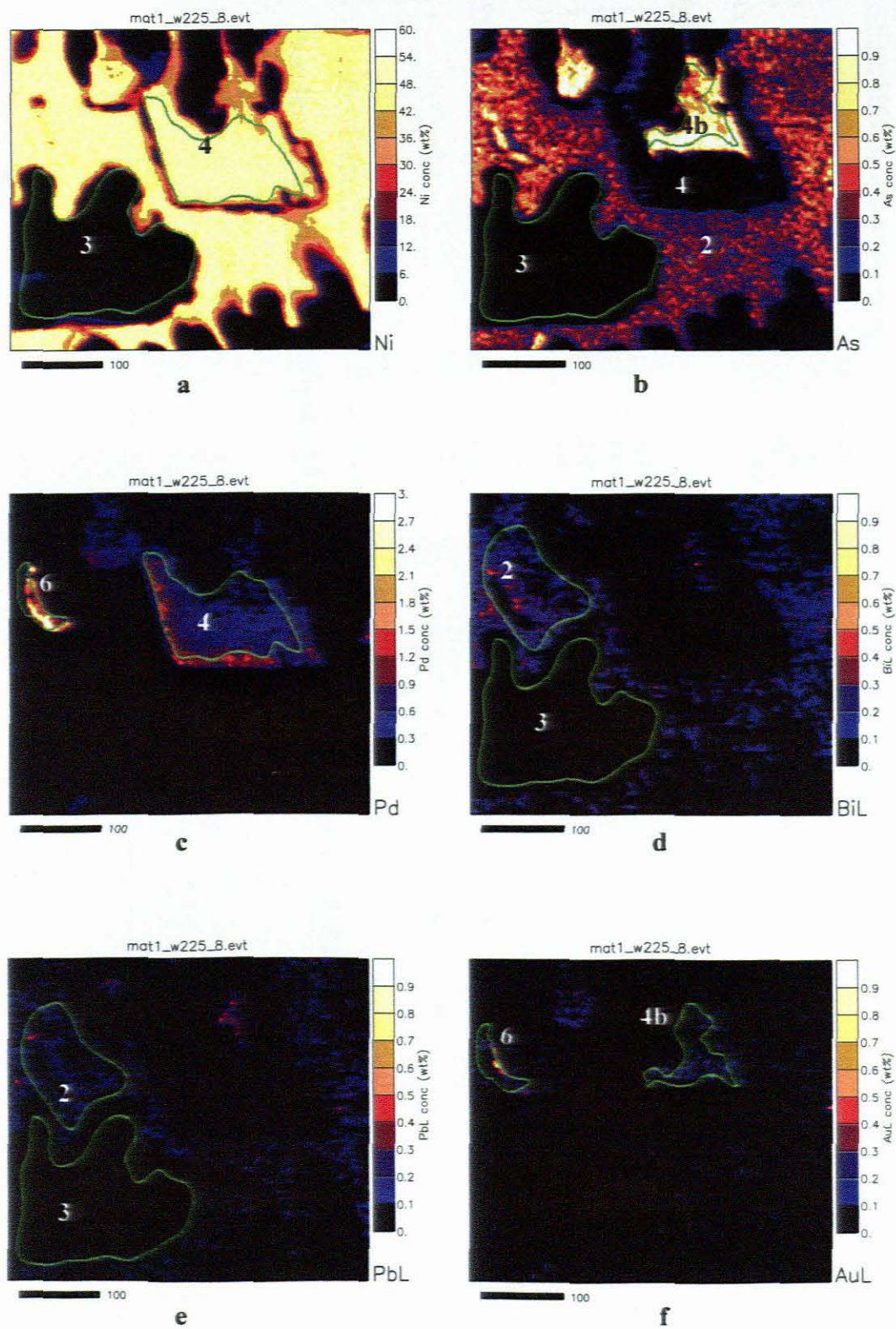


Figure 3.3.3 PIXE maps of spiked converter matte showing the distribution of As, Pd Bi Pb and Au in Ni-Cu alloy, heazlewoodite and chalcocite.

TABLE 3.3.2a

Concentration (ppm)		1	2	3	4	5	6	7	8	9	10	11	12
		Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ru	Rh
Phase 1	Ni-Cu alloy	46440	10050	670150	126760		14210					5600	3380
Phase 5	Ag alloy	10400	3550	200950	475080		2010	3170	<86.			<253.	<292.
Phase 7	Chalcocite	21240	4430	357360	447520	2750	998	1910				135	193
Phase 1a	Ni-Cu alloy	48740	11080	633800	128600		12300	<115.		149	<92.	9660	4500
Uncertainty (ppm)													
		Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ru	Rh
Phase 1	Ni-Cu alloy	417	407	2010	650		175					115	95
Phase 5	Ag alloy	643	409	2700	6840		156	139	39			126	122
Phase 7	Chalcocite	521	288	1900	13460	417	79	138				51	59
Phase 1a	Ni-Cu alloy	1171	531	2770	1190		224	121		75	39	307	290
Detection Limits (99% confid.)													
		Fe	Co	Ni	Cu	Zn	As	Se	Sr	Zr	Mo	Ru	Rh
Phase 1	Ni-Cu alloy	133	174	121	111		37					42	48
Phase 5	Ag alloy	396	481	554	254		80	74	86			253	292
Phase 7	Chalcocite	247	305	364	199	336	63	57				106	125
Phase 1a	Ni-Cu alloy	250	407	273	265		100	115		73	92	120	142

Nuclear Microprobe analyses of the principal phases present in Area 1 (A ratio of 1.25 was used)

TABLE 3.3.2b

Concentration (ppm)		13	14	15	16	17	18	19	20	21
		Pd	Ag	Sn	Sb	W L	Pt L	Au L	Tl L	Pb L
Phase 1	Ni-Cu alloy	5360	202	525	4820	<505.	6260	996		<106.
Phase 5	Ag alloy	2520	104540		<1030					839
Phase 7	Chalcocite	6030	901		734	<1060	428		<150.	336
Phase 1a	Ni-Cu alloy	4590			3580		28080			<273.
Uncertainty (ppm)										
		Pd	Ag	Sn	Sb	W L	Pt L	Au L	Tl L	Pb L
Phase 1	Ni-Cu alloy	122	45	61	160	227	162	72		55
Phase 5	Ag alloy	274	1770		439					235
Phase 7	Chalcocite	290	127		211	371	234		68	127
Phase 1a	Ni-Cu alloy	248			375		528			143
Detection Limits (99% confid.)										
		Pd	Ag	Sn	Sb	W L	Pt L	Au L	Tl L	Pb L
Phase 1	Ni-Cu alloy	54	58	65	81	505	178	126		106
Phase 5	Ag alloy	345	418		1030					199
Phase 7	Chalcocite	151	182		439	1060	348		150	150
Phase 1a	Ni-Cu alloy	175			500		480			273

Nuclear Microprobe analyses of the principal phases present in Area 1 (A ratio of 1.25 was used)

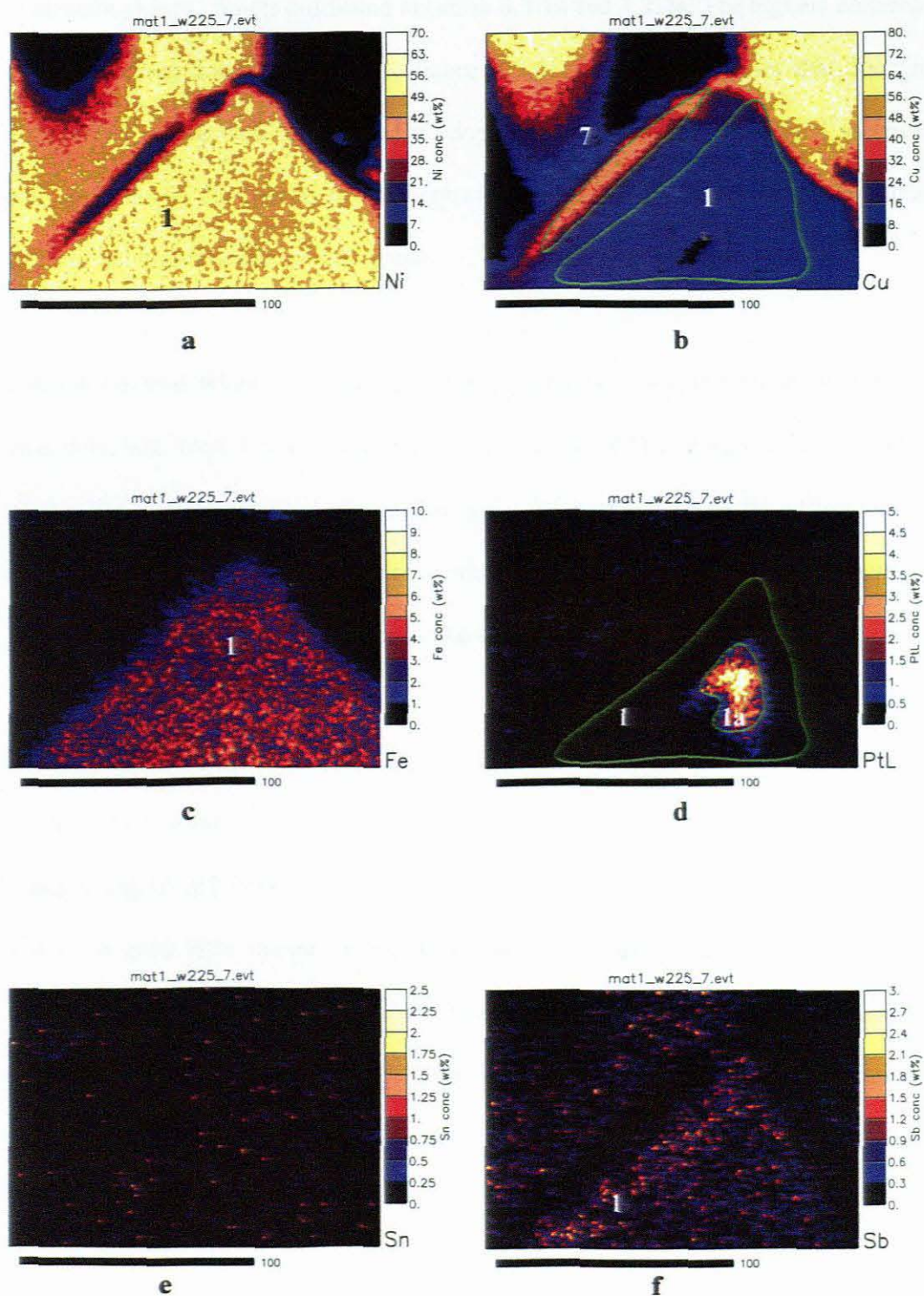


Figure 3.3.4 PIXE maps of spiked converter matte showing the distribution of Pt, Sn, Sb in Ni-Cu alloy.

Arsenic: Arsenic was present in all the phases with concentrations decreasing in the chalcocite phases, results are found in tables 3.3.1a and 3.3.2a. The highest concentration of Arsenic was found in phase 1, figure 3.3.5a. The image shows that As tends to concentrate in the core of the Ni-Cu alloy (phase1). Arsenic was found to have high concentration in the heazlewoodite (phase 2) regions, image 3.3.3b clearly shows its distribution in the heazlewoodite phase.

Ruthenium and Rhodium: The highest concentration of Ru and Rh was found in phase 1a and 4a, both these phases have high concentrations of Pt and they are found in the core of the Ni-Cu alloy (phase 1 and 4). Image 3.3.5 c and d show the affinity that these elements have for the core of the Ni-Cu alloy. Results of these phases are present in table 3.3.1b and 3.3.2a. The concentration of Ru and Rh decreased in phase 7.

Silver and Gold: Traces of Ag was found in all the phases, with the highest concentration being found in phase 5. Results of this phase is present in tables 3.3.2b. Image e figure 3.3.5 shows that Ag intensity increases towards the centre of phase 5. Traces of gold were present in the heazlewoodite phases but it was absent from the chalcocite phases, concentrations of Au increased in the Ni-Cu alloys. results are found in table 3.3.1b. Image f figure 3.3.3 shows how gold distributes its self in phase 4b and phase 6, phase 4b is rich in Arsenic and Pt.

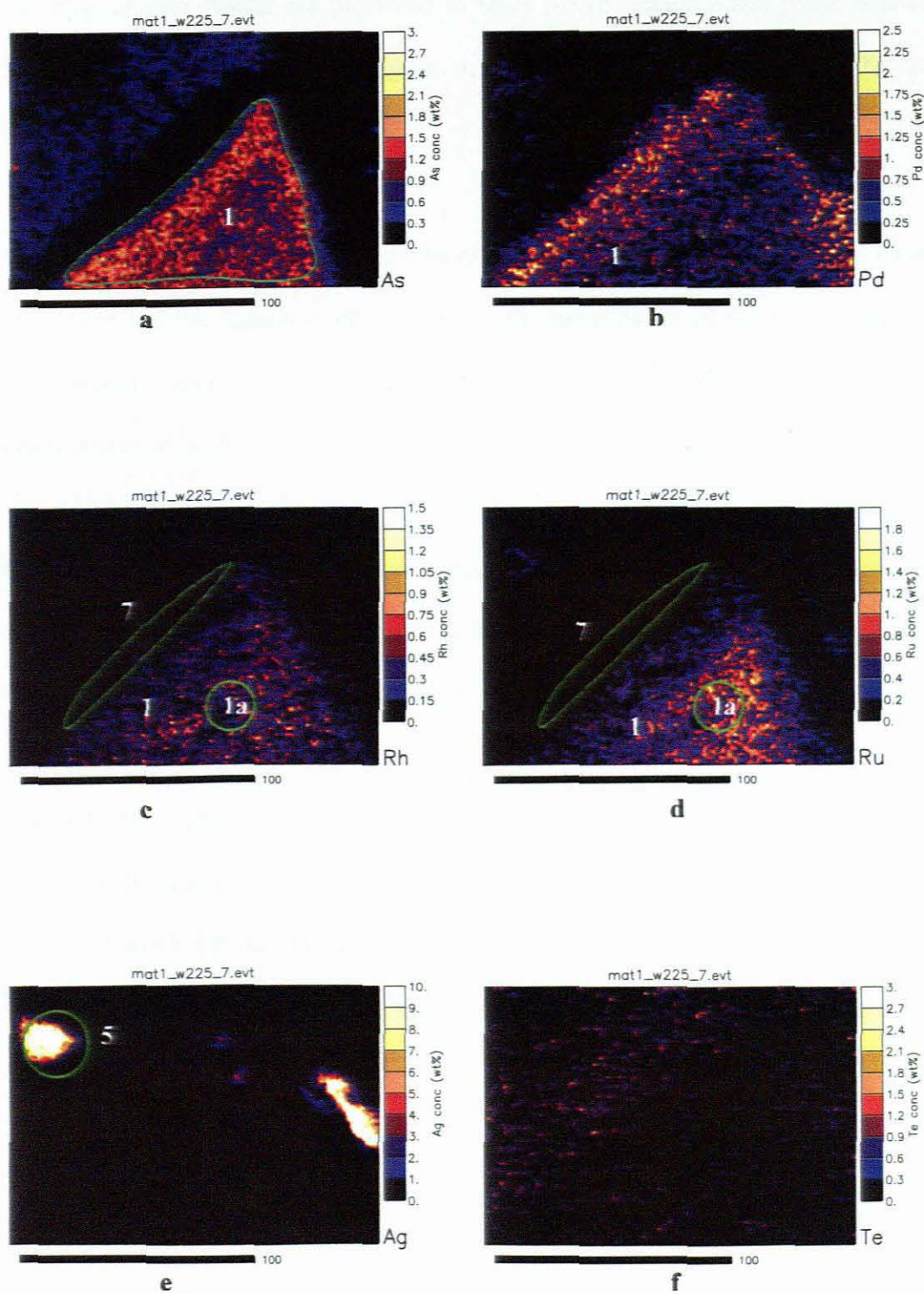


Figure 3.3.5 PIXE maps of spiked converter matte showing the distribution of As, Pd, Rh and Ru in Ni-Cu alloy, Ag in chalcocite and the distribution of Te in heazlewoodite.

Tellurium: Te was found present in most of the phases with concentrations decreasing in the alloy phases; results are presented in table 3.3.1b. Phase 2 and phase 6 have the highest concentrations of Te. Figure 3.3.5f shows the distribution of Te in the heazlewoodite phase.

Osmium and Iridium: The highest concentrations of Os and Ir were found in phase 4a, this phase has the highest concentration of Pt, some traces of Os were found in the heazlewoodite phase. Ir was only found present in the Ni-Cu alloy phase, results of this phase is present in table 3.1.1b.

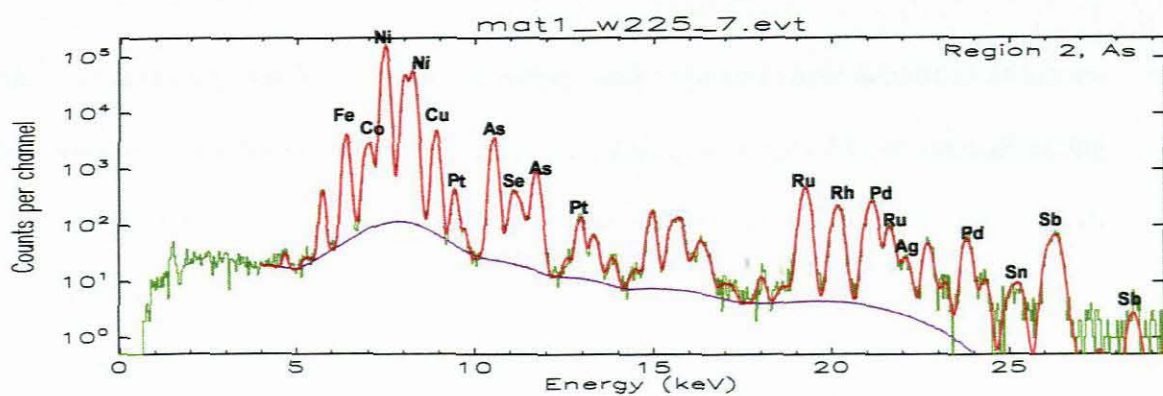
Chromium and Molybdenum: Low concentrations of both elements were detected, Cr and Mo were present in the heazlewoodite and chalcocite phases, results are presented in table 3.3.1a. Concentrations were too low to produce good images.

Zinc and Niobium: They were found in trace quantities in most of the phases, but no detectable concentrations were found in phase 5. The highest concentration of Zn was found in phase 7. Nb was found in low concentrations in the alloy phases, some traces of it was present in the heazlewoodite phase. Results of these phases are presented in tables 3.3.1a and 3.3.2a.

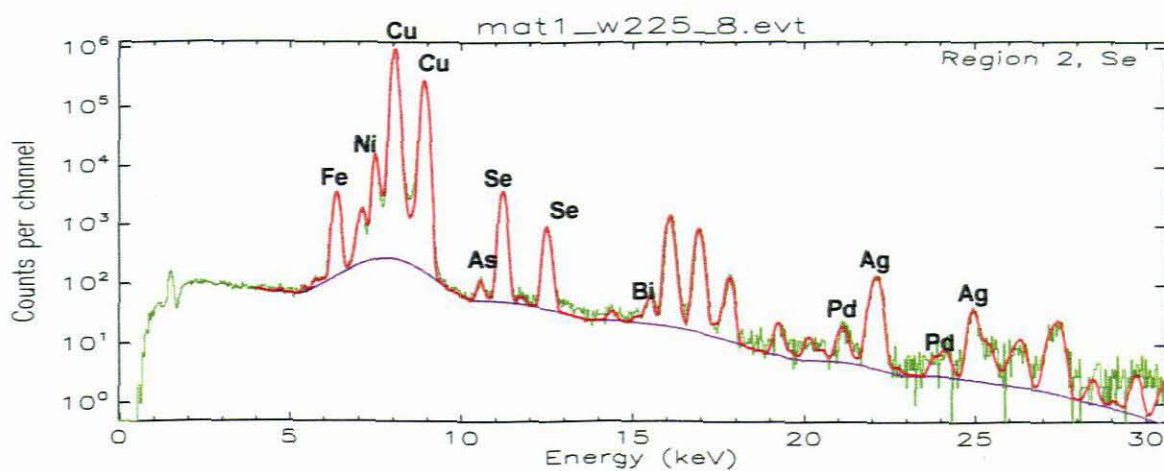
Zirconium and Cesium: Zr was found in phases where the Pt and Arsenic concentrations were very high, phases 4b and 1a are such phases. Cs was found to be present in the chalcocite phase only. Results of these phases are presented in tables 3.3.1a and 3.3.1b.

3.3.3 PIXE Spectra

Two spectra are presented in figure 3.3.6, one representing the Ni-Cu alloy phase and the other the chalcocite phase. Ni formed peaks of the highest intensity in the Ni-Cu alloy spectra, many other smaller peaks were also present in the spectrum as shown in figure 3.3.6. In the chalcocite spectra the highest intensity peaks were of Cu, smaller peaks for Se and Ag were also present.



Ni-Cu Alloy



Chalcocite

Figure 3.3.6 PIXE spectra of Ni-Cu alloy and chalcocite phases

3.3.4 Summary of analytical observations

This sample mostly consists of heazlewoodite, chalcocite and small quantities of alloys. The increase in heazlewoodite and Cu-sulphide phases has resulted in an increase in the Ni and Cu content of the sample. The alloy content in the sample also increased, which resulted in the increased concentration of the PGEs and Au. The highest concentrations of trace elements were found in heazlewoodite and chalcocite, the Ni-Cu alloys phases had the least. Heazlewoodite contains the most amounts of detectable elements and chalcocite contains the least. The highest concentration of trace PGEs and Au was found in heazlewoodite followed by chalcocite.

Ir and Os are definitely present in the Ni-Cu alloy phase, but in small concentrations, they were both found in the center of the alloy where the Pt concentration was high. Os was found in the heazlewoodite phase but in low concentrations. Both Bi and Pb concentrate in the Heazlewoodite phase, and Bi occurs as trace quantities in chalcocite. Ag was found in trace quantities in the alloy and heazlewoodite phase, but concentrates in chalcocite and occurs as small spots. Pd occurs as trace quantities in chalcocite and concentrates in the heazlewoodite and Ni-Cu alloy phases, concentrations were noticed to increase on the boundaries of the alloy. As and Co were found in trace quantities in chalcocite and at high concentrations in the heazlewoodite and Ni-Cu alloy phases. Se on the other hand had high concentrations in the chalcocite phases but was found in trace quantities in the Ni-Cu alloy phases. Arsenic concentrated mostly in the alloys followed by the heazlewoodite phase.

Both Sn and Sb have an affinity for heazlewoodite, Sn occurs in trace quantities in the Ni-Cu alloys and both occur in trace quantities in chalcocite. Sn and B show a positive correlation with Pb, when the concentration of Pd increased so did Sn and Sb. Both chalcocite and heazlewoodite hosted Ru and Rh but in trace quantities, concentrations increased in the alloy phases. Te occurs as trace quantities in the Ni-Cu alloy but concentrates in heazlewoodite

PIXE maps confirmed that Pt, Au, Ru, Rh, As, and Co tend to concentrate towards the core of the alloy phases. Maps also illustrated how As is distributed in the heazlewoodite phase. Maps showed the affinity that Se has for chalcocite followed by heazlewoodite. Se is absent in the Ni-Cu alloy phase. Pd was found in the alloy phases with the concentrations increasing towards the borders. Co was enriched in the Ni-Cu alloy phase, it was distributed evenly in both the alloy and heazlewoodite phase.

Maps showed low intensities of Te and Sb, but they can be seen present in the Ni-Cu alloy and Heazlwoodite phases.

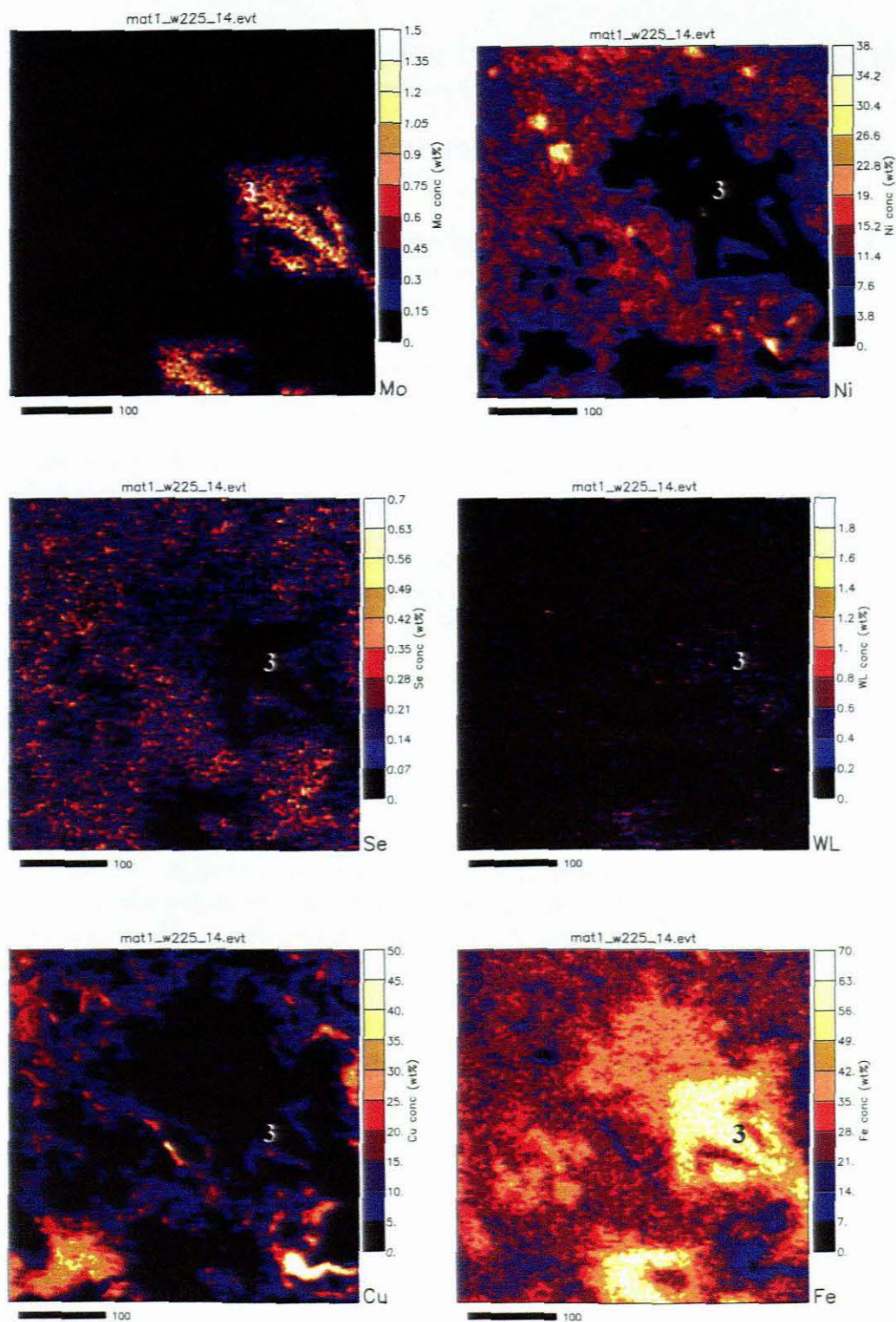
Chapter 4

4.1. Conclusion

- Oxidisation is the principle mechanism which influences the concentration of precious metals into an alloy phase.
- In both furnace and converter mattes the alloys were the main repositories for PGE's and Au. In the spiked converter matte the Ni-Cu alloy was found to also have the highest concentration of PGE's and Au.
- Trace PGE's and Au were found to concentrate in oxides and sulphides which had a high concentration in Fe or Cu relative to the Ni concentration.
- In furnace and converter mattes the most amounts of trace elements were found in the oxides and the sulphides which had high concentrations of Fe and Cu relative to the Ni concentration, sulphides such as pyrrhotite and chalcocite and the alloys contained the least. In spiked converter matte heazlewoodite and chalcocite contained the most amounts of trace elements and the Ni-Cu alloy phase contained the least.
- Bi, Pb and Se occurred in reasonable concentrations in the alloys that were found in furnace matte, but occurred as trace elements in the alloys which were present in converter matte; Bi and Pb were found in trace quantities in heazlewoodite and Se concentrated in chalcocite.

- Pd had a tendency to concentrate along the borders of the alloys that formed in the converting stage; high concentrations were also noticed in the heazlewoodite phases.
- The oxide which hosted Ru and Rh in trace quantities is trevorite, both elements were detected with concentrations below 300 ppm.
- Both Rh and Ru were present in pyrrhotite but in trace quantities. Pyrrhotite has 38 ppm Rh and 490 ppm Ru.
- Os and Pt occurred in trace quantities in some of the sulphides, Pt concentrated in core of most of the alloys, Ir on the other hand was found in low concentrations in alloys that contained high concentrations of Pt.
- Mo and W have an affinity for Fe oxides and were detected in reasonable concentrations in the magnetite phase, W occurred in concentrations several times less than Mo. These two elements occurred as oxides in the magnetite phase.
- The converting process reduced the concentration of both Ag and Au to trace quantities in most of the phases present in the converter matte, but there was an increase in concentration of Ag and Au in the spiked converter matte.

Appendix



The distribution of Se, W and Mo in magnetite

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