Characterization of nickel speciation in soils near Kalgoorlie, Western Australia
Abstract

Nickel has been identified as an element of concern in soils surrounding the city of Kalgoorlie, Western Australia. The area’s geology is naturally nickel-enriched, and there is also a large nickel smelter near the city. Nickel is of interest because all Ni compounds are carcinogenic and many cause respiratory diseases. This study attempts to characterize the nickel-hosting minerals in the soil, as they may have significant impacts on the health risk posed by inhalation or ingestion. Previous work in the area had come to different conclusions regarding the nickel mineralogy, which this study will endeavour to resolve. Also, this study will assess the degree of anthropogenic influence on soil nickel; this is of interest mainly due to the proximity of the smelter. Scanning electron microscopy (SEM), powder X-ray diffraction (XRD) and petrographic analysis of thin sections were used to accomplish these goals.

Results suggest that nickel is mainly hosted by nickel iron oxides, of the trevorite-magnetite solid solution. Nickel sulphides, likely pentlandite and haezlewoodite, likely also represent significant forms of nickel. Nickel carbonates, elemental nickel, adsorbed nickel, and nickel substituted in into iron oxides such as hematite and goethite were determined to be minor phases. Anthropogenic influence on soil composition was found to be very important near the smelter, in the form of nickelliferous slag particles in the soil. However, no significant anthropogenic influence was detected in soils in the city and background locations.
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1.0 Introduction

This study focuses on the town of Kalgoorlie, located in the Goldfields region of Western Australia. The town of about 28 000 people was founded in 1893 during a gold rush, and is still today in the heart of the region’s mining industry. It features a large open-pit gold mine and a nearby nickel smelter. Kalgoorlie is considered an asthma hotspot and has elevated levels of respiratory diseases and cancer (Lee et al, 2006; HDC, 2004). This has been attributed to the region’s history of mining activity as well as high airborne dust concentrations. The region has low precipitation and fine-grained red soils which are can easily become airborne. Although these soils contain various potentially toxic metals that could contribute to the health issues, nickel is of particular concern, as it is a well-documented carcinogen (Doll et al., 1970; Pederson et al., 1973). Nickel is naturally abundant in the bedrock of the region, and is also was released during the region’s long history of mining and smelting activity. Nickel occurs in a variety of mineral forms, some of which are more toxic than others (Grimsrud et al., 2002). While nickel has been studied before in this region, it has not been conclusively determined which mineral species host nickel in these soils (Drysdale, 2008; Segnit, 1976; -77). While it is expected that some of the nickel in the soil is of natural origin, the proximity of the smelter is also of concern and raises the possibility of significant levels of anthropogenically-introduced nickel, which may have important implications regarding mining and smelting regulations.

The objectives of my research were to identify and assess the abundance of nickel-hosting minerals present in the soil, and also to evaluate the degree of natural versus anthropogenic nickel mineralization. Surface soil samples were collected in 2008 by my supervisor, Dr. Heather Jamieson, and one of her graduate students, Mallory Drysdale, who was researching nickel bioaccessibility in the area. The samples were collected from locations near the smelter, in the city, and outside the influence of both city and smelter. These samples were analysed via several techniques in order to get more accurate results, including Scanning Electron Microscope (SEM), reflective light petrography, and X-ray Diffraction (XRD).
1.1 Geology

Kalgoorlie is located on the central eastern portion of the Yilgarn Craton, and overlies Archean-age rocks of the Southern Cross Domain and the Eastern Goldfields Superterrane. The craton covers most of Western Australia, and hosts a variety of ore deposits, including nickel, iron, gold, uranium, and Platinum Group Elements (PGEs). The basement rocks in the region consist of a mix of granite, gneiss and greenstone. The greenstone belts contain a mixture of metamorphosed mafic to ultramafic rocks, felsic volcanic rocks and metasedimentary rocks. This bedrock has been extensively weathered to thick layers of laterite (a type of Fe-rich, tropically-weathered soil), which in turn is overlain by recent alluvial, colluvial and aeolian deposits (Tille, 2006).

The local geological unit, the Kalgoorlie Terrane, consists of felsic volcanics overlying mafic lava sequences and intruded by mafic-ultramafic sills. These formations are found near surface 55km south of Kalgoorlie in the famous mining center of Kambalda, where they host large nickel deposits. In Kalgoorlie, the bedrock nearest the surface is the metasedimentary Black Flag sequence, which overlies the Paringa Basalt, an ultramafic basalt unit. These formations are intruded by a set of mafic sills, including the Golden Mile Dolerite, which hosts the majority of the area’s gold deposits (Phillips, 1986). The bedrock at Kalgoorlie is buried under 40-50m of relatively homogeneous overburden, developed both from weathering of the bedrock and from aeolian input (Sergeev & Gray, 2001). The local geology near Kalgoorlie is shown below in Figure 1.
The Kalgoorlie area consists of an extensive plateau, with flat to undulating plains and small valleys. Duricrust, claypans and playa lakes are common in the area. The soils in the area are very fine-grained and have a characteristic reddish colour, derived from their high iron oxide content. The soils are characterized by extensive areas of calcareous loamy earths, red loamy earths, red deep and shallow loamy duplexes (Tille, 2006).

A typical profile of the regolith near the city consists of a thin gravel layer overlying a 1-2m thick layer of calcareous clay-rich red soil with ferruginous granules. The soil transitions to a
sandy clay with sand lenses, and decreasing carbonate concentrations with depth (Drysdale, 2008). A thin mica-rich layer marks the unconformity between the sandy clay soil and the underlying clay-rich saprolite, which extends down to bedrock (Lintern, 2004).

While the underlying bedrock affects the regolith mineralogy of Kalgoorlie to some degree, there is also very significant influence from aeolian transport at the surface. Common surface soil minerals include iron oxides such as hematite and goethite, as well as kaolinite, quartz, and carbonate minerals. The soil pH is generally above neutral, and can go above 9 in some areas due to high carbonate content (Anand & Paine, 2002; Drysdale, 2008).

Evaporated lakes, or playas, are common in the area, and there are several near the city of Kalgoorlie. These differ somewhat from the surrounding soils; while the lake beds have similar mineralogy to the surrounding soils, evaporation of saline waters results in the precipitation of minerals like halite and gypsum, which can form large crystals near the surface and have a significant influence on soil chemistry (Clarke, 1994).

1.3 Kalgoorlie Nickel Smelter

The Kalgoorlie Nickel Smelter, owned by BHP Billiton, is located 12km south of Kalgoorlie along the Goldfields Highway 94. The ore processed here is shipped by rail from surrounding nickel deposits, including Kambalda to the south, and Leinster and Mt Keith to the north. The ore consists of massive and disseminated nickel sulphides, hosted by komatiites or within olivine cumulates (Barnes, 2004). The primary ore minerals are pyrrhotite and pentlandite, with minor chalcopyrite and pyrite (Hill et al., 2004).

The Kalgoorlie Smelter is an Outokumpu-type flash smelter, a design developed in Finland that is similar to the INCO smelter in Sudbury. The nickel sulphide ore is mixed with pre-heated oxygen-rich air, which causes the oxidation of iron and sulfur, separating the nickel-rich matte and slag. A converter then further oxidizes the matte, producing more iron-oxide slag. In
this type of smelter, the converter and the furnace are combined (Apelt et al., 1995; Tan & Neuschutz, 2001).

The smelter currently processes 100 000-110 000 tonnes of granulated nickel matte per year, with an average nickel content of 68%. Renovations in 1993 increased its production capacity from 540 000 to 750 000 tonnes per year (Apelt et al., 1995).

The slag produced by the smelter has the potential to contribute nickel to the soils in and near the city of Kalgoorlie, and by extension become inhaled by the residents as windblown dust. Segnit (1976) analysed the composition of the smelter’s converter slag, and found pyroxene, olivine, wustite, magnetite, and a few sulphides. He found accretions on the heart of the flash furnace which were predominantly magnetite with minor olivine, which was similar to the composition found for the flash furnace slag. He also found nickel ferrite and nickel iron olivine on the walls deposits. He determined that the final composition of the slag contains about 0.45-0.6% nickel. Further work by Segnit in 1977 analysing different mattes produced by the smelter found that the matte from the flash furnace contained a mixture of pentlandite, haezlewoodite, and minor metallic nickel. The electric furnace matte was mainly an iron-nickel alloy with pentlandite, while the converter matte consisted mainly of haezlewoodite and metallic nickel.

1.4 Previous research and possible nickel hosts

This project builds on Mallory Drysdale’s graduate research. In her paper, she suggested, based on SEM and sequential extraction evidence, that nickel was mainly hosted by sulphides, although a particular sulphide mineral was not mentioned (Drysdale, 2008). This was not the major focus of her research, so she did not look into it much further. After she finished her paper, Dr. Jamieson decided to pursue the matter further and analyzed the samples via X-ray Absorption Near-Edge Structure (XANES); the results are shown below in Figure 2. Based on this, she and her colleague Dr. Jeffery Warner arrived at a completely different conclusion: that
nickel was primarily hosted by nickel ferrite, also known as trevorite, a mineral with the formula NiFe$_2$O$_4$. Resolution of this discrepancy between data became the basis for my research.

Both are quite reasonable possibilities. Nickel sulphides are the major type of ore found in the area, and so could be released into soils either by weathering or as waste from the smelter and mining operations. On the other hand, iron oxides are very abundant in the soils, giving them their characteristic reddish colour. As such, it is plausible that some of them contain nickel, and as mentioned earlier, Ni-Fe oxides were known to be produced in the smelter. This section will discuss all nickel-bearing minerals that were hypothesized to possibly be present in these soils.

![Figure 2: XANES spectra for the soil samples, compared to reference spectra for various nickel species. Sample spectra seem to best match that of the mineral trevorite, NiFe$_2$O$_4$ (Data collected by H. Jamieson and processed by J. Warner).](image)

Trevorite, NiFe$_2$O$_4$, is an unusual iron oxide mineral. It is a spinel that is rarely found in nature in its pure form, but forms a solid solution series with the much more common mineral magnetite, Fe$_3$O$_4$, with nickel substituting for iron. Thus, even if pure trevorite is not present, a nickel ferrite mineral with an intermediate composition somewhere in the solid solution could be a candidate. This possibility is supported by Segnit’s 1976-77 work mentioned earlier, and
also by evidence by Hudson and Travis (1981) of nickel iron oxide-dominated hydrothermal veins in the Mount Clifford deposit in Western Australia (about 200km north of Kalgoorlie). These veins were typically zoned from “cores of nickeloan magnetite to rims of ferroan trevorite”, demonstrating a natural example of the nickel ferrite solid solution. Li and his colleagues (2009) also identified magnetite in slags from Vale Inco’s Sudbury nickel smelter, and found that most of the Ni existed as oxides, with a minor portion as sulphides.

We also theorized that the nickel might be hosted by goethite, FeO(OH), and/or hematite, Fe$_2$O$_3$. These two iron oxides are common minerals found in lateritic soils such as this, and both minerals are capable of incorporating a variety of elements, including Ni, as impurities in their crystal structure, via substitution for iron (Singh and Gilkes, 1992; Elias et al, 1981; Zeissink, 1969). In a study of an Indian laterite, Som and Joshi (2002) quantified the degree of substitution in goethite, finding Ni:Fe ratios ranging from about 1:50 to 1:26. Singh et al. (2000) found that up to 6 mol% Ni can substitute for Fe in the hematite structure. While only small amounts of nickel can thus substitute in the crystal structure, these minerals could nonetheless be an appreciable source of nickel given their abundance in these soils.

In terms of nickel sulphide minerals, there are several possibilities. One is pentlandite, (Ni,Fe)$_9$S$_8$, a common sulphide which is an important ore mineral in the nickel deposits in the Kalgoorlie area. Another is pyrrhotite, Fe$_{(1-x)}$S (x = 0 to 0.2) which often contains nickel, substituting for iron, and is another major ore mineral. There are other nickel sulphides which are less common, including millerite, NiS, which is also found in the area’s nickel deposits, haezlewoodite, Ni$_3$S$_2$, as well as violarite, FeNi$_2$S$_4$, which forms by weathering and oxidation of pentlandite (Dunn & Howes, 1996).

Another possibility is that nickel might be hosted as nickel carbonates. This possibility was suggested by the XANES results, and carbonates are a common phase in these soils.

A final possibility is that nickel is simply adsorbed onto the surfaces of soil grains, rather than incorporated into a particular mineral structure. Small particles – such as these very fine grained soils – can develop charged surfaces through a variety of mechanisms, enabling them to attract cations, like nickel, and bind them weakly. Different minerals have different adsorption affinities, although Fe and Mn hydroxides are among the highest.
A phase stability diagram for the Fe-O-Ni system is shown below in Figure 3. Trevorite (outlined in red) is stable at neutral to high pH and in slightly reducing to oxidizing conditions. At low pH, aqueous nickel species are stable.

Figure 3: Phase diagram for the Fe-O-Ni system at ambient conditions (Modified from Thompson et al., 2000). The dotted lines represent the redox potentials for hydrogen (lower) and oxygen (upper) saturation at one standard atmosphere. The domains that are doubly labeled for the case of two component alloys (I believe this paper was intended for metallurgical purposes).
1.5 Toxicological implications of nickel speciation

Speciation of any element has important effects on its toxicity. Speciation can be expressed in different ways. In ionic/aqueous form, many elements have different valance forms, which are separate species. Nickel has several oxidation states, including Ni$^0$, Ni$^+$, Ni$^{3+}$, and Ni$^{4+}$, but the most common form is Ni$^{2+}$ (Greenwood & Earnshaw, 1997; Nieboer et al., 1984). Elements can also form complex ions in aqueous solutions, each of which have different properties and are considered a species. Finally, elements can have a variety of solid mineralogical species, which is the focus of this study.

Each mineral has its own unique physical and chemical properties, which affect its toxicity to humans and other organisms. One important property is solubility. The higher a mineral’s solubility, the more nickel will be released when it enters the body, and thus enter cells and cause damage. Minerals are also only stable under certain pH and oxidation conditions. For example, from Figure 3, it is evident that trevorite is only stable at neutral to alkaline and oxidizing conditions; if it were exposed to a more acidic or reducing environment, it would break down. Thus, a mineral that is stable in the soil may not be stable once it enters the body, or may dissociate if soil conditions changed.

Elemental nickel is insoluble in water at ambient conditions. However, nickel compounds may be water soluble. Nickel chloride is most water soluble; 553 g/L at 20°C, to 880 g/L at 99.9°C. Nickel carbonate has a water solubility of 90 mg/L, whereas other nickel compounds, such as nickel oxide, nickel sulphide and nickel tetra carbonyl are water insoluble, limiting their potential harm (Lenntech, 2009). However, nickel adsorbed onto particles is bound only weakly, and can easily be dissolved. Nickel sulphides are also considered more toxic than other insoluble nickel compounds, due to their potential to oxidize and become soluble and their ability to react with epithelial cell fluid. The mineral heazlewoodite, Ni$_3$S$_2$, commonly referred to as nickel sub-sulphide, is considered the most toxic form of nickel (Oller et al. 1997).

All nickel species are considered potential carcinogens, although, as mentioned, some are more potent than others. Other respiratory diseases caused by nickel include asthma and
allergic reactions. These are due to high accumulations of nickel in the lungs, which cause an inflammatory reaction (Ligeiro de Oliveira et al., 2004). Both soluble and insoluble nickel compounds can cause inflammation, although Benson et al. (1986) found the reaction to be faster for soluble compounds, as they are immediately dissociated. Nickel carcinogenesis and respiratory diseases are also the result of nickel that manages to enter the cell nucleus and cause genetic mutations; this process tends to occur with insoluble nickel, like haezlewoodite. Very high nickel concentrations can also result in precipitation of nickel compounds in the lungs, permanently diminishing lung function (Lehert, 1990).

Nickel toxicity is also dependant on the path of exposure. Inhalation represents the major route of nickel exposure, with gastrointestinal and dermal absorption being less common routes. Absorption of nickel by cells is generally due to the soluble Ni\(^{2+}\) ion, but sparingly soluble crystalline nickel compounds may be phagocytosed by cells and then gradually dissolve (Costa & Mollenhauser, 1980; Abbracchio et al., 1982). These sparingly soluble compounds have also been known to increase in solubility in various bodily fluids (Ung & Furst, 1983; Kuehn & Sunderman, 1986).

Much research has studied the toxicity of inhaled nickel particles, mainly focussing on occupational exposure (Doll et al., 1970; Pedersen et al., 1973). It has been found that workers in the nickel industry have higher than normal incidences of nasal and respiratory cancers. Grimsrud et al. (2002) assessed the toxicity of different nickel species, analysing levels of lung cancer by exposure. The results are shown below in Figure 4. Unfortunately, little to no research has been done to assess the toxicity of specific nickel minerals like trevorite, pentlandite and pyrrhotite.
Figure 4: Smoking-adjusted odds ratios for lung cancer by cumulative exposure to four forms of nickel in a nested case-control study of Norwegian nickel-refinery workers observed between 1962 and 1995. The graphs show odds ratios for exposure variables categorized by quintiles among exposed controls. Odds ratios are plotted according to the median exposure value among cases and controls within each category. Each graph shows the odds ratio on a logarithmic scale unadjusted for the other forms of nickel. The vertical bars show 95% confidence intervals. (from Grimsrud et al., 2002)
2.0 Methodology

Mallory Drysdale and Dr. Jamieson collected soil samples from 13 locations near the smelter, around the city, in playa lakes, and geogenic (background) soil areas near the city. Only undisturbed, natural soils (with the exception of smelter soils) were taken, all overlying the same geologic formation (except playas), at least 20m from the road in the case of non-city soils, and all accessible to the public. At each location, samples were collected using plastic trowels from the top 5cm of soil, which was assumed to be the portion most likely to become airborne or come from an airborne source. Three sub-sites were taken at most locations to control for small scale variability. No freezing or drying of the samples was required. Samples are described below in Table 1.

Mallory then performed sequential extractions using different leaches of various pH’s and compositions to solubilize elements in different phases in the soils, as well as in-vitro pulmonary bioaccessibility tests using a simulated lung fluid. This was done to determine the mobility, origin, bioaccessibility and transport of elements and compounds. The sequential extraction results indicated found that most of the nickel was bound in the oxidizable fraction, which she interpreted as sulphides, consistent with her limited electron microprobe analysis results (Drysdale, 2008).

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample Location</th>
<th>Easting</th>
<th>Northing</th>
<th>Location Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Playa 1</td>
<td>381973</td>
<td>6442014</td>
<td>Evaporite playa along highway, north of Norseman</td>
</tr>
<tr>
<td>2a</td>
<td>Smelter East</td>
<td>356357</td>
<td>6583783</td>
<td>1.4km east of smelter along smelter road, relatively undisturbed terrain</td>
</tr>
<tr>
<td>2b</td>
<td>Smelter East</td>
<td>356374</td>
<td>6583776</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>Smelter East</td>
<td>356368</td>
<td>6583805</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>Smelter/Slag</td>
<td>356307</td>
<td>6583991</td>
<td>East of smelter next to fence around slag piles.</td>
</tr>
<tr>
<td>3b</td>
<td>Smelter/Slag</td>
<td>356315</td>
<td>6583979</td>
<td>Collected due to presence of small metallic particles at surface, potentially slag.</td>
</tr>
<tr>
<td>3c</td>
<td>Smelter/Slag</td>
<td>356317</td>
<td>6583991</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Playa 2 pit</td>
<td>352067</td>
<td>6585482</td>
<td>Old pit off side-road used for dirt biking. NW of smelter</td>
</tr>
<tr>
<td>5a</td>
<td>Railway</td>
<td>354583</td>
<td>6584226</td>
<td>Taken from side-road along railway north of the smelter.</td>
</tr>
<tr>
<td>5b</td>
<td>Railway</td>
<td>354586</td>
<td>6584223</td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>Railway</td>
<td>354588</td>
<td>6584218</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>School</td>
<td>354158</td>
<td>6595873</td>
<td>Small natural park next to primary school on Lionel Street.</td>
</tr>
<tr>
<td>6b</td>
<td>School</td>
<td>354113</td>
<td>6595917</td>
<td></td>
</tr>
<tr>
<td>6c</td>
<td>School</td>
<td>354133</td>
<td>6595892</td>
<td></td>
</tr>
</tbody>
</table>
Table 1: Sample Locations and Site Descriptions (from Drysdale, 2008).

<table>
<thead>
<tr>
<th></th>
<th>Location</th>
<th>Site Code</th>
<th>Site Phone</th>
<th>Site Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>7a</td>
<td>Kalgoorlie West</td>
<td>352251</td>
<td>6598139</td>
<td>Small undeveloped area next to large filled park in residential community.</td>
</tr>
<tr>
<td>7b</td>
<td>Kalgoorlie West</td>
<td>352245</td>
<td>6598126</td>
<td></td>
</tr>
<tr>
<td>7c</td>
<td>Kalgoorlie West</td>
<td>352230</td>
<td>6598150</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>Superpit</td>
<td>355683</td>
<td>6593586</td>
<td>Small undeveloped patch of land in a small park next to the railroad tracks. Directly off the main street in downtown Boulder.</td>
</tr>
<tr>
<td>8b</td>
<td>Superpit</td>
<td>355683</td>
<td>6593593</td>
<td></td>
</tr>
<tr>
<td>8c</td>
<td>Superpit</td>
<td>355699</td>
<td>6593580</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Playa 2</td>
<td>359501</td>
<td>6582148</td>
<td>Evaporite playa southeast of the smelter.</td>
</tr>
<tr>
<td>10a</td>
<td>South Kalgoorlie</td>
<td>352248</td>
<td>6595152</td>
<td>Large undeveloped field attached to new residential neighbourhood.</td>
</tr>
<tr>
<td>10b</td>
<td>South Kalgoorlie</td>
<td>352253</td>
<td>6595161</td>
<td></td>
</tr>
<tr>
<td>10c</td>
<td>South Kalgoorlie</td>
<td>352241</td>
<td>6595178</td>
<td></td>
</tr>
<tr>
<td>11a</td>
<td>Geogenic 1</td>
<td>347571</td>
<td>6591405</td>
<td>All undeveloped land along highway west of Kalgoorlie.</td>
</tr>
<tr>
<td>11b</td>
<td>Geogenic 1</td>
<td>347557</td>
<td>6591382</td>
<td></td>
</tr>
<tr>
<td>11c</td>
<td>Geogenic 1</td>
<td>347573</td>
<td>6591368</td>
<td></td>
</tr>
<tr>
<td>12a</td>
<td>Geogenic 2</td>
<td>343507</td>
<td>6587993</td>
<td></td>
</tr>
<tr>
<td>12b</td>
<td>Geogenic 2</td>
<td>343520</td>
<td>6587994</td>
<td></td>
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<tr>
<td>12c</td>
<td>Geogenic 2</td>
<td>343506</td>
<td>6587969</td>
<td></td>
</tr>
<tr>
<td>13a</td>
<td>Geogenic 3</td>
<td>349346</td>
<td>6593222</td>
<td></td>
</tr>
<tr>
<td>13b</td>
<td>Geogenic 3</td>
<td>349331</td>
<td>6593243</td>
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<tr>
<td>13c</td>
<td>Geogenic 3</td>
<td>349360</td>
<td>6593254</td>
<td></td>
</tr>
</tbody>
</table>

It was decided that the bulk of my research would focus on the SEM, so we needed to decide how best to analyze the samples with this method. Nickel is ferromagnetic, and the iron oxide magnetite also forms a solid solution with trevorite (NiFe$_2$O$_4$), which was predicted to be present by previous XANES analysis, and pyrrhotite is also magnetic, so it was hypothesized that the nickel in the soils could be concentrated by separating the magnetic fraction of the soil.

To accomplish this, a hand-held magnetic separator was used. This device has a plunger that could be depressed to magnetize its surface. A small quantity of sample was laid out on weigh paper. The separator was then magnetized, gently pressed against the soil, and moved around in a circular motion for a few seconds. During this process, a small amount of magnetically-charged soil would adhere to the separator. The separator was then lifted over a fresh piece of weigh paper and demagnetized, dropping the soil. This process was repeated several times until the amount of soil picked up by the separator became negligible. It should be noted that earlier separation attempts involved simply slowly passing the separator above the sample, rather than directly pressing against it. This method was deemed much less
effective, probably because internal cohesion between the very fine-grained particles counteracted the fairly weak magnetic force generated by the separator.

As a considerable portion of the soil seemed to be weakly magnetic, this initial separate was then refined further. In this step, the separator was passed over the soil, similarly as mentioned above. In this case, the method was successful because of the much lower volume of material and its refined nature. In doing so, characteristic black magnetic particles would adhere to the separator, leaving behind the weakly magnetic reddish soil. After the whole process was repeated to a satisfactory degree, the black magnetic separates were combined and placed in a labelled vial.

All samples produced a small quantity of magnetic material, on the order of a few percent of the total sample. Although the amount was not precisely quantified, it was observed that the samples closer to the smelter produced more magnetic material than those in the city and background locations. Since Mallory determined that total soil nickel was highest near the smelter (Figure 5), this seemed to support the conclusion that the majority of the nickel was being extracted in the magnetic separation procedure.

These separates were then later made into SEM stubs. The stubs were then carbon-coated for use under high-vacuum, for improved resolution; the carbon counteracts charge build-up from the electron beam of the SEM. As well as stubs for magnetic separates of most of the samples, two additional stubs were created for sample MD-03, one which represented the remaining soil after separation of the magnetic portion, and one which represented the soil as a whole, including the magnetic portion. These were used for comparison purposes.

![Figure 5: Total nickel concentrations at different sample locations (from Drysdale, 2008).](image-url)
3.0 Results

3.1 Scanning Electron Microscopy

The scanning electron microscope (SEM) was a valuable tool for the characterization of these soils. While the instrument is often used to visualise sample morphology, we were more interested in the backscattered electrons. These electrons have interacted with sample atoms, and thus can give us chemical information. In the resulting image, areas where the average atomic number is high appear brighter, relative to those with low average atomic number. Nickel is relatively high on the periodic table, so we could easily visually identify nickel-rich grains, based on their brightness. Another advantage of the SEM is that when the electron beam interacts with the sample, X-rays are produced, unique for each element. In this manner, we could confirm which elements were present in a grain of interest, and quantify their relative abundances. However, it cannot give the exact mineralogy, so it leaves much to interpretation, a significant shortcoming of the methodology.

One important result of SEM analysis is the observation of very distinct slag particles present in some of the samples, ranging in size from about 15-50µm. It was observed that the slag particles were only found in samples near the smelter. These particles are smooth and spherical in shape, and show textures characteristic of rapid cooling, such as spinifex (Figure 6). Sample MD-05, next to the smelter railroad (which was itself made of slag, and used to transport ore, matte, and slag), had the highest slag content (~30-50%); most of these spherules contained nickel, and a few contained sulfur as well.

Figure 6: Spherical slag particle, showing cooling textures.
All the grains analysed (both natural and slag) were high in oxygen, iron, silicon, and aluminum, with smaller amounts of magnesium, calcium, and potassium common as well (roughly in that order of abundance). A significant number of the bright particles also contained nickel and/or sulfur (Figure 7).

The stub made from the MD-03 post-magnetic separation soil also contained a few nickeliferous grains (one with S and two without); it also contained no slag. The unseparated soil MD-03 sample contained a few grains with both Ni and S, and had some slag. No nickel or sulfur were found in the city or background soils.

All grains scanned were converted to weight and molar percentages; the overall average composition was about 57.7% O, 19.9% Fe, 5.8% Ni, 2.8% S, 4.8% Al, 6.8% Si, 1.4% Mg, 0.5% Ca, 0.1% K, and some grains had trace (<1%) Mn, Cr, and Ti. Molar S:Ni ratios were calculated for grains containing both elements. Values ranged from 0.02 to 14.87; discounting the few very high outlier values (essentially no Ni), the mean was 0.62 and median 0.42.

Figure 7: X-ray absorption spectrum showing the elemental composition of a sample grain hosting Ni.
The results for all samples are summarized below in Table 2.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th># of grains analysed</th>
<th>Natural grain composition</th>
<th>Slag present?</th>
<th>Slag composition</th>
<th>Comments/observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD-02</td>
<td>10</td>
<td>Several grains with Ni only, one with some S, and one with both Ni and S</td>
<td>Yes, fairly common</td>
<td>One grain with S and Ni, rest barren</td>
<td>Range of grain shapes; most grains have smaller grains stuck to surface</td>
</tr>
<tr>
<td>MD-03</td>
<td>6</td>
<td>Two grains with very high S, two with both Ni and S high</td>
<td>Yes, fairly common</td>
<td>All barren</td>
<td>Grains are somewhat cleaner than MD-02; one of the high-S grains was crystalline and disintegrated under beam (very weak)</td>
</tr>
<tr>
<td>MD-03 (mag. depleted)</td>
<td>8</td>
<td>Two grains with very high S, two grains with Ni, and one with both Ni and S</td>
<td>None</td>
<td>n/a</td>
<td>Bimodal distribution in grain size. Few bright grains, and most present were only bright in some areas (patchy appearance)</td>
</tr>
<tr>
<td>MD-03 (full soil)</td>
<td>8</td>
<td>Two grains with both S and Ni, two with just Ni and one with just S</td>
<td>Some</td>
<td>Three with Ni</td>
<td>Similar to MD-02... perhaps incomplete magnetic separation for MD-02?</td>
</tr>
<tr>
<td>MD-04</td>
<td>3</td>
<td>One with just S</td>
<td>Yes, many</td>
<td>All barren</td>
<td>Very 'clean'-looking sample. Slag spheres show nice cooling textures.</td>
</tr>
<tr>
<td>MD-05</td>
<td>40</td>
<td>7 with high S, 4 with Ni, and one with both both Ni and S</td>
<td>Yes, very many (30-50%)</td>
<td>Most contained just Ni, a few with both Ni and S or barren</td>
<td>Scan biased towards slag. One spot with some bright “flakes”, very rich in Ni, interpreted as elemental Ni.</td>
</tr>
<tr>
<td>MD-06</td>
<td>3</td>
<td>Only S found</td>
<td>None</td>
<td>n/a</td>
<td>No grains of interest.</td>
</tr>
<tr>
<td>MD-07</td>
<td>0 (several were analysed but no scans were saved)</td>
<td>No Ni or S</td>
<td>None</td>
<td>n/a</td>
<td>No grains of interest.</td>
</tr>
<tr>
<td>MD-08</td>
<td>2</td>
<td>No Ni or S</td>
<td>Few</td>
<td>Barren</td>
<td>No grains of interest other than the occasional small slag grain.</td>
</tr>
<tr>
<td>MD-13</td>
<td>3</td>
<td>No Ni or S</td>
<td>None</td>
<td>n/a</td>
<td>Most grains large and rounded. Very few bright grains. Some grains with Mn or Cr.</td>
</tr>
</tbody>
</table>

Table 2: Summary of SEM observations. Samples in bold are from near the smelter; normal text samples were taken in the city; italics indicate background samples. All grains also contain Fe, O, Si, Mg, Al ± Ca, K.
3.2 Petrography

Mallory made polished thin sections for samples MD-02, 03, 05, 06, and 08. They were analysed with reflective light microscopy to see if they could shed any further clues as to the nickel mineralogy. Reflected light is useful for studying minerals like oxides and sulphides, which are opaque in transmitted light. The grains which are likely of interest appear shiny and silvery under reflected light.

The majority of the bright grains were hematite. Some of the hematite grains also had inclusions of magnetite, with textures indicating that magnetite was being altered to hematite. Many of the hematite grains themselves were being altered to iron oxides/hydroxides, which are the dominant soil minerals. A few grains of pyrite, which were brighter and yellower than the magnetite/hematite grains, were also found in most samples. Pyrite was the only sulphide mineral identified. Figure 8 illustrates some of the minerals and textures observed.

Slag particles were also visible in thin section. Although they were often difficult to differentiate from the background grains, it was observed that they seemed more abundant in smelter soil samples than those from the city and background locations, confirming SEM results.
Figure 8: Minerals and textures of the Kalgoorlie soil samples under reflected light microscope. A) Bright grain of hematite. B) Hematite with a Fe-hydroxide alteration rim, center left, and pyrite, brighter, center right. C,D) Lathe-like alteration of magnetite (brownish) to hematite (yellow in C, grey in D). E) “Blebby” alteration of magnetite (inner grey-brown mineral) to hematite (silvery) to Fe-hydroxides (outer, reddish-brown mineral). F) Slag spherule (upper center) and magnetite with a hematite alteration rim (lower center).
3.3 X-ray Diffraction (XRD)

XRD allows one to identify the mineral composition of a sample based on x-ray peak data, unique to the crystal structure of each mineral. Sample MD-06 was analysed to test the usefulness of this method (scan shown below in Figure 9). The scan indicated that the soil was composed primarily of quartz, hematite, and kaolinite. It also identified calcite, ankerite, and nullaginite, three carbonate minerals, the latter containing Ni. However, these fits are not very strong, and offer only a tentative identification.

Figure 9: Powder XRD spectra of sample MD-06, showing quartz (red lines), iron oxide (blue), ankerite (Fe-carbonate, green), calcite (Ca-carbonate, brown), kaolinite (teal), and nullaginite (Ni-carbonate, pink).
4.0 Discussion

The SEM scans for all grains contained a variety of elements, as mentioned earlier, suggesting that the grains are composites of multiple minerals, including quartz, iron oxides (hematite, goethite, etc), and kaolinite. This interpretation is supported by the XRD results, and the fact that most grains are fairly similar in appearance, and rounded and lacking a distinct crystalline shape that would be indicative of just a single mineral.

It was concluded that the main Ni-hosting mineral was trevorite, or more accurately, likely an intermediate phase in the trevorite-magnetite solid solution. There are several lines of evidence to support this. The majority of Ni-bearing grains analysed by SEM contained Ni, Fe and O, and were devoid of S. The petrography results indicated that pyrite was likely the main sulphide mineral, and also demonstrated the existence of magnetite (the literature is inconclusive whether trevorite differs significantly from magnetite optically). These near-surface soils are exposed to oxidizing conditions, so they would be expected to be dominated by oxide minerals; they are also particularly iron-rich. These conditions are conducive to the formation and stability of iron oxides like magnetite/trevorite. However, they would also lead to the oxidation and hence destabilization of reduced sulphide minerals, which is evidenced by the fact that relatively few pyrite grains were found in thin section. The literature also supports this conclusion; magnetite has been shown to form naturally in these soils, and is also a component in the slags from this smelter and others, and trevorite was found naturally in nearby deposits, on the Kalgoorlie smelter walls and in Sudbury smelter slags (Hudson and Travis, 1981; Segnit, 1976-77; Li et al., 2009).

The fact that there were several SEM-scanned grains that had Fe and S but no Ni, also supports the existence of pyrite (pure pyrrhotite being the only other iron sulphide; for the purposes of this study, it doesn’t really matter which mineral it is). It was then concluded that the occasional grain containing Fe and both Ni and S likely were simply grains that included both trevorite and pyrite. Molar S:Ni ratios for these grains were also calculated, and for most of grains were quite low, suggesting that even if Ni-sulphides did exist, other nickel species would also be present (since the lowest S:Ni ratio in nickel sulphides is 0.67, in haezlewoodite).
Nonetheless, it is possible, even probable, that there are some nickel sulphides in the soil, although in lesser amounts than trevorite. Although it was interpreted that the Fe-Ni-S grains were composites with trevorite and pyrite, it is possible that at least some of them contained nickel sulphides or nickel iron sulphides. This conclusion is supported by the fact that nickel sulphides are the ore minerals for the smelter, so it is possible that some remain in the slag, or are present naturally in the soils, since they constitute an important part of the bedrock. Segnit (1976-77) also found small amounts of unidentified sulphides in the smelter slag, possibly nickelliferous, and also identified haezlewoodite and pentlandite in some of the mattes. This supports the possibility that at least some of the nickel in the slag fraction of the soils is in sulphide form, and if so, that it is probably as haezlewoodite and/or pentlandite. This is of potential concern, as haezlewoodite is highly carcinogenic (Oller et al., 1997).

Nickel carbonates, likely nullaginite, Ni$_2$(CO$_3$)(OH)$_2$, may also be present as a minor nickel species in the soils. XANES analysis suggested there might be some nickel carbonate, and the XRD results weakly fitted a nickel carbonate to the peak pattern. SEM results showed a small calcium peak for most grains, suggesting the presence of calcite (CaCO$_3$). If calcite is found in the soils, it is possible that nickel carbonate may as well. Dissolution tests were also performed, where 10% HCl was applied to soil samples; HCl reacts with carbonates, releasing CO$_2$. All soils tested produced a quite strong reaction, indicating the presence of carbonate minerals. However, as the carbon data from the SEM is influenced by the carbon-coating, as well as any organic matter in the soils, it is difficult to accurately quantify the importance of carbonate as a Ni-hosting species. Sequential extraction results from Mallory’s thesis, however, indicate that carbonate-bound Ni represents less than about 5% of the total Ni in most samples (see Figure 10, below) (Drysdale, 2008).

Another concern with the SEM is that it would not likely be able to detect nickel in low concentrations, such as if it were hosted by substitution in the crystal structure of minerals like goethite and hematite, or adsorbed onto surfaces of grains. It is predicted that some Ni is hosted by these two cases, since other studies in similar soils have found Ni substitution, and cations like Ni$^{2+}$ have maximum adsorption rates at high pH’s like those found in these soils. However, adsorption and substitution in this manner are likely of lesser importance, in light of
numerous grains detected by SEM which host large quantities of Ni in other minerals, as discussed above. Furthermore, Ni in this form would likely not be influenced as much by the smelter, while results indicate that Ni concentrations decrease significantly away from the smelter, suggesting that smelter-sensitive phases are the dominant Ni hosts. Mallory’s sequential extraction results also support the conclusion that adsorbed Ni is of very minor overall importance.

As mentioned earlier, slag particles were found in considerable abundance in soils near the smelter, but are rare in city or background samples. These slag particles were also found to be important Ni hosts in smelter soils. This suggests that there is significant anthropogenic nickel input to the smelter soils, but influence is limited in city and background samples. This is likely due to the higher mass of the slag particles inhibiting them from becoming airborne for large distances. This observed trend, coupled with Mallory’s finding that total Ni shows a similar trend, also implies that the majority of the nickel contained in the smelter soils was hosted by the slag. This in turn supports the conclusion that the primary Ni host (at least in smelter soils) is trevorite, as most slag spheres with nickel contained iron and oxygen, but no sulphur.

Some of the slag particles were also barren of Ni. If it is assumed that the slag melt from which they crystallized was of more or less uniform composition, and therefore the freshly-cooled slag being uniform as well, the presence of barren and nickeliferous slag would suggest that Ni is leachable from the slag at ambient conditions, with the barren slag representing older, more weathered material. This scenario is reinforced by petrographic evidence showing magnetite/trevorite altering to hematite, likely releasing some or all of the Ni contained in the process. If this is indeed the case, the slag would represent a potential source of contamination to the local groundwater.

A final Ni species observed was elemental nickel, found as small flakes in sample MD-05. As this was the only observed occurrence, it is likely of very minor significance.

Although my conclusions confirm the XANES results, they differ from Mallory’s conclusion that Ni was mainly hosted by sulphides. She determined this based on interpretation of EMPA data and her sequential extraction results. It is of interest to determine why her conclusions differed from the XANES results and the results of this study.
The SEM/EMPA data is simple enough to explain, as the data is inherently inconclusive and open to interpretation. The grains she saw containing Fe, N, and S, she interpreted as simply nickel iron sulphides, while I concluded them to be primarily grains containing trevorite and pyrite. Her sequential extraction results are more difficult to explain. The dominant phase is ‘oxidizable’ Ni, which she interpreted as sulphide-bound Ni. The next most abundant form was ‘reducible’ Ni, interpreted as oxide-bound Ni (Drysdale, 2008). However, these phase labels differ from those used in the outline of her sequential extraction procedure, so it is difficult to determine which minerals are actually included in these groupings. The data discrepancy may be due to interpretation issues, or perhaps even a problem in the procedure itself (e.g. some oxide-bound Ni dissolving during the step intended only to dissolve sulphides). Further analysis may shed more light on this matter.

![Sequential extraction results for soil samples](image)

**Figure 10: Sequential extraction results for soil samples (Drysdale, 2008).**

It should also be noted that mineralogical interpretations could be biased in favour of trevorite by the magnetic separation process. However, the full-soil stub prepared for MD-03 showed no significant differences to the magnetically-separated samples, suggesting that the effect of such bias to be minimal. Also, the magnetically-depleted stub showed a distinct lack of slag, strengthening evidence of trevorite in the slag, as well as confirming the effectiveness of the technique in separating it.
5.0 Conclusion

While there is a degree of uncertainty in the results, it was concluded that nickel in the Kalgoorlie soils is hosted predominantly by trevorite (or an intermediate phase in the trevorite-magnetite solid solution). It is probable that nickel sulphides, likely pentlandite and haezlewoodite, are also significant nickel species. Nickel carbonates, substituted and adsorbed nickel, and elemental nickel are also likely present, but as very minor phases. SEM and petrographic analyses indicates the existence of significant amounts of anthropomorphitic slag particles in the soils near the smelter, much of which contains appreciable amounts of nickel. However, very little slag was found in city and background soil samples, suggesting that anthropogenic enrichment of soil nickel is limited to the immediate area surrounding the smelter, possibly due to the heavier mass of the slag particles preventing them from being windblown. Due to the lower nickel concentrations in the city and the fact that nickel is predominantly in the less toxic oxide form, risk to city residents’ health due to nickel exposure is minimal, although exposure to anyone in the vicinity of the smelter may be higher. Evidence also suggests that the nickel minerals in the soil may be unstable, releasing nickel into the environment, which may pose a threat to groundwater quality.
6.0 Summary of key findings

- Nickel iron oxide (trevorite) is likely the main Ni-hosting mineral in the Kalgoorlie soils, with nickel sulphides (pentlandite and/or haezlewoodite) being of secondary importance.

- Nickel carbonates (nullaginite), adsorbed, substituted and elemental nickel may also be present in small amounts.

- Anthropogenic influence on soil nickel composition near the smelter is high, and is represented by spherical slag particles; the abundance of slag (and overall nickel) decreases dramatically away from the smelter, and is virtually absent in city and background soils.

- It is unlikely that soil nickel minerals pose a serious health risk to residents of Kalgoorlie.
7.0 Acknowledgements

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