

Characterisation of Tailings at Prohibition Mine Site, Waiuta, Westland

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Abstract

The Prohibition Mill gold mine, located within the Birthday Reef of the Reefton Goldfield, was operational from 1938 until 1951. It is situated near the town of Waiuta in the Victoria Forest Park, Westland and is now administered by the Department of Conservation. An exclusion zone is in place on the processing site where extremely high arsenic values (up to 40 wt%) have been identified due to the historic processing and roasting of arsenopyrite-rich ore. This paper reports on a field portable XRF survey of an area outside the exclusion zone, to extend knowledge of the wider site for management and potential remediation purposes. Samples were also collected for further analysis of samples using XRD and SEM. The survey has identified four hotspots outside the exclusion zone which have elevated As, Pb, Zn, Cu, and Hg, however these four extensions to the metal-enriched site at Waiuta have relatively low levels of potentially toxic metals compared to the adjacent exclusion zone. The historic tailings identified in one of the hotspots are the focus of this study. The tailings are predominantly composed of hematite and quartz with relatively uniform As levels of 4000-9000 ppm. SEM analysis of the tailings shows that the distribution of As is not uniform and is closely associated with the iron oxides and minor sulphides which have not been completely roasted.

Keywords: Arsenic, Prohibition Mill, gold mine, environment, tailings, historic site.

Introduction

The main processing and roasting site at the Prohibition Mill gold mine has previously been characterised by Haffert (2009); following her work an exclusion zone has been put in place around the processing mill and roaster site (Fig. 1). The worst of the contaminated area has As residues up to 40 wt%. Government funding of \$3 million has been allocated to undertake a clean up the Prohibition Mill and Alexander Gold Mine sites, also situated in the Reefton Goldfield which has As values of up to 38 wt% (Malloch, 2015). In this study, we report on an additional area of processing tailings at the Prohibition site that has not previously been quantified.

For environmental purposes it is important to understand the chemical processes that occur in mine tailings over longer time periods as they are long term features and once capped are difficult to study. The tailings at Prohibition Mill mine site have been left undisturbed and unremediated for over 60 years and therefore provide an analogue for the potential processes that can occur within these systems in modern mines. In particular, the Prohibition processing system involved roasting of sulphide minerals to release the included gold. This is broadly similar to the pressure oxidation process that is currently being used at Macraes gold mine in Otago (Craw, 2003). Therefore, examination of the Prohibition tailings should provide some insight into the long-term stability of pressure oxidation tailings material at Macraes.

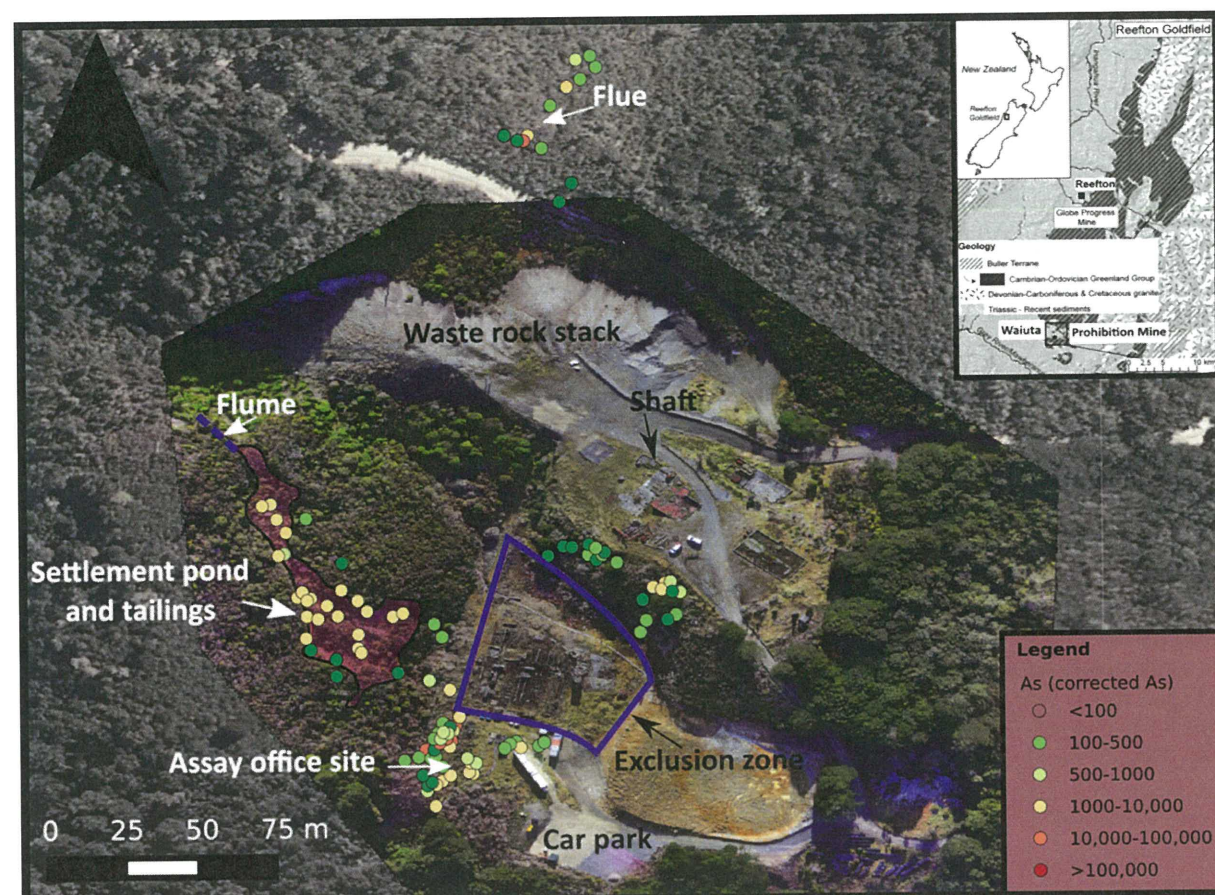


Figure 1. Site map with the regions of mine site and location map (inset modified from Haffert & Craw, 2005).

Site description

The Birthday Reef that formed the source for the ore, which was processed at Prohibition site was As rich. The ore at Prohibition Mill was primarily auriferous quartz containing 2-2.5% sulphides. The ore contained both free gold and refractory gold within the sulphides, with the analysis of the sulphide concentrates at Blackwater having a ratio of approximately quartz:pyrite:arsenopyrite of 3:2:1 (Hutton, 1947).

The main roaster area at the Prohibition site has the greatest levels of arsenic, and that is now in the exclusion zone (Fig. 1). Following further investigation of the Prohibition Mill site an extension of the contaminated area has been discovered by Department of Conservation staff. Characterisation of this area was undertaken as part of this study through a FP-XRF survey on site, and laboratory XRD and SEM analysis of samples. This study focuses on the tailings settling pond and tailings discharge areas (Fig. 1). These areas are difficult to access. They are partly revegetated from natural colonisation, and many parts of the tailings deposits are water-saturated.

The area consists of an original settling pond which was built from wooden boards and 44 gallon drums filled with the red tailings material. The settling pond is ~10 x 15 m while the spillover from the pond covers an area of ~30 x 35 m with a corridor of tailings heading NW ~50 m long and 5-10 m wide (Fig. 1). There are also tongues of tailings which run into low spots in the surrounding regenerated forest. The tailings have elevated As, Pb, Cu, and Zn, with As being the principal element of environmental concern.

The corridor of tailings connects into where there was a flume leading off the edge of the bank. The remaining footprint of the flume is ~50 m long and is thought to have been aerial from the processing plant over the settlement area (pers. comm. Jim Staton) where it joins in to the flume which is still present. The base of sections of the flume has red tailings and a non-roasted quartz based sand with As up to 20,000 ppm in places. Towards the NW end the flume contains organic soil with elevated As levels up to 3000 ppm in places.

The tailings vary in depth from a few cm to >50 cm. The forest has regenerated over much of the area, but there is less cover over the main tailings area which can be seen as the shaded area in Fig. 1. The regenerated forest predominantly consists of manuka, kanuka and gorse with brown-top grass mix growing directly into the tailings as well as several varieties of mosses which also form platforms for shrub growth. The paste pH of the tailings is 4.8-5.3 while the organic soil in the flume has a paste pH of 3.7-5.

Results

Field-portable XRF

Errors for the FP-XRF have many causes, with the two of concern in this study being heterogeneity of the substrate and moisture. The reading window for the XRF is 1 cm wide. Therefore variation on this scale can give errors of several thousand ppm. The recommendations of Haffert (2009) of ensuring the smoothest surface possible and removing any loose debris overlying the substrate was done. All of the red tailings and soil samples collected for these surveys had moisture contents between 23-44% which exceeds the threshold of 20% where the moisture content is minimal (EPA, 2007). Over 20% moisture content will yield an underestimation of As concentration (Fig. 2).

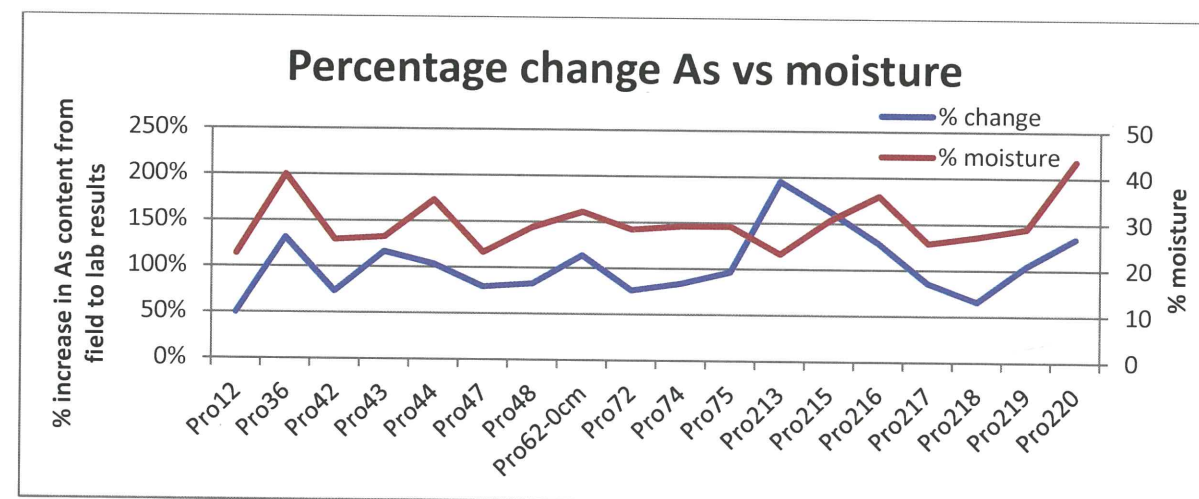


Figure 2. Graph showing the percentage increase in the As level from the field readings, which are wet and have not been homogenised, to the Hills Laboratories XRF As levels, which are dried and homogenised (blue line) compared to the percentage of moisture in the sample (red line).

To deal with this underestimation a calibration curve (Fig. 3) was created using dried, homogenised samples that were analysed by Hills Laboratories. A correction factor of 0.57 for the tailings has been calculated and applied to field readings. The 40 cm depth value was excluded as an outlier.

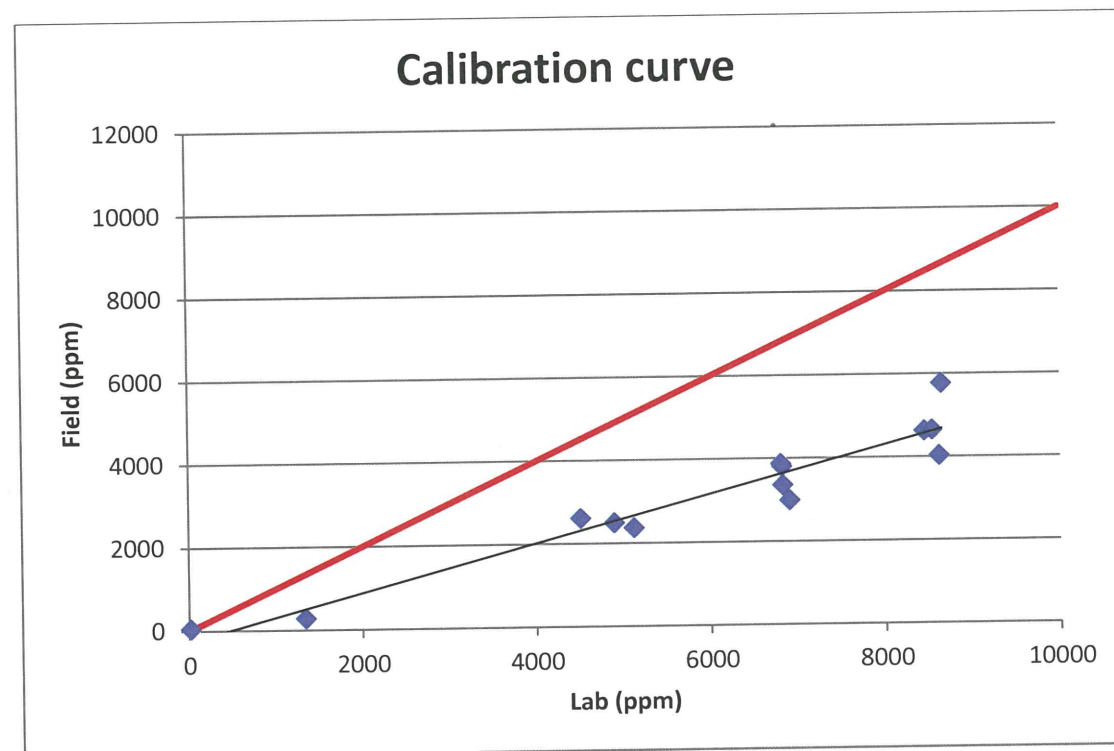


Figure 3. FP-XRF calibration curve for correction from the field values to the laboratory values for the tailings at Prohibition Mill Mine site giving a correction factor of 0.57. The red line is a 1:1 line between the field and laboratory readings.

The tailings material has broadly uniform grain size (sand) with a small amount of layering containing increased quartz sand visible to the eye. The concentration of As is variable on the 1 cm scale of the FP-XRF analyses throughout the area and with depth. The XRF survey undertaken over 2 days showed that the tailings have As levels between 4000-9000 ppm, with the exception of a very wet sample, with 64% moisture content, taken from 40 cm depth with an As level of 14,700 ppm. The flume has elevated As up to 3000 ppm in the organic soil with tailings present in some of the length of the flume, especially towards the processing site. There is also non-roasted milled debris in the flume which recorded the highest As in this area of 10,800 ppm. Elsewhere the soil surrounding the red tailings has a much lower level of As in the 10-100's of ppm.

X-Ray diffraction

The XRD shows that the composition of the tailings material is uniform, with the primary minerals present being hematite and quartz. In the flume, used to discharge waste beyond the tailings area, there was a non-red sandy waste with an As value of up to 20,000 ppm (field corrected). This waste does not contain hematite and is primarily quartz in composition.

Scanning electron microscopy

Under the SEM the iron oxides (predominantly hematite) appear as porous grains which are brighter than the surrounding grains of quartz (Fig. 4). Some of the iron oxide grains have maintained their euhedral shape from their parent pyrite or arsenopyrite throughout the roasting process. The porous texture has arisen because the roasting process has driven off volatile S and As from the sulphide grains. There are rare scattered relict sulphides still present, which appear to be completely encased in quartz.

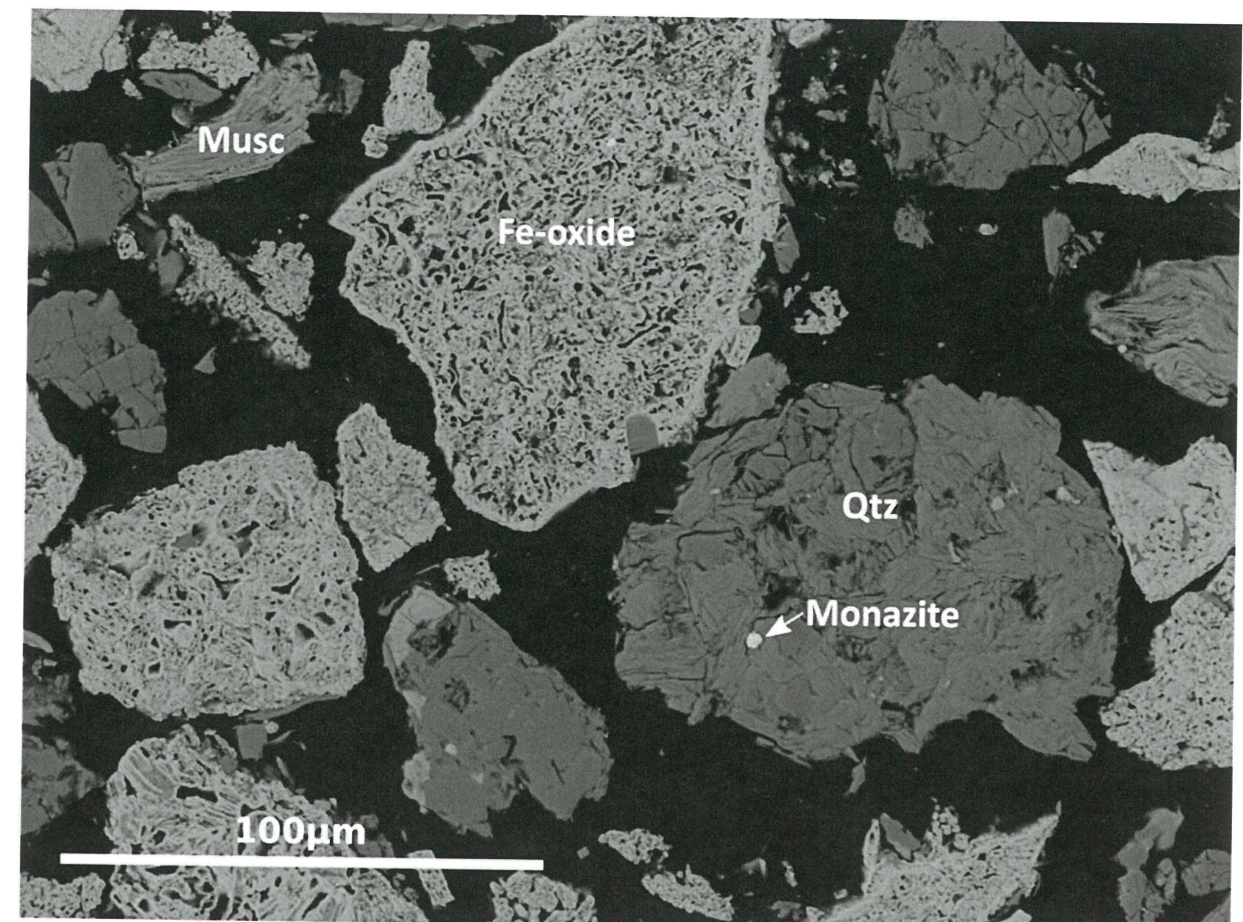


Figure 4. SEM image of the tailings with iron oxides (light grey, porous), with associated quartz, muscovite and monazite present.

The SEM images in Fig. 5 shows closer views of tailings iron oxide bearing grain. The upper image shows a quartz grain with iron oxide inclusions which have high porosity as a result of the roasting process. The oxidised grains all occur near the edge of the quartz host. In contrast, the pyrite grain which has not been oxidised is fully encapsulated within the quartz grain and has not been exposed to the oxidising effects during the roasting process. Distance from the oxidising front is one of the factors affecting incomplete oxidation during roasting of ore of this type (Puktunc et al., 2006). The shape of some of the pyrite grain inclusions in the quartz appears to have been maintained as can be seen by the euhedral nature of some of the oxides. The lower image in Fig. 5 shows textural zonation with different amounts of decomposition during roasting.

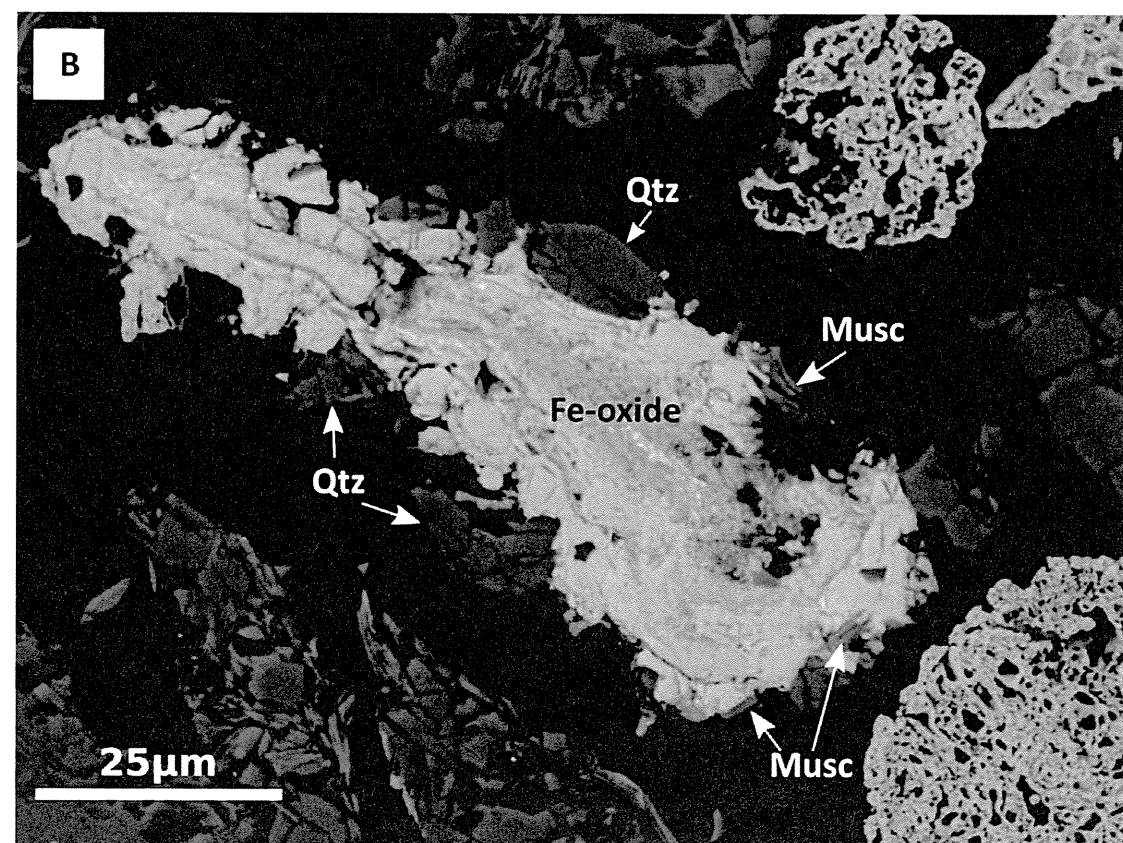
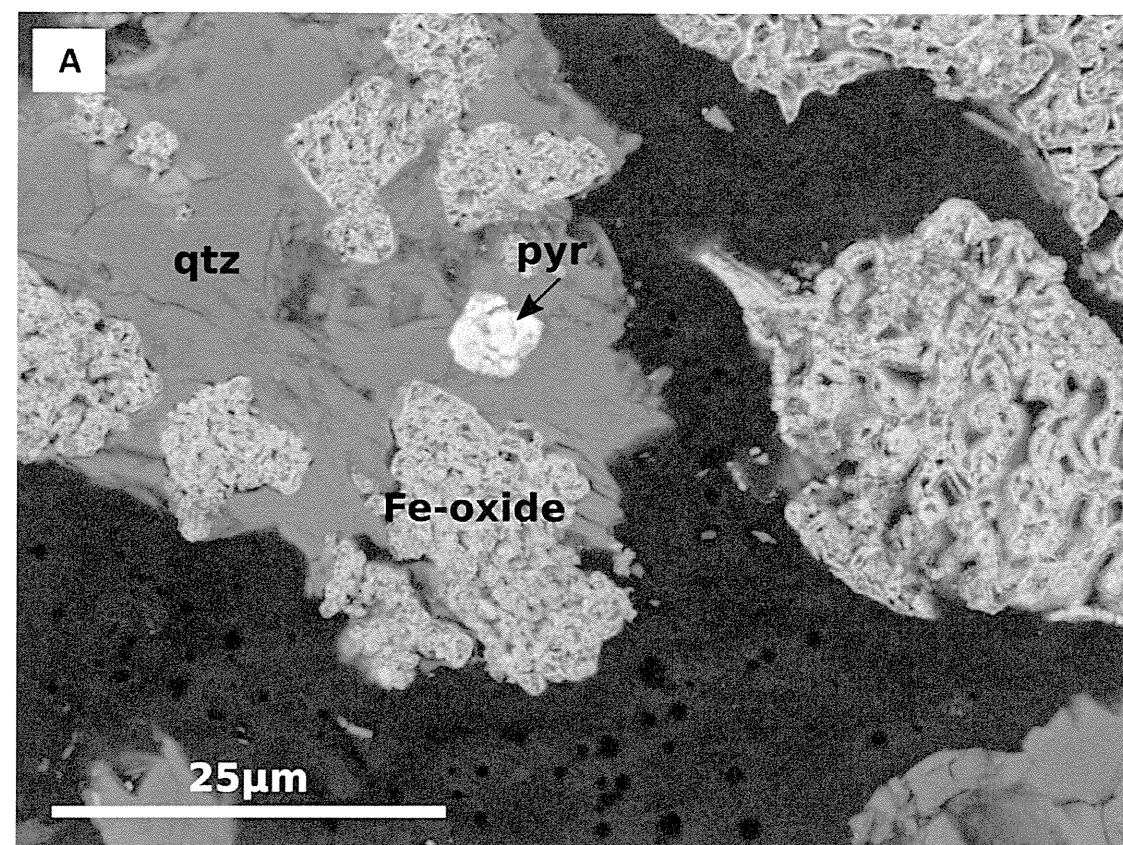


Figure 5. SEM backscatter images of tailings. (a) Image of a quartz grain (left) within the tailings with embedded iron oxide and pyrite. Other more porous oxidised grains are to right. (b) Image of a zoned oxidised sulphide grain.

SEM energy dispersive analytical examination shows that the As is not evenly distributed throughout the tailings material, but is irregularly enriched in some iron oxide grains. SEM detection limit for As in this material is ~0.5 wt%, and some of the dispersed As in the iron oxides is below this detection limit. The grain in Fig. 6 is zoned and mostly oxidised to iron oxide but has a rim of As rich (up to 15 wt% As) Fe-As-S oxide compound.

Relict quartz and muscovite are also present mostly on the outer rim of the grain in Fig. 6, and where there are holes in the grain. The muscovite can be seen in the K and Al maps while the quartz is seen in the Si map.

The oxidised arsenopyrite grain in Fig. 7 contains sites with up to 15 wt% As which shows up in the As element map as bright red. The grain is zoned with higher As zones especially towards the centre of the grain. Comparing the As and Fe maps it can be seen that the areas of higher As concentration correspond to lower Fe concentration. In the centre of the grain is an oxidised pyrite grain, which shows as a void in the As map.

Discussion and conclusions

The sandy tailings at Prohibition site consist of two principal components: hematitic pseudomorphs of roasted sulphide grains, and quartz grains with other silicates. Quartz is the dominant component of the tailings. It is unlikely that all the quartz would have been passed through the roaster during historic processing, as this would have required substantial additional energy input. We assume that a sulphide concentrate was roasted, and the residue after cyanidation was remixed with the quartz-rich component prior to discharge to their present position. This is the process undertaken at the modern Macraes mine (Craw, 2003).

Our results with field portable XRF show that the As contents of the tailings show a broadly uniform range of between 4000-9000 ppm. The As variations occur laterally and vertically within the tailings piles, on the centimetre to metre scales. The variations in As contents probably reflect variations in the proportions of sulphides in the original ore, and incomplete mixing during discharge.

On the microscopic scale the As is seen to be much less evenly distributed. As is located almost exclusively in iron oxide grains, either as Fe-As-S oxide compounds of variable composition, or as rare relict sulphide grains encapsulated in quartz. These Fe-As-S oxide compounds are common products of mineral processing oxidation processes (Paktunc et al., 2006) and occur in the tailings discharged at the modern Macraes mine (Craw, 2003). SEM analysis shows that some iron oxide grains can contain As up to 15 wt%, whereas other grains have As contents below the SEM detection limit (~0.5 wt%). The highest As contents occur in grains that show the least porous texture. This may be a result of incomplete volatilisation of the As (and S) during roasting.

There is decreased As contents towards the outside of many iron oxide grains. This may be a result of more complete volatilisation of As on the rims during roasting. Alternatively, the As on the outsides of the grains may have been leached from the grains during the subsequent 70 years of wet storage on the site. However, Fe-As-S compounds from roasting processes are deemed to be the most stable As-bearing products for long-term storage of As-bearing residues (Paktunc et al., 2006).

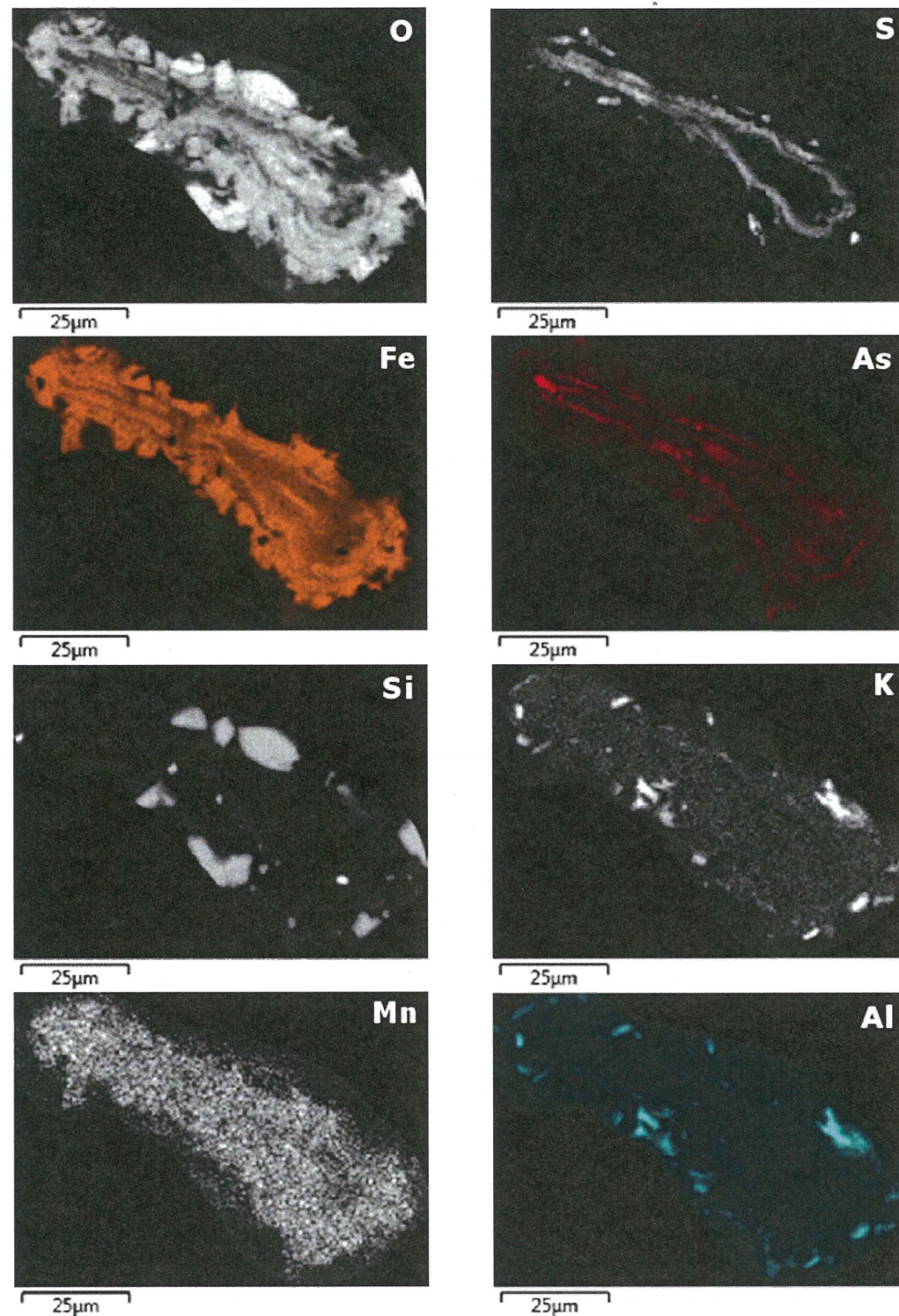


Figure 6. SEM element mapping of the zoned iron oxide grain in Fig. 5b, with a prominent As-rich S-bearing zone. Embedded relict quartz and muscovite, which can be seen in the K and Al maps, occur around the rim and in holes in the grain.

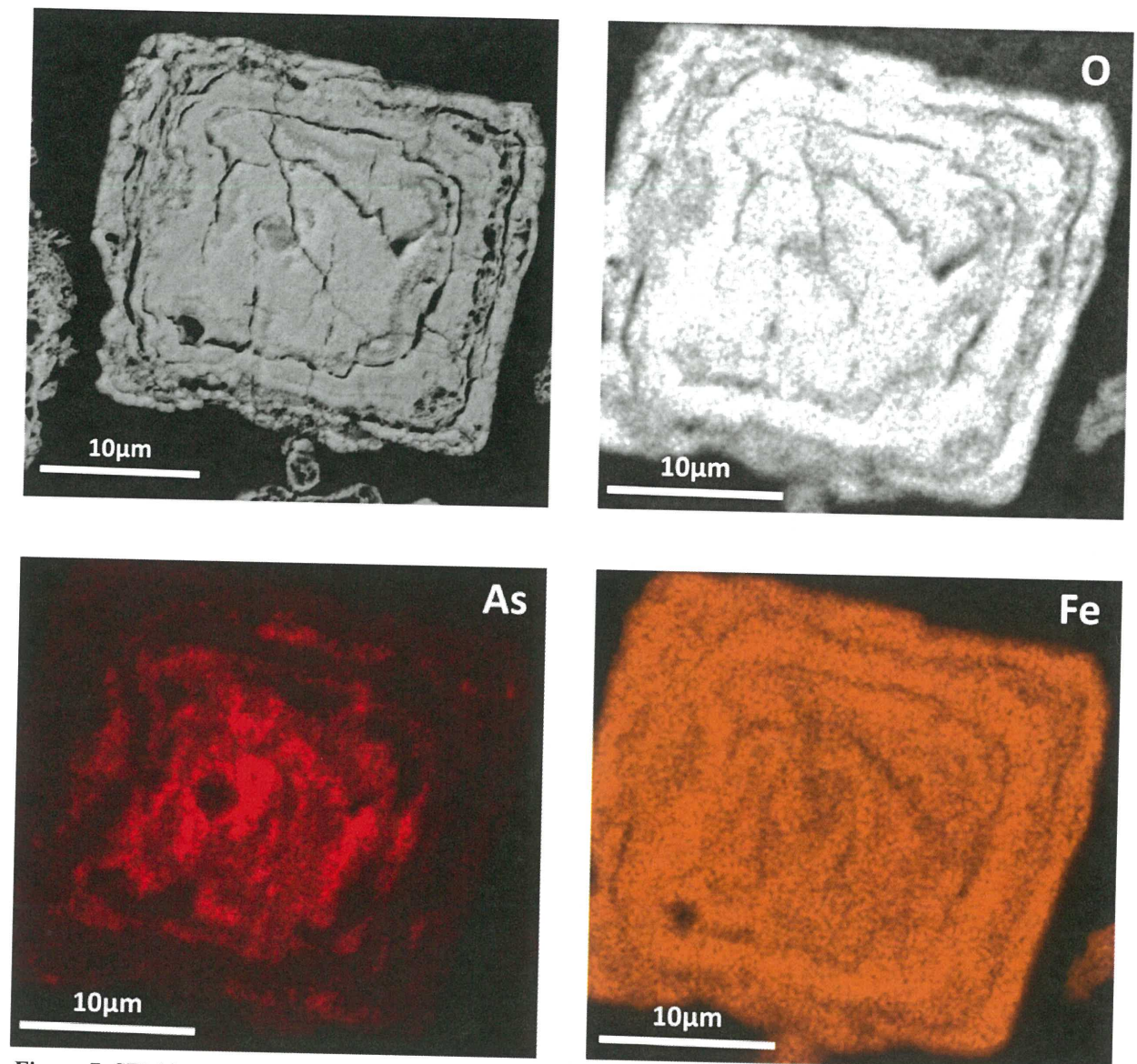


Figure 7. SEM image of a zoned iron oxide with the euhedral shape of the parent arsenopyrite. The high As and low Fe correlate in the element maps. A small cubic pyrite pseudomorph is seen in the centre as a void in the As map.

Acknowledgements

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