



Mineralogical controls on environmental mobility of arsenic from historic mine processing residues, New Zealand

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Abstract

Processing of arsenopyrite ore took place at Blackwater Au mine, New Zealand, between 1908 and 1951 and no rehabilitation was undertaken after mine closure. High As concentrations in solid processing residues (up to 40 wt% As) are due to secondary As minerals. Site pH regimes vary from 4.1 to circum-neutral. Originally, all processed As was present as arsenolite (arsenic trioxide polymorph, As^{III}), a by-product of arsenopyrite roasting. Near the roaster, scorodite precipitated as a result of the high dissolved As concentration during arsenolite dissolution. The formation of scorodite has two major consequences. Firstly, the scorodite precipitate cements the ground in the vicinity of the roaster area, thereby creating an impermeable surface crust (up to 30 wt% As) and encapsulating weathered arsenolite grains within the cement. Secondly, formation of scorodite temporarily immobilizes some of the dissolved As that is generated during nearby arsenolite dissolution. Where all the available arsenolite has dissolved, scorodite becomes soluble, and the dissolved As concentrations are controlled by scorodite solubility, which is at least two orders of magnitudes lower than arsenolite solubility. Downstream Eh conditions fall below the As^V/As^{III} boundary, so that scorodite does not precipitate and dissolved As concentrations are controlled by arsenolite solubility. Dissolved As reaches up to 52 mg/L in places, and exceeds the current WHO drinking water guideline of 0.01 mg/L by 5200 times. This study shows that dissolved As concentrations in discharge waters at historic mine sites are dependent on the processing technology and associated mineralogy.

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1. Introduction

Arsenic is a trace metalloid element that is commonly associated with metallic mineral deposits. In mesothermal Au deposits, As can be enriched up to levels of hundreds to thousands of times above respective average crustal abundance (1.7 ppm, Wedepohl, 1995), mainly in the form of arsenopy-

rite (FeAsS) and arsenian pyrite (Clara and Magalhães, 2002; Crow et al., 2004; Salzsauler et al., 2005). Arsenic is considered to be toxic in the environment at relatively low (ppb) levels (e.g. Foy et al., 1978; Gebel, 1997; Loebenstein, 1993; Smedley and Kinniburgh, 2002; Turner, 1993). The World Health Organisation (WHO, 2001) drinking water limit currently lies at 0.01 mg/L and freshwater ecosystems are affected at concentrations as low as 0.8 µg/L of As (ANZECC, 2000). Thus, As mobility from mineralized rocks is of considerable environmental significance. The release of As into

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the environment occurs naturally by oxidation of exposed sulphide minerals (e.g. Ashley and Lottermoser, 1999; Howell, 1992; Clark and Raven, 2004). In addition, the mining and beneficiation of Au, which is commonly intergrown with the sulphide phases, produces As-rich mine wastes, thereby accelerating the natural processes of As mobilization (Langmuir et al., 1999; Leblanc et al., 1996; Roussel et al., 1998; Shuvaeva et al., 2000). Historic mines are especially well known for elevated metalloid site output (Ainsworth et al., 1990; Ashley et al., 2003; Baroni et al., 2000), because they were commonly abandoned with little or no rehabilitation of the mine site, or provision for attenuation of potential As-rich discharge from excavations exposed to oxidation. Rehabilitation of historic As-rich mine sites requires some knowledge of the As minerals at the site and the solubility of these minerals in the present environmental conditions. Based on this knowledge, predictions of the levels of dissolved As leaving a site can be made. Attenuation of As-bearing waters can then be facilitated by natural dilution and sorption (Craw et al., 2000), and/or anthropogenic intervention (e.g. Clara and Magalhães, 2002; Ferreira da Silva et al., 2004). Hence, a scientifically based rehabilitation programme can be constructed based on a geochemical understanding of the processes controlling As mobility.

This study quantifies the mineralogical controls on As mobility at historic mine sites in New Zealand where spectacularly high As contents (up to 40 wt%) of mine residues are exposed to the environment. The sites examined occur in a wet climate, so As is being mobilized on a daily or weekly basis. The As phases present at these sites were identified and their solubilities evaluated and compared in the current environmental setting. The selected sites also provide information on the temporal and spatial control on As mobilization, especially with respect to secondary As minerals, arsenolite (As_2O_3 polymorph) and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). This information can supply a context for a rehabilitation programme that will be started in the near future.

1.1. General setting

The studied mine sites are part of the Reefton goldfield (Christie and Brathwaite, 2003). Two historic mine sites, associated with the Blackwater Mine, have been selected for this study: the Snowy River Battery (Snowy site) and the Prohibition Mill

mine site (Prohibition site), which are both in the vicinity of the abandoned mine town of Waiuta (Fig. 1). Mining at Waiuta was mostly confined to one large vein, known as the Birthday Reef (Christie and Brathwaite, 2003). The host rock consists of alternating sandstone and mudstone of the lower Palaeozoic Greenland Group (Cooper, 1974) (Fig. 1). The sandstones are feldspathic litharenites, with detrital grains of quartz, rock fragment, muscovite, plagioclase and biotite, of which the latter two have been altered to albite and chlorite, respectively, during greenschist facies metamorphism. Subsequent hydrothermal alteration of the sandstone has developed a mineral assemblage of K-mica, ankerite carbonate, chlorite, pyrite and arsenopyrite. Stibnite is common in some lodes but rare in the Waiuta area (Christie and Brathwaite, 2003), and no stibnite was observed in remnants of ore at either site. The sulphosalts bournonite (PbCuSbS_3), zinkenite (PbSb_2S_4) and tetrahedrite/tennantite can also be present in trace quantities (Leach et al., 1997; Williams, 1974). The rocks have high acid-neutralising capacity (ANC), typically between 4 and 9 wt% CaCO_3 (equivalent) and can reach 12 wt% CaCO_3 (equivalent) (Hewlett et al., 2005; Williams, 1974).

The Waiuta area is located on a plateau of moderate elevation (~ 400 m asl), which is dissected by two major drainages, the Snowy and Blackwater Rivers. The Prohibition site lies within the Blackwater River catchment and is located at the top of a hill at an elevation of ~ 560 m asl. The Snowy site is positioned in a steep sided valley adjacent to the Snowy River at an elevation of ~ 240 m asl. Annual precipitation from orographic rainfall averages 2300 mm. Seasonal distribution of rainfall has spring and autumn maxima, and minima in late summer and midwinter (Mew and Ross, 1994). The mean annual temperature is 12°C , with prevailing westerly winds. Vegetation is dense, consisting of secondary growth beech forest and associated thick under-bush. Original and present forest generated an organic layer, which overlies thin soils consisting of lithic material that is colluvial in places.

1.2. Mineral processing techniques

The Snowy site processed Waiuta's Au-bearing quartz from 1908 to 1938, involving crushing, flotation and cyanidation. Refractory Au in sulphide minerals was heated in an Edwards Roaster (Hut-

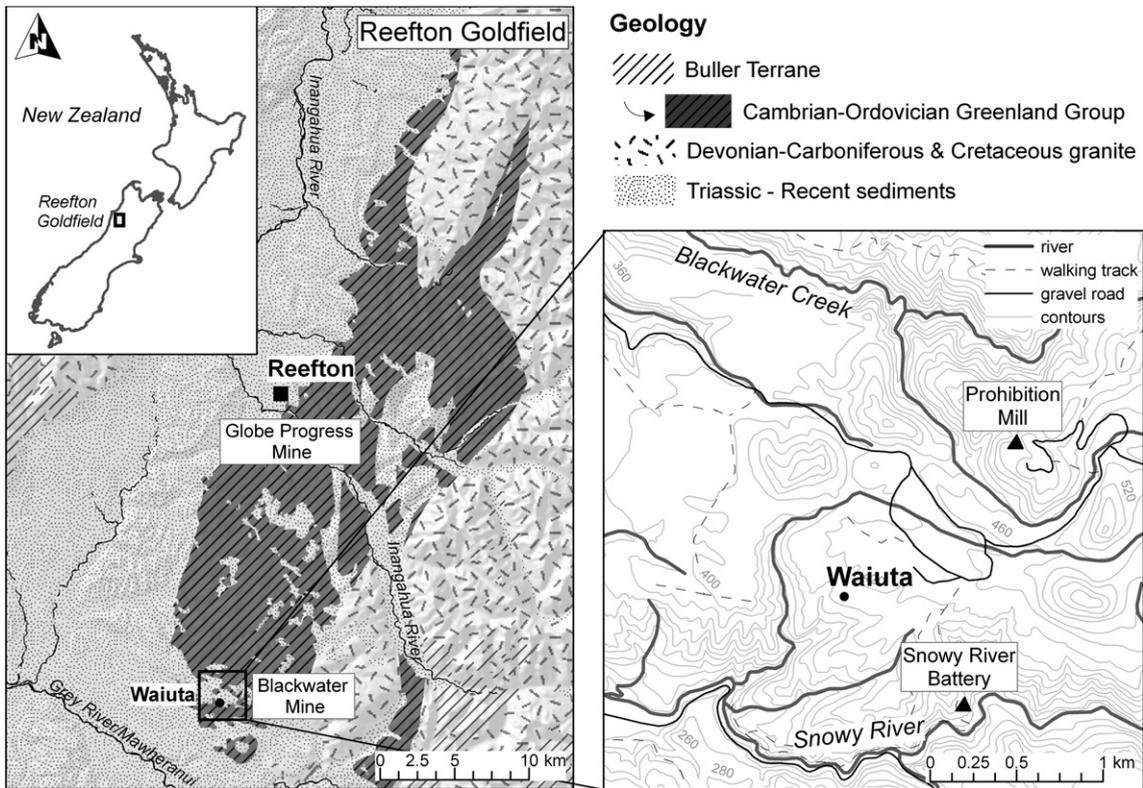
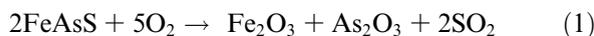


Fig. 1. General setting of the Reefton goldfield and the historic Waiuta mining area, including the geological setting of the Reefton goldfield and an overview of the Blackwater Mining area.

ton, 1947). In 1938 the ore processing operations were shifted to the Prohibition site, where operations were broadly similar including an Edwards Roaster (Hutton, 1947). The Edwards Roaster introduced a secondary As product, As_2O_3 . At temperatures of about 650 °C, arsenopyrite is ultimately converted to hematite (Fe_2O_3), As_2O_3 and SO_2 according to the overall reaction (La Brooy et al., 1994):



Arsenic trioxide, a roasting by-product, emerged from the furnace either as dust or vapour. The Snowy site did not accommodate a facility specifically for collecting and potentially recovering the As_2O_3 . Thus, a significant amount of As_2O_3 dust entered the atmosphere and only some of the As_2O_3 remained on site by precipitation along the flue system or as atmospheric fallout.

At the comparatively advanced Prohibition site, collection of the dust and condensation of volatile As_2O_3 was performed on discharge volatiles (<120 °C, Marsden and House, 1992) to save the

As. Production of As_2O_3 for 1945 was ~17 tonnes (Hutton, 1947). Dust contained by the final unit, a water spraying chamber, was largely washed out to waste. However, complete removal of As from any of the dust collecting chambers was difficult to achieve, resulting in a build up of As_2O_3 throughout the roaster gas discharge system (Hutton, 1947), and this was disposed of on site (Fig. 1). In 1951 mining at Waiuta ceased.

1.3. Site descriptions

The Prohibition site includes concrete foundation remains and scattered timber and iron debris. The most distinct feature is the condenser tower from the Edwards Roaster (Fig. 2). Large areas of the site are un-vegetated, especially in the vicinity of the roaster and flue system. The site receives only minimal surface run-off from the surrounding terrain, because it is located close to a topographic high. Site run-off drains into an adjacent small wetland (~10 m wide, ~100 m long), which is constrained at the northern side by a man-made dam (Fig. 2).

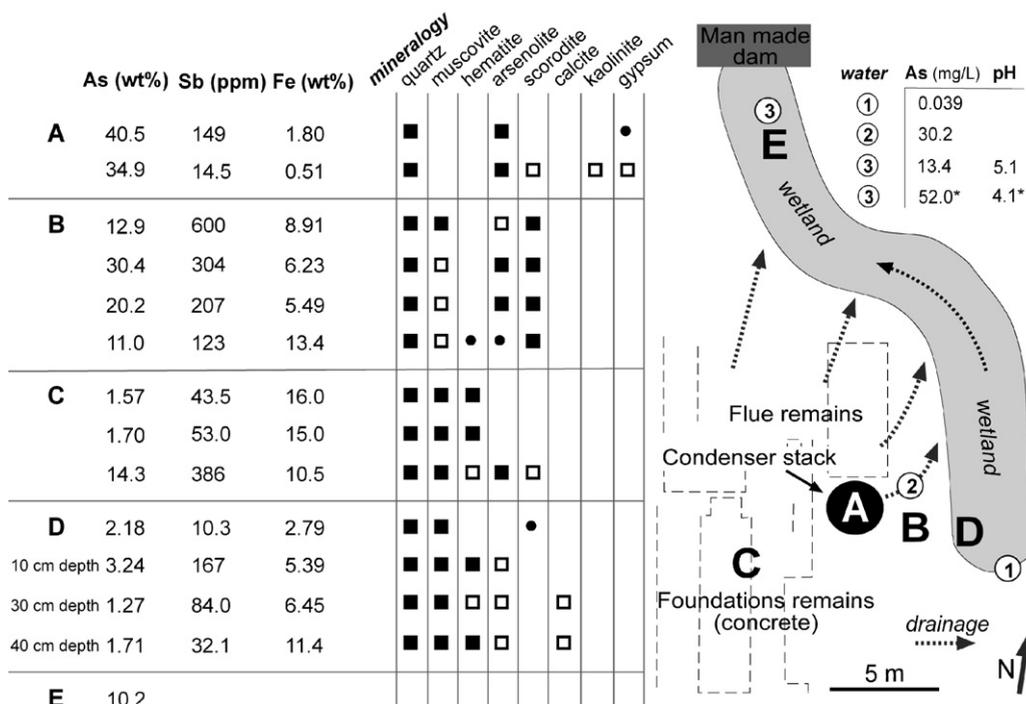


Fig. 2. Analytical results (As, Sb, Fe) and mineralogy from processing residues at the Prohibition Mill site, including main (full squares), subordinate (hollow squares) and trace (dots) mineral constituents. Sample locations (bold letters) are plotted in a present day outline of the site (after Hancox, 1985). A table of dissolved As concentrations and their locations (circled numbers) is also included. Most water samples were collected in May 2007 during a rain period. The sample with the asterisk was collected during a dry period in May 2005.

Water percolating through the dam emanates on the other side at the foot of a scree slope and eventually enters the Blackwater Creek (Fig. 1).

The Snowy River Battery plant is located in a steep sided valley immediately adjacent to the Snowy River. Like the Prohibition site, the Snowy site is characterised by concrete foundation remains and scattered timber and iron debris. A simplified present day outline of the site is depicted in Fig. 3. The site is only partly vegetated. Un-vegetated areas, which include the ground in the vicinity of the roaster foundations as well as the area between the tanks and the river, have a light grey/greenish surface crust. The crust is approximately 30 cm thick at the river bank. The site receives surface run-off from adjoining elevated ground. The drainage of the site occurs via surface run-off and via sub-surface seepage along the river bank (Fig. 3). Downstream of the cyanide tanks, surface run-off is partly channelled in a trench (Fig. 3), which originally drained the Au bearing cyanide solutions from the tanks. All run-off water is eventually transported away by the Snowy River (Figs. 1 and 3).

2. Methods

2.1. Sampling

To understand the nature of the As source, 28 solid samples were extracted from the Prohibition site and the Snowy site. At the Prohibition site (Fig. 2), these include the precipitate from the inside walls of the condenser tower (location A), the ground draining the condenser tower (area B) as well as the ground among the foundation remains (area C), and sediments from the wetland at the upstream end (location D), and from the lower end of the wetland (location E). Wetland sediments were extracted at different depths (up to 40 cm below the surface). At the Snowy site (Fig. 3) samples were obtained from the water-filled drainage tunnel (location A), tailings from the cyanide tanks (locations B and C), the ground draining the roaster area (area D), the ground draining the cyanide tanks (area E), an overgrown drainage trench (area F), and a composite sample from the river bank (location G).

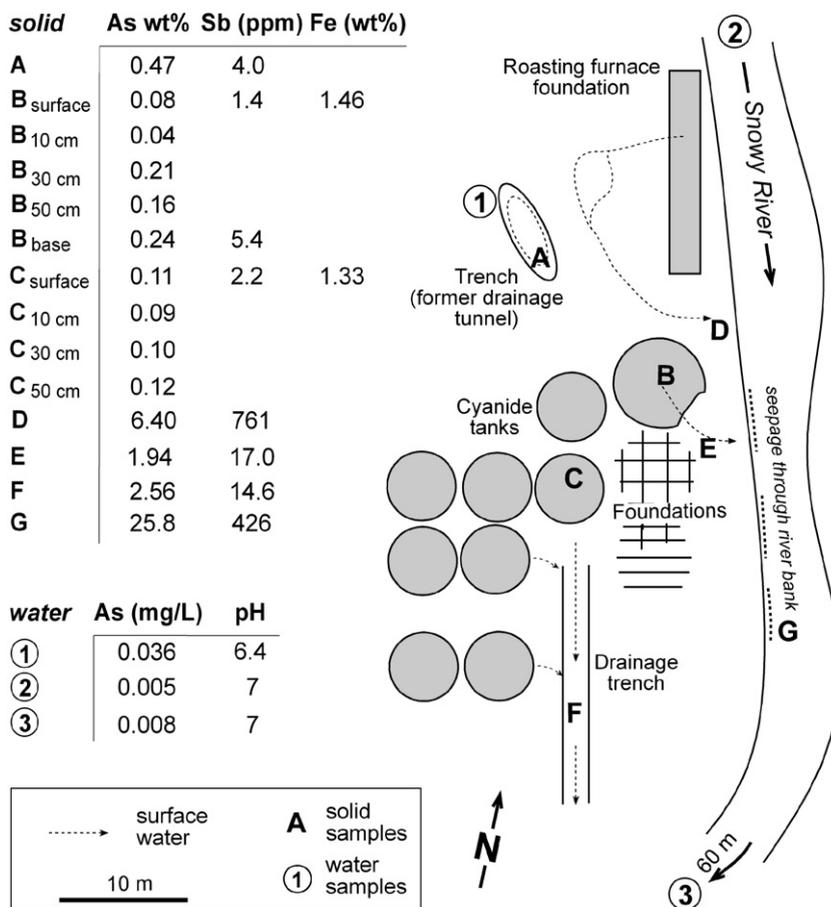


Fig. 3. Analytical results (As, Sb, Fe) from the Snowy River Battery mine site and a map of the present day site outline (after Hancox, 1985). Sample locations are included as bold letters for processing residues (A–G) and as circled numbers for water samples (1–3). Water samples were collected during a dry period in May 2005.

Only a small number of water samples could be extracted from the sites, because only few locations allow for surface water to accumulate outside rain events. At the Prohibition site, water from the upper and lower end of the wetland was extracted (location 1 and 3, Fig. 2). Surface run-off was collected ~1.5 m downstream from the condenser tower. At the Snowy site, water from the drainage tunnel (location 1, Fig. 3) and the adjacent Snowy river (locations 1, 3, 4, Fig. 3) was sampled. Water samples were filtered *in situ* (0.45 μm) and collected in HNO_3 -washed plastic bottles for dissolved As analysis. At the same time, the pH of the sample was lowered to a pH of 2 with HNO_3 . Water sampling was accompanied by *in situ* pH measurement using an Oakton PC10 field pH meter. The same instrument also measured electrical conductivity (EC) and water temperature. Paste pH of solid materials was deter-

mined on site on slurries made with distilled water in a clean plastic container (Sobek et al., 1978).

2.2. Analytical

Water samples were analysed for major ions and dissolved As by ICP-MS at Hill Laboratories, Hamilton, and Chemsearch Laboratories, Dunedin, New Zealand, which are internationally accredited laboratory (detection limit 0.001 mg/L). Methods comply with standard methods for the examination of water and waste water (APHA-3125, 1998). These include a four point standard calibration curve (0.005, 0.010, 0.025, 0.050 g/m³), filter blanks and bottle blanks and a synthetic control reference standard per run. All blanks and standards are made with ultra pure, trace metal free water. At least one duplicate sample is run every 20 samples.

All solid samples were oven dried at 45 °C. Stream sediment samples were subsequently sieved to less than 120 µm, thus excluding quartz-rich material principally inactive in As mobilization and transport. A cut off limit lower than 120 µm was not possible due to a lack of sediments in smaller grain size ranges. Mine processing residues were manually ground by mortar and pestle. Samples were then analysed for total recoverable As and, in most cases Sb and Fe, by HNO₃/HF digestion (EPA 200.2; US EPA, 1994) followed by solution analysis by ICP-MS (Hill Laboratories, Hamilton, NZ). Interference of ⁴⁰Ar³⁵Cl on ⁷⁴As analysis was corrected by measuring ⁷⁷Se and ⁸²Se and establishing the interference of ⁴⁰Ar³⁷Cl on ⁷⁷Se. This was then related to the ⁴⁰Ar³⁵C interference by adjusting for the natural abundance of both Cl isotopes.

Mineral constituents were identified, where possible, by X-ray diffraction (XRD) on pressed-powdered discs using a PANalytical X'Pert-Pro MPD PW3040/60 at the Geology Department, University of Otago, New Zealand. The scanning was conducted with Cu Kα radiation at a rate of 0.05°/s. Results were interpreted with the support of the PANalytical High Score software package.

A cemented sample of the ground adjacent to the condenser stack at the Prohibition Mill site and another from the former roaster area at the Snowy Battery site, were polished and examined under a semi-automated JEOL JXA-8600 electron microprobe analyzer (EPMA) at the University of Otago, New Zealand. Methods include scanning electron microscopy (SEM), energy dispersive (EDS) and wavelength dispersive (WDS) spectrometry. Antimony and As element maps of a small area (0.50 × 0.45 mm) of the polished sections were generated by applying the WDS at 25 kV by automated stepping (1 µm steps) across the area.

3. Description of processing residues

3.1. Prohibition mill site

The analytical results and their respective locations are displayed in Fig. 2. Arsenic is abundant at this site in two secondary As minerals. No unoxidized pyrite or arsenopyrite from the ore persisted through the processing plant to the residues.

The inside wall of the condenser tower is covered in white rosette-like crystals, which are friable and give off an unpleasant onion-like odour. A photo-

graph of the material (white/light grey) on brick (dark grey) is displayed in Fig. 4B along with a XRD spectrum (Fig. 4A) and a reference pattern for arsenolite (Fig. 4C). The material is mainly composed of arsenolite crystals (<0.004 mm), which occur as aggregates (<0.5 mm) and as an interstitial material in-between mainly quartz (sub-angular, ~0.5 mm) and some gypsum (tabular, <1 mm) (Fig. 2). The precipitate possesses the highest As concentrations encountered at the studied sites (up to 40 wt% As). Another precipitate from the same sample location (A, Fig. 2) is light brown, friable and consists of quartz grains and aggregates of parallel fibrous gypsum (~2 mm × 0.05 mm) cemented loosely by arsenolite crystals (<4 µm) and scorodite (<4 µm).

The un-vegetated sedimentary substrate adjoining the condenser tower (area B, Fig. 2) is grey and variably cemented. Clast sizes can be as small as 0.01 mm and generally do not exceed several mm. These are mainly composed of monocrystalline and some polycrystalline quartz (sub-angular, 0.01 mm–5 mm), which are commonly fractured. Some clasts consist of friable aggregates (1–0.01 mm) of arsenolite crystals (<4 µm), as seen in Fig. 5. Arsenolite aggregates exhibit irregular edges and tend to occur as localised clusters (Fig. 5). Some arsenolite occurs as individual euhedral crystals (0.3–0.5 mm). Glass fragments are also present. These exhibit curved cavities and possess a sieved texture under the microscope. Subordinate muscovite (tabular, ~0.01 mm) and trace hematite (fibrous, <1 mm) with an iridescent lustre can also be found. All clasts are coated in light brown equant particles (<4 µm) that also make up the interstitial material in cemented parts of the material. These particles consist predominantly of a botryoidal scorodite precipitate (FeAsO₄ · 2H₂O) (Figs. 5 and 6A), which can form a globular cement (Fig. 6B). Generally, the scorodite cement is continuous (Fig. 6A) with low porosity.

Element maps of As and Fe of the same area as Fig. 6A are displayed in Fig. 6C and D, respectively. The grey shading corresponds to the element concentrations. Lithic fragments are dominated by quartz, which occurs as white grains in both maps. An arsenolite grain is identifiable in the upper left hand corner by its dark grey colour in the As-map (~75 wt% As) and white colour in the Fe-map (0 wt% Fe). Hematite occupies the upper left hand corner of the image and is characterised by its dark grey colour in the Fe-map (~70 wt% Fe) and white

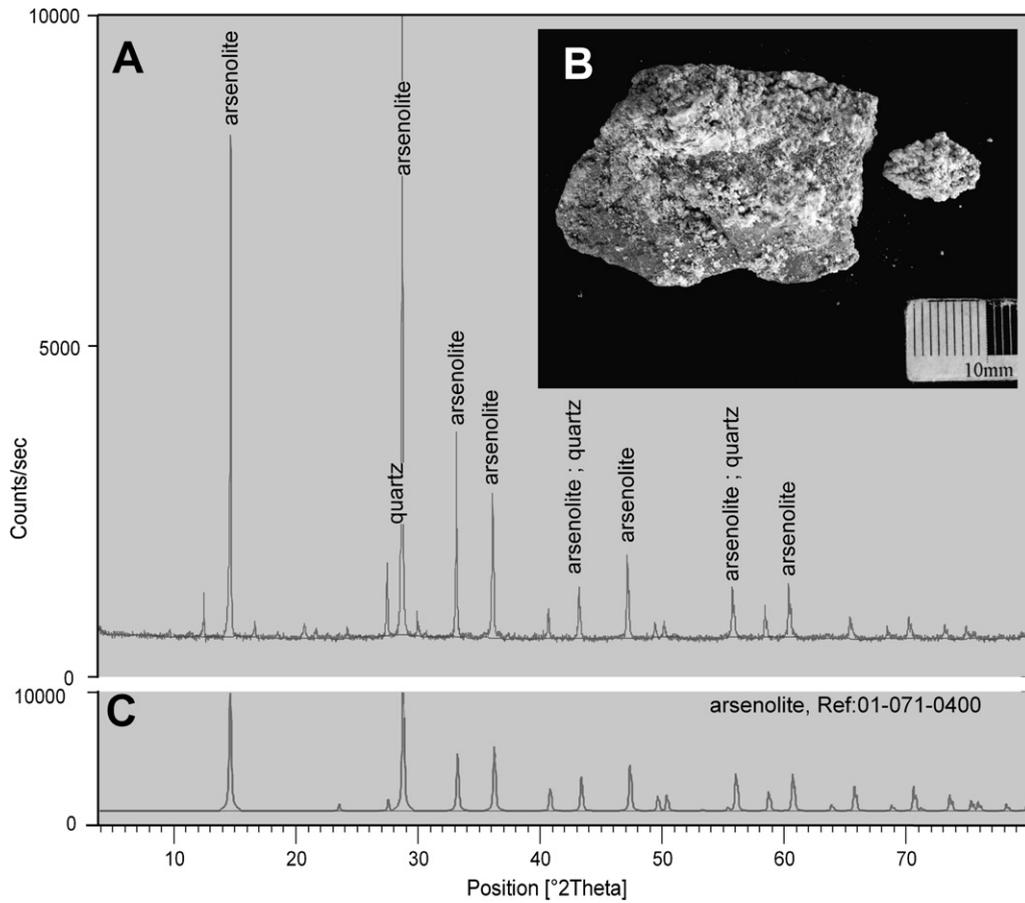


Fig. 4. (A) X-ray powder diffraction pattern of the arsenolite condensate from inside the condenser stack, Prohibition site. Scanning was conducted with Cu $K\alpha$ radiation at a rate of $0.05^{\circ}/s$. (B) photograph of arsenolite condensate (white material) on brick (dark grey) and (C) reference X-ray powder diffraction pattern for arsenolite (01-071-0400).

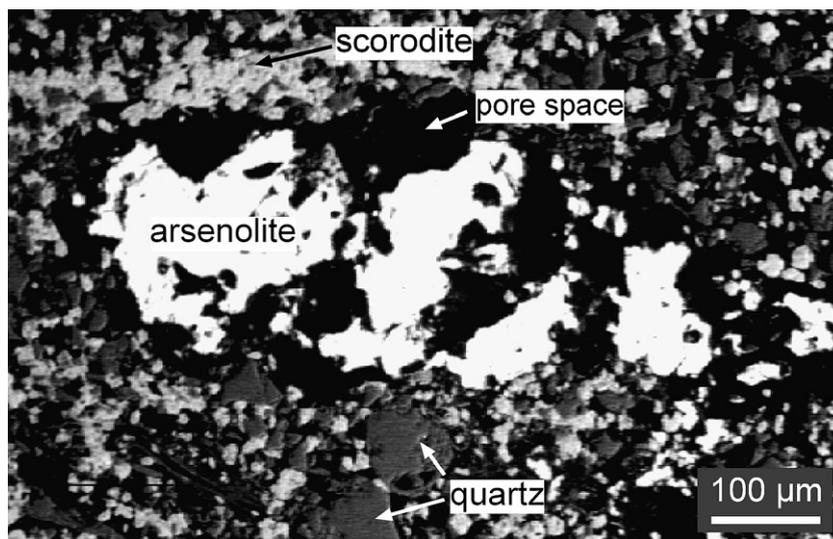


Fig. 5. Scanning electron microscopy (SEM) image of material from the crust surrounding the Prohibition condenser stack: arsenolite aggregate (white) surrounded by scorodite spherules (light grey) and quartz (dark grey). Black areas are pore space.

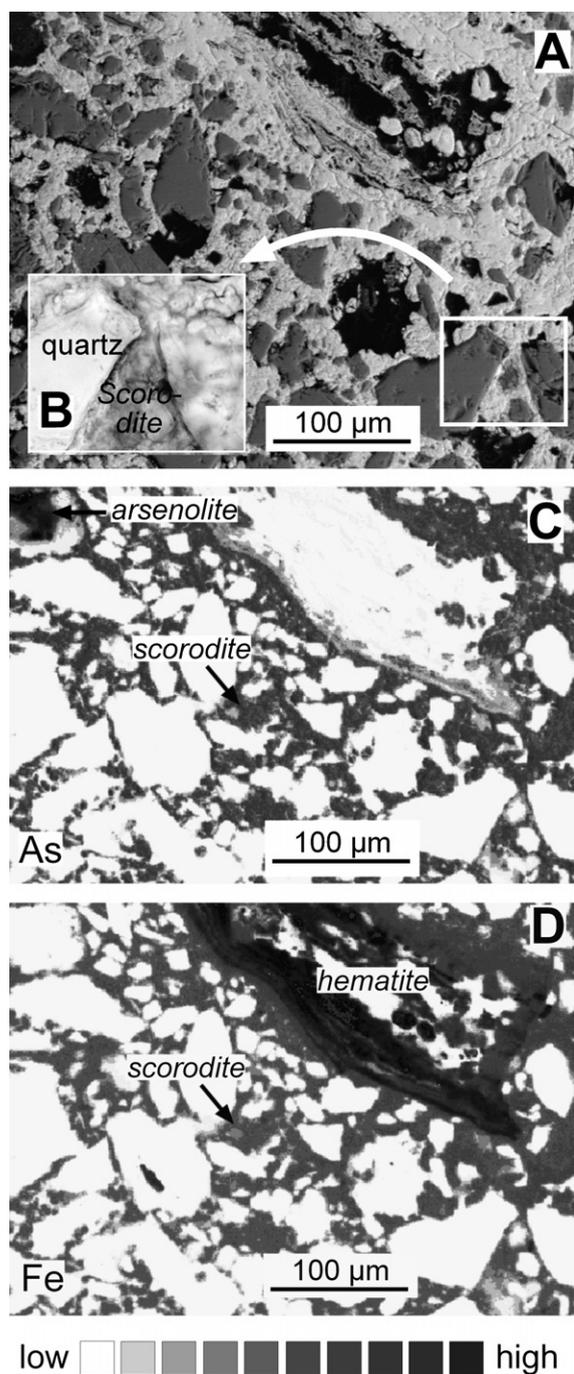


Fig. 6. Globular scorodite cementing hematite and quartz grains at the Prohibition site: (A) backscatter scanning electron image (SEM) image, showing the pervasive nature of scorodite, (B) microscope image, showing scorodite spherules cementing quartz grains, (C) microprobe element map of As. Darkness of grey shade correlates to As concentration. Medium grey areas represent scorodite (~30 wt%) and dark grey areas represent arsenolite grains (~75 wt%) and (D) microprobe element map of Fe. Darkness of grey shade corresponds to Fe concentration. Medium grey areas represent scorodite (~20 wt%) and dark grey areas represent hematite (~70 wt%).

colour in the As-map (0 wt% As). Scorodite occurs in the As-map (~30 wt% As) and Fe-map (20 wt% Fe) as grey interstitial material. Arsenic concentrations are homogeneous within individual As phases such as arsenolite (dark grey, Fig. 6C) and scorodite (medium grey, Fig. 6C). Similarly, Fe concentrations show little variation within scorodite cement (medium grey, Fig. 6D), confirming that scorodite is the only cementing phase. Overall As concentrations in the crust around the condenser tower can reach up to 30 wt% and up to 13 wt% Fe. The paste pH of this material was around 3.

Tailings and other unconsolidated material from among the concrete and timber remains (area C, Fig. 2) comprise dark brown moderately well sorted silty sediment, consisting mainly of quartz (sub-angular), muscovite (tabular), hematite (botryoidal) and glass fragments with curved cavities. Arsenolite crystals (~0.05 mm) and subordinate scorodite spherules (<4 µm) were also identified. Arsenic concentrations ranged from 2 to 15 wt% and Fe concentrations typically stayed between 11 and 16 wt%.

At the margin of the upper wetland (location D, Fig. 2), surface sediments are light grey and loosely cemented in places. The sediment is bimodal, with the coarser fraction comprising mainly coarse sub-angular quartz grains and tabular muscovite. Coarse grains are coated by light grey silty particles including trace scorodite. Carbonaceous material constitutes ~1% of this material. With depth, the coarse quartz fraction is replaced by dark brown silt which includes coarse clasts of quartz, hematite, glass and subordinate aggregates of arsenolite crystals (<4 µm). Arsenolite aggregates are detrital and closely resemble the condenser precipitate (location A, Fig. 2). There is no evidence of *in situ* arsenolite precipitation. Arsenic concentrations are significantly lower in this material (below 4 wt% As, Fig. 2) compared to other mine residues at this site. Fe concentrations can reach up to 11 wt% (Fig. 2).

Sediment from the lower end of the wetland, location E (Fig. 2), is less cohesive, and lighter in colour. The sediment is also bimodal, consisting of coarse sub-angular quartz and occasional brown stained aggregates of arsenolite crystals (<4 µm). The coarse fraction is coated in brown particles (<4 µm) making up at least 30% of the sample. Individual arsenolite crystals (~0.2 mm) were also identified. Carbonaceous material is present at ~2%. Arsenic concentrations can be as high as 10.2 wt% As.

In contrast to As concentrations, there is comparatively little Sb present in the mine waste. Anti-

many concentrations range from 10 to 600 ppb and are on average 3 orders of magnitude lower than As concentrations (Fig. 2). This is in agreement with observations made from remnants of ore containing at least 10 times more arsenopyrite than stibnite.

3.2. Snowy river site

The analytical results of the solid samples collected at the Snowy site and their locations are displayed in Fig. 3. A red colloidal precipitate accumulated at the base of a water-filled trench, which has collapsed upstream and downstream allowing water to accumulate (location A, Fig. 3). The colloidal material is brown when dried and contains occasional coarse (~1 mm) clasts of muscovite, quartz and carbonaceous fragments. Arsenic concentrations were relatively low in the material (0.5 wt% As) and no As phase could be detected. The water was up to 40 cm deep and rich in reddish particulates. Dissolved As levels in this water were also relatively low (0.036 mg/L, pH 6.4, location 1, Fig. 3).

Tailings from the cyanide tanks and from spillage underneath the tanks (locations B and C, Fig. 3) consist of light coloured medium-coarse well sorted sediments. These are mainly composed of sub-angular quartz and some sub-angular schist fragments and occasional well-rounded reddish aggregates of micro-particles (<4 µm). Trace scorodite was also identified in the XRD spectra. Inside the cyanide tanks, As concentrations average 0.1 wt% As in tank C (vegetated) displaying no significant variation in As content with depth (Fig. 3). Tank B (un-vegetated), in contrast, reveals slight variations in As concentrations with depth, with a maximum of 0.2 wt% As at 30 cm below the surface (Fig. 3). Arsenic concentrations are highest at the base of the tanks, reaching 0.24 wt%. Iron concentrations are just above 1 wt% at the surface of the tanks.

The site substrate is covered by a surface crust with a thickness of ~30 cm at the river bank. The crust is white/greenish, loosely cemented and only sparsely vegetated. The material takes on a light brown colour upon drying and is composed of detrital material and interstitial particles (<4 µm). The material closely resembles the surface crust in the vicinity of the condenser tower at the Prohibition Mill site (location B, Fig. 2). Clasts are mainly composed of sub-angular quartz grains (0.5–2 mm) and subordinate tabular muscovite (0.01–0.1 mm), glass fragments (<0.1 mm) with curved cavities, trace

scattered friable aggregates (~0.5 mm) of arsenolite crystals (<4 µm), trace euhedral arsenolite crystals (~0.5 mm, Fig. 7) and trace schist fragments (~0.5 mm). Trace anhedral ilmenite, as lamellar exsolutions in tabular hematite, is also a constituent of the clast fraction. Similarly to the surface crust at the Prohibition site, the clasts are cemented by light brown equant particles (<4 µm), which consist predominantly of a botryoidal scorodite precipitate (Fig. 7A). In the vicinity of arsenolite crystals, scorodite can form a globular cement (Fig. 7B). Compared to the Prohibition site, scorodite precipitation was less intensive at the Snowy site. As a consequence, the surface crust at the Snowy site has a higher porosity (Fig. 7) and the dominant scorodite morphology is more commonly individual dispersed scorodite spherules (Fig. 7A) rather than a continuous globular cement. Accordingly, As

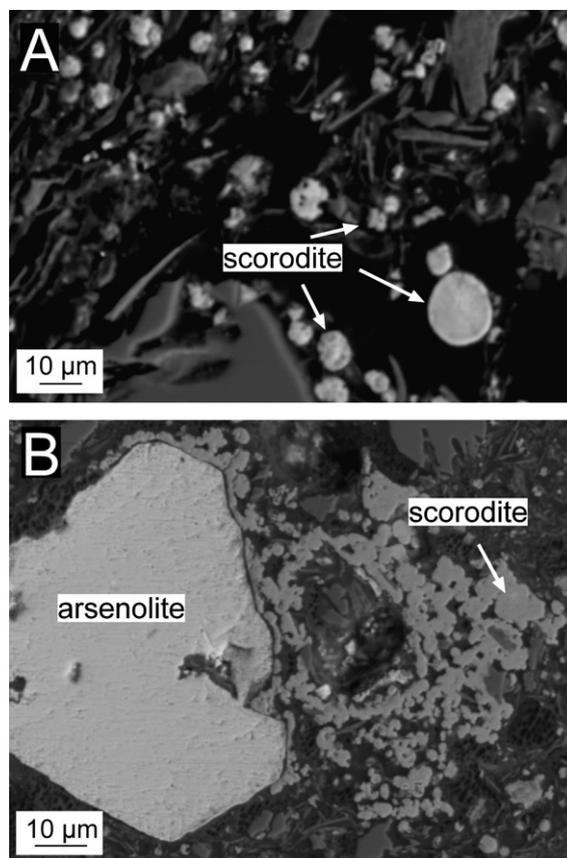


Fig. 7. Scanning electron microscope (SEM) backscatter image of material from the Snowy site showing (A) scorodite spherules (light grey) growing unrestricted in pore space (black) and (B) scorodite cement (medium grey) developing around arsenolite grain (light grey).

concentrations are lower in the surface crust, reaching 6.4 wt% along the surface drainage path of the former roaster area (location D, Fig. 3) and 2 wt% along the surface drainage path of some of the cyanide tanks (location E, Fig. 3).

Another drainage path of the cyanide tanks is via a man-made trench (location F, Fig. 3). The trench is filled with unconsolidated dark brown, organic rich sediment, which were water saturated at the point of sampling. These consist of fine to clay sized particles (<4 µm) and occasional coarse clasts of sub-angular quartz, aggregates of arsenolite crystals (<4 µm), and tabular muscovite. Scorodite was not detected nor any evidence for an *in situ* precipitated phase. Arsenic concentrations reached 2.6 wt%.

The site substrate is exposed along the river bank. At location G (Fig. 3) the bank is between 2 and 3 m high and exposes water saturated compacted sediment which is covered by a green bio-matt (0.5 cm thick). Sediments are sand sized at the bottom of the exposure and gradually thin upwards so that the material just under the surface crust is of clay size (<4 µm). Sediments are well sorted and are composed mainly of quartz and arsenolite and subordinate muscovite and scorodite. A composite sample from the bank was extracted at different elevations, which contained the highest As concentration encountered at this site (26 wt%, Fig. 3).

In accordance with the findings at the Prohibition site, there is little Sb present at the Snowy site. Antimony concentrations range from 0.1 to 76 ppb (Fig. 3) and are generally one order of magnitude lower than at the Prohibition site.

4. Water chemistry

Background water of the catchments hosting the Prohibition site and the Snowy site are of the Na–Mg–HCO₃–Cl and Mg–Na–Ca–HCO₃–Cl type, respectively (Table 1). Wetland water at the Prohibition site is of the As–Ca–SO₄ type (Table 1) and is characterised by low pH (pH ~4, Fig. 2). Major

ions are mainly controlled by gypsum and minor carbonate dissolution, resulting in high SO₄ (216 µmol/L) and Ca (322 µmol/L) concentrations, and lower Na (131 µmol/L) and Mg (106 µmol/L) concentrations (Table 1). Bicarbonate is comparatively low (16 µmol/L) and the Ca/Mg ratio is 3:1 reflecting the absence of significant carbonate dissolution, which would result in HCO₃ concentrations exceeding Ca concentrations and a Ca/Mg ratio of 2:3 as seen in the typical downstream catchment water (Table 1). The chemically anomalous signal emanating from the Prohibition site prevails 500 m downstream, at which point a tributary dilutes the site drainage water to the typical background water type.

The upper wetland water at the Prohibition site (position 1, Fig. 2) contained elevated dissolved As (0.039 mg/L) after at least two days of moderate rain. Surface run-off from the area around the condenser tower contained 30.2 mg/L As during a rain event (position 2, Fig. 2). Arsenic concentrations in wetland water downstream from the roaster area (position 3, Fig. 2) contained up to 13.4 mg/L (pH 5.1) during the same sampling campaign. At the same location, water containing 52.0 mg/L (pH 4.1) was sampled during a dry spell two years prior. At the Snowy site, subsurface site drainage towards the river occurs through the river bank via continuous seepage. The river water approached the Snowy site with a dissolved As concentration of 0.005 mg/L (pH 7) (location 2, Fig. 3), which dropped to 0.008 mg/L (pH 7) 60 m further downstream from the site (location 3, Fig. 3).

5. Discussion

Arsenic concentrations in mine residues at the Prohibition site and the Snowy site are alarmingly high, reaching up to 40 and 26 wt% respectively (Figs. 2 and 3). The current NEPC (1999) As guideline for parks and recreational open space lies at 0.02 wt% (200 mg/kg), which is exceeded

Table 1

Major ion analysis of the Prohibition wetland water and of background samples from the Snowy River and Blackwater River catchment

	PH	Alkalinity (mg/L CaCO ₃)	HCO ₃ (µ mol/L)	Ca (µ mol/L)	Mg (µ mol/L)	Na (µ mol/L)	K (µ mol/L)	Cl (µ mol/L)	SO ₄ (µ mol/L)
<i>Wetland water</i>									
③, Fig. 2	4.1	<1	<16	322	106	131	27	110	216
<i>Background</i>									
Prohibition site	7.0	12	246	43	59	237	10	152	13
Snowy site	7.1	14	279	53	84	167	10	104	11

in every sampled material from the Prohibition site (Fig. 2). Arsenic concentrations at the Snowy site are generally lower (Fig. 3) but still exceed the NEPC guideline in every sample. Arsenic is present as the secondary minerals arsenolite and scorodite, which contain 76 wt% and 33 wt% As, respectively. Scorodite is the most prevalent natural form of Fe^{III} arsenate and is common in many types of oxidation zones and mine wastes (Dove and Rimstidt, 1985; Foster et al., 1998). Arsenolite, as well as its polymorph claudetite, can also form naturally as weathering products of As sulphides but are more commonly found as the oxidation products of the roasting or As-bearing ore minerals or coal. Overall Sb levels are approximately 3 orders of magnitude lower than As concentrations, which is in accordance with low Sb concentrations in primary ore (Christie and Brat-hwaite, 2003).

Useful guidelines for site waters include the ANZECC (2000) freshwater trigger value for a highly disturbed ecosystem (<80% species survival), which lies currently at 0.14 mg/L As^V, and the provisional drinking water threshold of 0.01 mg/L proposed by the World Health Organisation (WHO, 2001). Thus the wetland water at the Prohibition site exceeded these guidelines by up to 370 and 5200 times, respectively.

5.1. Theoretical arsenic mineral stabilities

Weathering and solution of As minerals occurs at the Waiuta processing sites, especially as a result of rainfall events, and dispersion of As into the local ecosystem follows. Arsenolite is highly soluble, and water in equilibrium with arsenolite can contain up to ~10–16 g/L As (Pokrovski et al., 1996). Thus, rainwater will dissolve the exposed arsenolite according to the following equation (Vink, 1996):



Rainwater is unlikely to reach equilibrium with arsenolite due to the short contact between surface run-off and the arsenolite.

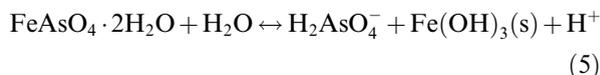
In the surficial environment (oxidizing conditions) arsenite, H₃AsO₃(aq), is unstable in the presence of arsenite-oxidizing microbes (Green, 1918; Tamaki and Frankenberger, 1992; Turner, 1949) or a strong oxidant and will eventually oxidize to arsenate, H₃AsO₄(aq). The following reaction may occur between pH 2.2 and 6.7 (Fig. 8A) (Appelo and Postma, 1999):



To predict the stability of scorodite in the given settings, an Eh–pH diagram in an H–O–As–Fe–S system was constructed in the “Act2” program available in the “Geochemist’s Workbench” package using the LLNL database (Bethke, 1996). The scorodite solubility product was replaced by the revised value of p*K* = 24.4 from Krause and Ettel (1989), which takes into account the crystallinity of the scorodite phase. In addition, goethite has been suppressed from the system, based on the fact that goethite is neither visible on any of the site surfaces nor analytically identified in any of the samples. Thus the stability field of scorodite is calculated with respect to the metastable precursor of goethite, an amorphous ferrihydrite (Fe(OH)₃) phase, as suggested by Salzsauler et al. (2005). The diagram shows that, in oxidising conditions, even at concentrations as low as [As] = 10^{−6} mol/L, metastable scorodite is predicted to precipitate as long as the pH is below 5 (Fig. 8B). In circum-neutral solutions, scorodite precipitation can be expected if [As] > 10^{−4} mol/L, which is the case in most Prohibition site waters (Fig. 2):



If site conditions change, and no longer fall inside the scorodite stability field, scorodite is predicted to dissolve. The solubility of scorodite has been investigated and discussed by many authors (e.g. Dove and Rimstidt, 1985; Krause and Ettel, 1989; Nordstrom and Parks, 1987; Robins, 1987; Vircikova et al., 1995). At pH > 2.3 (23 °C, Krause and Ettel, 1989) scorodite dissolves incongruently according to the equation:



The upper limit of dissolved As concentrations produced by scorodite dissolution is pH dependent:

$$\log K_{\text{incongruent}} = \log[\text{H}_2\text{AsO}_4^-] - \text{pH} \quad (6)$$

A composite equilibrium constant for Eq. (6) was established from the equilibrium constants for a set of related reactions (Allison et al., 1991).

$$\log K_{\text{incongruent}} = -10.1$$

Assuming a local pH of 5, dissolved As concentration as a result of scorodite dissolution could be up to 0.6 mg/L (Fig. 9), which is considerably lower

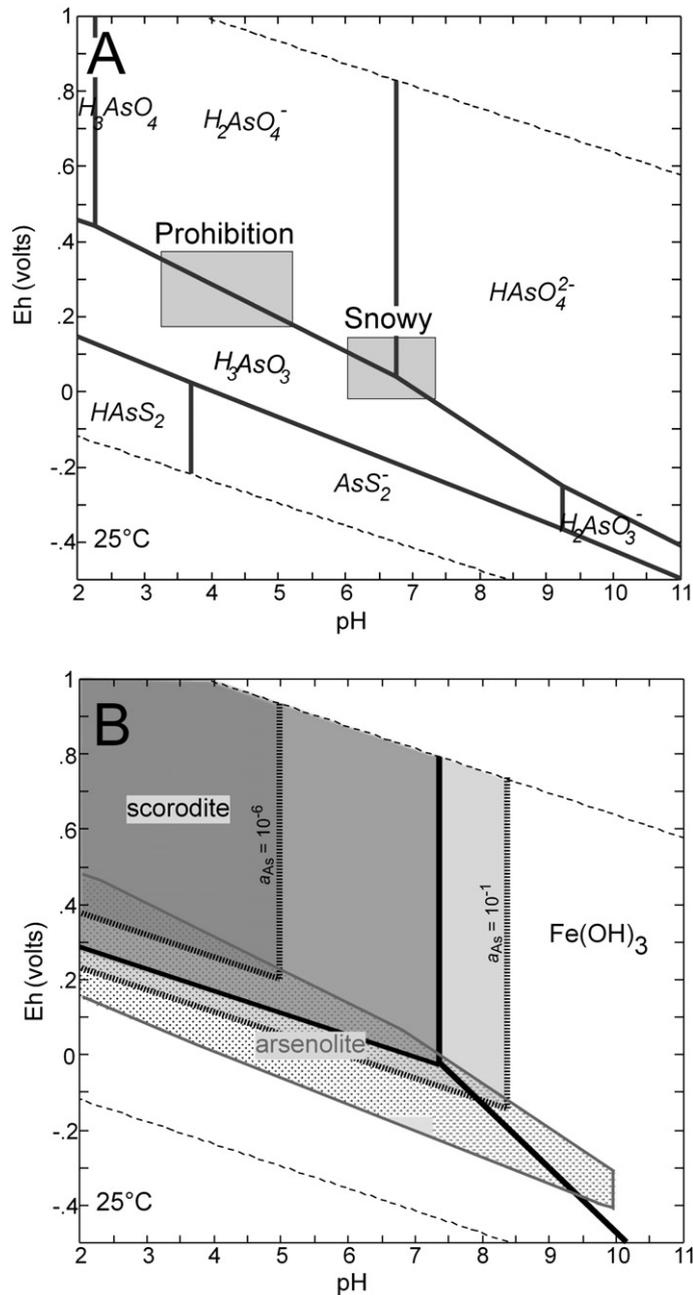


Fig. 8. Diagrams of H–O–As–Fe–S built in Eh–pH space at 25 °C and 1 bar total pressure showing (A) aqueous As species and (B) scorodite with respect to amorphous Fe(OH)₃, and arsenolite with respect to scorodite. Solid lines represent typical site concentrations for As (Fig. 2) and SO₄ (Table 1) and an estimated Fe concentration: [As] = 10⁻⁴ mol/L, [SO₄] = 10⁻⁴ mol/L, [Fe^{II}] = 10⁻⁴ mol/L. The conditions of the Prohibition and Snowy site are added as shaded boxes in (A).

than the solubility of arsenolite (~10–16 g/L As, Pokrovski et al., 1996). It is noted that both studied sites are well drained and do not allow for surface water to accumulate easily. Thus, theoretical mineral stabilities are constrained by the absence of water outside rain events.

5.2. Site pH

To interpret the findings with respect to As mineralogy, a brief consideration of site pH is necessary. The Greenland group host rocks are known to generate circum-neutral surface waters because

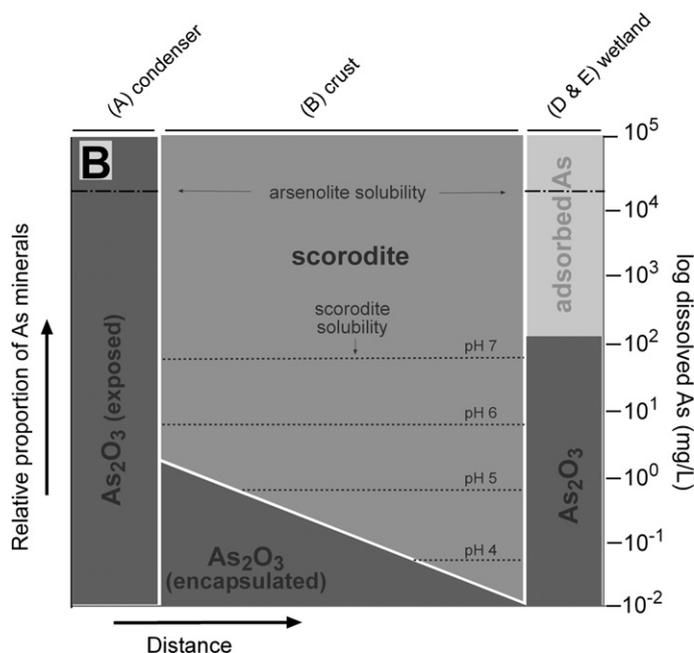


Fig. 9. A schematic diagram of the relative proportion of As minerals (primary y -axis) with distance from the roaster condenser tower at the Prohibition Mill site (x -axis). Dark grey represents arsenolite, medium grey corresponds to scorodite and light areas symbolizes adsorbed As. Mineral solubilities (secondary y -axis) for arsenolite (dashed-dotted line) and scorodite (dotted lines) are added.

they include abundant carbonate minerals (Table 1) (Christie and Brathwaite, 2003; Haffert et al., 2006; Hewlett et al., 2005). The Snowy site is located in a valley and therefore receives ample surface run-off water that has interacted with the surrounding carbonate-bearing host rocks (Table 1), ensuring that Snowy site waters remain circum-neutral (pH 6.4, Fig. 3). In contrast, the Prohibition site does not receive circum-neutral surface run-off, and local controls on pH are more pronounced. Pyrite and other minerals that potentially liberate protons during dissolution are absent in the processing waste (Fig. 2). The low site pH (pH 4–5, Fig. 2) is likely to be caused by the oxidation of arsenite oxyanions, which are produced during arsenolite (As^{III}) dissolution (Eq. (3)).

5.3. Observed mineral stabilities

Ample scorodite and arsenolite are present at both sites. Their stabilities and consequent impact on the downstream environment depends largely on mineral exposure and dissolved As concentrations in site waters. Most of the arsenolite is present encapsulated in the surface crust by a scorodite precipitate and therefore unavailable for weathering. At the Prohibition site some arsenolite is still

exposed inside the condenser tower and dissolves during rain events generating high dissolved As site waters (up to 52 mg/L, Fig. 2). Scorodite is present as interstitial globular cement of varying porosity. At the Prohibition site scorodite precipitation was intense (Fig. 6), resulting in low porosity in scorodite cemented samples. At the Snowy site, scorodite morphology resembles an early stage of scorodite precipitation (Fig. 7A) (Salzsauler et al., 2005). This is characterised by dispersed scorodite spherules, rather than globular cement and results in higher porosity (Fig. 7A). The differences in scorodite morphology can be related to the differences in the thermodynamic settings of the sites. Scorodite precipitation is most favoured in acidic waters (if $[\text{As}] > 10^{-6}$ mol/L) or very As-rich waters ($[\text{As}] > 10^{-1}$ mol/L) (Fig. 8B). At pH 7, scorodite can precipitate only if $[\text{As}] > 10^{-4}$ mol/L, which is two orders of magnitudes higher than at pH 5 (Fig. 8B).

At the Prohibition site, the presence of arsenolite has generated As-rich ($[\text{As}] \sim 10^{-3}$ mol/L) and acidic (pH 4–5) waters, which are not diluted with surface run-off from surrounding terrain. Thus conditions at the Prohibition site plot in the scorodite precipitation field in the revised Eh–pH diagram (Fig. 8B). In contrast, at the Snowy site high-carbonate circum-neutral surface run-off controls site pH (Table 1)

and dilutes As-rich waters. Thus, conditions for scorodite precipitation are less frequently met at this site. In addition, processing technologies did not allow for effective condensation of arsenolite gas and therefore less As was initially present at this site.

At present, arsenolite dissolution is still taking place in the exposed precipitate inside the condenser tower at the Prohibition site (location A, Fig. 2). Thus, dissolved As concentrations are not likely to decline in the near future and scorodite will continue to build up in this setting. At the Snowy site all available arsenolite has been dissolved and As concentrations are generally lower ($[As] \sim 10^{-6}$ mol/L). Consequently, the Snowy site falls outside the precipitation stability field of scorodite (Fig. 8B) and, instead of scorodite build up, scorodite dissolution can be expected.

At location A (Fig. 2) and locations A and F (Fig. 3) no scorodite was detected even though ample arsenolite was present, indicating Eh regimes below the As^V/As^{III} boundary (Fig. 8B). Arsenolite occurs exclusively as detrital aggregates, which derived from the gas flue system. *In situ* arsenolite precipitation is unlikely to occur because dissolved As concentrations outside the range found at the studied sites (<52 mg/L) would be required.

5.4. Effects of time on substrate stabilisation/possible controls on arsenic mobilisation

Arsenolite (As^{III}), the main As source at the studied sites, is unstable in the surficial environment and will eventually be mobilised. The transition between As in arsenolite and dissolved As entering the hydrosphere includes the oxidation of As^{III} to As^V and possible precipitation of temporary scorodite from As^V -rich waters in oxidising conditions. The mineralogical evolution and associated dissolved As concentrations are likely to contribute to the observed differences between the Prohibition site and the older Snowy site. Originally all As was present as arsenolite. Over time arsenolite dissolves. Thus, during this stage dissolved As concentrations are dominated by arsenolite dissolution, accompanied by intense scorodite precipitation, as seen at the Prohibition site.

Once all available arsenolite has dissolved, dissolved As concentrations decline. If $[As]$ decreases (e.g. by dilution during rain) to $<10^{-4}$ mol/L (~ 7 mg/L) in a circum-neutral pH regime, scorodite becomes unstable according to Fig. 8B. During this stage, dissolved As concentrations are controlled by

scorodite, with theoretical As concentrations at least two orders of magnitude lower than arsenolite solubility. It is probable that the Snowy site is currently at this stage of site evolution because all remaining arsenolite has been encapsulated by scorodite and is, therefore, not available for dissolution. Furthermore, there was no As 'hot spot' identified at this site, instead maximum As concentrations were found in the substrate along major drainage pathways (locations D, E, F, G; Fig. 3).

5.5. Spatial control on As mineralisation

Spatial variation of As mineralogy and mineral solubilities are outlined for the Prohibition site (Fig. 9). Initially, As was present solely as exposed arsenolite inside the condenser tower (location A, Fig. 2) or as mine spillages (location B, D, and E, Fig. 2). Resultant high dissolved As concentrations flowing from the condenser tower area (Fig. 2) are alleviated by the formation of scorodite (Figs. 2, 9). The strong control by scorodite on the dissolved As output under oxidizing conditions has also been noted by other authors (Ashley and Lottermoser, 1999; Borba et al., 2003; Craw et al., 2000; Deutsch, 1997; Garcia-Sanchez and Alvarez-Ayuso, 2003; Krause and Ettel, 1988; Smedley and Kinniburgh, 2002; Vink, 1996; Williams, 2001). Thus, with increasing distance from the condenser (x-axis) scorodite becomes comparatively more important. Furthermore, arsenolite crystals, present in the surface crust, became encapsulated by scorodite (Fig. 5) and therefore unavailable for dissolution.

Water draining the site is collected in a wetland (D and E, Figs. 2 and 9) before entering the Blackwater catchment (Fig. 1). Conditions in the wetland are below the As^V/As^{III} boundary (Fig. 8B) such that scorodite is not stable (Fig. 8B) and arsenolite is the only crystalline As phase (Fig. 2). Wetland water contained up to 52 mg/L As at a pH of 4.1. This value exceeds scorodite solubility (0.06 mg/L, pH 4, Fig. 9) by almost 3 orders of magnitude (Fig. 2), confirming that in this setting arsenolite solubility is the controlling factor. Some As is also expected to be adsorbed onto soil colloids (Sadiq, 1995), particularly clay surfaces (Sadiq, 1995; Xu et al., 1991), as these are known to adsorb As^V and to a lesser extent As^{III} (Lin and Puls, 2000). It should be noted however, that the boundary in Fig. 9 between adsorbed As and arsenolite in the wetland is solely schematic and has no quantitative basis.

6. Conclusions

Ample scorodite and arsenolite is present at both sites, however, their impact on the downstream environment depends largely on the mineral exposure and dissolved As concentrations in site waters. Processing of the arsenopyrite ore at the historic Waiuta sites has resulted in As-rich mine residues which act as a point source for As in the downstream environment. A strong mineralogical control on As mobility has been observed and year-round precipitation ensures that climatic-rate controls are kept at a minimum. Original site chemistry with respect to As minerals was found to depend mainly on the historic processing technology. Roasting of arsenopyrite ore at Waiuta introduced arsenolite (As_2O_3 polymorph, As^{III}) and the complexity of the roaster flue system controlled the quantity of arsenolite retained on site. The presence of arsenolite distinguishes these sites from historic processing sites, where roasting of the ore did not take place and arsenopyrite is the main As source. Arsenolite occurs as spillage in the surface crust and, at the Prohibition site there is ample arsenolite precipitate still exposed on the inside of the condenser tower. Arsenolite dissolution and oxidation results in locally high dissolved As^{V} concentrations. In oxidizing conditions some of the dissolved As is temporarily immobilized by the formation of scorodite (As^{V}). Scorodite precipitation is most pronounced in acidic conditions in the presence of ample exposed arsenolite, as seen at the Prohibition site. Less scorodite precipitated at the Snowy site where site pH is generally circum-neutral and less arsenolite was originally precipitated on site. This agrees with theoretical predictions based on an Eh–pH diagram, which shows that scorodite can precipitate in circum-neutral pH conditions as long as dissolved As concentrations are high such as during arsenolite dissolution. Scorodite precipitates as an interstitial precipitate cementing the ground around the former roaster area. Thus scorodite formation not only controls dissolved As output during arsenolite dissolution, but also encapsulates arsenolite spillages on the ground, making arsenolite unavailable for further weathering. At present, dissolved As concentrations at the Prohibition site are controlled by arsenolite dissolution, and scorodite continues to build up. At the Snowy site, dissolved As concentrations are predicted to be lower, since all the available arsenolite has dissolved and scorodite is no longer stable. Thus, dissolved As concentrations at

the Snowy site are likely to be controlled by scorodite solubility, which is two (pH 7) to five (pH 4) orders of magnitude lower than arsenolite solubility. In Eh conditions below the $\text{As}^{\text{V}}/\text{As}^{\text{III}}$ boundary, such as in the wetland or water-saturated trench, scorodite is not stable and arsenolite is the main As mineral phase. The findings from these sites are applicable to other historic processing sites where roasting of arsenopyrite ore took place in a year-round wet climate.

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