Formation of arsenic sulphide in gold mine processing wastes, West Coast, New Zealand

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Abstract

We have identified low temperature (<30°C) arsenic sulphide forming in arsenic-rich processing wastes at the historic Blackwater gold mine (1906-1951) on the South Island of New Zealand. Roasting wastes and tailings from the mine are stored within several man-made dams on site. Sediments within the dams contain up 10 wt% As, and up to 330 mg/L As and 20 mg/L SO_4 in pore water. Water pH in the waste material ranges from acid to neutral (pH 2.8-6.7). Bright yellow, macroscopic arsenic sulphide occurs in patchy horizons, 15-45cm below the surface. It is associated with organic matter within the sediments in suboxic to anoxic conditions. Scanning electron microscope imaging of the arsenic sulphide shows a dense network of filamentous As-S nanotubes (100 nm to 2 µm diameter) and poorly-developed nano-crystalline aggregates (< 1 µm). X-ray diffraction and Energy-dispersive X-ray spectroscopy analysis confirms realgar (As_4S_4) as the most likely As-S mineral present. This study provides quantification of this naturally-occurring reduction process and provides insights into the environmental conditions necessary to drive the process. Our findings also have implications for the management of mine wastes and development of novel waste treatment systems.

Keywords: Arsenic sulphide, low temperature, processing wastes, gold mining, realgar.

Introduction

Gold mining in New Zealand in the late 19th and early 20th century has left a legacy of arsenic-rich deposits throughout the gold-mining regions. Mechanical and chemical processing of gold-bearing ore releases arsenic contained within sulphide minerals and historically, very little site remediation work occurred. The potential negative impact this mobilised arsenic may have on the environment and human health depends largely on the ability of dissolved arsenic to be sequestered into stable solid phases through either adsorption or precipitation processes. In recent years, researchers have mostly focused on the formation and stability of secondary arsenic minerals under oxic conditions, or the adsorption to or coprecipitation of arsenic with other minerals. This study identifies rare low temperature arsenic sulphide forming in reduced arsenic-rich processing residues of the historic Blackwater gold mine on New Zealand's West Coast. Through field investigations, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) techniques, this study quantifies the environmental conditions necessary for the formation of this unusual low-temperature arsenic sulphide.

Geology and mining history

Blackwater mine

The Blackwater Mine is located on the West Coast of New Zealand's South Island (Fig. 1) and operated from 1906 until 1951. At its peak, Blackwater was the deepest hardrock gold mine in New Zealand operating over 16 levels with two major shafts, Blackwater and Prohibition, sunk 563.7m and 979.5m respectively. Over its lifetime, Blackwater mine produced 732,907 oz. of gold from 160 Mt of ore (Christie and Braithwaite, 2003). Mining ceased abruptly on 9th July 1951 when the Blackwater shaft collapsed, cutting off ventilation, power and water supplies. Attempts to reopen the shaft immediately after the collapse were unsuccessful and the mine closed on 17th July 1951 (Morris, 1986). In recent years, there has been interest in resuming mining activity at Blackwater, although the collapse of Blackwater shaft and significant post-closure deterioration of Prohibition shaft requires the development of alternative access to the ore body. Construction of a new twin decline directly to No. 16 level is considered the most feasible option at present (OceanaGold, 2015).

The mine targeted the Birthday Reef, a single gold-quartz lode that averages 0.64m in width with a strike length of 1070m (Christie and Braithwaite, 2003). The reef has a N-NNE strike, is subparallel to bedding and steeply dipping. The ore contains abundant arsenopyrite and rare pyrite (Christie and Braithwaite, 2003). Birthday Reef is part of the wider Reefton goldfield, hosted by the Cambrian-Ordovician Greenland Group metasediments (Fig, 1; Cooper, 1974; Adams et al., 1975). The Greenland Group consists of alternating sandstone and mudstone turbidites that underwent Silurian-Devonian greenschist facies regional metamorphism (Adams et al., 1975). The Greenland Group is bordered to the north and east by granitoid plutons of the Late Devonian to Early Carbonifereous Karamea Suite and Early Cretaceous Rahu Suite (Tulloch, 1983). Mafic dykes of various ages cross-cut the Greenland Group (Mortimer et al., 1995). The age and origin of the gold-bearing lodes of the Greenland Group has been debated. Some workers theorize that mineralisation occurred during the late stages of regional metamorphism (Braithwaite and Pirajno, 1993), while others suggest the mineralisation is of a magmatic origin, related to the Rahu Suite or post-Jurassic mafic instrusions (Hunt and Roddick, 1993).

Snowy Battery and Prohibition Ball Mill

From 1908-1938, ore from Blackwater mine was processed at Snowy Battery (Morris, 1986). Over its lifetime, the battery underwent several modifications and upgrades to improve gold recovery. The most significant of which was the addition of the Edwards roasting furnace in 1924. Prior to 1924, concentrates were shipped to Australia for processing or, in the case of low-grade material, stockpiled at the battery (Wright, 2007). Processing of ore at Snowy Battery was a simple process. Ore and water fed through a 30-head stamping battery formed a pulp that passed over mercury-coated copper plates to capture any free gold. This process alone accounted for 80-83% of total gold production. The remaining pulp was classified as coarse (sands) or fine (slimes). Wilfley tables separated the denser sulphides from the coarse fraction. These sulphides passed through the Edwards roaster to oxidise in preparation for the subsequent cyanidation process. Both roasted and unroasted ore were piped to the cyanide plant, filling large steel vats. Any remaining water drained through the base of each vat, and a cyanide solution (0.4% NaCN) was added. The ore would remain in this solution for up to 48 hours, at which point the gold-bearing cyanide solution was piped to the zinc extraction room and the tailings were sluiced out through the base of the tank, along drainage channels feeding

directly into the Snowy River. The cyanide solution, once passed through the zinc boxes, was piped into a storage vat for reuse and the gold, now bound to the zinc shavings, was extracted by further refining (Wright, 2007).
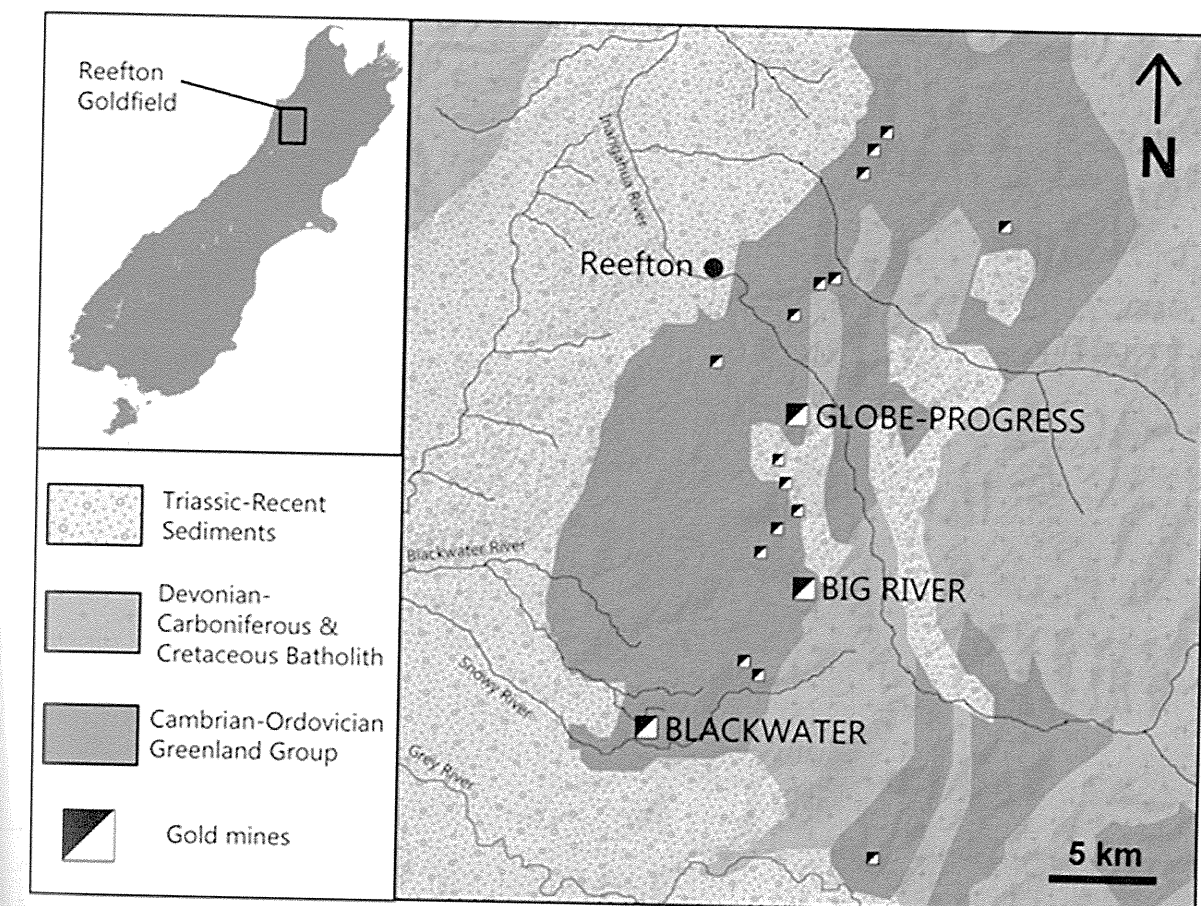

Figure 1. Simplified geological map of the Reefton Goldfield showing location of Blackwater mine and other recent and historic gold mines.

From 1938 until the mines closure in 1951, ore was processed at the Prohibition Ball Mill (Morris, 1986). The mill included several new gold extraction technologies such as flotation cells and strakes, and replacement of the stampers with a ball mill (Morris, 1986). The addition of an arsenic condenser attached to the Edwards roasting furnace enabled the capture of As[III] trioxide dust to sell as a by-product (Wright, 2007).

Methods

Site description and sampling

Blackwater mine is located in a mountainous region 30 km south of the township of Reefton. The site is characterised by a high orographic rainfall (Reefton mean = 2200/yr; Mew and Ross, 1994) and the mean annual temperature is 12°C.

An Olympus Innov-x Omega field portable X-ray Fluorescence Spectrometer (fp-XRF) was used to identify elevated arsenic levels at Snowy Battery. As the majority of tailings from the battery were discharged directly into the Snowy River, and any left on site were reprocessed when Prohibition Ball Mill opened in 1938, only minor quantities remain today. However, fp-

XRF analysis shows that there are localised areas around the site where very high arsenic levels (up to 53 wt%) persist. These 'hotspots' occur at the remains of the roaster and flue, and the foundation remains of the drying room in which Wilfley table sulphide concentrates were stored prior to roasting (Fig. 2a).

In contrast to Snowy Battery, tailings dams and settling ponds were constructed on the slopes surrounding the Prohibition Mill to contain waste materials. The extent of the main tailings impoundment is visible in aerial photos and covers an area of approximately $1400m^2$. A second tailings impoundment (~ 1000 m^2) on the NE edge of the site forms a long trench and has developed into a wetland (Fig. 2c). The composition of this wetland is considerably more complex than the western tailing dam, as it contains tailings, arsenolite (As_2O_3) and As-rich run-off from the adjacent roaster, deconstructed iron cladding and wooden framing from the mill buildings and mine, and an abundance of organic matter. Both tailings dams were targeted for sampling. This study draws on the large amount of data already published on the chemistry of the Prohibition Ball Mill site (Haffert, 2009).

The vibrant yellow to orange colour of orpiment (As_2S_3) and realgar (As_4S_4) was a useful indicator when sampling (see Fig. 2) and was easily identified in the field. Samples were collected at three different sites – Snowy River drying room foundations (Figs 2a, b), Prohibition wetland (Figs 2c, d) and Prohibition main tailings dam (Figs 2e, f). To prevent oxidation reactions, samples were tightly wrapped up and frozen immediately after collection. Once in the laboratory, samples were dried in a low temperature oven (35°C) prior to analysis.

XRD

For identification of arsenic sulphide, mineral samples were separated from closely associated organic material by hand picking under a light microscope. Samples were powdered in an agate mortar and pestle and mounted on glass slides. X-ray diffraction was conducted on a PANalytical X'Pert PRO MPD PW3040/60 diffractometer with a CuK_α source (λ=1.5406Å). Continuous scan data were collected at diffraction angles between 3° and 60° operating at 40 kV and 30 mA with a step size of 0.008° and 10.075 seconds per step. Analysis and data processing was performed with X'Pert HighScore v4.0 and the ICDD PDF-4+ database.

SEM

A sample of the sulphide concentrate from Snowy Battery was made into a standard polished thin section (30 µm thick). The thin section was examined with a polarized light microscope to select suitable areas for more detailed examination. Samples of arsenic sulphide from each site were mounted on pin stubs using double-sided carbon tape. The polished thin section and stub-mounts were carbon coated using an Edwards E306A vacuum coating system. Samples were examined with a Zeiss Sigma VP FEG scanning electron microscope with an Oxford Instruments XMax 20 Si drift energy dispersion X-ray detector (EDX) at the Otago Centre for Electron Microscopy (OCEM). The EDX analytical system was operated at 15 keV. Spot analyses were obtained with a tightly focussed beam that interacted with sample volumes with diameters of ~2 µm. Analytical uncertainties for Na and heavier elements are ±0.2 wt.%.

Figure 2. Arsenic sulphide samples in the field. A) Remains of the concentrates drying room at Snowy Battery. Heaps are now largely composed of weathered sulphides and timber framing. B) Sample collected from the waste pile. C) The Prohibition wetland containing tailings, discarded timber and iron cladding. Note the vegetation mats. D) Sample collected from Prohibition wetland. E) Sediments in the western tailings dam. Arsenic sulphide forming on the surface of buried organic matter (red circles) retrieved from a depth of ~40cm. F) fp-XRF measurement of of the tailing material in the western tailings dam.

Results

Characterisation of sample sites

The three samples sites chosen for the study have the typical characteristics of arsenic-rich gold mine waste, although they differ from one another in composition. Material collected from Snowy Battery is highly heterogenous, composed of unroasted sulphide ore concentrate, small fragments (up to 2 cm) of weathered Greenland Group greywacke, organic material and fragments of timber and concrete. The sulphide minerals are highly weathered and the material is amalgamated with a pale green secondary cement. A pH of 2.8 was determined from a paste pH of the sample. Arsenic levels in the material, as measured by fp-XRF, are extremely variable and range from ~1400 ppm to 21 wt%.

The tailings in the western dam at Prohibition Mill cover an area of approximately 1400 m^2 and vary in depth from <5 cm to ~40 cm. The tailings are composed of cm-scale layers of red silt and sand sized sediments derived from the cyanidation and roasting processes. As levels, as measured by fp-XRF, typically range from 1000-8000 ppm within the tailings impoundment although the As content of the material measured in the immediate vicinity of the arsenic sulphide sample was ~11,000 ppm. A pH of 5.0 was determined from paste pH of the sample material.

Previous work by Haffert (2009) has extensively characterised the mineralogy and geochemistry of the Prohibition wetland site. The sediments are composed predominantly of quartz, muscovite and haematite, minor arsenolite, with trace quantities of scorodite occurring only at the surface. Arsenic levels in the wetland sediments vary from 1.7-10.2 wt%. Arsenic concentrations in surface water in the wetland range from 4-52 mg/L, with pore water containing up to 370 mg/L As and pH ranging from 3.2-6.7 (Haffert, 2009). A pH of 3.7 was determined from paste pH of the wetland material collected in this study.

Mineralogy of the sites

XRD patterns of the bright yellow mineral collected at each site confirm the presence of arsenic sulphide in near-surface tailings. The diffraction pattern shows that the arsenic sulphide is crystalline rather than amorphous (Fig. 3). Comparing the diffraction pattern to the ICDD database indicates that realgar (As_4S_4) is the most likely mineral species present. Semiquantitative EDX analysis confirms the arsenic sulphide is composed of ~70% As and ~30% S indicating a As:S ratio of 1:1 providing further evidence of an As_4S_4 crystal form, rather than orpiment (As_2S_3). SEM imaging (Fig. 4) of the arsenic sulphide shows two main forms; filamentous nanotubes (100 nm to 2 μm in diameter; Figs 4b, 4c, 4d) and poorly developed crystalline aggregates (<1 μm; Fig. 4d). The arsenic sulphide samples collected from the wetland commonly occur in close association with detrital arsenolite from the roasting furnace (Fig. 4c).

XRD and SEM analysis confirms that the concentrates at Snowy Battery are mainly composed of variably weathered arsenopyrite with minor pyrite, quartz, muscovite and other phyllosilicates. This material is cemented by scorodite ($FeAsO_4 \cdot 2H_2O$; Fig. 4a). Although arsenolite (As_2O_3) is present in other areas of the site, e.g. the roaster flue remains, it has not been identified in the ore concentrates. The sample collected from the western tailings dam contains quartz, hematite, muscovite and other minor phyllosilicates. Arsenolite and Scorodite have not been identified by XRD.
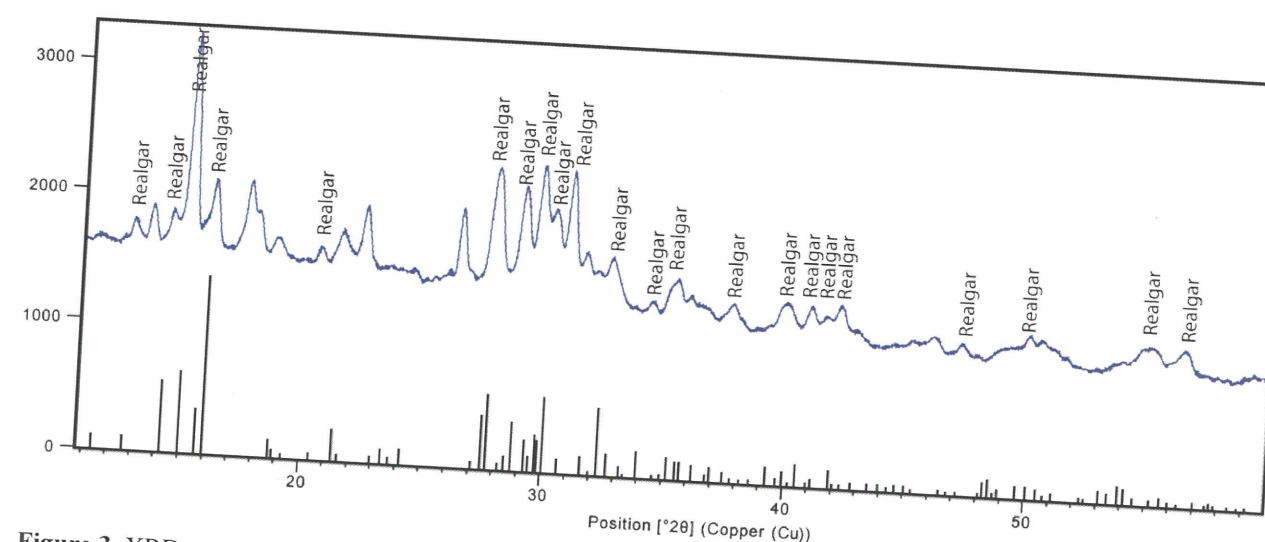
Figure 3. XRD pattern of arsenic sulphide sample collected from Prohibition wetland. Black peaks represent ICDD diffraction pattern 01-081-8782 – Realgar (As_4S_4).

Discussion

Arsenic transformations

The arsenic at the Blackwater processing sites originates as mesothermal arsenopyrite (FeAsS). Roasting of the ore produces arsenolite (As_2O_3) which undergoes dissolution, along with weathering and dissolution of primary arsenopyrite. This dissolution process forms dissolved As phases (e.g. H_3AsO_3, H_3AsO_4) which will either undergo sorption onto iron oxyhydroxides or precipitation as secondary As minerals i.e. scorodite ($FeAsO_4 \cdot 2H_2O$). Secondary arsenolite and scorodite are well documented on site, but arsenic sulphide has not previously been identified.

Currently at Blackwater mine, environmental conditions permit the formation of rare low-temperature realgar. Of note is the presence of realgar in three different settings; weathered sulphide concentrates, iron-rich quartzose tailings, and iron-rich quartzose tailings mixed with abundant arsenolite and organic matter. In the western tailings dam and wetland at Prohibition, realgar occurs 10-40 cm below the surface in suboxic to anoxic conditions. At Snowy Battery, realgar also occurs at the surface in close association with scorodite and highly weathered primary sulphides. Geochemical modelling by O'Day et al. (2004) indicated that in reducing acid waters with high As-levels (μM/L) low temperature arsenic sulphide can form. They predicted that in waters with high iron and low sulphate concentrations, excess iron will prevent the formation of soluble thioarsenic species causing realgar to precipitate. Conversely, in high sulphate, low iron waters limited precipitation of iron sulphides will cause orpiment to precipitate. The waters at Blackwater mine are consistent with those described in their study (Fig. 5). They are acidic (pH range = 2.8 – 5.0; this study) and anoxic to suboxic at depth. The presence of arsenopyrite and pyrite provide a source of iron at Snowy Battery, while haematite from the roasting process provides a source of iron in the wetland and tailings dam. Higher levels of sulphate could be expected in the wetland and at Snowy Battery where dissolution of gypsum from the roaster, and dissolution or arsenopyrite respectively, occur. Previous work by Haffert (2009) characterised the waters of the Prohibition wetland; sulphate concentrations were 6.9-20.7 mg/L, and iron concentrations were 0.71-34.2 mg/L. Several years after those measurements were taken, corrugated iron

roofing and iron waste drums from the mill building were added to the wetland (Fig. 2c), potentially providing an additional source of iron. The largest quantities of realgar are seen in the wetland where it is dispersed in large (cm-dcm scale) mat-like structures just below the surface. However, the realgar appears to have been absent during the extensive site characterisation undertaken by Haffert (2009). It is possible that formation of realgar in the wetland was initiated by the increase in dissolved iron concentration when the waste materials were added.
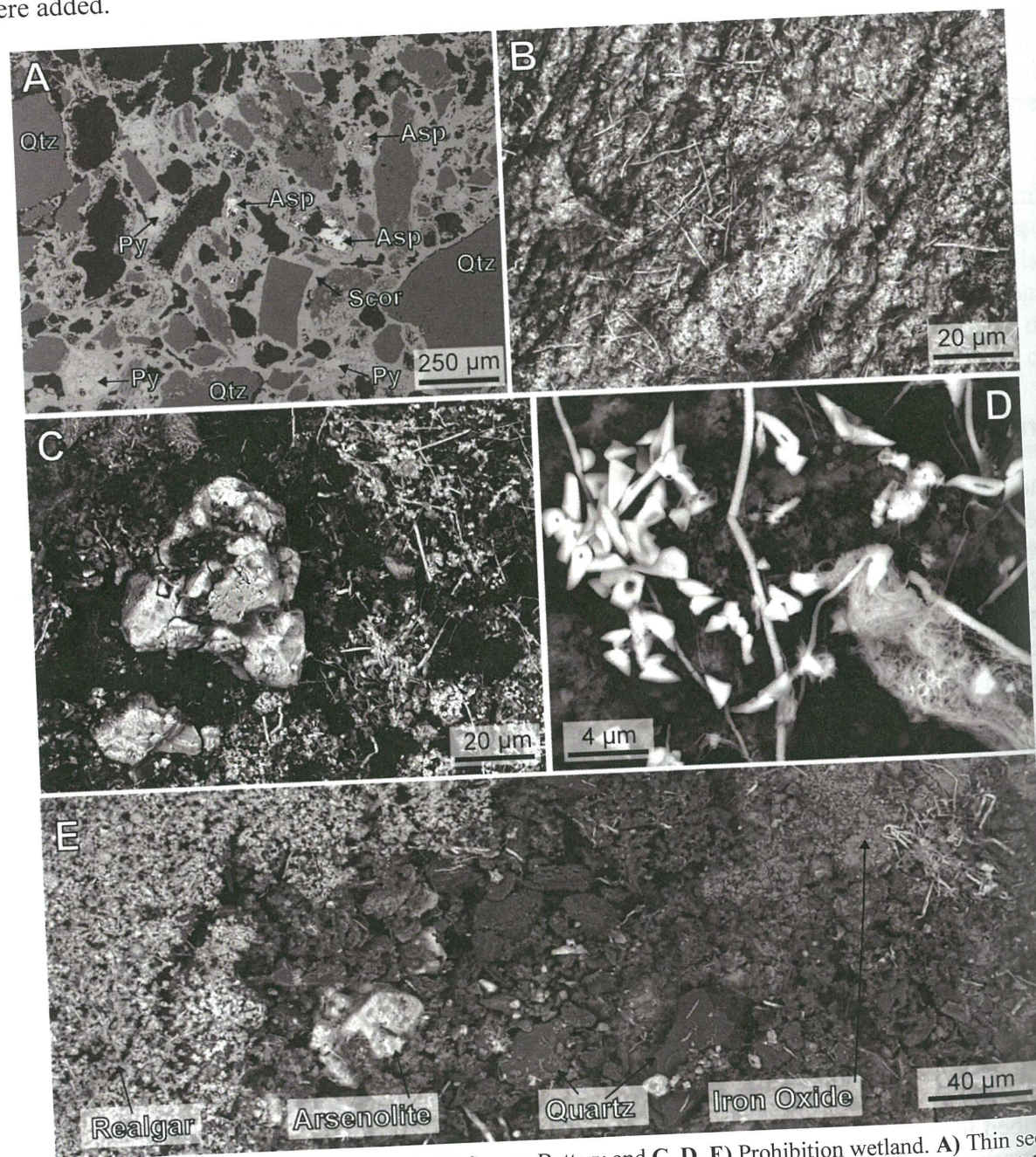
Figure 4. SEM images of samples from **A, B)** Snowy Battery and **C, D, E)** Prohibition wetland. **A)** Thin section image of weathered sulphides, showing alteration of arsenopyrite (*Asp*) and pyrite (*Py*). Scorodite (*Scor*) has formed a secondary cement. **B)** Realgar (*white*) forming on the surface of wood. **C)** Detrital crystal of arsenolite (*centre left*) dissolving with nanocrystalline realgar forming around it. **D)** View of nanocrystalline aggregates of realgar and filamentous realgar nanotubes. **E)** Section across the surface of a fragment of tailing material showing detrital iron oxide, arsenolite and quartz with realgar crystals forming on the surface.
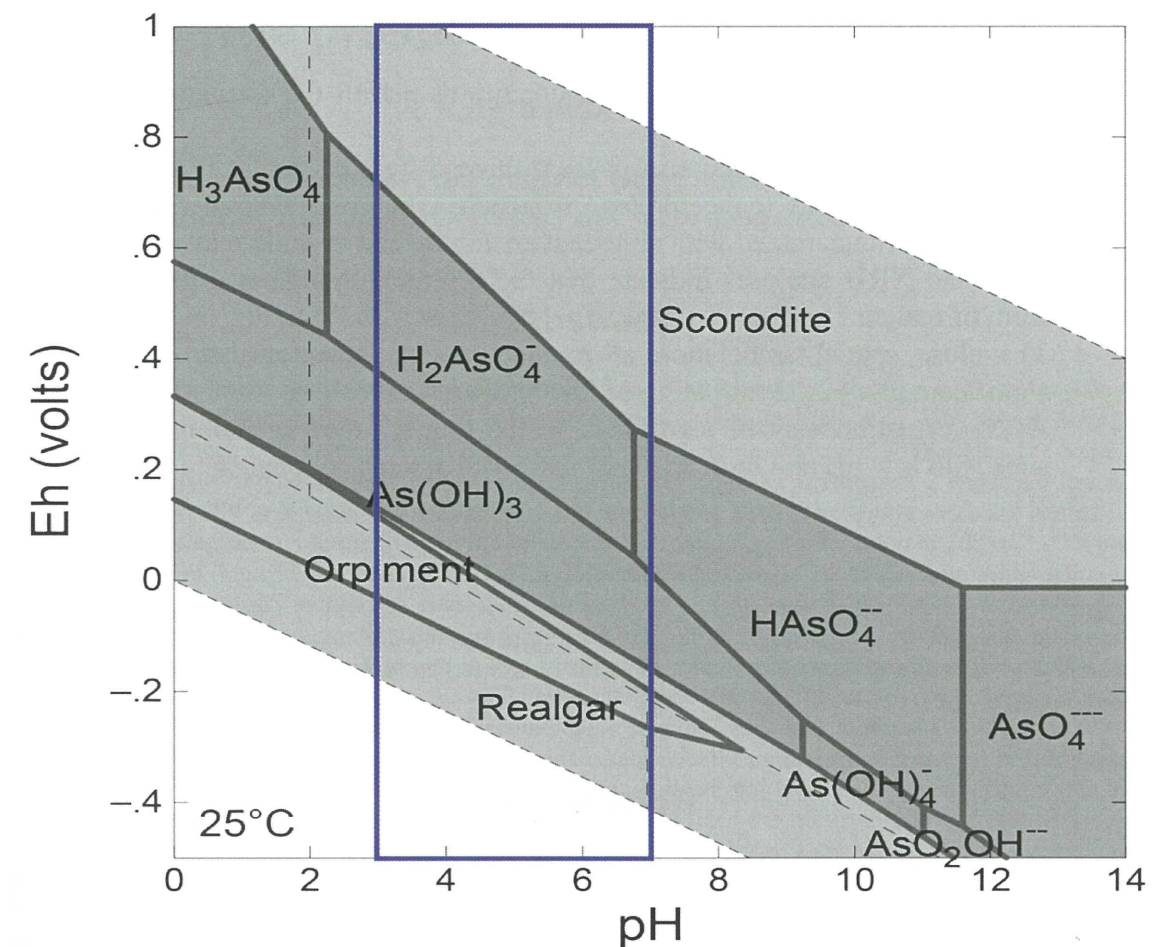
Figure 5. Eh-pH diagram of the H-O-As-Fe-S system at 25°C and 1 bar total pressure showing aqueous As species, scorodite and realgar. Concentrations are $[As]=10^{-3}$ mol/L, $[SO_4^-]=10^{-5}$ mol/L, $[Fe^{2+}]=10^{-4}$ mol/L. The environmental conditions at Snowy Battery and Prohibition Mill are contained within the blue box.

The occurrence of low-temperature arsenic sulphide is a relatively recent discovery and at present, not much is known about the solubility. Although pH, iron and sulphide concentrations are important factors in the solubility of low temperature realgar, geochemical modelling suggests that dissolved arsenic concentration is the main control. O'Day et al. (2004) predicted that the solubility threshold of realgar is 10-100μM. At Blackwater mine, arsenic levels are likely to remain above this level, although in very high rainfall events, dissolved arsenic levels may temporarily decrease causing the realgar to dissolve.

The role of organic material in the formation of arsenic sulphide at Blackwater mine is not yet understood. The close spatial correlation (mm- to cm-scale) of organic material and realgar is a strong indicator that organic material is involved in the reduction process, either directly as a reductant or through the enhancement of microbial reduction. Interestingly, in the western tailings dam realgar is only present where organic material such as tree branches or fragments of timber framing are encapsulated at depth (Fig. 2e). This phenomenon is also observed at Snowy Battery where the realgar is forming directly on timber fragments (Figs 2b, 4b) or is very closely associated with it. The abundant organic material in the wetland may provide an explanation for the more widespread realgar deposits.

Conclusions

- At Blackwater mine, environmental conditions permit the formation of rare low temperature arsenic sulphide.
- The arsenic sulphide occurs in at least three different sites at Blackwater mine: weathered sulphide concentrates, iron-rich quartzose tailings, and iron-rich quartzose tailings mixed with abundant arsenolite and organic matter.
- SEM and XRD analyses indicate that the arsenic sulphide is a low-temperature form of realgar (As_4S_4).
- The close spatial association of organic matter indicates that it may play a significant role in the formation of low temperature realgar.
- As_4S_4 formation may be significant in the sequestration of mobilised arsenic in sites with low pH and high levels of dissolved arsenic, sulphate and iron.

Acknowledgements

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