



# Authigenic realgar and gold in dynamic redox gradients developed on historic mine wastes, New Zealand

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## ARTICLE INFO

Editorial handling by Kate Marie Campbell

### Keywords:

Redox  
Arsenolite  
Realgar  
Scorodite  
Gold  
Authigenic  
Tailings

## ABSTRACT

Complex redox and pH microenvironments have developed on arsenic-rich (percent level As) mine wastes at two gold mine processing areas in southern New Zealand that were abandoned 70–80 years ago. Redox conditions range from surficial zones that are being actively oxidised, with formation of authigenic scorodite and Fe oxides, to zones of active chemical reduction around organic debris where authigenic As sulfides, mainly realgar, are actively forming. Authigenic realgar is forming in low-redox microenvironments in a high-sulfur setting with decomposing primary pyrite and arsenopyrite, and in low-sulfur pre-oxidised As-rich mine tailings. Realgar has formed in close proximity (micron scale) to authigenic and/or detrital arsenolite at one low-sulfur site, and in close proximity (cm scale) to authigenic scorodite at the sulfur-rich site. The latter site also has minor accumulations of authigenic gold, which is nanoparticulate and microparticulate and dispersed through a coating of Fe oxyhydroxide and biofilm on authigenic scorodite. Gold was probably mobilised by ephemeral metastable thiosulfate complexes during oxidation of primary auriferous sulfides, and redeposited as those complexes decomposed. Detrital gold has not been noticeably dissolved and redeposited in the low-sulfur mine wastes. The dynamic redox gradients that have developed on these mine wastes are distinctly different from those that form on most mine wastes elsewhere, where an oxidation front progressively penetrates into primary sulfide residues. The dynamic redox gradients can persist at these New Zealand sites until all the organic debris has decomposed, after which the more reduced components including authigenic realgar will become oxidised.

## 1. Introduction

Arsenic-bearing residues are common around gold mines, and these residues can become progressively oxidised unless they are buried and encapsulated (Blowes and Jambor, 1990; Hudson-Edwards et al., 2011; Hayes et al., 2014). The most common result of oxidation is a redox gradient within the residues that extends from the most oxygenated zone into less oxygenated primary material that commonly contains sulfide minerals (Blowes and Jambor, 1990; Hayes et al., 2014). The oxidation front moves progressively into the primary material over time and the oxidised zone expands to ultimately incorporate all the waste material. In contrast, some redox gradients in mine wastes and in natural settings can be more dynamic, so that the low-redox ends of these gradients host active reductive reactions (O'Day et al., 2004; Rigaud et al., 2013; Johnson et al., 2014; Gorny et al., 2015; Bentz and Peterson, 2017). In these latter cases, precipitation of new authigenic low-redox minerals can occur within, or instead of, the primary reduced material. This paper reports on examples of dynamic redox gradients in

which the arsenic sulfide mineral realgar (AsS) is being precipitated. Near-surface, low temperature deposition of realgar is rare (O'Day et al., 2004; Demergasso et al., 2007; Langner et al., 2012; Drahota et al., 2013; Bentz and Peterson, 2017), and our examples in mine wastes constrain the geochemical processes and time scales in which authigenic realgar can form.

Despite gold's reputation as a “noble metal”, there is abundant evidence for gold dissolution and reprecipitation at ambient temperatures in surficial geological environments (Mann, 1984; Webster and Mann, 1984; Stoffregen, 1986; Bowell, 1992; Reith et al., 2010, 2012). The time scales of this gold mobility are poorly understood because of the rarity of authigenic gold occurrences in sites that can be dated with precision (Shuster et al., 2017). On the other hand, experimental studies have shown that gold mobilisation can occur under laboratory conditions on a time scale of months, under both inorganic and biologically-mediated conditions (Webster, 1986; Vlassopoulos and Wood, 1990; Usher et al., 2009; Shuster et al., 2016). In this study, we present evidence for microparticulate and nanoparticulate gold precipitation in

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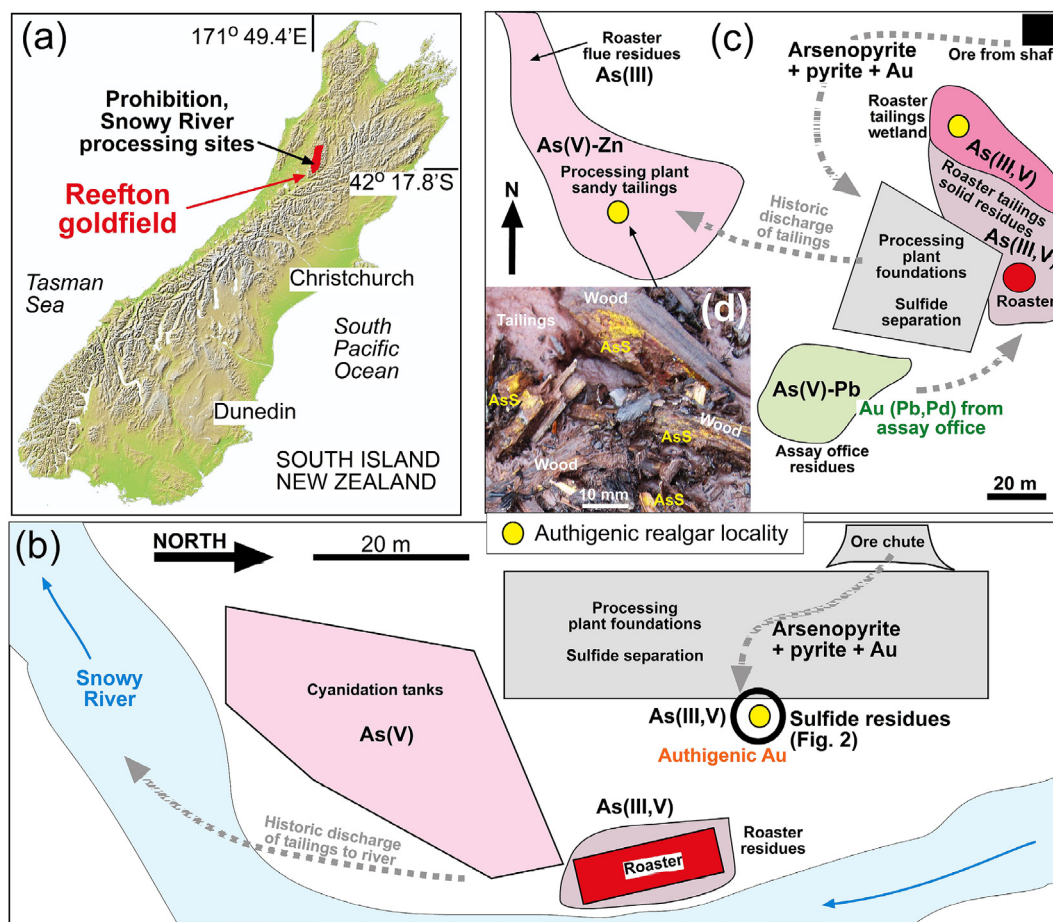
E-mail address: [dave.craw@otago.ac.nz](mailto:dave.craw@otago.ac.nz) (D. Craw).

<https://doi.org/10.1016/j.apgeochem.2018.08.009>

Received 4 June 2018; Received in revised form 8 August 2018; Accepted 20 August 2018

Available online 22 August 2018

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**Fig. 1.** Locality maps for the Reefton goldfield mine wastes described in the text, with authigenic realgar occurrences. General As oxidation states and principal accompanying metals for various processing residues are indicated. (a) Regional map showing location of Reefton goldfield. (b) Map of Snowy River processing site (abandoned 1938), with location of sulfide residues described in text. (c) Map of Prohibition processing site (abandoned 1951) prior to rehabilitation in 2016. (d) Photograph of wood fragments excavated from bottom of tailings deposit at Prohibition site in c, with authigenic realgar coatings (AsS; yellow-orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

a dynamic redox gradient containing authigenic realgar, in sulfur-rich mine wastes of known age. From these observations we construct a conceptual model for the inter-relationships of As, S and Au during microenvironmental evolution in mine wastes on human time scales.

## 2. General setting

The Reefton goldfield, in which the sites described in this study are located, lies on the western side of the South Island of New Zealand (Fig. 1a). The goldfield lies on the windward side of the main mountain chain (Fig. 1a), and consequently receives frequent high orographic rainfall events throughout the year. Average annual rainfall is ~2300 mm under warm temperate conditions, with mean temperature of 12 °C (Mew and Ross, 1994). Topography is moderate to steep, with streams incised into bedrock between ridges cloaked in rainforest.

The goldfield hosts a set of Paleozoic orogenic gold deposits that are dominated by steeply dipping quartz vein systems (Christie and Braithwaite, 2003; Hamisi et al., 2017). Ore from these deposits contains some free macroscopic gold, and abundant pyrite and arsenopyrite in which micron-scale gold is encapsulated (Christie and Braithwaite, 2003; Hamisi et al., 2017). The most productive mining area, near the southern end of the goldfield, occurred in what was locally known as the Birthday Reef (Christie and Braithwaite, 2003; Hamisi et al., 2017). Historic processing of this ore involved sulfide mineral separation and oxidative roasting, and cyanidation for gold extraction. Two separate processing sites were developed during the life of the mining area:

Snowy River site from 1906 to 1938, followed by Prohibition site from 1938 until the mine finally closed in 1951 (Fig. 1b and c).

The processing sites were abandoned after they were no longer required, without rehabilitation. Consequently, there are residues of various components of the processing systems lying around the sites (Fig. 1b and c; Table 1), and these residues have been exposed to rainfall incursion and oxidation since these sites were abandoned. Tailings from the Snowy River site were discharged into the river during normal operations (Fig. 1b) and these have since been removed by flood events. However, small amounts of residues that spilled during operations remain at the site, and in this study we focus on deposits of sulfide mineral concentrates that remain adjacent to the main processing plant foundations (Fig. 1b; Table 1). Tailings and various spilled residues largely remained on the Prohibition site during operations and after abandonment (Fig. 1c; Table 1). However, subsequent identification of extremely high arsenic concentrations in residues at the Prohibition site (Haffert and Craw, 2008a; b; Haffert et al., 2010) led to rehabilitation of some of the site in 2016. Sampling for this study was carried out before and during this rehabilitation process, in residues in which the ore sulfides had been through the roasting oxidation system so only minor sulfur remained (Fig. 1c; Table 1).

## 3. Methods

Samples were selected for this study from shallow (< 1 m) spade excavations through deposits of variably oxidised mine wastes at the

**Table 1**

Summary of the chemical and mineralogical<sup>a</sup> features of As-rich processing residues from mining of the Birthday Reef in the Reefton goldfield, New Zealand (Fig. 1a–d). Data from this study, with additional information from Haffert and Craw (2008a), Haffert et al. (2010), Hamisi et al., 2017, and McLachlan and Craw (2018).

Site	Snowy River plant	Prohibition plant	Prohibition plant
Age	Abandoned 1938	Abandoned 1951	Abandoned 1951
Residue type	Sulfide concentrate sand	Roaster tailings; sand, metallic mineral matter	Sandy process tailings
Dissolved sulfur environment	High sulfur; perennially moist	Low sulfur; wetland; $\text{SO}_4^{2-} = 7\text{--}21 \text{ mg/L}$	Low sulfur; water-saturated
Silicate content	Low	Low	High
Original metallic minerals	Pyrite; arsenopyrite; trace chalcopyrite, galena, sphalerite, cobaltite, Bi-minerals	Arsenian hematite & maghemite; scorodite, arsenolite, minor gypsum	Arsenian hematite & maghemite; scorodite; rare arsenolite,
pH range	3–7	3–7	4.5–5.5
Redox mineral range	Basal sulfides, surface oxides	Basal sulfides, surface oxides	Basal sulfides, surface oxides
Organic material as reductant	Remnants, wooden retaining structure	Relict forest debris, pollen	Relict forest debris
Dissolved As	Not determinable	50–370 mg/L	< 0.3 mg/L
Dissolved $\text{Fe}^{2+}$	Not determinable	20–40 mg/L	Not determinable
Authigenic oxidised As minerals	As-bearing Fe oxyhydroxide	Scorodite	As-bearing Fe oxyhydroxide
Authigenic intermediate redox As minerals	Scorodite; kañkite	Arsenolite	Not present
Authigenic reduced As minerals	Realgar; trace uzonite, alacranite, orpiment	Realgar; trace uzonite, alacranite, orpiment	Realgar
Original Au	Auriferous sulfides; rare free particles (~5% Ag)	Particle from assay; trace Pb, Pd, Mo, Cd, Pt	Rare free particles
Authigenic Au	Microparticulate, nanoparticulate, with scorodite	None detected	None detected

<sup>a</sup> Arsenic mineral formulae: **arsenopyrite** =  $\text{FeAsS}$ ; **scorodite** =  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ; **kañkite** =  $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$ ; **arsenolite** =  $\text{As}_2\text{O}_3$ ; **realgar** =  $\text{AsS}$  or  $\text{As}_4\text{S}_4$ ; **uzonite** =  $\text{As}_4\text{S}_5$ ; **alacranite** =  $\text{As}_8\text{S}_9$ ; **orpiment** =  $\text{As}_2\text{S}_3$ .

two processing sites (Fig. 1b and c; Table 1). The excavations extended to buried wood fragments that typically occur at and near the base of the waste deposits. Some of that wood is anthropogenic building material, and some is relict forest debris, and distinguishing these is not always possible because of advanced degradation. All the excavated material was at least moist throughout, and most wastes were fully saturated with water when sampled. Material from the roaster tailings wetland at the Prohibition site (Fig. 1c) was excavated after the wetland had been partially drained in the early stages of the recent site rehabilitation activity. This drainage of the wetland permitted access that was not available when an earlier study of the fully-saturated wetland was undertaken with coring tubes pushed through a water cover and underlying sediment (Haffert et al., 2010). Sampled material was collected in clean plastic bags, and dried at 25–30 °C in a laboratory oven.

General concentrations of arsenic and metals in the mine wastes around the sampling points were analysed with an Olympus Innov-X Systems model XPD-4000 field portable X-ray fluorescence instrument (FP-XRF). The FP-XRF model is similar to the one used elsewhere at the Prohibition processing site (Haffert and Craw, 2009; McLachlan and Craw, 2018) using similar field protocols. Calibration curves for As contents of different materials were constructed using sets of samples of differing As contents between ~50 and ~50 000 mg/kg. These samples were analysed with the FP-XRF instrument while wet and after drying, and then analysed in a commercial laboratory (cf McLachlan and Craw, 2018).

Minerals in the mine wastes were examined and identified with standard incident light microscopy in polished resin blocks. Hand-picked mineral material was identified by X-ray diffraction (XRD), using  $\text{Cu K}\alpha$  radiation on a PANalytical X'Pert Pro MPD PW3040/60 instrument housed in the Geology Department, University of Otago. Resultant diffraction patterns were analysed using a PANalytical High Score software package. Further examination of mineral textures and compositions were done on a scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) analytical facility. Flakes of dried realgar-bearing material were mounted on carbon tape on aluminium holders for placing in the SEM. These samples were carbon-coated to limit charging prior to examination with a Zeiss Sigma VP (variable pressure) SEM fitted with a HKL INCA Premium Synergy Integrated EDS system at the Otago Centre for Electron Microscopy (OCEM), University of Otago.

## 4. Results

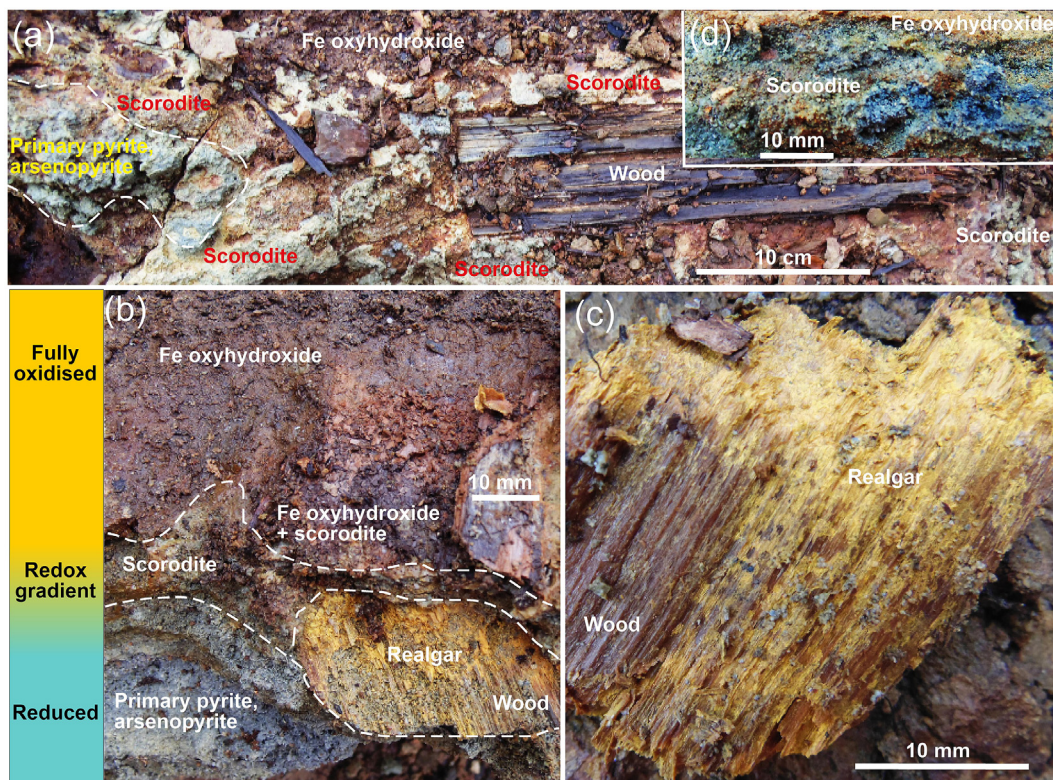
### 4.1. Snowy River site: sulfur-rich mine wastes

Residues of mine wastes at the Snowy River processing site have wide ranges in As contents, typically between ~1000 and ~50 000 mg/kg, with localised patches reaching 59 wt% As. The highest As contents occur in localised patches rich in arsenolite, especially around the remains of the roaster building (Fig. 1b). Residual sulfide mineral concentrates at the margin of the principal processing plant area (Fig. 1b; 2a–d; Table 1) consist of quartz-bearing sand rich in pyrite (predominant) and arsenopyrite (Table 1), with As contents between 1400 mg/kg and 21 wt%. Pyrite from the ore is variably arsenian and can contain up to 1 wt% As (Hamisi et al., 2017).

The sulfide-bearing sands have become cemented with incipient alteration products and now form hardened zones in remnant outcrops (Fig. 2a,c). There are steep redox gradients on the centimetre scale between residues that contain largely original sulfides and pervasively oxidised residues that contain no sulfides and consist of almost pure Fe oxyhydroxide (Fig. 2a and b). Within the redox gradients, scorodite is an intermediate phase, which contributes to cementation of the sulfides and dominates in a zone between sulfides and iron oxyhydroxide, before decreasing in proportion into the iron oxyhydroxide zone (Fig. 2a and b). Paste-pH measurements show that the most sulfidic parts of the redox gradient have pH as low as 2.8 as a result of oxidative acidification. However, most of the residues in the redox gradients have paste-pH of 3.5–4, rising to > 6 in the most oxidised Fe oxyhydroxide material and the surrounding environment.

Scorodite occurs in a wide range of forms within the redox gradients, and ranges in colour from green-grey to blue-green (Fig. 2a,b,d). Minor kañkite is intergrown with scorodite. Near the zones of relict sulfides, scorodite has pseudomorphously replaced arsenopyrite, with minor ragged relict arsenopyrite cores remaining in some particles. This pseudomorphous scorodite is typically well-crystallised and has molar Fe/As ratios near 1, similar to the original arsenopyrite. These pseudomorphs are cemented by poorly-crystalline Fe arsenate material with variable As contents between 20 and 45 wt%. Much of this amorphous Fe arsenate material is finely intergrown with As-bearing (~5 wt%) Fe oxyhydroxide. The pseudomorphous scorodite textures become less discernible through the redox gradient as Fe oxyhydroxide becomes more abundant. Nevertheless, even the most oxidised material contains highly variable As contents, between 5 and 20 wt%, within the Fe





**Fig. 2.** Environments and mineralogy in sulfide residues at Snowy River processing site. (a) Variably cemented and oxidised sulfide residues partially impounded by wooden framework. (b) Close view of the redox gradient between primary sulfides (lower left) and the most oxidised material (top), with intermediate realgar and scorodite. (c) Realgar-coated wood from the redox gradient in b. (d) Blue-green scorodite in roaster residues. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

oxyhydroxide.

#### 4.2. Authigenic realgar at Snowy River site

The sulfide residues were originally impounded by low wooden walls, which have now largely collapsed. Fragments of wood are irregularly intermixed with the residues and locally cemented within the variably oxidised primary sulfides (Fig. 2a–c). Wood fragments adjacent to the primary sulfide remnants have become coated and impregnated with yellow-orange authigenic As sulfides that are dominated by realgar (Fig. 2b and c). XRD analysis of hand-picked near-pure separates of this material shows that in addition to the dominant realgar, there are indications of several other As sulfides, including orpiment, uzonite, and alacranite (Fig. 3a; cf Lee et al., 2007). Pararealgar appears to be absent or only a minor component (Fig. 3a). The realgar and associated authigenic As-S minerals are microcrystalline and form thin (~10 μm) coatings on the wood (Fig. 4a–c). In addition, these coatings are accompanied by hair-like fibres of As sulfides that are irregularly distributed over the wood surfaces (Fig. 4a–c), similar to As-sulfide nanotubes described by Lee et al. (2007).

#### 4.3. Authigenic gold at Snowy River site

A polished section was prepared from a sample of partially oxidised sulfide residue from the steep redox gradient (Fig. 2b). This residue has become cemented to form a hard rock-like material, and was discovered to contain minor amounts of authigenic gold (Fig. 5a–d) in addition to rare primary free gold. The residue specimen is dominated by angular silicate particles and relict sulfide mineral particles pseudomorphously replaced by scorodite, and has been pervasively cemented by scorodite and related Fe-As rich precipitates (Fig. 5a). One free gold particle (~50 μm) is present in the polished part of the section, and a cavity in

the section contains one particle of a Bi-rich mineral (Fig. 5a–d) that is a rare component of the primary ore (Hamisi et al., 2017).

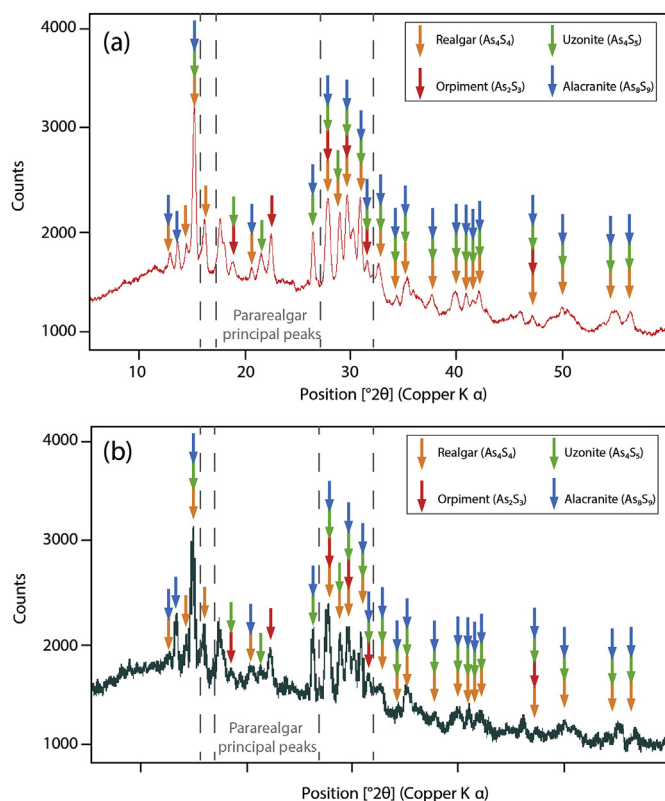
The sectioned specimen was treated with epoxy resin for sectioning purposes, but the scorodite cementation inhibited incursion of the resin into the interior of the specimen. The grinding process during section-making has exposed a resin-free interior cavity with abundant scorodite cement forming botryoidal masses (Fig. 5a–c). The cavity surface is coated with a thin electron-transparent film of amorphous iron oxyhydroxide intermixed with abundant light elements (C-O-H?) of presumed organic material (biofilm). This coating lacks the characteristic chemical signature (especially Cl) of the resin used in the sectioning process.

Irregularly shaped nanoparticulate and microparticulate gold occurs scattered across the surface of this cavity (Fig. 5a–d). Some of the gold appears suspended above the mineral surfaces in SEM images (Fig. 5a–d) because that gold is hosted within the electron-transparent surface film. Some of the gold has clearly been deposited on the exterior surface of botryoidal scorodite cement (Fig. 5a–d), and therefore the gold deposition post-dated the cementation processes. The gold contains no detectable Ag, or other metallic impurities, although precise analyses are not possible on these small and irregularly shaped particles.

#### 4.4. Prohibition site: low-sulfur mine wastes

The processing system at the Prohibition site was essentially the same as that at the Snowy river site, but no sulfide residues remain at the Prohibition site. Instead, the processing residues are dominated by tailings deposits that contain products of the sulfide roasting component of the operation. The roasting process removed almost all the sulfur from the sulfide concentrates and oxidised the iron. Most sulfur was discharged to the atmosphere as SO<sub>2</sub> during the historic processing





**Fig. 3.** X-ray diffractograms for hand-picked yellow-orange As sulfide coatings on wood, with inferred mineral identifications of principal peaks. Dashed grey lines indicate four principal peak positions of pararealgar, which appears to be minor or absent from these samples. (a) Snowy River sulfide residues (Fig. 2b,c), (b) Prohibition roaster tailings wetland (Fig. 6a). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

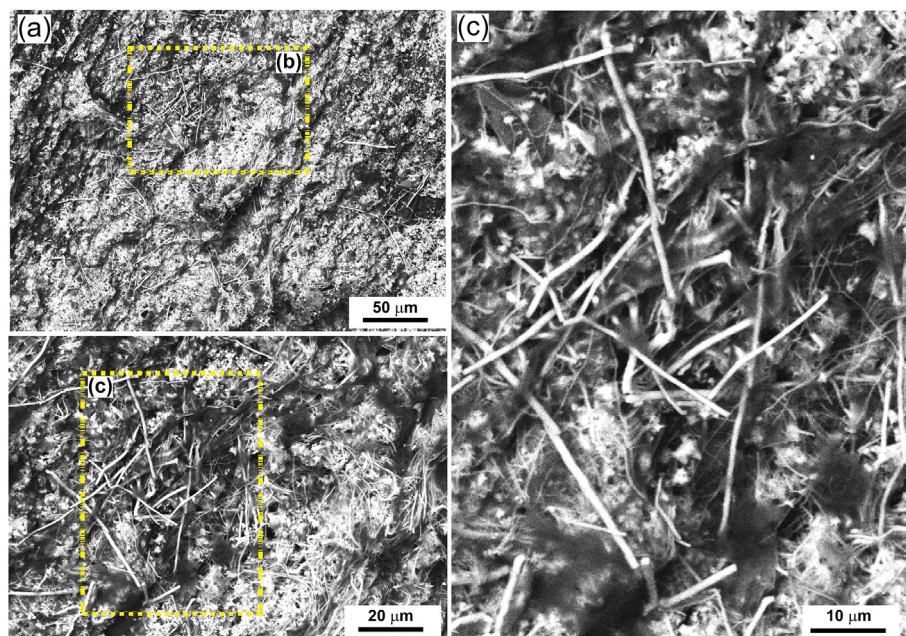
activity, with minor amounts of gypsum remaining in residues around the roaster site. Likewise, arsenic from arsenopyrite was volatilised during roasting, and some was lost to the atmosphere with the sulfur. Most of the volatilised arsenic was deliberately condensed as arsenolite in the roaster system, and was sold as a byproduct.

There are two different tailings disposal areas at the site (Fig. 1c), and the minerals present in these tailings are similar but mineral proportions are variable. Residues near the roaster and in the adjacent wetland are dominated by arsenolite, scorodite and hematite (Table 1), and general As contents range from 10 000 to 400 000 mg/kg (1–40 wt % As). In contrast, the processing plant tailings are dominated by silicate sand from crushed ore with subordinate scorodite and hematite, and rare arsenolite deposited directly from the roaster, with general As contents of tailings ranging from 4000 to 9000 mg/kg. Hematite in all the tailings typically contains 1–3 wt% As in solid solution (McLachlan and Craw, 2018).

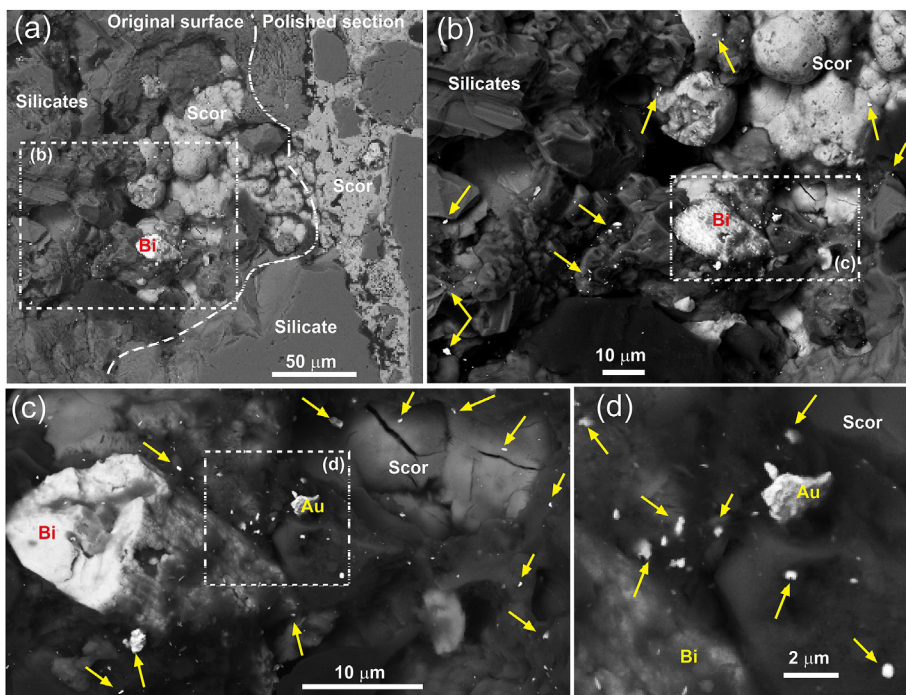
The sandy tailings from the processing plant have broadly uniform pH near  $5 \pm 0.5$  in their pore waters, and low dissolved As contents ( $< 0.3$  mg/L; McLachlan and Craw, 2018). The compositions of waters near the roaster have been comprehensively documented previously (Haffert and Craw, 2008b; Haffert et al., 2010). Rainfall runoff water had  $\sim 50$  mg/L dissolved As as it flows to the wetland, and the wetland had surface waters with 50–70 mg/L dissolved As, and deeper pore waters in the wetland had up to 370 mg/L dissolved As in conjunction with arsenolite in the solids. These runoff waters were acidified to pH  $\sim 3$ –4 by the As-dominated chemical system, and this was neutralised at depth in the wetland where lower redox conditions prevailed. Dissolved sulfur is low ( $< 50$  mg/L) in all the tailings waters (Haffert et al., 2010).

#### 4.5. Authigenic realgar at Prohibition site

Yellow-orange coatings of authigenic realgar occur on woody material at the base of water-saturated sandy hematitic tailings (Fig. 1d) and at the base of the wetland that contains roaster tailings (Fig. 1d; 6a–e). The best samples of this realgar were obtained from the roaster tailings wetland (Fig. 6a) and this material is crystalline with a well-defined XRD powder pattern (Fig. 3b). There are additional XRD peaks in the diffractogram that may reflect minor coexisting As-S minerals



**Fig. 4.** SEM backscatter electron images of realgar coatings (white) on wood from Snowy River sulfide residues (Fig. 2b and c). (a) General view of realgar coating. (b) Contrasting realgar textures within the coating. (c) Detailed view of hair-like fibres of realgar.



**Fig. 5.** SEM backscatter images of a polished section of sulfide residue from Snowy River site, with authigenic gold deposited in a cavity exposed during sectioning. Scor = scorodite cement; Bi = primary bismuth mineral; Au and yellow arrows indicate some of the authigenic gold particles. (a) General view of the edge of the exposed cavity (left), with polished surface on right and dashed line at boundary. (b)–(d) Closer views of authigenic gold particles and their textural contexts within a film composed of light elements that coats the cavity. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

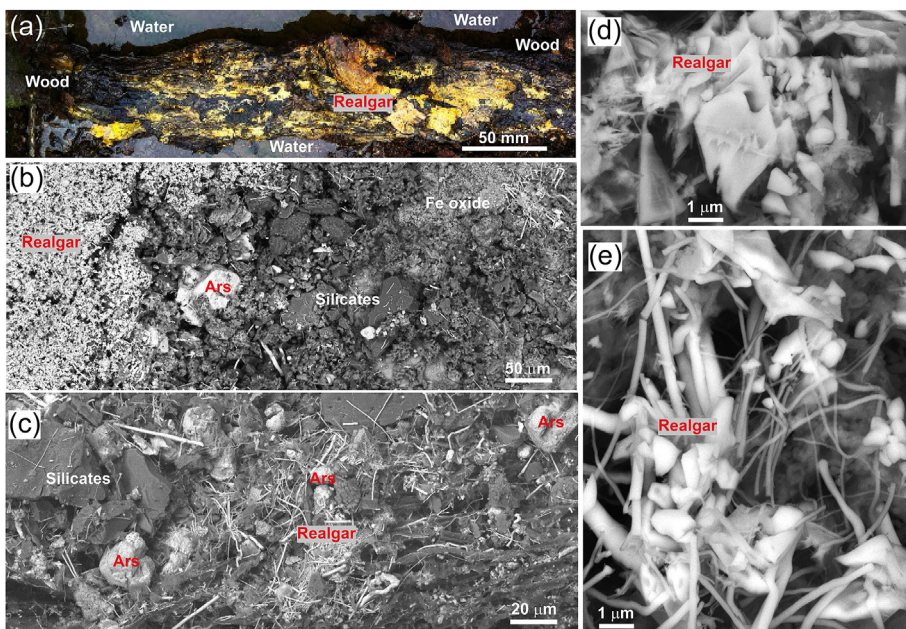
such as alacranite, uzonite and/or orpiment, as in the Snowy River material (Fig. 3a and b). As for the Snowy River site, pararealgar appears to be absent or only a minor component (Fig. 3b).

At the microscopic scale, the authigenic realgar coatings on the wood from the roaster tailings wetland are intermixed with, or deposited on, sandy tailings residues that adhere to the wood (Fig. 6b–e). In detail, the authigenic realgar coatings are similar to those of the Snowy River site (above), and are made up of microcrystalline, acicular, and hair-like grains that form a loose network (Fig. 6b–e). These tailings residues contain numerous arsenolite particles and realgar has locally grown in close association with some of those arsenolite particles (Fig. 6b and c; 7a,b). Some of the arsenolite particles are rounded and chemically corroded, and are probably of detrital origin from the nearby roaster site (Fig. 2c; 6b,c; 7a). However, some well-formed arsenolite crystals also occur in the tailings deposits, and may be of

authigenic origin (Haffert et al., 2010), in close association with authigenic realgar (Fig. 7b).

#### 4.6. Detrital gold at Prohibition site

One flake of realgar-bearing material from the Prohibition roaster tailings wetland that was examined in the SEM was found to have a micron-scale gold particle resting on the exposed substrate (Fig. 7c and d). This particle is an angular fragment with a layered internal texture (Fig. 7c and d). The particle contains traces of a range of metals, mainly Pb and Pd, with traces of Pt, Mo, Cd although precise analysis was not possible. The Pd content ranged between < 1 and 16 wt% across the particle (semiquantitative EDS analysis), implying the presence of dispersed microparticulate Pd-rich inclusions. This particle is presumed to be detrital material derived from the nearby assay office (Fig. 2c). The



**Fig. 6.** Realgar coating wood from the roaster tailings wetland at Prohibition site. (a) Photograph of freshly-exposed realgar (yellow-orange). (b)–(e) SEM backscatter electron images of realgar textures with remnants of tailings, including presumed detrital arsenolite particles (Ars). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



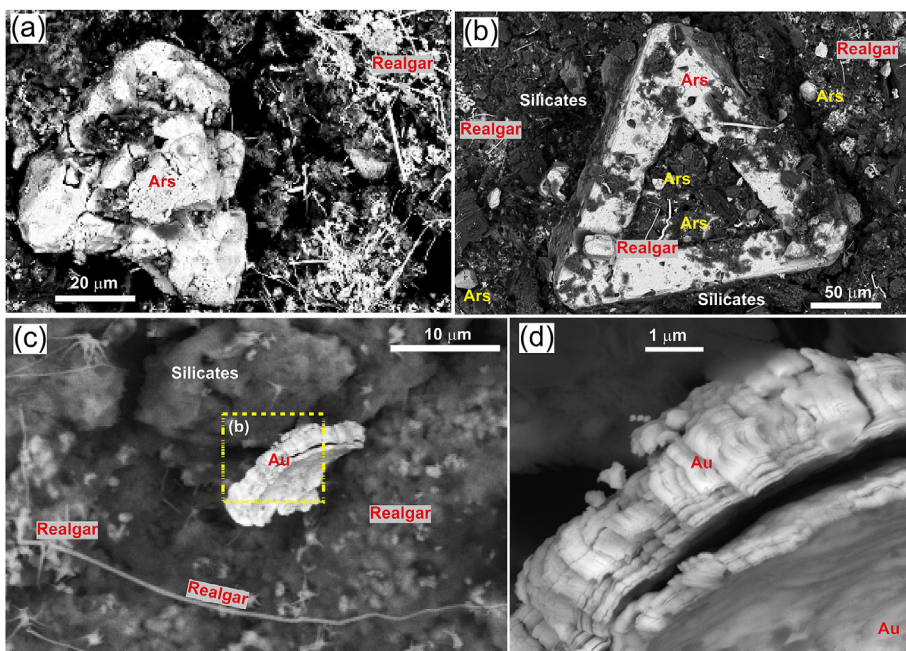


Fig. 7. SEM backscatter electron images of arsenolite (Ars), gold (Au) and realgar from the roaster tailings wetland at Prohibition site. (a) Corroded and rounded arsenolite crystal (left) with adjacent and coating realgar. (b) Hollow arsenolite crystal (possibly authigenic) with scattered finer grained associated realgar. (c) Layered detrital gold particle containing Pb, Pd, Mo, Cd, and Pt, presumed to be derived from the nearby assay office (Fig. 1c). (d) Close view of the delicate layering in the detrital gold particle. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

traditional fire assay technique routinely produces small artificial gold concentrates using added lead compounds, and these gold concentrates commonly include platinum group elements (Chow and Beamish, 1967; Hoffman et al., 1999). The resultant Pb-rich residues are widely distributed near the historic assay office at the Prohibition site upslope of the roaster wetland (Fig. 2c; McLachlan and Craw, 2018). Assuming a detrital origin for this gold particle, there is no textural evidence of corrosion or dissolution of gold from the delicate textures of the particle after deposition within the tailings repository, or for nearby authigenic gold redeposition (cf Snowy River site; Fig. 5a–d; Table 1).

5. Discussion

5.1. Redox gradients

Typical oxidation zones on mine wastes (e.g., Fig. 8a) are relatively simple, with a zone of primary sulfides into which an oxidation front progressively migrates (Blowes and Jambor, 1990; Hayes et al., 2014; Majzlan et al., 2014). Oxidation of primary sulfides occurs in the region of the migrating front, via a combination of bacterial and inorganic processes (Blowes and Jambor, 1990; Gould and Kapoor, 2003;

Hamamura et al., 2013; Hayes et al., 2014). Waters in contact with the primary sulfides may contain reduced sulfur species, but oxidation of the sulfides releases dissolved sulfate ions, commonly with metastable thiosulfate ions ( $S_2O_3^{2-}$ ) as an intermediate species (Fig. 8a; Goldhaber, 1983; Rimstidt and Vaughan, 2003; Melashvili et al., 2015). Oxidation of arsenopyrite also releases dissolved As, initially as arsenite ions and then as arsenate and/or thioarsenate ions, and these processes are also driven by a combination of inorganic and bacterial reactions (Fig. 8a; Corkhill and Vaughan, 2009; Suess and Planer-Friedrich, 2012; Hamamura et al., 2013; Amend et al., 2014; Majzlan et al., 2014). Periodic evaporation can lead to precipitation of arsenic minerals, including arsenolite and scorodite (Fig. 8a; Majzlan et al., 2014; Kerr et al., 2015).

The presence of chemically reactive reducing agents such as organic debris in a redox profile causes the redox zone to be more dynamic, with active reduction reactions in parts of the profile while oxidative reactions are occurring elsewhere (Fig. 8b). The dissolved As and S species are broadly similar in the dynamic redox gradients to those in the simpler oxidation gradient (Fig. 8a and b). Dynamic redox zones are common in water-saturated natural settings such as river sediments and wetlands (O'Day et al., 2004; Rigaud et al., 2013; Johnson et al., 2014;

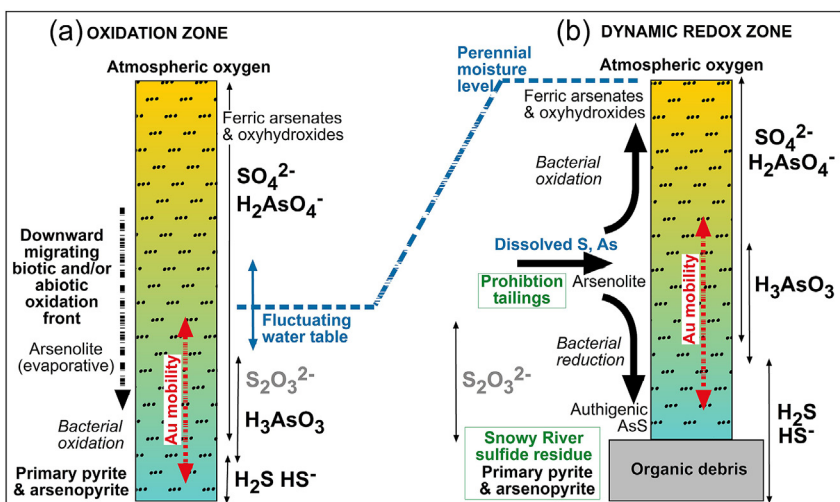


Fig. 8. Cartoon sketches of contrasting redox profiles developed on arsenic-bearing gold mine wastes. (a) Simple oxidation zone with migrating oxidation front. (b) Dynamic redox zones with active reduction reactions at base that is forming authigenic realgar. Different settings for Snowy River and Prohibition sites (this study) are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Gorny et al., 2015; Bentz and Peterson, 2017) but are less common in mine wastes because of the general lack of reductants. The mine wastes described herein (Table 1) provide examples of dynamic redox gradients: a sulfur-rich system at Snowy River, and low-sulfur systems at the Prohibition site (Fig. 8b).

## 5.2. Arsenic minerals

Scorodite and related As-bearing Fe oxyhydroxides are among the most common minerals formed in oxidised As-rich mine wastes in general (Majzlan et al., 2014; Craw and Howell, 2014), and these minerals are widespread in the mine wastes of this study. These minerals are relatively insoluble under weakly acidic conditions that prevail at the sites described in this study (Krause and Ettel, 1989; Langmuir et al., 2006; Craw and Howell, 2014). In contrast, arsenolite is highly soluble, and formation in oxidising mine wastes typically requires evaporative concentration of pore waters (Fig. 8a; Kerr et al., 2015). There was apparently insufficient evaporation of the ambient moisture in the Snowy River sulfide residues to permit arsenolite precipitation at that site (Fig. 2a–c). Conversely, the very high dissolved As concentrations in wetland pore waters of the Prohibition roaster tailings has permitted persistence of detrital arsenolite and possibly precipitation of authigenic arsenolite under intermediate redox conditions (Fig. 6b–d; 7a,b; Haffert et al., 2010).

Active reduction reactions around organic matter have facilitated precipitation of authigenic As sulfides, principally realgar, at three sites described in this study (Fig. 8b; Table 1). Authigenic realgar is rare in surficial environments, but examples from diverse settings have been reported recently (O'Day et al., 2004; Demergasso et al., 2007; Drahota et al., 2013; Bentz and Peterson, 2017). The dynamic redox gradients in which the authigenic realgar deposits we describe herein are broadly similar to these previously-reported environments. Surficial evaporation has been important for some natural realgar deposition (Demergasso et al., 2007; Bentz and Peterson, 2017), and some evaporative effects may have played a role in the perennially moist, but not fully water-saturated, sulfide residues at Snowy River site (Fig. 2b and c), and the wetland occurrences of realgar reported by Drahota et al. (2013). Conversely, the occurrences of authigenic realgar in fully saturated Prohibition tailings (Fig. 1c and d) are more akin to the water-saturated environment described by O'Day et al. (2004), albeit with substantially higher dissolved As concentrations in the Prohibition roaster tailings.

Observations by O'Day et al. (2004) and Bentz and Peterson (2017) suggest that authigenic realgar is most likely to precipitate in reducing conditions when dissolved As is relatively high in relation to reduced dissolved sulfur concentrations. In addition, Drahota et al. (2017) suggest that authigenic realgar precipitation is limited by the rate of reduction of available dissolved sulfate. The Prohibition occurrences of realgar in this study occur in relatively low-sulfur settings, where sulfides were removed during mine processing. Dissolved sulfate concentrations were low in the surficial waters (< 21 mg/L; Table 1), and dissolved reduced sulfur concentrations are presumed to have been even lower at depth, where the realgar was forming. Dissolved iron occurs as Fe<sup>2+</sup> up to 40 mg/L in the Prohibition wetland pore waters (Table 1; Haffert et al., 2010) but no authigenic Fe sulfides have been recognised at the site (cf Kirk et al., 2010).

We have no analyses of waters from the Snowy River sulfide residues, but that occurrence of authigenic realgar is in a relatively sulfur-rich environment where primary sulfides are undergoing oxidation and the resultant dissolved sulfate is being locally reduced (Fig. 2a and b; 9a). Hence, dissolved sulfate is probably locally elevated at the Snowy River site because of this on-going sulfide mineral oxidation. However, the rate of reduction of dissolved sulfate to sulfide may limit the availability of reduced sulfur for authigenic sulfide precipitation, as suggested by Drahota et al. (2017), thereby controlling the rate of precipitation of authigenic realgar.

The Prohibition roaster tailings wetland has strongly elevated dissolved As concentrations (Table 1) and the Snowy River sulfide residues probably have locally elevated As concentrations as well. The low redox conditions and reduction reactions that facilitated deposition of authigenic realgar are likely to have been facilitated by bacterial processes (O'Day et al., 2004; Demergasso et al., 2007; Drahota et al., 2013, 2017; Bentz and Peterson, 2017; Sancho-Tomas et al., 2018). Reductive bacteria that are tolerant of As-rich environments, or even have a preference for As, are becoming increasingly identified in natural environments (Oremland and Stolz, 2005; Ledbetter et al., 2007; Lee et al., 2007; Amend et al., 2014). Hence, the complex and irregular textural networks of Snowy River and Prohibition authigenic realgar precipitates at the micron scale (Fig. 4a–c; Fig. 6b–e) are probably results of biological reductive processes, associated with decomposition of the hosting organic material that maintains the low redox environments, as also reported by Drahota et al. (2013, 2017). Laboratory experiments by Lee et al. (2007) have shown that bacterial processes can yield texturally similar As-sulfide products to those described herein.

## 5.3. Au mobility and deposition

Gold dissolution and subsequent microparticulate and nanoparticulate gold precipitation in near-surface environments results from a combination of inorganic and biologically mediated geochemical processes (Mann, 1984; Webster and Mann, 1984; Stoffregen, 1986; Hough et al., 2008; Reith et al., 2010, 2012; Kerr and Craw, 2017). Experimental studies show that gold mobilisation and deposition during oxidation of auriferous sulfide minerals is at least partly controlled by formation and decomposition of Au-thiosulfate complexes (Webster, 1986; Grosse et al., 2003; Shuster et al., 2016). Chloride complexes may also have contributed to gold dissolution and reprecipitation under acid oxidising conditions (Mann, 1984; Usher et al., 2009), as some evaporative concentration of marine aerosols (up to 34 mg/L Cl<sup>-</sup>; Haffert et al., 2010) does occur in the area.

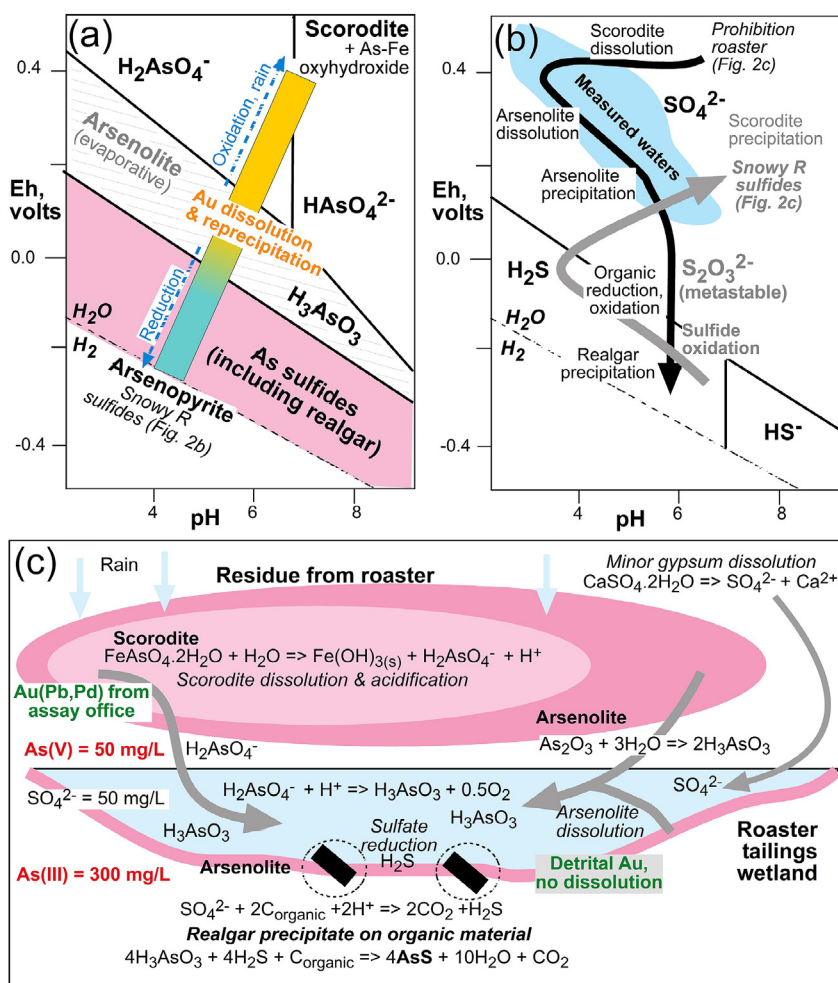
The authigenic gold identified in Snowy River sulfide residues in this study has probably been redistributed from the auriferous sulfides to a surficial microenvironment within the dynamic redox gradient being developed on those sulfides. The authigenic gold is at least partially associated with authigenic scorodite in the intermediate to relatively oxidised portion of the redox gradient, rather than with the authigenic realgar that occurs a few centimetres away (Fig. 2a–c; Fig. 5a–d). This occurrence of authigenic gold in mine wastes that are only 80 years old helps to confirm the inferences of Shuster et al. (2017) that biologically-mediated gold mobility can occur on decadal time scales.

In contrast to the sulfur-rich Snowy River site, no authigenic gold has been found at the sulfur-poor Prohibition sites examined in this study. On the contrary, the one piece of gold discovered, in the Prohibition roaster tailings is detrital in origin (Fig. 7c and d). This gold particle has delicate textures that appear to have remained unaffected by the relatively extreme geochemical environment in which it has remained buried and water-saturated for almost 70 years. One of the main differences between the Snowy River and Prohibition sites is the lack of oxidising sulfides in the latter. Consequently, dissolved sulfur is low (~50 mg/L) at Prohibition, and this dissolved sulfur is solely present as sulfate ions with no available source of metastable thiosulfate ions to complex with gold (Fig. 8b). Hence, the lack of authigenic gold at the Prohibition sites is probably a direct result of this low sulfur, thiosulfate-absent environment.

## 5.4. Environmental geochemical evolution

The geochemical environments of the mine wastes described herein are dominated by As-bearing minerals and solutions reflecting wide ranges of redox potentials and pH (Fig. 9a–c). The geochemical systems in the mine wastes have evolved a set of redox and pH microenvironments, and authigenic realgar has formed at the more reduced end of





**Fig. 9.** Geochemical environments and processes for As and Au mobilisation and redeposition in examples of dynamic redox environments described in this study (Fig. 8b). (a) Sketch Eh-pH diagram for As minerals and dissolved species, with overlain redox profile from Snowy River sulfide residues (Fig. 2b). (b) Sketch Eh-pH diagram for sulfur species, with inferred evolutionary path for sulfide oxidation (Snowy River sulfide residues; grey arrow and lettering). Contrasting evolutionary path for the Prohibition roaster tailings wetland (black line) is partially calibrated with data from Haffert et al. (2010; blue field). (c) Cartoon showing the mineralogical and geochemical spatial relationships in the Prohibition roaster tailings. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dynamic redox gradients, similar to the wetland setting described by Drahotka et al. (2013). Within this general context, there have been two contrasting geochemical evolutionary pathways in the mine wastes, reflecting the differences in original materials and the settings in which the mine wastes were placed (Fig. 9a–c; Table 1).

The sulfide concentrate residues at Snowy River site have well-defined As mineral redox gradients at the centimetre scale (Fig. 2; 9a), with localised acidification driven by sulfide mineral oxidation (Fig. 9b), possibly augmented by organic acids. At the same time, thiosulfate ions generated by sulfide oxidation have contributed to mobilising gold from those sulfides into solution (Fig. 9a and b). The acidic conditions have dissipated in the more oxidised parts of the redox profile, where scorodite and As-bearing Fe oxyhydroxide have precipitated with dilution and neutralisation by abundant rainfall (Fig. 9a and b). Decay of the metastable thiosulfate ions has caused precipitation of authigenic gold in the relatively oxidised scorodite zone (Fig. 9a and b). At the other end of the redox gradient, decomposition of woody material in a perennially moist environment has countered the incursion of oxygen and is actively maintaining sufficiently low redox conditions for realgar to form and be preserved. The dynamic redox profile will remain until the woody material has completely decomposed, after which the realgar will become oxidised along with the remnants of the primary sulfide concentrate. Hence, the observed mineral spatial relationships are temporary and do not reflect chemical equilibrium, so replacement of the more reduced minerals by oxidised minerals is likely to occur over time.

The Prohibition roaster tailings wetland has a different geochemical evolutionary path as a result the relatively oxidised, arsenic-rich, and sulfur-poor starting materials. The Prohibition sandy tailings have

similar mineralogy and have followed a similar geochemical evolutionary pathway, albeit with less spectacular arsenic-rich water compositions. At the Prohibition sites, scorodite and Fe oxides are among starting materials, not end products as seen in Snowy River sulfide residues. Dissolution of scorodite under oxidising conditions at Prohibition site caused localised acidification (Fig. 9b and c), but this has been neutralised by reduction of arsenate ions ( $\text{As}^{\text{V}}$ ) to arsenite ions ( $\text{As}^{\text{III}}$ ) in more reduced (intermediate redox) conditions in water-saturated mine wastes (Fig. 9b and c). The general geochemical environment at depth within the roaster tailings wetland was dominated by  $\text{As}^{\text{III}}$ , with both dissolution and precipitation of arsenolite (Fig. 9b and c; Haffert et al., 2010). The persistence of detrital arsenolite, a highly soluble mineral derived from historic mine processing, in this water-saturated setting has been attributed to slow dissolution kinetics (Haffert et al., 2010).

Decomposing woody material at the base of the Prohibition wetland created localised reduced microenvironments for deposition of authigenic realgar (cf Drahotka et al., 2013, 2017) in close spatial relationships with arsenolite (Fig. 6; Fig. 9b,c). Authigenic realgar has precipitated with low-redox sulfur species despite the relatively low dissolved sulfur concentrations in the saturating waters, with that sulfate derived from dissolution of gypsum in the mine wastes (Fig. 9c). As for the Snowy River site, the spatial relationships between the minerals do not reflect redox equilibrium, and replacement of one arsenic mineral by another is likely to occur as the microenvironments evolve with time.

## 6. Conclusions

Well-defined redox gradients have developed over 70–80 years on As-rich mine wastes at two abandoned gold mine processing areas in southern New Zealand. The scales of these redox gradients are highly variable around the processing areas, but are typically at the centimetre to metre scale. The redox gradients are strongly affected by inherited materials, and in particular there are steep reductive gradients around organic debris of both natural and anthropogenic origin. Active reduction reactions around this organic debris have caused precipitation of authigenic As sulfides, principally realgar, at three sites. The authigenic realgar is distinctly yellow-orange in colour and well-crystallised with respect to XRD identification, but morphologically the realgar is highly irregular, fine grained (micron scale), and locally forms hair-like nanotubes. Some of this authigenic realgar has developed in localised microenvironments where steep redox gradients have led to close spatial associations with authigenic and/or detrital arsenolite, and realgar also occurs in close proximity to authigenic scorodite. These spatial relationships do not reflect chemical equilibrium, and replacement of one As mineral by another is likely as the microenvironments evolve. Authigenic realgar has formed in high sulfur environments where primary sulfides are being progressively oxidised, and in low-sulfur environments where As-rich, S-poor oxidised mine tailings have been deposited. Formation of the redox microenvironments has been facilitated by microbiological processes acting on the heterogeneous hosting substrates, especially the organic debris. Despite the high-rainfall climate in which these mine sites are located, some evaporative concentration of near-surface solutions may have occurred, and this evaporation probably facilitated deposition of authigenic minerals within the redox gradients.

Gold is a rare component of the mine wastes and occurs as detrital particles or disseminated in primary sulfide minerals. Some of this gold has been chemically mobilised and redeposited in a sulfur-rich redox gradient developed on oxidising primary sulfides. This authigenic gold is nanoparticulate and microparticulate in form and occurs scattered through a thin coating of iron oxyhydroxide and biofilm that developed on top of authigenic scorodite. The authigenic gold was precipitated in a moderately oxidised part of the redox gradient that developed over 80 years since the hosting site was abandoned. The gold was probably mobilised by metastable thiosulfate complexes formed ephemerally within that redox gradient, although mediation by chloride complexes and/or organic geochemical processes cannot be discounted.

## Acknowledgements

This research was supported financially by the Marsden Fund administered by the Royal Society of New Zealand, and a research contract from the NZ Ministry for Business Innovation and Employment. Discussions with Kathy Campbell (University of Auckland) and Karen Hudson-Edwards (University of Exeter) were helpful in formalising some ideas expressed herein. The NZ Department of Conservation provided logistical assistance and we are particularly grateful for the enthusiastic support of Jim Staton. Kirstine Malloch and Christine McLachlan provided field assistance, expert knowledge and helpful discussions. Brent Pooley conducted sample preparation of difficult material, and Kat Lilly and Marianne Negrini assisted with SEM work at the Otago Centre for Electron Microscopy. Positive and constructive comments from two anonymous reviewers substantially clarified some aspects of the text.

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