Natural attenuation of extreme metalloid contents in historic mining residues, Big River Mine, NZ

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Abstract

Remediation of historic mine sites has been the topic of much debate in New Zealand in recent years. The Big River Mine is located in the West Coast of the South Island of NZ, only 8 km away from the Prohibition Mine at Waiuta - the most recent example of a site being cleaned-up with the help of the government's Contaminated Sites Remediation Fund. Arsenic and antimony are two metalloids associated with orogenic gold deposits which are often found at elevated levels in soils and waters at historic mine sites. Both elements are potentially toxic at low levels in the environment and their mobilisation from decomposing sulphide minerals into mine waters is facilitated by circum-neutral pH. The Big River Mine site was found to contain up to 25 wt% As and 3.6 wt% Sb in mining residues. Mine water concentrations are elevated only locally, up to 0.85 mg/L As and 0.007 mg/L Sb. In contrast, As concentrations in water at the Prohibition Mine site are known to be considerably more elevated, up to ~30 mg/L. Dissolved metalloids are effectively immobilised at the Big RivTableer Mine through the formation of secondary mineral phases (scorodite, iron sulphoarsenate, amorphous iron arsenate) and adsorption onto iron (hydr)oxides and clay mineral surfaces. This successful attenuation is possible due to the presence of acidic conditions in water and mining residues (pH 2-4). In comparison, at the Prohibition Mine site As is present, amongst others, in the form of arsenolite. This secondary mineral is environmentally mobile and becomes readily dissolved on contact with precipitation water. Despite the extremely high metalloid concentrations present, the Big River Mine site is considered to be geochemically stable. Provided that adequate safety measures are implemented at this DoC-owned site, it is not considered to be in need of urgent remediation.

Keywords: Gold mining, mining residues, arsenic, antimony, metalloid mobility, attenuation.

Introduction

Remediation of historic mine sites has received a considerable amount of attention in New Zealand in recent years. Efforts undertaken at sites such as Tui mine on the Coromandel Peninsula and Prohibition and Alexander Mines in the West Coast were made possible thanks to government grants, such as the Contaminated Sites Remediation Fund. Given New Zealand's rich mining history, there is a need for a comprehensive assessment of historic mining sites in the country with respect to the existing environmental impacts as well as sites' geochemistry and their geochemical stability. It is likely that some of the sites, even though disused for decades, continue to contribute negative impacts to local environments, as was shown to be the case with the Prohibition Mine in Waiuta (Haffert and Craw, 2009).

The gold mining legacy on the South Island of New Zealand frequently involves high arsenic (As) and antimony (Sb) concentrations in soils, waters and remaining mining wastes. The two metalloids are found in sulphide minerals which are naturally closely associated with gold in orogenic vein systems (Groves et al., 1998; Ashley et al., 2003). Both arsenic and antimony are considered potentially toxic at low levels (e.g. < 0.01 mg/L in water) and for this reason, their presence at elevated concentrations in water and soil is an issue of environmental concern.

This paper aims to provide an example of geochemical characterisation of an historic gold mine, including a preliminary assessment of environmental impacts on a local and regional scale. The study involved quantification of metalloid concentrations in mining wastes and waters, as well as description of the nature and mineralogy of processing residues found on site. The study also aims to highlight the importance of understanding of particular geochemical settings at mining sites, including their controls, on a case by case basis. This is to ensure that the assessments of environmental (and human health) risks and prioritisation with respect to possible remediation requirements are undertaken appropriately. As part of this effort, a comparison between the Big River and Prohibition Mine sites has been undertaken as part of this study. The study was carried out in 2011/12 as part of a PhD project at University of Otago, and more details are contained in Druzbicka and Craw (2015).

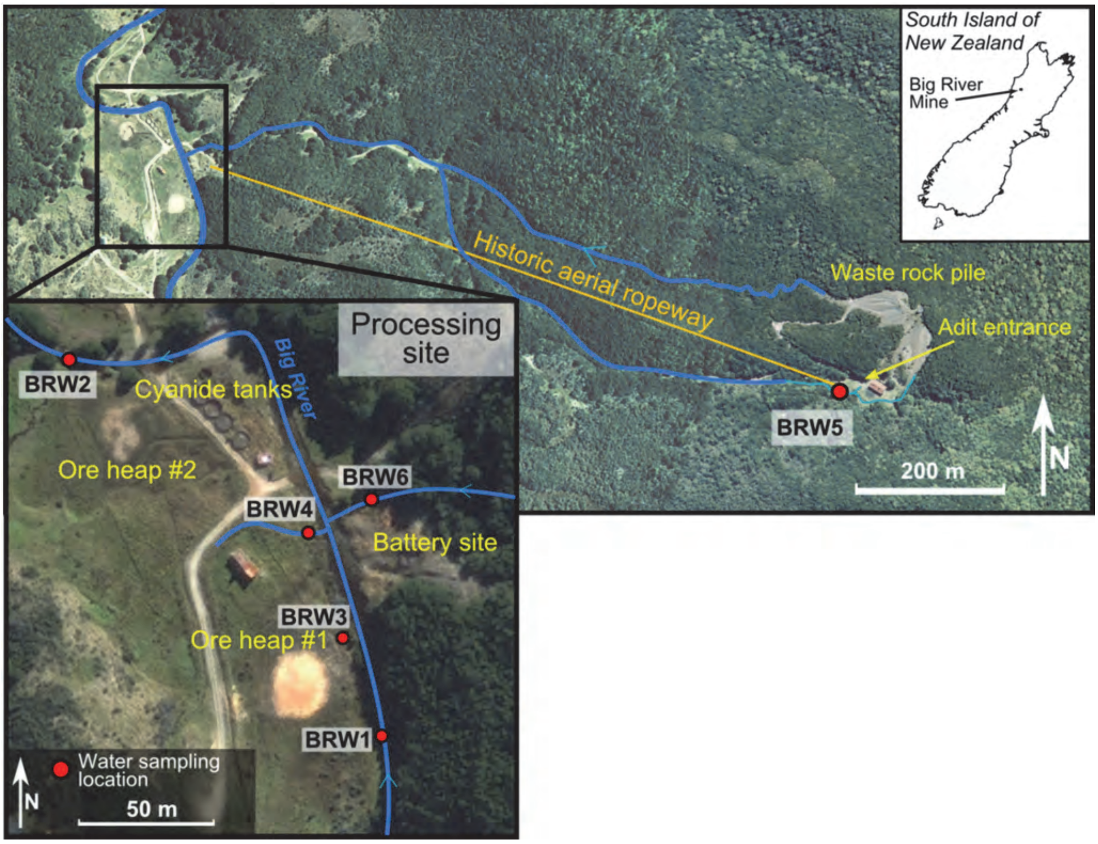

Figure 1. Location maps showing site features and water sampling points.

General setting and geology

The Big River Mine site is located 13 km south of Reefton township in the West Coast region of the South Island. The mine belongs to the Big River Group of mines within the Reefton Goldfield and is located south of the currently mined Globe-Progress mine. The site lies within the Victoria Conservation Park, at an elevation of 700-800 m above sea level. The area is drained by Big River which joins Grey River to the west. The region is characterised by high orographic rainfall of more than 2000 mm annually and the mean annual temperature is 12ºC. The vegetation cover is composed of predominantly mixed beech and podocarp forest. The site is located on a tramping and mountain biking track and is popular with visitors.

Basement rocks in the Big River Mine area comprise alternating sequences of weakly metamorphosed greywackes and argillites belonging to the Paleozoic Greenland Group of the

Buller Terrane (Cooper, 1974; Christie et al., 2000).The naturally high acid neutralising capacity (ANC) of the Greenland Group rocks generally exceeds their maximum potential acidity (MPA) (Haffert et al., 2006).

The mined deposit is of orogenic (mesothermal) type. Gold in the Reefton Goldfield occurs predominantly in association with sulphide minerals (pyrite, arsenopyrite and stibnite) in shear zone-hosted quartz lodes (Christie et al., 2010). It is also present in sulphide-rich pug (clay-rich fault breccia), in disseminated sulphides of the surrounding host rocks and in free form (minor) (Barry, 1993; Christie et al., 2003).

Mining history

Mining of the Big River deposit targeted gold-bearing quartz veins. An aerial ropeway was used to transport extracted ore to the processing site (Fig. 1), where it was crushed in the 10 stamp head battery. The recovery of gold was performed using blanket tables and amalgamation and/or cyanidation techniques. Only the coarse-grained free gold was extracted at the Big River processing site. The recovery of refractory gold was less straightforward and required finer crushing and/or roasting of the concentrates to oxidise the pyrite, as was later done at other sites in New Zealand (e.g. Prohibition Mine at Waiuta; Haffert and Craw, 2009). No roaster has ever been installed at the Big River Mine's processing site (Wright, 1993).

At the time when mining was undertaken at the Big River Mine no environmental controls were in place to regulate the industry. The metalloid-rich concentrates and tailings were disposed of on-site or directly into the Big River running through the middle of the processing site. No remediation or rehabilitation efforts have ever been attempted at the site since its closure in 1942 and the post-closure management included mainly the dismantling of the various buildings and mining machinery. The mine is administered by the Department of Conservation and efforts have been made to preserve it as a site of historic interest.

Site description

The Big River mining area, including the processing and historic settlement sites, has historically been cleared of native bush and to this day the majority of the sites are either covered by low-growing vegetation or remain bare (Fig. 1). The entrance to the mine shaft is surrounded by a mullock heap, formed by discarding waste rocks down the sides of the hill. Two small streams drain this waste rock pile. They merge further downstream and join the Big River within the mine processing area.

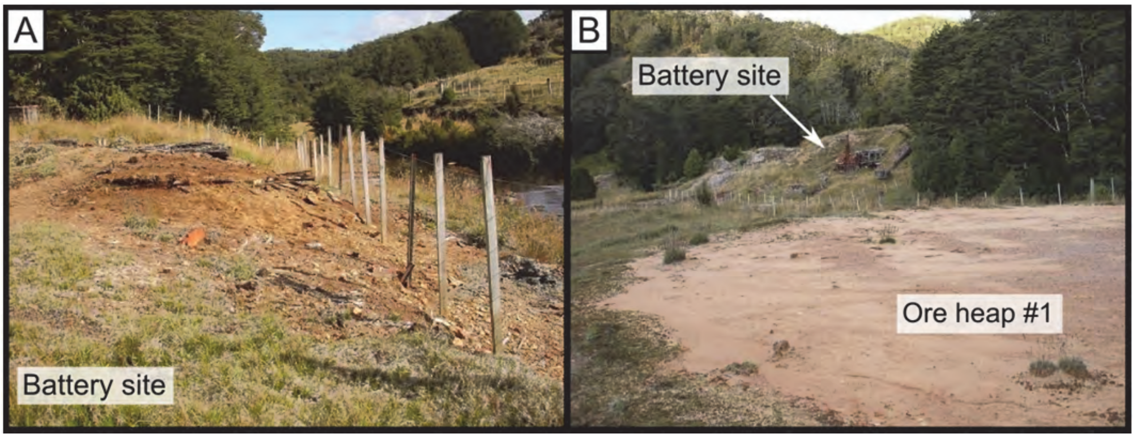

Figure 2. Photographs showing mining residues at the battery site **(A)** and in the ore heap #1 **(B)**.

The mine's processing site is located along the Big River, with the battery site situated on a partly-sloping river bank (Fig. 2A). Large parts of the site remain un-vegetated and contain distinctive brown/orange mining residues (Figs 2A, B). Fences have been erected around the various parts of the processing site, including the battery site. Two scarcely vegetated ore heaps and a cyanide plant remain at the processing site (Fig. 2B). The ore heaps are surrounded by a number of waterlogged/swampy areas.

Site characterisation

Mining-related processing residues are found in four general areas around the mine's processing site: battery site, two ore heaps (#1 and #2) and the cyanide plant. The processing residues at the battery site are predominantly brown-coloured and appear to be both physically and chemically heterogenous, including materials varying with respect to grain-size distribution and the level of sorting and cementation. Examples of two distinctive substrates identified include well-cemented greenish-brown hardpan (sample B-1) and yellow clay-like materials (samples B-2 and B-3). Substrates identified at the two ore heap sites include orange/brown medium-grained sand (ore heap #1) and a brown clay-rich substrate (ore heap #2).

Field-portable XRF was used for determination of metalloid concentrations on-site (see Haffert and Craw (2009); Druzbicka and Craw (2015) for methods). Metalloid results were plotted against laboratory XRF results obtained from the same samples. An equation of the best fit line was derived for each of the analytes and used for the correction of the FPXRF result dataset collected from the field. Maps in Figs 3A, B show arsenic and antimony concentrations (corrected values) recorded across the processing area of the mine using the FPXRF method. A wide range of metalloid concentrations were encountered with the majority ranging between 0.1 and 5 wt% for arsenic and 0.01 to 0.5 wt % for antimony. Two distinct areas of 'hot spots' were identified within the battery site where As and Sb concentrations were recorded exceeding 5 wt% and 1 wt%, respectively. The highest metalloid contents were encountered at those locations and reached 25 wt% for arsenic and 2.8wt% for Sb. In general, antimony is present at concentrations one order of magnitude lower than As.

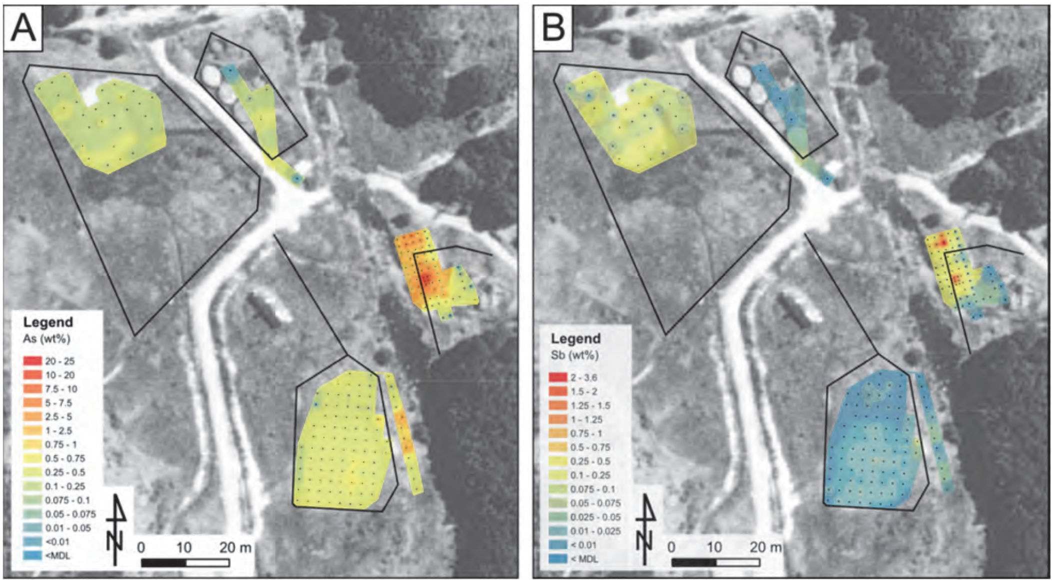

Figure 3. Maps showing As **(A)** and Sb **(B)** contents distribution (in wt%) at the Big River Mine's processing site. The maps were created using corrected results of the FPXRF analyses. Solid lines show existing fences.

The summary of laboratory XRF analytical results for 36 substrate samples is presented in Table 1. The paste pH measurements range from <2 to 6.2, with the majority of the results lying between 2 and 4. The highest As and Sb concentrations recorded reached 23 wt% for As and 3.6 wt % for Sb.

Table 1. Summary of analytical results for 36 substrate samples (As, Sb by XRF; Spectrachem, Wellington).

Location	Statistic/ sample name	paste pH	As (mg/kg)	Sb (mg/kg)
Battery site	min	1.6	2200	298
	max	3.43	231300	35606
	average	2.3	67196	9196
Ore heap #1	min	3.27	514	10
	max	3.78	6350	315
	average	3.5	3463	124
Ore heap #2	OH2-1	5.35	3460	1226
	OH2-2	5.83	2850	1983
	OH2-3	5.8	2440	770
Cyanide plant	CT-1	6.2	2290	435
	CT-2	3.97	2660	218

Table 2. Summary of water analysis results (Hill Laboratories, Hamilton).

Sample	pH	As (mg/L)	Sb (mg/L)
BRW1	4.5	<MDL	<MDL
BRW2	5.1	<MDL	<MDL
BRW3	3.8	0.85	<MDL
BRW4	6.3	0.04	<MDL
BRW5	7.1	<MDL	0.007
BRW6	7.3	<MDL	0.005

The majority of water analyses results were below the minimum detection limits of the methods used (0.02 mg/L for As and 0.004 mg/L for Sb; Table 2). The highest As concentration (0.85 mg/L) was recorded in seepage emanating from ore heap #1, while the creek draining the waste rock pile was found to contain the highest Sb concentration (0.007 mg/L) (Fig. 1, Table 2). Both arsenic and antimony were undetectable in Big River water. The field-measured pH ranged from 3.8 (ore heap #1 seepage) to 7.3 (creek draining waste rock pile).

Table 3. Mineralogy of 15 samples analysed by XRD, including sample descriptions.

Sample name	Mineralogy (XRD)	Description
B-1	Qtz, py, scor, musc, aspy	Green/brown fully cemented residue (hardpan)
B-2	Qtz, bukovskyite(?)	Yellow partially cemented residue
B-3	Amorphous(?), qtz	Yellow fine-grained residue
B-4	Qtz, musc, aspy	Grey fine-grained substrate
B-6	Qtz, musc, kaol	Brown well-sorted fine-grained sand
B-8	Qtz, musc	Brown poorly-sorted residue
B-11	Qtz, musc, kaol	Brown fine-grained residue
B-12	Qtz, musc	Yellow fine-grained residue
B-13	Qtz, musc, kaol	Orange fine to medium-grained sand
B-16	Qtz, musc, kaol	Brown medium-grained sand
OH1-1 + OH1-3	Qtz, musc, kaol	Orange well-sorted medium-grained sand
OH2-1 + OH2-2	Qtz, musc, kaol	Orange clay-rich residue
CT-1	Qtz, musc, kaol	Brown mine soil

Notes:
B = battery site, OH1 = ore heap #1, OH2 = ore heap #2, CT = cyanide tanks
Aspy = arsenopyrite, kaol = kaolinite, musc = muscovite, py = pyrite, qtz = quartz, scor = scorodite

Mineralogy of processing residues

The most distinctive feature of the battery site is a square relict of a timber structure. Mining residues in this area form a hardpan which extends down the ~1 m slope towards the river, which is where the B-1 sample material has been collected. X-ray diffraction, petrographical and scanning electron microscope EDS analyses results for this substrate indicate the presence of quartz, scorodite, arsenopyrite, pyrite, and muscovite (Table 3, Figs 4-6).

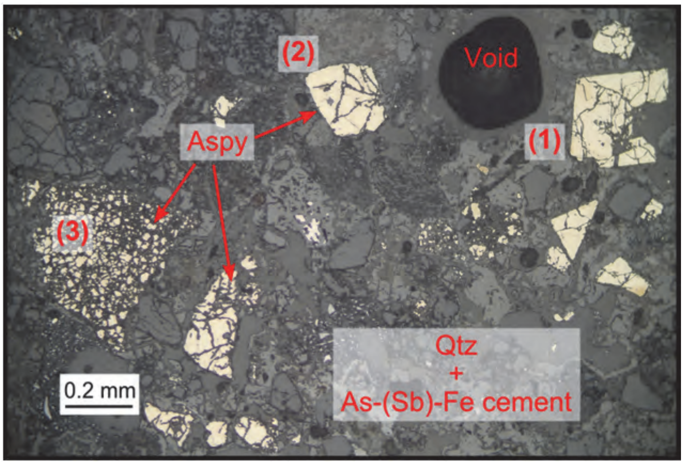

Figure 4. Reflected light microscope (REF) image of sample B-1 showing arsenopyrite grains at different stages of decomposition.

Arsenopyrite and minor pyrite grains appear to have undergone varying degrees of partial decomposition. Fig. 4 demonstrates examples of such grains: (1) grains that retain much of their euhedral shape, (2) grain with serrated edges and (3) grains comprising a collection of small (<30 µm) shards. The interstitial space between primary sulphide minerals and quartz is filled with two phases, of which one is a pale green-grey scorodite ($FeAsO_4 \cdot 2H_2O$) and the other appears orange in plane polarised light (PPL).

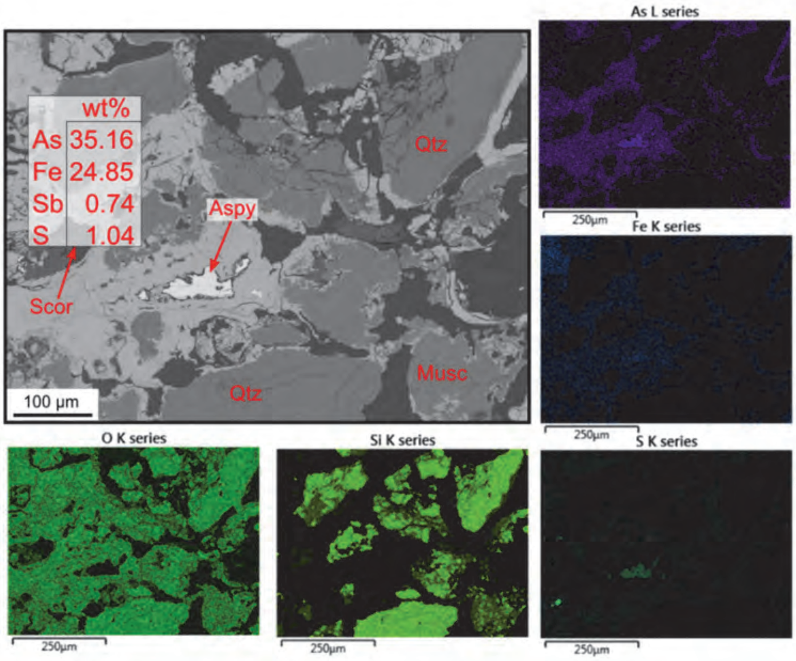

Figure 5. BSE image showing a decomposing arsenopyrite grain, with corresponding elemental (As, Fe, S, Si, O) maps. Results of selected EDS spot analysis are also shown.

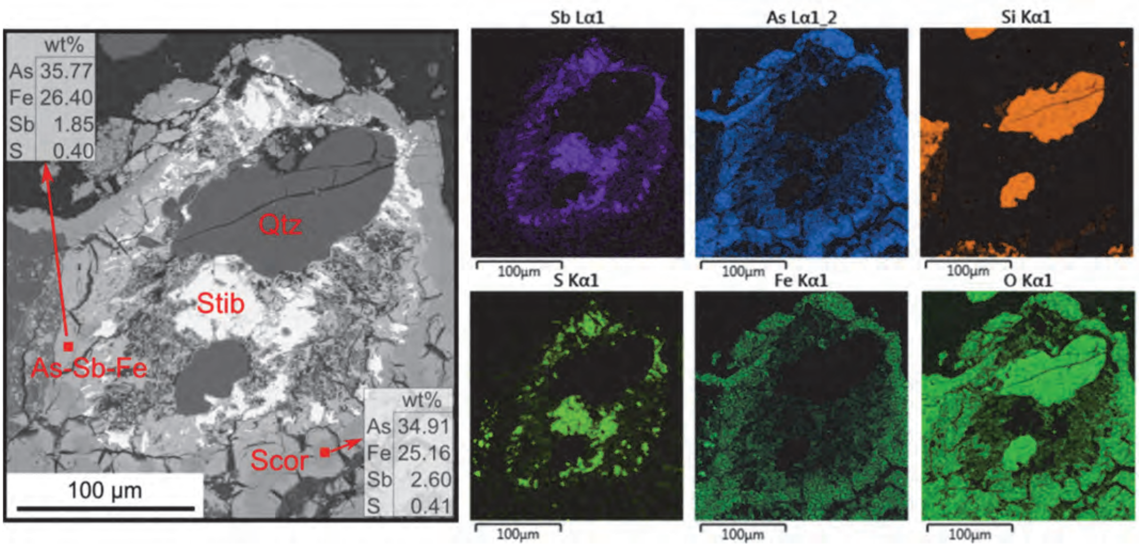

Figure 6. BSE image showing a decomposing stibnite grain, with corresponding elemental (Sb, S, As, Fe, Si, O) maps. Results of selected EDS spot analyses are also shown.

Backscatter electron (BSE) images and element maps of sample B-1 show the partial decomposition of arsenopyrite (Fig. 5) and stibnite (Fig. 6) grains and the cementing nature of the surrounding As–(Sb)–Fe phases. Point analyses of the observed phases provided qualitative data which enabled the identification of scorodite around the decomposing arsenopyrite and stibnite minerals (Figs 5, 6). Scorodite (darker grey) was observed to appear as globular inclusions in another As-Sb-Fe phase (light grey) around the stibnite grain (Fig. 6).

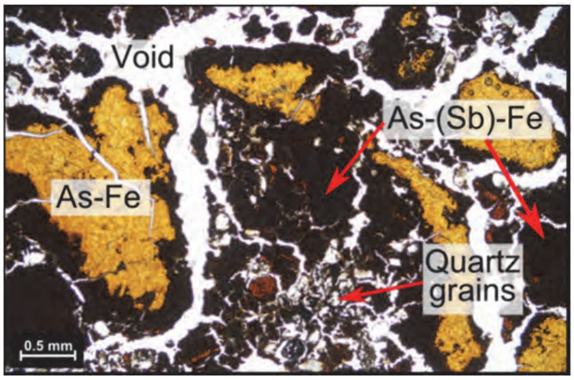

Figure 7. Microphotograph of sample B-2, taken under plane-polarized light (PPL), showing subrounded quartz grains and two distinctive secondary mineral phases.

A distinctive creamy-yellow coloured residue was also sampled from beside the timber structure (sample B-2, Table 3). The material appeared as a fine-grained clay-like loose material and contained more consolidated fragments (aggregates) on a centimetre scale in hand specimen. The material was subjected to an XRF analysis and was shown to contain ~16 wt% of As and ~1 wt% of Sb. Microscope observations of the material (under PPL) indicate that, apart from sub-rounded quartz grains (arrowed, on average 0.1 - 0.2 mm in size), two other phases are present (Fig. 7). Dark brown-coloured phase (EDS results: 30 wt% Fe, 27 wt% As, 3.5 wt% S and 1.5 wt% Sb) tends to surround a bright orange-coloured mineral (EDS results: 30 wt% Fe, 22 wt% As and ~8 wt% S), forming a rim. The boundary between the two phases is uneven and the brown phase appears to act as cement as it was observed coating the quartz grains present (Fig. 7). Unlike sample B-1, no residual sulphide minerals were found in sample B-2. The closest match found for the material during the XRD analysis was an iron arsenate sulphate mineral, bukovskyite ($Fe_2[AsO_4][SO_4][OH]\cdot 7H_2O$) (Table 3).

A brightly yellow-coloured substrate sampled from the battery site (sample B-3, Table 3) was a clay-like powdery material. This substrate was found to contain extremely high As and Sb contents (23 wt% As and 3.6 wt% Sb; Table 1). High background intensities and no clear peaks (except for quartz) were detected during the XRD analysis, which is thought to beindicative of a highly disordered (amorphous) nature of this material (Table 1). Sample B-4 was collected from an area near the Big River's water edge at the battery site. The substrate was fine-grained, distinctly grey-coloured, and contained visible quartz sand grains. The presence of arsenopyrite in this substrate was confirmed by the XRD analysis performed (Table 1).

Discussion

The mobilisation of arsenic and antimony occurred generally on a metre-scale at the Big River Mine's battery site but detailed investigations of some of the substrates, especially the cemented scorodite-bearing hardpan material, demonstrated mobilisation occurring on a cm and even mm-scale. Metalloid mobility is controlled (indirectly) by the environmental conditions present on site. The pH is of particular importance, as it governs the precipitation and dissolution of secondary phases that formed over time. The low pH character of the Big River Mine's battery site enables the sustained presence of the mineral scorodite, which is known to be relatively stable in acidic conditions and to re-dissolve at pH 7–8 (Langmuir et al., 2006). The continued presence of scorodite represents an arsenic sink contributing to the minimisation of As mobility at the battery site.

Secondary mineral formation is one of the known mechanisms of As retention in sulphidic mining wastes (Ashley and Lottermoser 1999; Giere et al., 2003; Haffert et al., 2010). The visual observations of the colouring of the processing residues and the known presence of iron-bearing sulphide minerals in the mineralised zone, suggest the presence of iron oxides or iron hydroxides, even though in the majority of cases the XRD analyses failed to successfully identify them in the sampled substrates (Table 1). These phases are known and have been experimentally demonstrated to be important scavengers of As and Sb are here presumed to represent additional metalloid sinks at the Big River Mine's historic processing site (Courtin-Nomade et al., 2003; Haffert et al., 2010; Alvarez-Ayuso et al., 2013). The mechanisms responsible for metalloid association in Fe-rich phases are mainly co-precipitation and adsorption.

Adsorption onto clay mineral surfaces represents another possible - and likely - sink for both metalloids at the Big River Mine. Adsorption of arsenic and antimony oxyanions is considered particularly likely in acidic conditions when clay particles are positively charged (Sadiq, 1997; Xi et al., 2010). Kaolinite has been found in a number of processing residues analysed and this mechanism of metalloid retention is considered likely to be occurring at the site.

The formation of a hardpan layer and the precipitation of secondary metalloid phases are responsible for the immobilisation of the metalloids and isolation (e.g. through encapsulation by secondary phase formation) of the primary sulphide minerals (arsenopyrite, pyrite, and stibnite) from the surficial environment, thereby preventing their further disintegration and decomposition. The presence of non-oxidised residues (sample B-4) indicates that burial in a saturated, reducing environment represents another way of arsenopyrite stabilisation which prevents its decomposition.

The mobilisation of arsenic and antimony from decomposing sulphide minerals into mine waters is facilitated by circum-neutral pH. It was found that only approximately 1 L/s (combined, during dry weather) of water draining the site contained detectable metalloid concentrations. Some results were found to exceed the environmental guideline value for protection of aquatic ecosystems of 0.001 mg/L for As (ANZECC, 2000). However, the small volume of water affected and the immediate natural remediation that occurs on confluence with the Big River as a result of dilution, ensure that no serious environmental risks are posed. It appears that the impact of the mine site on water quality is only localised as no metalloids were detected in the receiving Big River downstream of the site.

A comparison of the Big River Mine processing site's chemistry and mineralogy with the nearby Prohibition Mine reveals how the different site-specific conditions influence the chemical stability of historic mining sites and the extent of possible associated environmental impacts. The Prohibition Mine has been investigated in 2009 and as a result of the extreme metalloid contents in soil/processing residues and water documented, it is currently undergoing extensive remediation. The principal difference between the two sites is that the Prohibition Mine site contains arsenolite. Arsenolite (As_2O_3) is a by-product of roasting of a sulphide-rich ore concentrate which has been undertaken in an Edwards-type roaster. The primary source of acidity at this site is the oxidation of arsenolite. The dissolved As run-off is partially immobilised by the formation of scorodite cement but large quantities of As (in water) were shown to be leaving the site (Haffert and Craw, 2009). It is the lack of mobile arsenolite at the Big River Mine which allows for it to be much more chemically stable than the Prohibition Mine site.

Conclusions

The Big River site undoubtedly represents a disrupted ecosystem (lack of vegetation cover etc.). However, the understanding of the site chemistry allows for an assessment of metalloids mobility and the site's chemical stability. In this case, particularly when compared to the nearby Prohibition Mine site, the investigation was able to conclude that the extremely elevated metalloid concentrations are contained within the site, primarily in the form of secondary mineral phases which act as As and Sb sinks. These metalloids do not travel far from the site provided that the conditions (including chemical controls) persist that are favourable for the stability of secondary minerals and the adsorption of metalloids onto iron oxides/hydroxides and clays. Despite the presence of extreme metalloid contents in mining residues, the site is not considered in need of immediate remediation – especially when considered in the context of the nearby Prohibition Mine. In saying that, the site was identified to be unsuitable for human access and the fence currently present at the battery site should be moved and rebuilt to restrict public access as exposure to the extreme mining residues located on site may pose a human health risk.

Acknowledgments

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References

Alvarez-Ayuso, E., Otones, V., Murciego, A. and Garcia-Sanchez, A. 2013. Evaluation of different amendments to stabilize antimony in mining polluted soils. Chemosphere 90: 2233–2239.

ANZECC. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

APHA. 2005. Standard methods for the examination of water and wastewater, 21st edn. American Public Health Association, Washington DC.

Ashley, P. and Lottermoser, B. 1999. Arsenic contamination at the Mole River mine, northern New South Wales. Australian Journal of Earth Sciences 46(6): 861–874.

Ashley, P., Craw, D., Graham, B. and Chappell, D. 2003. Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. Journal of Geochemical Exploration 77(1): 1–14.

Barry, J. and Armstrong, B. 1993. The history and mineral resources of the Reefton goldfield. Resources Information Report 15, Energy and Resources Division, Ministry of Commerce. P. 59.

Blakemore, L., Searle, P. and Daly, B. 1987. Methods for chemical analysis of soils. New Zealand Soil Bureau Scientific Report 80: 71–76.

Christie, A. and Brathwaite, R. 2003. Hydrothermal alteration in metasedimentary rock-hosted orogenic gold deposits, Reefton goldfield, South Island, New Zealand. Mineralium Deposita 38(1): 87–107.

Christie, A., Corner, N., Bierlein, F., Smith, P., Ryan, R. and Arne, D. 2000. Disseminated gold in turbidite-hosted gold deposits of Reefton (South Island, New Zealand), Victoria (Australia) and Nova Scotia (Canada). In: Proceeding NZ Minerals and Mining Conference, Crown Minerals, Ministry of Economic Development, Wellington, New Zealand. Pp. 105–118.

Christie, A., Barker, R. and Brathwaite, R. 2010. Mineral resource assessment of the West Coast Region, New Zealand. GNS Science Report 2010/61. P 235.

Cooper, R. 1974. Age of the Greenland and Waiuta Groups, South Island, New Zealand (Note). New Zealand Journal of Geology and Geophysics 17(4): 955–962.

Courtin-Nomade, A., Bril, H., Neel, C. and Lenain, J-F. 2003. Arsenic in iron cements developed within tailings of a former metalliferous mine-Enguiale`s, Aveyron, France. Applied Geochemistry 18(3): 395–408.

Druzbicka, J. and Craw, D. 2015. Metalloid attenuation from runoff waters at an historic orogenic gold mine, New Zealand. Mine Water and the Environment (in press).

Giere, R., Sidenko, N. and Lazareva, E. 2003. The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). Applied Geochemistry 18(9): 1347–1359.

Groves, D., Goldfarb, R., Gebre-Mariam, M., Hagemann, S. and Robert, F. 1998. Orogenic gold deposits: a proposed classification in the context of their crustal distribution and relationship to other gold deposit types. Ore Geology Reviews 13(1): 7–27.

Haffert, L. and Craw, D. 2009. Field quantification and characterisation of extreme arsenic concentrations at a historic mine processing site, Waiuta, New Zealand. New Zealand Journal of Geology and Geophysics 52(3): 261–272.

Haffert, L., Craw, D. and Pope, J. 2006. Quantification and controls on As distribution in Westland, New Zealand. In: Proceedings of the 39th AusIMM New Zealand Branch Annual Conference.

Haffert, L., Craw, D. and Pope, J. 2010. Climatic and compositional controls on secondary arsenic mineral formation in high-arsenic mine wastes, South Island, New Zealand. New Zealand Journal of Geology and Geophysics 53(2–3): 91–101.

Langmuir, D., Mahoney, J. and Rowson, J. 2006. Solubility products of amorphous ferric arsenate and crystalline scorodite ($FeAsO_4$-$2H_2O$) and their application to arsenic behavior in buried mine tailings. Geochimica et Cosmochimica Acta 70(12): 2942–2956.

Sadiq, M. 1997. Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. Water Air Soil Pollution 93(1–4): 117–136.

Wright, L. 1993. Big River quartz mine 1882–1942: a worthwhile speculation. Friends of Waiuta Inc, Reefton.

Xi, J., He, M. and Lin, C. 2010. Adsorption of antimony (V) on kaolinite as a function of pH, ionic strength and humic acid. Environmental Earth Sciences 60(4): 715–722.