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A Geoenvironmental Model for Orogenic Gold Deposits to Predict Potential Environmental Effects

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Abstract Orogenic deposits are an important source of gold around the world, with associated environmental impacts. New Zealand has a broad spectrum of these orogenic deposits, providing an ideal setting to develop a general conceptual model that can be used to predict potential environmental issues associated with their exploration and mining. This model provides a practical and quantitative framework for permitting and managing mine operations, with a focus on downstream water quality. The model has been quantified using data collected from natural mineralised occurrences, two active mines, and numerous historic mine sites. Mine waters in and around orogenic deposits almost invariably have a pH of 7–8. Minor localised acidification occurs in excavations and waste rock, but it is readily neutralised by the abundant calcite in the host rock. The ore can have strongly elevated levels of As and Sb; the proportions of these metalloids are controlled by geological factors, especially the crustal level of emplacement and the structure of the mineralised rocks. Agitation of sulfide mineral slurries during processing and pressure oxidation in the processing system can lead to dissolved metalloid concentrations of tens to hundreds of mg/L in mine tailings waters. The gold also commonly contains Hg, up to 40 wt%, and discharge of this Hg to the atmosphere during processing is possible, but Hg is not significantly mobilised from other mine rocks. High metalloid concentrations are the most significant environmental issue, but are decreased by adsorption to iron oxyhydroxide as the water percolates through mine rocks and tailings. Even so, additional treatment may be needed to lower metalloid concentrations for discharge to rivers and lakes.

Keywords Arsenic · Antimony · Mercury · Adsorption · Treatment · Stream invertebrates · Suspended solids

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Introduction

Geoenvironmental models of mineral deposits provide predictions of potential environmental issues associated with particular types of deposits during mining and mineral processing (Goldfarb et al. 1995; Plumlee et al. 1999; Seal et al. 2002; Seal and Hammarstrom 2003). Development of a conceptual geoenvironmental model is useful for preventing or mitigating environmental issues before, during and after exploration, development of mining operations in a particular mineralised terrane and/or deposit type, and for assessing abandoned mine sites and their potential remediation requirements (Plumlee et al. 1999; Seal et al. 2002). Construction and validation of a the model involves compilation of empirical data on host rocks, primary and secondary mineralogy, and trace element geochemistry, combined with likely mining and ore processing methods, hydrology, topography, and climate (Goldfarb et al. 1995; Plumlee et al. 1999; Seal et al. 2002; Seal and Hammarstrom 2003).

Orogenic gold systems form a class of mineral deposits that have a broadly consistent set of geological and geochemical features around the world (Bierlein et al. 2004). In particular, orogenic gold systems that are hosted in metamorphosed sedimentary rocks are remarkably similar through geological time and space (Bierlein et al. 2004). Consequently, this deposit type has been amenable to construction of geoenvironmental models in several geographical locations (Goldfarb et al. 1995; Seal 1995; Seal and Hammarstrom 2003). These models have incorporated site-specific geochemical data, principally from abandoned historic mines, that contribute to quantification of mineralogy and potential water quality issues in a range of climatic and topographic settings.

In this paper, we have extended geoenvironmental modelling of orogenic gold deposits in metasedimentary terranes, using examples from southern New Zealand. Our conceptual model was developed for a broad spectrum of orogenic deposit types that have been formed at, and exhumed from, a range of geological depths. We quantified our model primarily with mineralogical and geochemical data from active mines, for a range of ore types and processing systems and strongly contrasting climates. These data were augmented with information from historic mine sites to extend the range of ore types investigated, contributing to a more generalised model that is applicable to southern New Zealand in particular, but is also transferable elsewhere in the world where similar topography and temperate climates prevail. In addition, we have incorporated on-going research on water treatment systems appropriate for these mine sites, and the inter-relationships between water discharge quality and consequent downstream biological implications. Hence, our integrated geological, mineralogical, geochemical and biological compilation underpins and quantifies the most comprehensive geoenvironmental model for orogenic deposits yet devised. Our model is mostly focussed on water quality, but we also incorporate some air quality issues, especially with respect to Hg, where these are related to the underlying geological features.

General Setting

The South Island of New Zealand (Fig. 1) is predominantly underlain by Paleozoic and Mesozoic metasedimentary terranes (Mortimer 2004). The metasedimentary rocks are dominated by greywackes with interlayered argillites in turbidite sequences (Mortimer 2004). Orogenic gold deposits were emplaced in these metasedimentary terranes in the Paleozoic and Mesozoic (Christie and Brathwaite 2003; Mortensen et al. 2010). Renewed uplift across the South Island occurred in the late Cenozoic, and additional orogenic deposits were emplaced in the mountains immediately east

of the Alpine Fault (Fig. 1). This orogenic hydrothermal system is still active, and metal-bearing warm springs are locally discharging at the surface (Fig. 1; Holley et al. 2010).

The South Island has a generally moderate, temperate, climate with mean annual temperatures in coastal and inland valley areas of 10–15 °C. However, the mountains along the length of the South Island (Fig. 1) produce strongly contrasting climatic zones. Areas west of the mountains receive abundant orographic rainfall, typically exceeding 2000 mm/year (Haffert et al. 2010), while the eastern side of the mountains are relatively dry and locally arid, with rainfall as low as 300 mm and high evapotranspiration rates (>700 mm/year; Druzbicka et al. 2015; Haffert et al. 2010).

Sources of Data

This paper is a product of a ten-year collaborative research programme involving mining and mineral exploration companies and regulatory and conservation bodies in New Zealand (Cavanagh et al. 2014). The research was aimed at developing a practical framework for permitting and managing mine operations, with a focus on water quality in streams and rivers in mined catchments. The research programme included all mined commodities, not just orogenic gold (Cavanagh et al. 2014). Most data for this paper were provided by mining and/or exploration companies operating in orogenic gold deposits from their routine environmental monitoring programmes, and some of the data have previously been published as part of more specific studies. Sampling and analytical methods are described in detail in those publications, which are referred to herein. The principal contributor of data has been OceanaGold Ltd, who operate the world-class Macraes Mine in the Mesozoic rocks of southeastern South Island, and the Globe-Progress Mine in Paleozoic rocks on the western side of the South Island (Fig. 1; Milham and Craw 2009).

Further data have been collected from two active mines and numerous historic mine sites by the authors, and analysed by techniques outlined in previous publications as well as those quoted herein. In addition, gaps in data sets and general environmental knowledge have been filled in with field and laboratory experimental work, most of which has also been published previously in some form, and quoted herein. In this paper, we compile relevant aspects of all these data sets into a unified and quantified description of environmental issues associated with orogenic gold deposits and their immediate downstream environments.

Geochemical and Mineralogical Features

The metasedimentary host rocks for orogenic gold deposits in southern New Zealand almost invariably have the greenschist facies mineral assemblage of quartz, albite,

Fig. 1 Hillshade image of the South Island of New Zealand, showing the locations of principal types of orogenic hydrothermal systems of differing ages
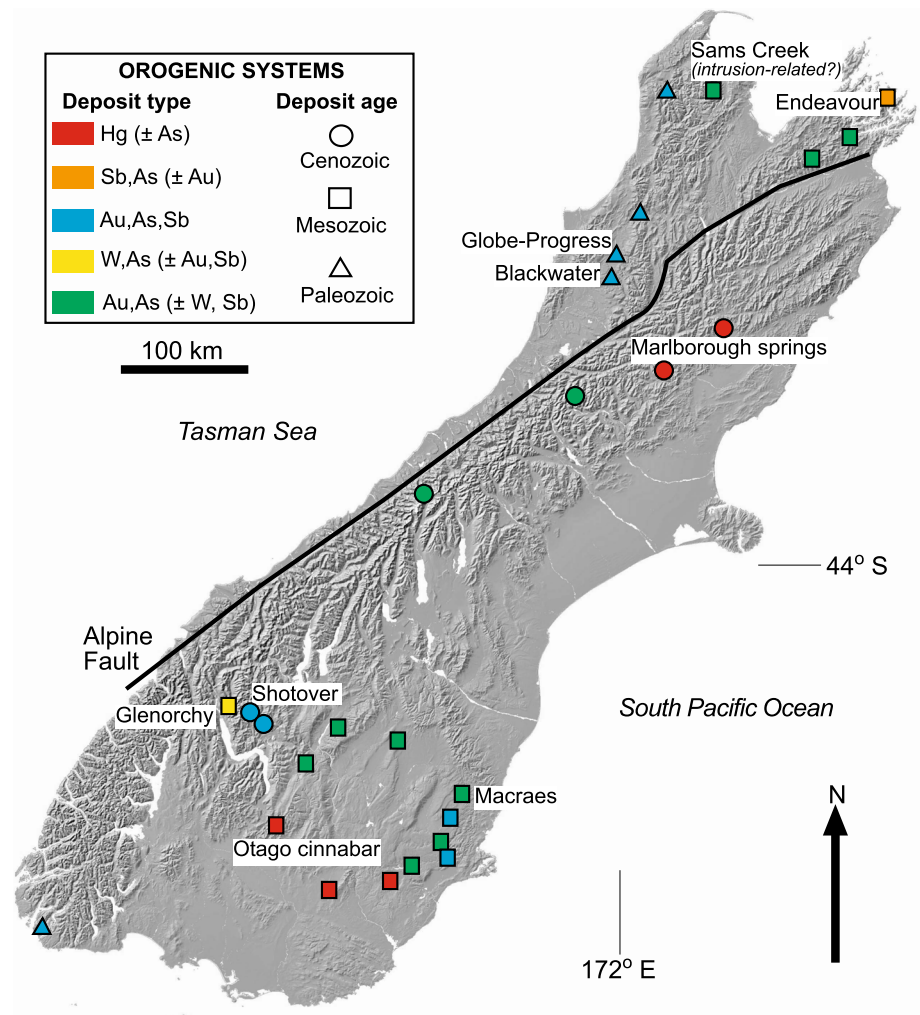
muscovite and chlorite, with abundant carbonate, especially calcite. The abundant carbonate in the host rocks is a very important feature from an environmental perspective, as it neutralises any acid generated by oxidation of sulfide minerals (Craw 2001). Consequently, the surface and ground waters associated with mineralised rocks, in natural and mined state, have near-neutral or weakly alkaline pH. This is an important distinction between the orogenic deposits described in this paper and epithermal gold deposits found elsewhere in New Zealand, as the latter commonly have widespread acid rock drainage (Craw 2001). In addition, most of the other minerals in the metasedimentary host rocks are relatively reactive in groundwater. Hence, water–rock interactions in host rocks of orogenic gold deposits, particularly partial dissolution of calcite, chlorite, and albite, are a major component of the geochemical system and are predictable across all of New Zealand's orogenic deposits (Craw 2001).

Despite the uniformity of the host rocks, the orogenic deposits themselves show a wide range of mineralogical and geochemical characteristics (Figs. 1, 2). These characteristics result from the formation processes of orogenic hydrothermal systems, in which different styles of deposits, with differing elemental makeup, were deposited at different structural levels in the deforming crust (Fig. 2). The full range of orogenic deposit styles extends over 10 km vertically in the original formational settings (Fig. 2; Craw et al. 2009; Milham and Craw 2009; Mortensen et al. 2010). The same general ranges of deposit styles, with some local variations, formed at different times in the different host terranes (Figs. 1, 2), and have been variably exposed by subsequent differential uplift and exhumation. In particular, deeper-formed gold deposits such as the Macraes mine (Fig. 1) contain abundant W and only minor Sb, whereas shallower-formed systems contain abundant Sb, locally without Au, although As is abundant throughout (Figs. 1, 2; Craw et al. 2009). The Globe-Progress deposit formed from at least two stages of mineralisation at different depths during uplift, with distinctly higher Sb in the later, shallower stage (Fig. 2; Milham and Craw 2009). The
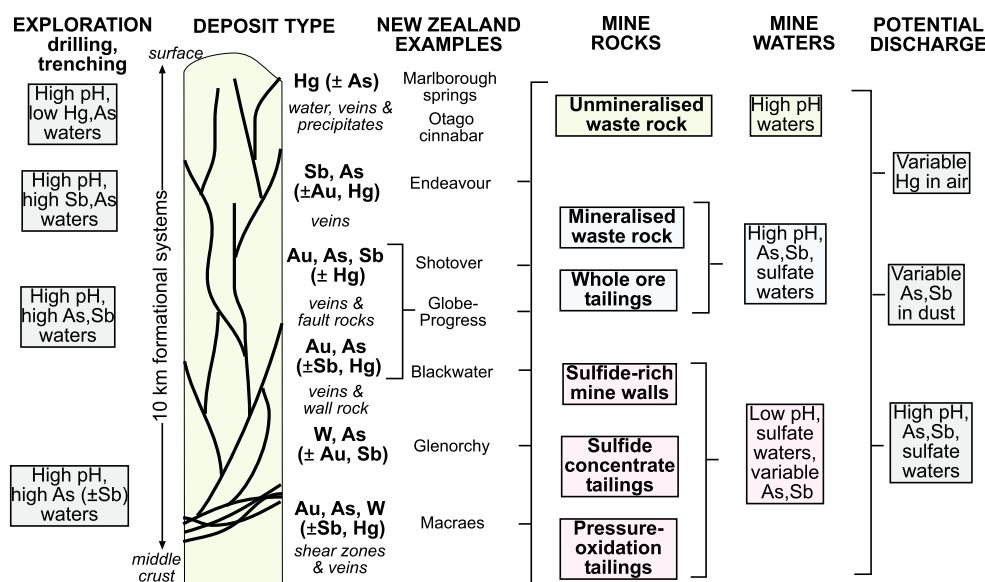
Fig. 2 Schematic depiction of general crustal scale zonation of orogenic deposit types (after Craw et al. 2009), with their typical element associations that are of environmental significance. New Zealand examples relevant to this paper are identified in Fig. 1. Principal potential environmental issues are indicated for exploration (*left*) and mining (*right*)

late Cenozoic orogenic system, which is still active in the mountains of the South Island (Craw et al. 2009), shows a similar range of deposit styles to the older orogenic systems, but has the additional component of active warm springs where Hg-bearing orogenic fluids, with some As, are reaching the surface (Figs. 1, 2; Holley et al. 2010). Details of the formation of the Sams Creek deposit (Fig. 1) are not yet fully understood, but the deposit occurs in a small Cretaceous granite intrusion that is hosted in greenschist facies Paleozoic metasedimentary rocks similar to those which host orogenic deposits nearby (Faure and Brathwaite 2006; Phillips et al. 2014; Windle and Craw 1991). From an environmental perspective, the Sams Creek deposit is broadly similar to the orogenic systems elsewhere in the South Island.

The depth of formation of orogenic deposits also affects the nature and extent of mineralised rocks, with varying proportions of veins and altered wall rocks (Fig. 2). Deepformed deposits have mineralised veins in localised sites that are typically irregular in shape, laterally discontinuous, and have commonly undergone post-mineralisation deformation and disruption. Extensive alteration of wall rock has typically occurred in these settings, with pervasive fluid flow in the host rock at the grain scale; the ore in such deposits is locally dominated by mineralised wall rock, rather than veins (Craw et al. 2009; MacKenzie and Craw 2007; Petrie et al. 2005). The Macraes deposit contains the most spectacular example of this style of mineralisation, where alteration and gold mineralisation occurs in variably sheared host rocks in a zone up to 250 m wide (Craw et al. 2009; Petrie et al. 2005).

In contrast, shallow-formed deposits are generally confined almost entirely to quartz veins in well-defined fractures and faults, with minor alteration and mineralisation of fault rocks and breccias (Fig. 2; Craw et al. 2009). These parts of the orogenic system are generally characterised by Sb-rich mineralisation, including the shallow-formed Endeavour Inlet Sb deposit that contains little Au at exposed levels (Wilson et al. 2004a, b). Well-defined gold-bearing quartz vein systems, with minor wall rock alteration and mineralisation, have formed at, or extend down to, intermediate depths, as at the historic Blackwater mine (Figs. 1, 2). The nearby, and genetically related, Globe-Progress deposit shows evidence for superimposition of late-stage mineralisation of fault rocks, with only minor vein formation, on to early-formed vein and wall rock alteration zones (Fig. 2; Milham and Craw 2009).

Metallic minerals that accompany gold in the various orogenic systems reflect the general zonation with formation depth, although pyrite (locally As-bearing) and arsenopyrite are almost ubiquitous (Fig. 2; Table 1). Scheelite is the principal W-bearing mineral in deeper-formed deposits and the Sams Creek deposit contains minor wolframite, but these minerals are of negligible environmental significance. Stibnite is the principal Sb mineral in shallower-formed systems, and this almost invariably contains some As (up to 5 wt%) in solid solution (Table 1; Milham and Craw 2009; Wilson et al. 2004a, b). Conversely, most arsenopyrite contains some Sb (typically <1 wt%; Milham and Craw 2009; Petrie et al. 2005). Minor Sb and As occur in tetrahedrite solid solution minerals in the Paleozoic systems, and in

Table 1 Principal metallic minerals in New Zealand orogenic gold deposits, with the most environmentally significant solid solution impurities

Mineral	Formula	Solid solution	Occurrence
Primary			
Gold	$\approx Au_{0.9}Ag_{0.1}$	Hg	All
Pyrite	FeS_2	As	All
Arsenopyrite	FeAsS	Sb	All
Stibnite	Sb_2S_3	As	All Sb-rich
Tetrahedrite	$\approx Cu_{12}Sb_4S_{13}$	As	Paleozoic
Boulangerite	$Pb_5Sb_4S_{11}$	As	Macraes
Chalcopyrite	$CuFeS_2$	As?	All (trace)
Sphalerite	ZnS	Cd	All (trace)
Galena	PbS	Ag	All (trace)
Scheelite	$CaWO_4$	Mo	All W-rich
Wolframite	$FeWO_4$	Mn	Sams Ck
Cinnabar	HgS	As	Otago
Oxidised			
Arsenolite	As_2O_3	Sb	Local, POX
Scorodite; kankite	$FeAsO_4$ hydrate	Sb?	All, POX
Ferric arsenate	Variable Fe, As, hydrated	Sb? SO_4	POX
Pharmacosiderite	$KFe_4(AsO_4)_3(OH)_4 \cdot 6H_2O$	Sb?	Local
Stibiconite	$Sb_3O_6(OH)$	As?	Local
Valentinite; senarmontite	Sb_2O_3	As	Local
Jarosite	$KFe_3(SO_4)_2(OH)_6$	As	Local, POX

Occurrences refer to Figs. 1 and 2

Local occurrences are typically in sulfide-rich rock in mines and oxidised outcrops

POX pressure oxidation

boulangerite at the Macraes mine (Table 1). Cinnabar occurs in some orogenic veins in Mesozoic rocks, but not in direct association with known gold deposits (Fig. 1; MacKenzie and Craw 2005). Minor cinnabar has been deposited in spring precipitates in the active orogenic systems in Marlborough (Fig. 1; Holley et al. 2010). Mercury is locally enriched in the gold of some orogenic deposits (Table 1), but the regional geological controls on this enrichment are not understood (MacKenzie and Craw 2005). Cu, Pb, and Zn, occur in chalcopyrite, sphalerite and galena in many orogenic systems, but generally in minor concentrations and with little or no enrichment (Petrie et al. 2005). However, the Sams Creek deposit has some localised enrichment of these minerals (Faure and Brathwaite 2006; Windle and Craw 1991).

Mine Rocks and Waters

Excavations and Waste Rocks

Mine excavations expose fresh rock to surface waters in a wide variety of settings, and the mineralogy and structure of these exposed rocks affects the resulting water compositions that have potential downstream environmental significance (Figs. 2, 3a–d). The resultant water quality is affected primarily by the nature and amount of metallic minerals present in the rocks. The examples in Fig. 3a–d are all from the Globe-Progress mine, in which two different styles of mineralisation yield different runoff water compositions. These examples at a single mine reflect processes that occur in separate mining areas, such as Endeavour Inlet (Sb) and typical Au–As orogenic deposits elsewhere (Fig. 1).

The most voluminous product of most mines is the waste rock, which includes overburden and other rock that has to be extracted to gain access to ore in complexly shaped ore bodies at both surface and underground mines. This waste rock is typically piled in the immediate vicinity, as permanent repositories that are revegetated, or as temporary stockpiles intended for replacement in exhausted excavations. Unmineralised waste rock has negligible environmental significance, and their runoff typically maintains high pH, with elevated levels of dissolved major ions derived from dissolution of silicate minerals and carbonates (Craw and Nelson 2000). Likewise, runoff from unmineralised rocks in excavations (Fig. 3a) evolves to high pH as a result of the same water–rock reactions. Water
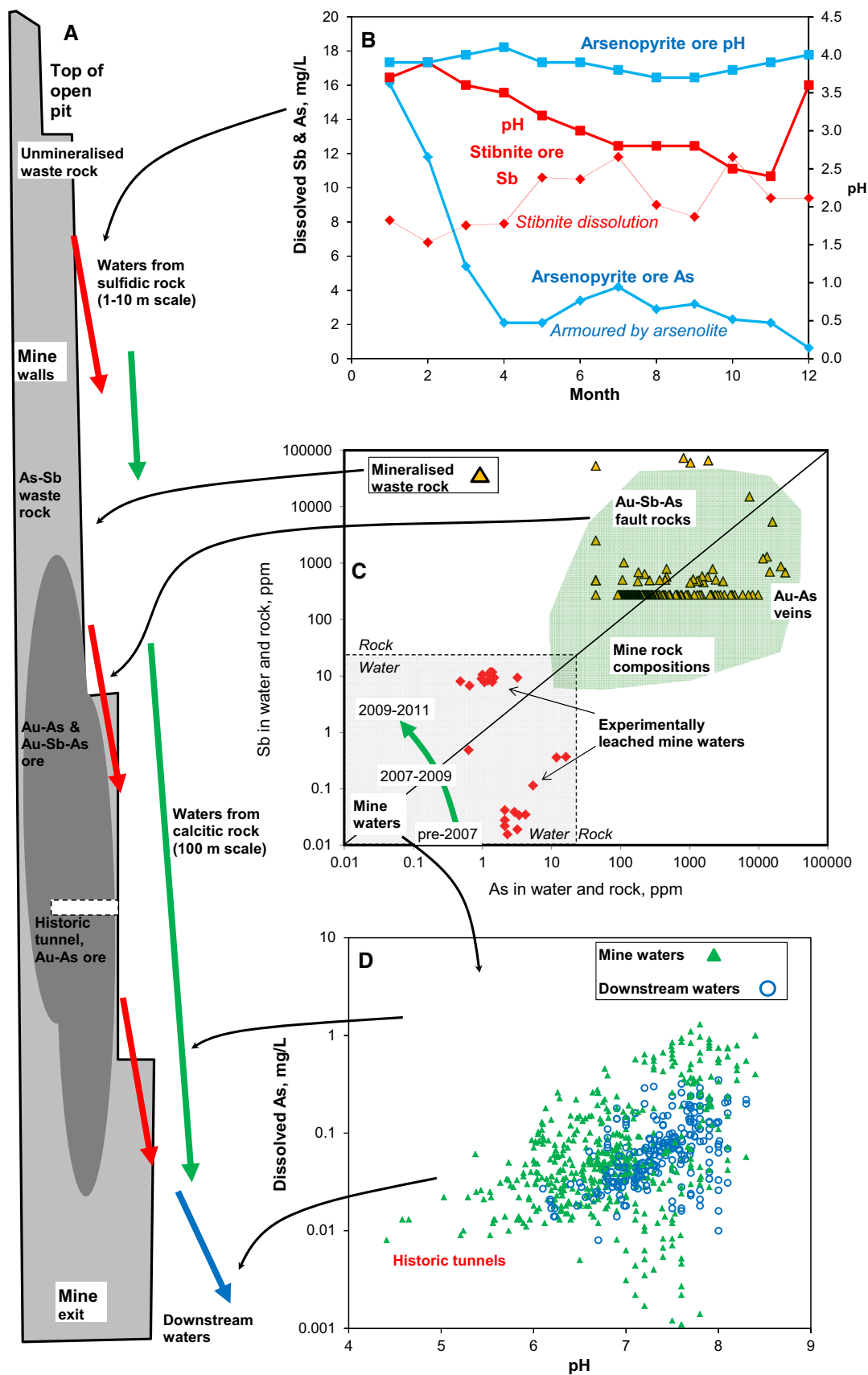
◄ **Fig. 3** Key features of mine excavations and their impacts on water compositions, based on the Globe-Progress mine in which early As-rich ore was overprinted by Sb-rich ore. **a** Sketch of open pit wall, outlining environmentally important rock types exposed, and associated water runoff. **b** Results of laboratory leaching of different sulfidic ore samples, showing the timescale and magnitudes of water compositional changes (after Kerr et al. 2015a). **c** Metalloid compositions of mine rocks, including mineralised waste rocks, and associated run-off water compositions (after Druzbicka and Craw 2013). Data from experiments in **B** are plotted for comparison. **d** The pH and As contents of mine waters and downstream waters, with trajectory of compositional evolution over time as increased amounts of Sb-rich ore were mined

from both these situations provide useful buffering and dilution capacity.

Runoff from sulfidic rocks can rapidly dissolve As and/or Sb from the abundant sulfides, in addition to dissolved sulfate. The rate of metalloid dissolution is difficult to quantify in situ, for practical reasons, but individual rain events in an open pit can produce large volumes of water with metalloid loads of several mg/L (Fig. 3c; Druzbicka and Craw 2013). Experimental leaching of stibnite- and arsenopyrite-rich ore samples in a laboratory, simulating repeated rain events and dry periods over 12 months (Kerr et al. 2015a), resulted in dissolved Sb > 10 mg/L and As > 3 mg/L (Fig. 3b, c). The lower levels of dissolved As arose because of armouring of arsenopyrite grains by arsenolite coatings (Fig. 3b), reflecting partial As oxidation (Kerr et al. 2015a). Stibnite did not develop significant secondary mineral coatings in this short time period. Longer periods of sulfide oxidation, including natural weathering, typically yield scorodite, kankite, or pharmacosiderite from arsenopyrite, and senarmontite, valentinite, and/or stibiconite from stibnite (Table 1; Craw et al. 2002, 2004; Haffert et al. 2010; Wilson et al. 2004a).

Localised acid generation (Fig. 3b) causes calcite dissolution in the host rocks; consequently, dissolved sulfate and bicarbonate rise in tandem (Fig. 4a) without a significant decrease in pH (Fig. 3d). Dissolved sulfate is remarkably persistent through mine water systems, and discharge waters commonly retain a strong dissolved sulfate signature (Fig. 4a). Likewise, water that has passed through waste rock that contains sulfide minerals also develops a strong sulfate-rich signature (Fig. 5a), reflecting its interaction with sulfides, carbonates, and silicates (Craw and Nelson 2000), and is distinctly different in composition from the rainwater, which is dominated by marine aerosols with a seawater composition (Fig. 5a). The sulfate concentrations of discharging waste rock waters decrease as the waste rock stacks are rehabilitated with caps and vegetation, thereby limiting water ingress, and the exposed sulfide grains become armoured with secondary minerals (Fig. 5a).
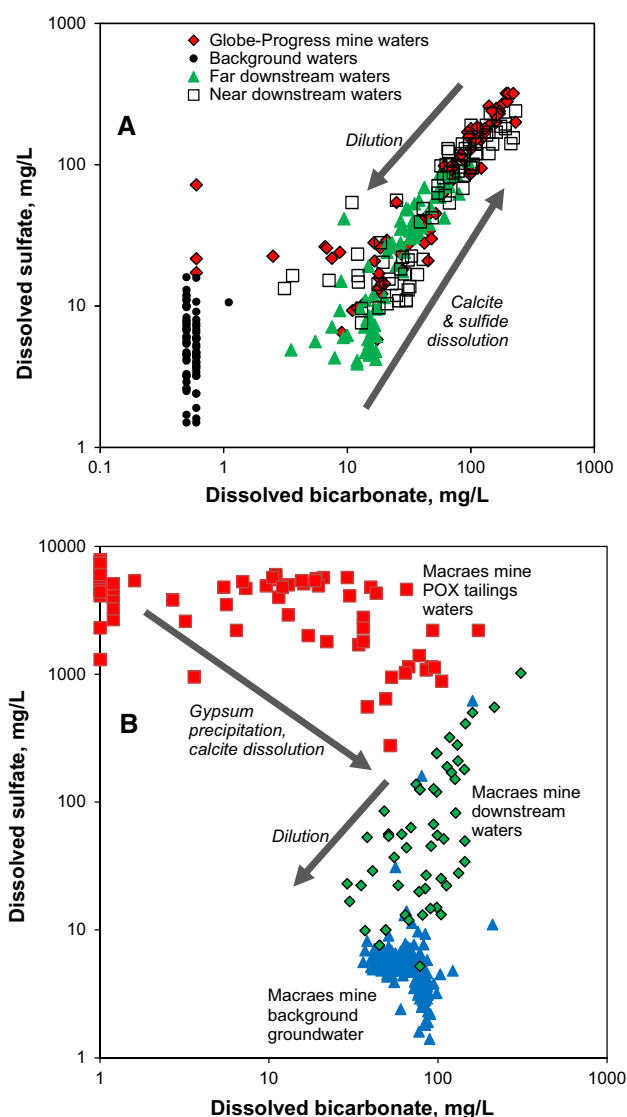
Fig. 4 Geochemical relationships between dissolved bicarbonate and sulfate in mine water, compared to background water. **a** Data for the Globe-Progress Mine, in which sulfide oxidation drives calcite dissolution, and downstream waters become diluted. **b** Data for the Macraes Mine, in which relatively acidic water from pressure oxidation (POX) of sulfides goes on to dissolve calcite and precipitate gypsum, and is then diluted downstream

Variable dissolution of metalloids and sulfate occurs in mineralised waste rock (Figs. 3c, d, 5a, b). Waste rock piles that have strongly elevated As and/or Sb contents (Fig. 3c) may require separate storage and possibly encapsulation in low permeability materials to limit water ingress and egress. Mineralised waste rocks have variable As/Sb ratios, depending on the minerals that are being extracted at the time, and the resultant runoff will have dissolved metalloid ratios that broadly reflect the compositions of the rocks they have encountered. Historic mines at the Globe-Progress site largely focussed on the earlier
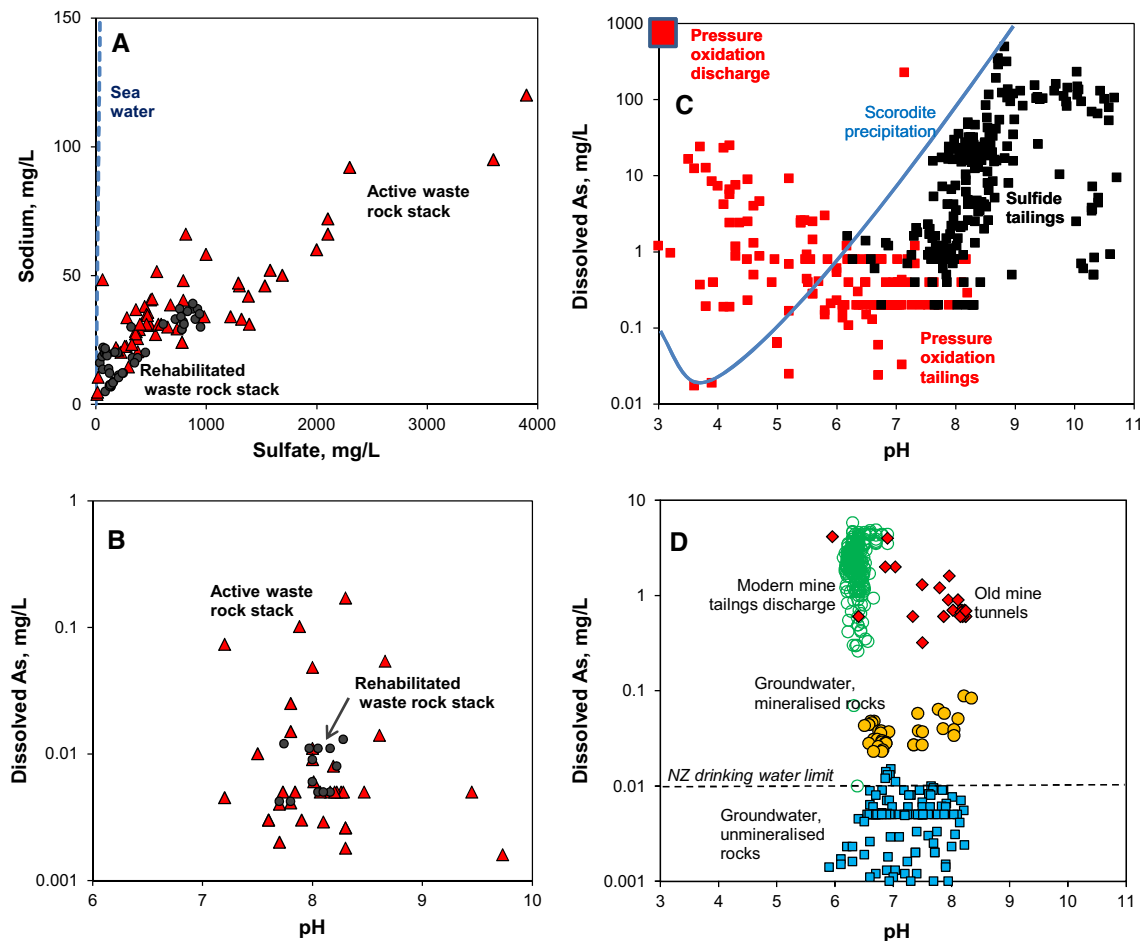
Fig. 5 Water compositions at Macraes mine. **a** Compositions of waters from waste rock stacks, showing evolution to elevated sulfate and Na contents because of interaction with sulfides and silicates respectively. **b** Same waters as in **a**, showing water pH and dissolved As contents. **c** The pH and As content of mine tailings waters from sulfide tailings before pressure oxidation was introduced, and from pressure oxidation processing. Scorodite precipitation line is from Krause and Ettel (1989). **d** The pH and As content of downstream mine waters, and background waters from mineralised and mineralised rocks

Au–As quartz veins via underground workings (Fig. 3a, c). The As/Sb ratio of mine waters evolved with time as the mine progressively extracted more ore and mineralised waste from the later, stibnite-bearing, mineralisation event (Fig. 3c; Druzbicka and Craw 2013). In contrast, the Macraes waste rock has low Sb, and so the water from waste rock stacks has a near-neutral pH, low to moderate dissolved As concentrations (Fig. 5b), but negligible dissolved Sb.

Pyrite that has been deposited from groundwater is a common feature of freshly exposed waste rock. This pyrite generally coats joints and fractures in a thin (<0.1 mm) film that is irregularly distributed through the rock mass. This pyrite is unrelated to gold mineralisation and contains no gold. Similar joint-coating pyrite occurs widely elsewhere in the metasedimentary host rocks, where it has been mobilised from metamorphic sulfides (pyrite or pyrrhotite), or deposited from groundwater after reduction of dissolved

sulfate (Youngson 1995). Oxidation of this type of pyrite is responsible for some or all of the elevated sulfate levels in water discharged from waste rock stacks at gold mines (Figs. 4a, 5a, b).

Mine Tailings

Modern orogenic gold mines almost invariably produce a sulfide-rich concentrate in the processing plant, as the sulfides contain some or all of the gold in the ore, as μm-scale inclusions or in solid solution in the sulfide mineral structure (Large et al. 2012; Petrie et al. 2005). This gold is made available for extraction by fine grinding, possibly augmented with additional artificial oxidation. The gold is then extracted from the concentrate by cyanidation, at pH > 10, and the residue is discharged as tailings. There are four principal types of tailings produced by gold processing systems: (i) sulfide-free tailings, from which the

sulfides have been extracted; (ii) sulfide tailings, from which the gold has been extracted; (iii) oxide tailings that contain oxidised sulfide residues from which the gold has been extracted; and (iv) mixed tailings that include some combination of the other three tailings types, remixed and discharged to the tailings impoundment (Craw 2003). Since only 1–10 g of gold is extracted from each t of ore, tailings constitute one of the largest components of the mining system. The tailings are generated as a slurry of water and fine-grained (typically <100 μm) crushed rock. Tailings are generally stored in large impoundments behind dams constructed of waste rock, with internal drainage systems and low-permeability liners (Craw and Nelson 2000). The solid component of the tailings slurry settles into the impoundment, a lake (decant pond) forms on the surface of the impoundment, and water variably percolates through the impoundment (Craw and Nelson 2000; Craw 2003). In some cases, these lakes become permanent water bodies and develop their own ecological communities.

Because of the extra grinding and processing involved in gold extraction, mine tailings waters typically have greater dissolved chemical contents than waters discharged from waste rocks. In particular, the initial tailings water, which collects on the tailings impoundment, will have the most extreme compositions on the mine site, and require careful management. Water associated with sulfide-free tailings is generally relatively benign, with compositions similar to, but with higher dissolved loads than water from waste rock piles. The elevated sulfate is associated with the sulfide-extraction processing system, and subsequent dissolution of minor remnants of sulfides, e.g. Fig. 4a.

Sulfide-rich tailings can develop strongly elevated metalloid content, especially dissolved As, up to hundreds of mg/L (Fig. 5c). Such high dissolved As occurs under highly alkaline conditions (pH > 8), and is limited by precipitation of iron arsenates, particularly scorodite (Fig. 5c; Craw et al. 2002; Haffert and Craw 2008; Haffert et al. 2010). As pH decreases towards neutrality in the tailings, the dissolved As decreases as scorodite precipitates (Fig. 5c; Craw et al. 2002). Localised acidification of the tailings can occur as sulfide minerals oxidise, further lowering the dissolved As content of the water (Craw et al. 2002; Haffert et al. 2010). Dissolved Sb content of the tailings water is typically less than the dissolved As, and generally does not exceed 10 mg/L (Milham and Craw 2009). However, dissolved Sb levels in contact with stibnite-rich solids can reach 50 mg/L (Ashley et al. 2003).

Oxidation of the sulfide concentrate at a processing plant typically occurs at elevated temperatures; the modern pressure-oxidation process (POX) occurs at >200 °C in a pressurised oxygen atmosphere (Craw 2003). The subsequent rapid oxidation of sulfides results in extreme acidification (pH < 1) of the processing slurry, with associated dissolved As concentrations up to thousands of mg/L (Fig. 5c; Craw

2003; Kerr et al. 2015b). The pH of this slurry is immediately raised >10 for cyanidation, but oxidation of residual Fe^{2+} causes temporary re-acidification (Fig. 5c; Craw 2003). This re-acidification is readily managed by mixing the oxidised tailings with sulfide-free tailings that contain abundant calcite, so that tailings water pH rises towards neutral on a time scale of months (Fig. 5c, d; Craw 2003). This neutralisation is important for lowering dissolved sulfate as well, as the reaction with calcite contributes to gypsum ($CaSO_4 \cdot 2H_2O$) precipitates in the tailings impoundment (Fig. 4b). Gypsum precipitation lowers dissolved sulfate from thousands of mg/L to ≈1000 mg/L, while bicarbonate concentrations increase (Fig. 4b; Craw 2003).

Mercury

Historically, Hg was commonly added to extract gold by amalgamation during ore processing at orogenic gold mines, resulting in Hg contamination of the mine sites and surrounding areas (Mains and Craw 2005; Holley et al. 2010). This Hg contamination generally exceeded any natural Hg content of the mineralised rocks (Mains and Craw 2005). However, modern mines do not use Hg amalgamation, so natural Hg content now controls the environmental Hg at these mine sites. Hg is most abundant in shallower-formed orogenic systems, culminating in Hg-rich near-surface deposits (Fig. 2). However, Hg occurs as a significant trace component of mineralised rocks throughout the orogenic hydrothermal systems (Fig. 2).

The variably elevated Hg contents of mineralised rocks results in dissolved Hg concentrations (≈0.001 mg/L) in the associated groundwater, which is similar in composition to the actively mineralising Marlborough springs (Fig. 6a). These Hg concentrations are more than an order
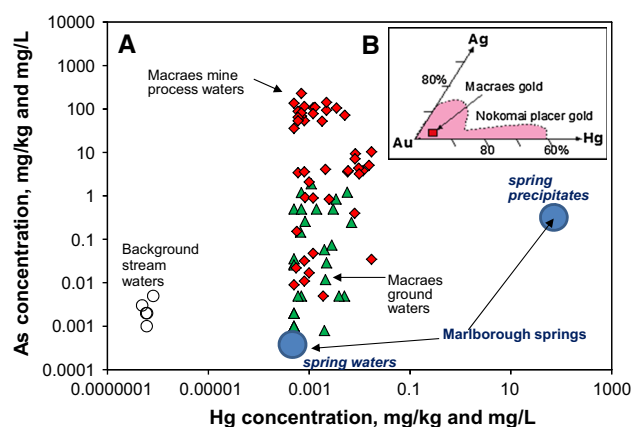

Fig. 6 Mercury in orogenic systems. **a** Comparison of dissolved Hg and dissolved As (after Holley et al. 2010) at Macraes mine (*diamonds* and *triangles*) and at active Marlborough warm springs (*large filled circles*). **b** Compositions of gold at Macraes, and in placer gold derived from orogenic systems related to the Otago cinnabar deposits (Fig. 1; after Youngson et al. 2002)

of magnitude higher than background waters (Fig. 6a; Holley et al. 2010). Hg dissolution is largely unaffected by the extreme water–rock interaction that occurs in a gold processing plant, where dissolved As concentrations can increase by several orders of magnitude, while the dissolved Hg increases by less than one order of magnitude (Fig. 6a).

Gold is an important repository for the Hg in mineralised rocks, and Hg can make up several percent of the gold (Table 1; Fig. 6b). For example, gold at the Macraes Mine contains up to 4 wt% Hg, and some orogenic veins in the region have up to 7 wt% Hg (Fig. 6b; MacKenzie and Craw 2005). Placer gold, which may have been derived from cinnabar-bearing orogenic veins in Otago, has up to 40 % Hg (Fig. 6b; MacKenzie and Craw 2005; Youngson et al. 2002). This Hg in the mineralised rocks has the greatest environmental significance, as it can be released to air during gold extraction and refining in the processing plant (Fig. 2). Careful control of Hg emissions is an important aspect of the processing plant air quality management system, for health and safety as well as environmental reasons, for Hg discharging in associated waterways can significantly affect the environment.

Downstream Water Quality

Untreated Discharges

Streams and rivers receiving discharges at most modern mine sites have consistently low metalloid contents: typically <1 mg/L at the Globe-Progress Mine (Fig. 3d) and >0.1 mg/L at Macraes (e.g. Fig. 5b). The receiving streams below the Macraes Mine are typically similar in composition to the natural background groundwater composition in the mineralised rocks (Fig. 5d). Downstream waters also have a high pH, although some low pH waters emanated from historic tunnels at both mine sites before the modern mines were developed (Figs. 3d; 5d). Dissolved sulfate concentrations in downstream waters remain elevated compared to background waters, but dilution with other water emanating from unmineralised rocks ensures that dissolved sulfate concentrations typically remain near 100 mg/L (Fig. 4a, b). This dilution depends on rainfall and associated groundwater recharge, which can be periodically limited in the dry and highly evaporative climate east of the mountains (Druzbicka et al. 2015). Abundant rainfall west of the mountains, as at the Globe-Progress Mine, ensures adequate dilution there.

Dissolved metalloids are readily extracted from mine water by adsorption to iron oxyhydroxide (HFO) that is typically abundant in variably oxidised mineralised rocks at the site (Craw et al. 2004; Druzbicka and Craw 2015; Roddick-Lanzilotta et al. 2002; Wilson et al. 2004a, b).

This adsorption process, possibly assisted by co-precipitation of secondary arsenates and Sb oxides (Table 1), can extract >90 % of the metalloids dissolved in mine waters (Craw et al. 2004; Druzbicka and Craw 2015; Roddick-Lanzilotta et al. 2002; Wilson et al. 2004a, b). For example, the very high initial dissolved As in the Macraes Mine tailings water (>100 mg/L; Fig. 5c) decreases to near 1 mg/L as the water percolates through the tailings impoundment on a time scale of weeks (Fig. 5d). This attenuation of metalloids by adsorption within the mine wastes is highly efficient as long as sufficient HFO is available. Water discharging for over >50 years at historic tunnels at the Globe-Progress site yielded widespread HFO with adsorbed As contents up to a million times higher than the dissolved As, and adsorbed Sb content up to 100,000 times the dissolved Sb (Fig. 7a; Craw et al. 2004). This
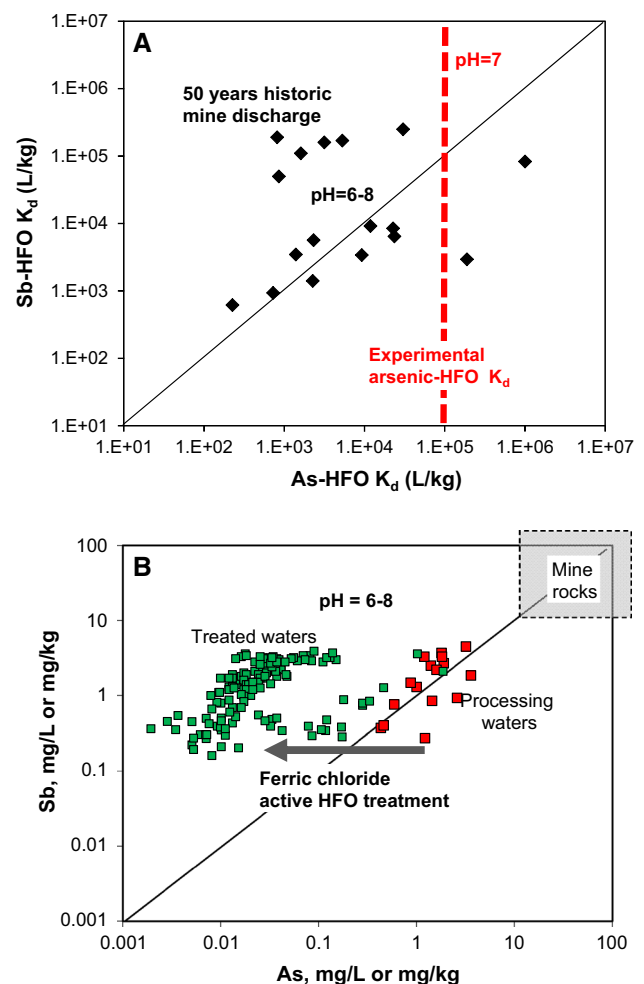

Fig. 7 Adsorption of metalloids to iron oxyhydroxide (HFO) at mine sites. **a**. Distribution ratios of As and Sb in HFO and associated mine water at historic tunnels at the Globe-Progress deposit, compared to experimental As results (after Roddick-Lanzilotta et al. 2002). **b** Water from an active treatment plant at the Globe-Progress mine, showing effective adsorption extraction of As, but not of Sb (partly after Milham and Craw 2009)

observed long-term As adsorption is comparable to experimental As adsorption using similar mine water (Fig. 7a; Roddick-Lanzilotta et al. 2002).

Suspended Solids

All mine excavations and processing activities involve disturbance of variably mineralised rock; this can lead to elevated levels of suspended solids (cf Druzbicka and Craw 2012). Excessive suspended solids in mine discharges can cause significant environmental impacts, especially if amounts exceed those of natural floods in absolute concentrations and duration. Suspended and deposited fine sediment can reduce the diversity and ecosystem health of stream communities (Burdon et al. 2013). The amount of suspended solids in mine water is affected by the nature of the substrate that is being disturbed, with clay-rich materials proving most problematic (Druzbicka and Craw 2012). Clay-rich substrates are relatively rare in orogenic gold deposits, where hydrothermal alteration of wall rocks is limited (Fig. 2). However, shallow-level fault activity in the hosting structures of orogenic systems can result in formation of fine-grained fault gouges that include clays (Milham and Craw 2009). These fine-grained materials can include As and Sb sulfides and/or their oxidised products, so that suspended solids in orogenic mine waters may have chemical as well as physical environmental significance (Druzbicka and Craw 2013). If properly designed and maintained, settling ponds positioned downstream of the mine activities can be an effective control mechanism; the required residence time in these ponds depends on the physical nature of the suspended mineral grains (Druzbicka and Craw 2012).

The amount and rate of suspended solids discharge is affected by climate. Major rain events can mobilise fine-grained sediment and at times can exceed the carrying capacity of settling ponds (Druzbicka and Craw 2013). Conversely, dry conditions can make fine sediment available for wind-blown redistribution; dust problems then arise downwind of the mine site. Furthermore, the dust particles can be deposited in waterways, contributing to suspended sediment loads, and potentially leading to widespread chemical as well as physical contamination. Hence, control of dust distribution can be a significant management issue, especially for dry tailings impoundment surfaces (Mains et al. 2006) and exposed waste rock piles.

Water Treatment

Metalloids can be extracted from mine waters by engineered treatment systems if the attenuation processes described above are insufficient. Active treatment typically involves a dedicated treatment plant constructed at the end of the mine processing system, where the highest metalloid concentrations arise. Active treatment systems need ongoing management, addition of appropriate reagents, and regular extraction and disposal of metalloid-bearing residues, and are therefore relatively expensive. Most active treatment systems for metalloids involve generation of additional HFO in the water by chemical means; ferric chloride is the most common reagent added for this purpose. The ferric chloride dissolves to release Fe^{3+}, which immediately hydrolyses in the neutral pH water to yield suspended HFO. The HFO, with adsorbed metalloids, is filtered out of the water before discharge. This process is most effective for removing dissolved As; competition between As and Sb for adsorption sites can limit the effectiveness of Sb extraction in this process (Fig. 7b; Milham and Craw 2009).

Passive treatment involves engineered systems that channel water through appropriate pathways to facilitate extraction of metalloids in a less organised way than active systems. Passive systems require less management than active systems, and can be left for years or decades with little maintenance, so are less expensive to operate. However, passive systems typically require long residence times and are most effective for removing small amounts of metalloids. A pilot-scale passive system involving bacterial reduction of Sb and sulfate in composted organic material has effectively precipitated stibnite and lowered dissolved Sb (Fig. 8a, b; Trumm and Hay 2012). This pilot system was constructed immediately downstream of the active (ferric chloride) treatment plant at Globe-Progress mine, which was less effective at extracting Sb than As (Fig. 7b). The passive bacterial reduction system was most effective with residence times of at least one day (Fig. 8a).

Low levels of dissolved As can also be extracted from discharging mine waters using engineered passive treatment systems containing HFO. The effectiveness of these passive adsorption systems depends, in part, on residence time within the engineered reactor, like the bacterial reduction system described above. The effectiveness is also strongly affected by the amount of available HFO adsorption sites in the reactor system. Pilot-scale passive HFO reactor systems at the historic Blackwater mine (Fig. 1) used HFO precipitates from two different acidic coal mine discharge water streams, with different proportions of iron oxyhydroxide (Fig. 8b; Rait et al. 2010; Trumm et al. 2012). The higher HFO content was most effective at removing As from the mine waters, but all experiments removed >90 % of the dissolved As (Fig. 8b).

Potential Downstream Biological Effects

New Zealand stream ecosystems are generally less complex than in many other countries, due to the high
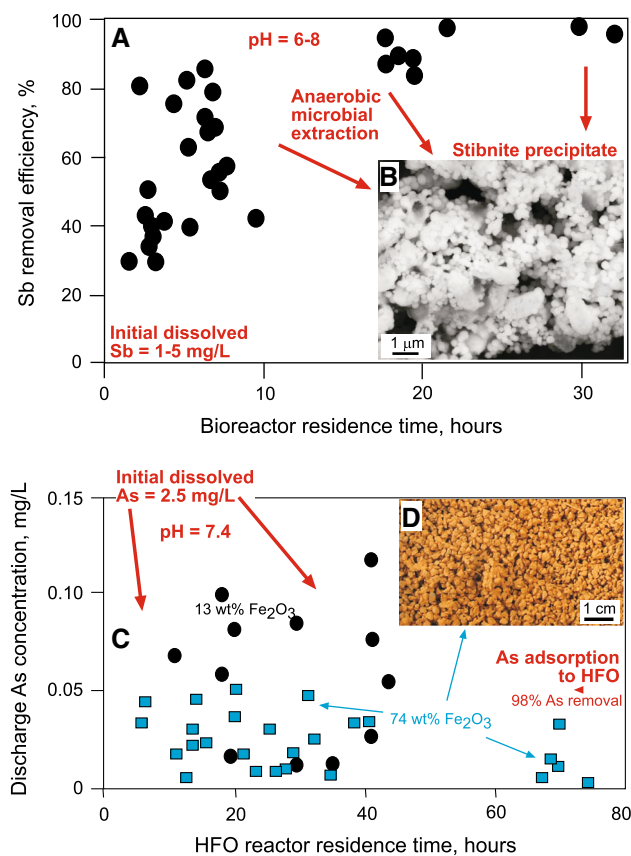
Fig. 8 Results of pilot-scale passive treatment of mine waters to extract metalloids (after Trumm et al. 2012; Trumm and Hay 2012). *a* Bacterial reduction with compost removes Sb, through stibnite precipitation (*b*; photo by K Lilly). *c* As extraction by adsorption on to HFO collected from coal mine acid rock drainage precipitates with differing Fe contents (Rait et al. 2010). *d* Coal mine HFO (74 wt% Fe_2O_3) coating gravel, used in the reactor in C

endemism and the absence of most freshwater amphibians, reptiles, and mammals. As a result, New Zealand streams, rivers and lakes are dominated by aquatic plants inverte-brates and fish. New Zealand's indigenous fish are entirely predaceous, feeding on invertebrates and other fish. Therefore, aquatic invertebrates play an important role in processing organic matter and as prey for fish species (Fig. 9a; Harding 2005; Hogsden and Harding 2012). Consequently, aquatic invertebrate communities are com-monly used as indicators of stream health, and changes to these communities downstream of mine sites can be indi-cators of negative environmental impacts. Qualitative and quantitative indices of relative stream health can be cal-culated from collections of key aquatic invertebrate taxa (e.g. Stark 1985, 1993; Stark and Maxted 2007). However, these indices were developed for assessment of agricultural impacts, such as nitrates and phosphates (Stark 1985), not

mining. Likewise, a similar index developed for acid mine drainage impacts (Gray and Harding 2012) is not directly applicable to the neutral pH to alkaline waters associated with orogenic gold mines (Figs. 3d, 5d). However, the effects of elevated suspended sediment concentrations from mining activities are similar to those from other earth disturbances, and Quinn et al. (1992) suggest that the average increase in turbidity and suspended solids should be limited to <5 NTU or <5 mg/L, respectively, to prevent substantial impacts on invertebrate communities.

Tolerance of aquatic invertebrates to elevated metalloid concentrations in circumneutral pH waters is poorly understood globally. Telford et al. (2009) found that Aus-tralian aquatic invertebrates with low ecological tolerances were not significantly impacted in waters with Sb $\approx$ 0.4 mg/L and As $\approx$ 0.05 mg/L, in near-neutral pH waters downstream of an orogenic Sb–Au mine. However, New Zealand's aquatic invertebrate fauna is highly ende-mic (Harding 2005), and little evaluation of metalloid tolerances of these endemic taxa has been done (e.g. Jeyasingham and Ling 2000). Preliminary ecotoxicological experiments on one of the most common New Zealand aquatic invertebrates, the mayfly *Deleatidium* (Fig. 9b), and on a common stonefly, *Zelandobius*, are summarised in Fig. 9c. Short-term elevation of dissolved As above $\approx$ 1 mg/L is apparently not deleterious, but longer-term exposure to such waters may be significantly deleterious (Fig. 9c). These experiments highlight the important eco-toxicological distinction between acute and chronic expo-sure on survival of mayflies (Fig. 9c). Minor elevated Hg associated with some orogenic gold is similar to, or less than, natural orogenic warm spring systems (Fig. 6a), and distinctly lower than geothermal spring systems elsewhere in New Zealand (Holley et al. 2010), so mine-related impacts on biota by Hg are unlikely to be distinguishable from natural systems.

The New Zealand recommended drinking water limits for As and Sb contents is 0.01 mg/L, though groundwater in mineralised rocks can substantially exceed that level without mining (Fig. 5d). Likewise, historic mining has commonly left a legacy of tunnels that at least in part focus the discharges of such groundwater with naturally elevated metalloid contents (Figs. 3d, 5d; Wilson et al. 2004a, b). Consequently, the distinction between natural and mine-impacted waters can be difficult to distinguish when dis-solved metalloids are less than $\approx$ 0.1 mg/L. Such water, whether natural or mine-impacted, is not suitable for long-term human consumption. Elevated dissolved sulfate, at the levels associated with mine waters (<1000 mg/L) is not considered to be toxic to humans or animals, though this dissolved load may affect the taste of that water (Backer et al. 2001; Gomez et al. 1995).

Fig. 9 Aquatic invertebrates downstream of mine sites. **a**. Schematic outline of stream ecosystems, showing the key position of aquatic invertebrates and the potential mine-related disruptions. **b** The most common and widespread invertebrate, the mayfly *Deleatidium*, that is commonly part of the evaluation of stream health and impacts. **c** Preliminary results of ecotoxicolgical experiments on aquatic invertebrates in metalloid-bearing waters (see text)
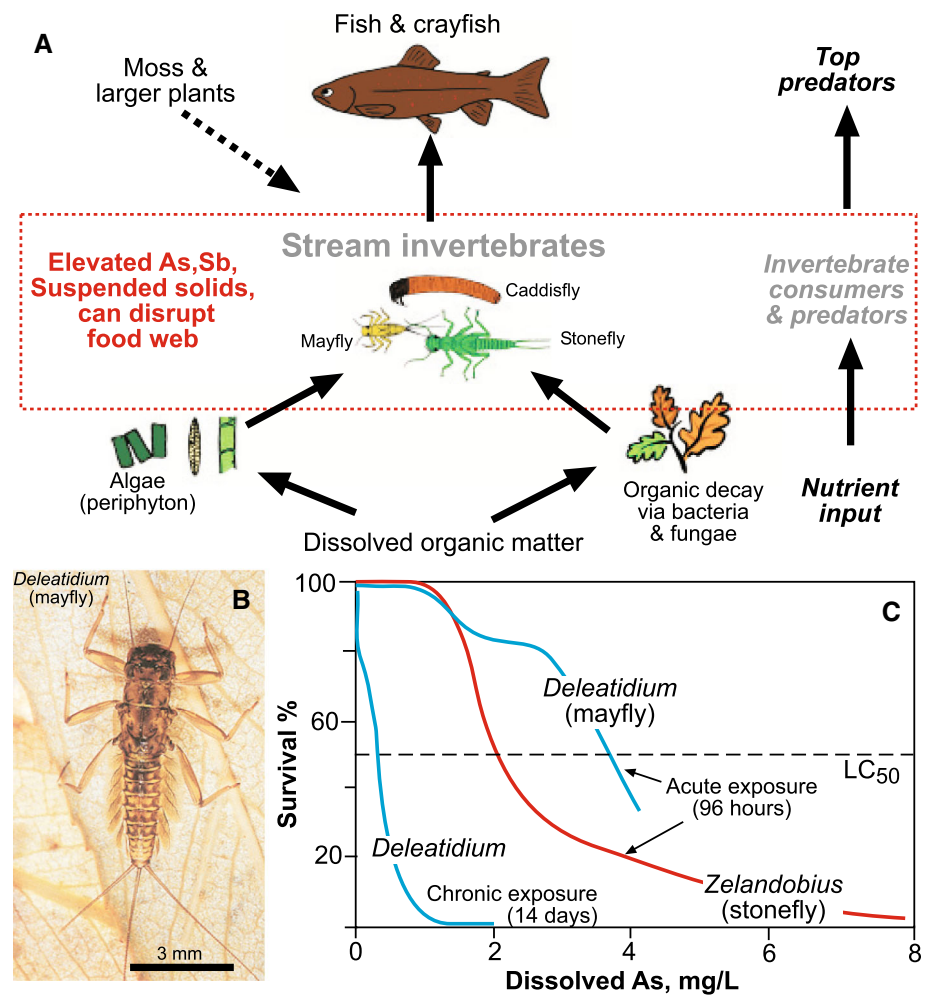

Fig. 10 Summary chart showing principal geological and geochemical features, and processing pathways (*right*, *pink* no oxidation/roasting; *left*, *blue* oxidation/roasting) of mines in orogenic deposits. These lead to predicted water compositions and other potential environmental issues, as indicated. Further geological and mineralogical variations relevant to this summary are presented in Fig. 2 and Table 1
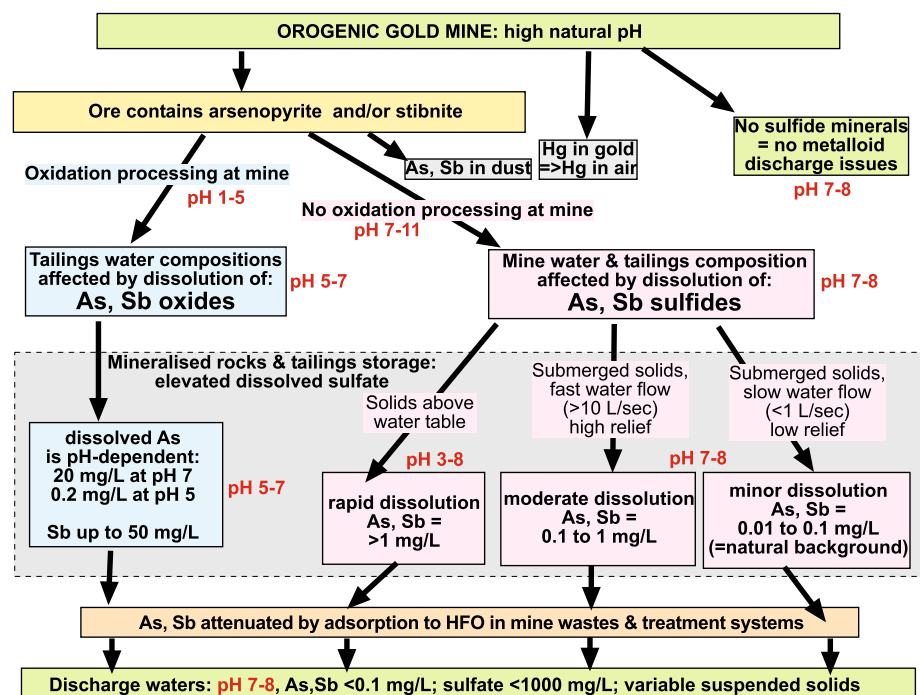
Model Summary and Conclusions

The data sets outlined above, combined with specific observations at active mine sites, can be summarised into a generalised model of water quality and associated environmental issues at orogenic gold mines (Fig. 10). Specific issues associated with different geological styles of orogenic deposits are outlined in Figs. 2 and 3a; these augment the generic flow paths in Fig. 10. Likewise, the potential environmental issues associated with initial exploration and mine feasibility studies, before mining is initiated, are summarised in Fig. 2 according to the underlying geological features of the different styles of orogenic deposits. The various components of the geoenvironmental model can be used to predict the nature and magnitude of environmental issues at various types of orogenic gold mines, at various stages of exploration, mine development, and processing operations. Importantly, the abundant calcite in host rocks ensures that pH remains circumneutral almost everywhere through exploration and mining activity, so that acid rock drainage is not a significant environmental issue.

The key features of the geoenvironmental model that arise from Figs. 2, 3a, and 10 are that water quality will inevitably be affected by elevation of dissolved As and Sb, with the relative significance of As and Sb being affected primarily by the depth of formation of the orogenic deposit (Fig. 2). Mine tailings are the principal source of dissolved metalloids on mine sites, so the geometry of tailings storage and the rate of throughput of water strongly affects the water quality immediately downstream of the tailings (Fig. 10). Likewise, the presence or absence of a sulfide oxidation stage in the ore processing system can affect the rate and amount of metalloid dissolution in the tailings impoundment (Fig. 10). Attenuation, by several orders of magnitude, of elevated metalloids occurs readily by adsorption to HFO in mine wastes, but additional water treatment may be required to further lower metalloid contents before water is discharged to the environment. Limited ecotoxicological data suggest that aquatic invertebrates can tolerate short-term (acute) metalloid contents of ≈ 1 mg/L, but longer-term (chronic) exposures at such high levels may be deleterious (Fig. 9c). The geochemical signals of the various types of orogenic gold mines that we have outlined for New Zealand are likely to be similar elsewhere in the world. However, the potential effects on biota described herein are relevant to New Zealand's unique endemic ecosystems, which are relatively tolerant of elevated metalloid concentrations.

Superimposed on this elevation of metalloids at a mine site is the relatively minor component of Hg mobilisation, which is primarily related to the gold itself. Processing of the abundant sulfide-bearing rocks inevitably raises dissolved sulfate concentrations, and waters emanating from waste rock piles also have elevated dissolved sulfate. Attenuation of highly elevated sulfate can occur at the mine site by precipitation of gypsum, and further attenuation occurs by dilution. However, elevated sulfate is an almost inevitable feature of mine discharge waters. Similarly, disturbance of the rock mass almost inevitably results in occasional elevated levels of suspended solids in discharge waters, which can have negative effects on the downstream ecosystem. Awareness of the potential development of these environmental issues ensures that appropriate management strategies can be put in place at any stage of an operation.

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