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Arsenic mobility in mildly alkaline drainage from an orogenic lode gold deposit, Bralorne mine, British Columbia

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ABSTRACT

The historical (1932–1971) Bralorne mine produced over 87 million grams of Au from an archetypal orogenic lode gold deposit in southwest British Columbia. High concentrations of As in mine drainage, however, represent an on-going environmental concern prompting a detailed study of effluent chemistry. The discharge rate at the mine portal was monitored continuously over a fourteen-month period during which effluent samples were collected on a quasi-weekly basis. Water samples were also collected on synoptic surveys of the adit between the portal and the main source of flow in the flooded workings. Total concentrations of As in the mildly alkaline ($pH = 8.7$) portal drainage average 3034 μg/L whereas at the source they average 5898 μg/L. As emergent waters from the flooded workings flow toward the portal, their dissolved oxygen content and pH increase from 0 to 10 mg/L and from 7.7 to 9, respectively. Near the emergence point, dissolved Fe precipitates rapidly, sorbing both As(III) and As(V). With increasing distance from the emergence point, dissolved As(III) concentrations drop to detection limits through sorption on hydrous ferric oxide and through oxidation to As(V). Concentrations of dissolved As(V), on the other hand, increase and stabilize, reflecting lower sorption at higher pH and the lack of available sorbent. Nonetheless, based on synoptic surveys, approximately 35% of the source As load is sequestered in the adit resulting in As sediment concentrations averaging 8.5 wt%. The remaining average As load of 1.34 kg/d is discharged from the portal. Partitioning of As(V) between dissolved and particulate phases in portal effluent is characterized by a sorption density of 0.37 mol As $(\text{mol Fe})^{-1}$ and by a distribution coefficient (K_d) of 130 L/g HFO. The relatively high sorption density may reflect co-precipitation of As with Fe oxyhydroxides rather than a purely adsorption-controlled process. Results of this study show that the As self-mitigating capacity of drainage from orogenic lode gold deposits may be poor in high-pH and Fe-limited settings.

1. Introduction

Orogenic gold deposits (Groves et al., 1998), also known as mesothermal, Mother Lode or greenstone-hosted deposits are the most widespread type of economic gold-bearing mineral occurrence (Groves et al., 2003). Because of their generally high grade and potentially large tonnage (Groves et al., 2003, and references therein), deposits of this class have long represented attractive targets for mineral exploration. Orogenic gold deposits are so named because they are typically hosted by greenstones and metasedimentary rocks in accreted geological terranes. Deposits consist of quartz veins usually containing carbonates, sericite, pyrite and arsenopyrite as well as Au. Vein alteration envelopes are ubiquitous and typical wall-rock mineral assemblages include quartz, albite, ferroan dolomite, sericite, pyrite and arsenopyrite (Ashley, 2002). From an environmental perspective, the most significant features of these deposits are their abundant carbonate content, low sulfide content and enrichment in As and occasionally Sb (Goldfarb et al., 1995). Because of the low sulfide content of the ore and the buffering capacity of the carbonates, acid drainage is not usually associated with this type of deposit, and base metal loadings are consistently low (Ashley, 2002). However, the circum-neutral to alkaline waters that result from contact with ore and altered wall-rocks also promote the mobilization of oxyanion-forming metalloids As and Sb (Ashley, 2002). These are potentially toxic and hazardous to human health and ecosystems (Edmunds and Smedley, 1996; Smith and Huyck, 1999).

The drainage geochemistry of orogenic gold deposits has been studied at mines in the Mother Lode district of California (Savage et al., 2000, 2009), Alaska (Goldfarb et al., 1997; Verplanck et al., 2008; Torrance et al., 2012) and New Zealand (Craw et al., 2004;

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Haffert and Craw, 2008; Druzbicka and Craw, 2013). This study extends these investigations to an archetypal Mesozoic orogenic gold deposit at the Bralorne mine in British Columbia, Canada (Leitch, 1990; Leitch et al., 1991). The contiguous Bralorne and Pioneer mines were, at one time, the largest gold producers in western Canada (Church and Jones, 1999). Large-scale production at the Pioneer mine started in 1928 and followed at the Bralorne mine in 1932. Although operations at the two mines were consolidated in 1959, the Pioneer mine closed in 1962 while the Bralorne mine continued operations until 1971. Total combined production from the Bralorne and Pioneer mines was 129,169 kg (4,152,882 oz) of gold and 29,582 kg (951,070 oz) of silver from 7,295,878 tonnes (8,042,328 tons) of ore mined (MINFILE, 2010, 092JNE001; 092JNE004). Since 1971, various companies have investigated the possibility of re-opening the mine and redevelopment activities are currently underway (Bralorne Gold Mines, 2014). However, with a modern environmental regulatory regime in place, the operator is faced with the challenge of managing high-arsenic drainage from the old workings.

Whereas a number of studies have investigated As mobility in acidic mine waters (Courtin-Nomade et al., 2005; Gault et al., 2005; Asta et al., 2010), the objectives of this study are to characterize drainage chemistry and As mobilization under higher pH (>8.5) conditions (Smedley and Kinniburgh, 2002), as encountered at the Bralorne mine.

Hydrogeochemical investigations at the Bralorne mine have been conducted previously by Strand (2007), Desbarats et al. (2011) and Beauchemin et al. (2012). Strand (2007) described the results of a synoptic survey of drainage, sediment and rock chemistry conducted along the main haulage adit (800-Level) of the historical mine. Desbarats et al. (2011) investigated the chemistry of drainage from a recent exploration adit on the Bralorne property exhibiting elevated concentrations of As and Sb. The authors characterized the mobilization and attenuation of As and Sb using geochemical mass balance modeling to estimate sulfide weathering rates. In their companion study of the same site, Beauchemin et al. (2012) described variations in As and Sb speciation and accumulation in drainage channel sediments, from the channel source to a wetland downstream. The present investigation revisits the drainage chemistry of the historical Bralorne mine. Drainage from 800-Level was sampled on a quasi-weekly basis over a 14-month period while portal discharge rate was monitored continuously. This temporal analysis of drainage chemistry was complemented with new synoptic surveys conducted on the adit level between the portal and the main source of mine water where flooded workings overflow. Results of this investigation contribute to understanding of the geoenvironmental characteristics of orogenic lode gold deposits (Ashley, 2002; Seal and Hammarstrom, 2003) and the As self-mitigating capacity of their drainage. This understanding can be used to anticipate and better manage drainage issues associated with future development of newly discovered ore bodies of this class.

2. Site description

2.1. Physiographic and climatic setting

The Bralorne mine (lat: 50.778476 N; long: 122.820626 W; Elev. 975 m) is located 175 km north-east of Vancouver (Fig. 1) within the deeply-incised valley of Cadwallader Creek which separates the Bendor and Cadwallader Ranges of the southern Coast Mountains. Elevations in the area vary between 950 m on Cadwallader Creek and over 2800 m on the nearest summits of the Bendor Range. Cadwallader Creek forms part of the headwater drainage of the Bridge River which joins the Fraser River at Lillooet.

The property lies in the rain shadow of the Coast Mountains, at the transition between a moist Marine West Coast climatic zone in the west and a semi-arid Continental Interior climatic zone in the east. Because of this climatic gradient and strong local orographic effects, extrapolation of climatic data from the nearest active weather stations to the Bralorne site is problematic. However, based on historical meteorological records for Bralorne available between 1934 and 1963 (Environment Canada, 2009), mean annual precipitation averages 652 mm, including an average snowfall equivalent of 244 mm. Mean temperatures in the hottest (July) and coldest (January) months of the year are 15 °C and −7.3 °C, respectively.

2.2. Geological setting

The geology of the Bridge River mining camp has been reviewed by numerous authors including Church (1996), Church and Jones (1999) and Hart et al. (2008). The geology of the Bralorne mine has been described in detail by Leitch (1990) and Leitch et al. (1991).

The Bralorne property is underlain by fault-bounded wedges of metasedimentary rocks and greenstones from the Bridge River and Cadwallader accreted terranes. Deposits of the Late Paleozoic Bridge River terrane consist of ribbon cherts with intercalated argillite, greenstones and thin limestone beds of oceanic origin. Deposits of the Triassic Cadwallader terrane reflect an island-arc origin and consist of argillites, volcanics and turbidite wackestones of mixed provenance. Interleaving of Bridge River and Cadwallader terranes occurred during a Jurassic plate collision which resulted in reverse faulting, imbricate thrusting and stacking of oceanic and ocean-margin lithologies with fault-bounded lenses of underlying gabbroic and ultramafic rocks. Late Cretaceous and Tertiary granitic plutonism, folding and faulting completed the complex structural fabric of the region, characterized by panels of diverse rock types bounded by major northwest and north-trending faults. Bridge River and Cadwallader terranes are cut by a major steeply dipping fault system known as the Cadwallader "break" and interpreted as a crustal transform fault. In the Bralorne area, the strike of this fault changes abruptly from northwest to north forming a bend which is subtended by a splay known as the Fergusson fault. These two faults form the boundaries of a lozenge-shaped domain 5.5 km long and 0.8 km wide which contains all the productive gold-quartz veins of the Bralorne and Pioneer mines. Along the Cadwallader break, rocks of the Bridge River and Cadwallader terranes are intruded by a narrow belt of steeply dipping, partially-serpentinized ultramafic rocks and elongated felsic to basic stocks. The largest of these intrusions, known as the "Bralorne diorite", hosts the most productive veins. Younger intrusions include a large body of sodic granite flanking the diorite on the northeast and Late Cretaceous albitite dikes. To the southwest, the veins end abruptly against the serpentinite marking the Cadwallader break. To the northeast, the veins tend to become narrow, erratic and non-productive as they die out in sodic granite or argillite.

Most veins are between 1 and 2 m thick and are composed of quartz with minor carbonates, sericite, sulfides, scheelite and native gold. The sulfide content of the veins is generally less than 3% and consists mainly of pyrite and arsenopyrite. Sphalerite, chalcopyrite, pyrrhotite, galena, tetrahedrite and stibnite may also occur in trace amounts. Vein formation and gold mineralization was accompanied by widespread and intense carbonatization, silicification and sericitization of host rocks. Wall rock alteration exhibits a well-defined mineralogical zonation (Leitch et al., 1991). In diorite, the outer alteration zone is characterized by the presence of abundant chlorite and epidote. The intermediate zone is characterized by an assemblage of carbonates, albite and sericite. Nearest the veins, wall rocks are replaced almost entirely by

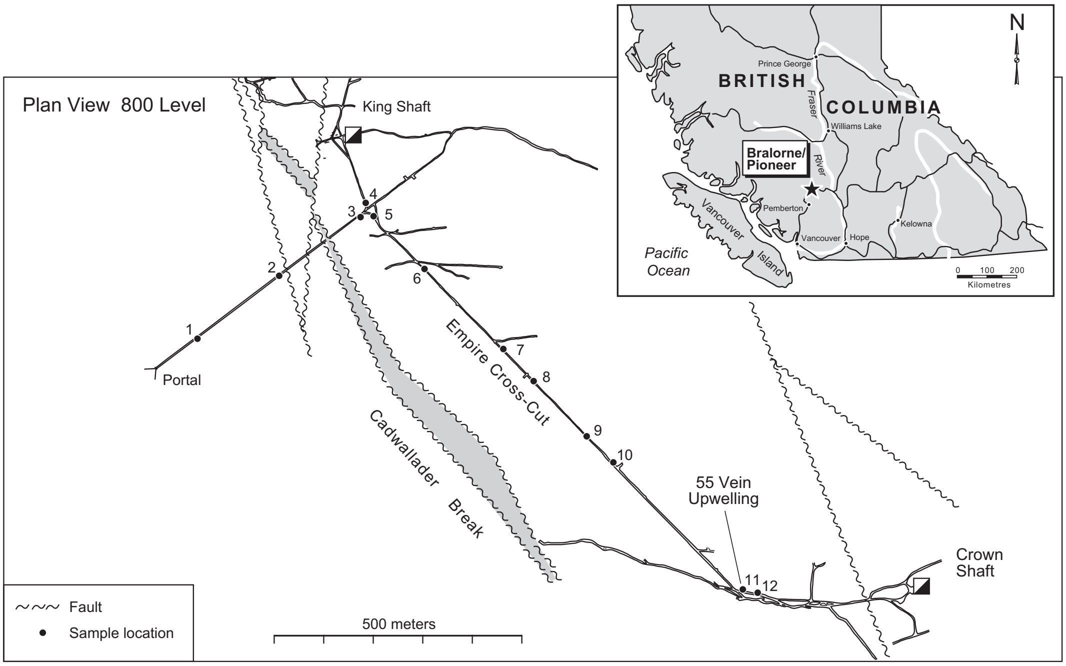

Fig. 1. Plan view of 800-Level showing the monitoring site location at the portal and the numbered sampling locations for the synoptic surveys. The map inset shows the location of the study area.

quartz, sericite and carbonates. The dominant carbonate mineral varies from almost pure calcite in the intermediate zone to mainly ferroan dolomite or ankerite closer to the veins. The sulfide content of the inner zone is generally less than 5 wt% and consists mainly of disseminated pyrite and arsenopyrite.

2.3. Sampling locations

The 30 veins on the amalgamated Bralorne-Pioneer property were developed by over 80 km of tunneling on 44 levels, the lowest of which is at a depth of 1900 m below ground surface. Workings below 800-Level, the lowest adit level, are currently flooded. All drainage from the mine discharges through the 800-Level portal. Most of this drainage originates at the “55 Vein Upwelling” where the flooded lower levels decant to 800-Level through a partially obstructed ore pass. The 800-Level adit also collects drainage from the Upper Crown workings and the Upper King workings (Fig. 1). A temporal analysis of mine drainage was performed by sampling effluent at the portal on a quasi-weekly (every 6–8 days) basis between October 15, 2007 and December 7, 2008, for a total of 60 sampling events. Additional synoptic surveys of water quality were performed on 800-Level by sampling effluent at 12 points between the portal and the “55 Vein Upwelling”, on October 8–9, 2007, June 19 2008, and October 15, 2008 (Parsons et al., 2012). The general layout of 800-Level and locations of the sampling points are shown in Fig. 1.

3. Methods

3.1. Flow measurements

Discharge from the 800-Level portal was measured using an H-type flume (Gwinn and Parsons, 1976; US EPA, 2001) with $D = 0.305$ m (1 ft). Stage (water level) in the flume was measured using an ultrasonic proximity sensor mounted in a stilling well. Discharge (Q) was determined from stage (H) according to:

$$Q = 48.12\,H^{1.5} + 923.775\,H^{2.5}$$

where Q is in L/s and H is in m. The coefficients of the equations depend on flume geometry and on measurement units. They were estimated here by least-squares regression on tabulated stage-discharge relations (Grant and Dawson, 1997).

The flume was sited approximately 10 m beyond the portal, at the edge of an embankment, in order to provide free-flow conditions for discharge. Freeze-up of the flume over the winter months was not a concern because of the warm temperature of the effluent and the relatively high flow rate. In addition to the ultrasonic proximity sensor, electrical conductivity (EC) and water temperature sensors were also deployed at the monitoring site. However, rapid build-up of carbonate scale on these sensors made measurements unusable. The sensors were connected to a data logger recording at 6-h intervals.

3.2. Water chemistry

For each quasi-weekly sampling event, effluent temperature, pH and electrical conductivity were measured in the field, using instruments calibrated daily. A 1-L High-Density Polyethylene (HDPE) bottle, triple-rinsed with sample water, was filled with effluent and transported to a clean indoor location for the preparation of a set of water samples. Each set consisted of three 60 mL HDPE bottles containing unfiltered (total) cations, filtered (dissolved) cations and anions, respectively. Samples for cations were acidified to $\text{pH} < 2$ using ultrapure nitric acid. Samples for dissolved cations and anions were filtered (Sterivex®) to <0.45 μm. Samples were then refrigerated and stored in a dark location pending shipment in batches every four weeks to the Inorganic Geochemical Research Laboratory of the Geological Survey of Canada in Ottawa. Each batch shipment (8 sets of three samples) was supplemented by at least one sample blank, one acid blank, one travel blank and a field duplicate sample.

In the June and October 2008 synoptic surveys on 800-Level, water samples were also collected for analysis of inorganic arsenite [As(III)] and arsenate [As(V)] concentrations. Samples were filtered (Sterivex®) in the field to <0.45 μm and collected in opaque 60 mL HDPE bottles. Within 12 h of sample collection, the As species in each 60 mL sample were stabilized by adding 3 mL of 0.25 M EDTA. Samples were then stored in the dark at 4 °C until analysis at the Inorganic Geochemical Research Laboratory of the Geological Survey of Canada. Details of the water sampling protocols are provided in Desbarats et al. (2010) and in Parsons et al. (2012).

Analyses of major elements were performed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) using a Perkin-Elmer 3000 DV. Analyses of trace elements were performed using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) with a Thermo Corporation X-7 Series II. Determinations of anion concentrations were made with a Dionex DX-600 ion chromatograph using an AS-18 column and gradient elution. Alkalinities were determined using a PC-Titrate System. Samples for As speciation were analyzed by liquid chromatography-ICP-MS using a Dionex AS7 anion exchange column and gradient elution with 2.5–50 mM HNO3 in 2% methanol as the mobile phase to separate As(III) and As(V) (Parsons et al., 2012). For each sample batch, analyses were performed on one or more certified standards of known concentrations. Element suites analyzed by each method and their corresponding detection limits are provided in Desbarats et al. (2010).

During the June 2008 synoptic survey on 800 Level, the concentrations of dissolved ferrous iron (Fe^{+2}) and total dissolved sulfide ($H_2S + HS^-$) were measured to assess the redox conditions controlling mine drainage compositions. Samples were filtered (Sterivex®) in the field to <0.45 μm and collected in opaque 60 mL HDPE bottles to prevent Fe(II) oxidation. Both Fe(II) and total sulfide were measured in the field within 12 h of sample collection using a HACH DR/2400 spectrophotometer. Sulfide was measured at 665 nm wavelength using a methylene blue method (Hach method 8131). Ferrous Fe was measured at 562 nm wavelength using the FerroZine® method (Hach method 8147). The results of these measurements showed that the concentrations of sulfide and Fe(II) were below the instrumental detection limits (~10 μg/L for both analytes) for all samples except at the upwelling point (Parsons et al., 2012).

Charge balances were calculated for all filtered water samples. For the time-study, charge balance errors were less than ±4% for all 60 samples. For the October 2007 synoptic study, 10 of 12 samples had errors than ±3% and all had errors less than 8.5%. The geochemical datasets for all waters analyzed during this study are available in Desbarats et al. (2010) and in Parsons et al. (2012).

3.3. Speciation modeling

Speciation modeling of drainage chemistry and the calculation of mineral saturation indices (SI) were performed using PHREEQC (Parkhurst and Appelo, 1999) with the WATEQ4F thermodynamic database (Ball and Nordstrom, 1991). The database was supplemented with thermodynamic data for As complexes with Ca, Mg, Mn and Fe (Whiting, 1992; Bothe and Brown, 1999b) as compiled by Donahue and Hendry (2003). Solubility products for Ca-arsenate minerals were obtained from Drahota and Filippi (2009), and Bothe and Brown (1999b) as compiled by Donahue and Hendry (2003). Secondary arsenate minerals considered in speciation modeling were scorodite, weilite ($CaHAsO_4$), haidingerite ($Ca(AsO_3OH):H_2O$), pharmacolite ($(CaHAsO_4):2H_2O$), $Ca_3(AsO_4):4H_2O$, $Ca_4(OH)_2(AsO_4)_2:4H_2O$, and $Ca_5(AsO_4)_3OH$. Thermodynamic data were not available for Ca–Fe arsenate minerals or secondary arsenate minerals of the pharmacosiderite group (Drahota and Filippi, 2009).

4. Results

4.1. Time study of portal drainage

4.1.1. Discharge rate and field parameters

Over the period of investigation, the average flow rate at the 800-Level portal was 427 m^3/d (Fig. 2a). During the spring freshet of 2008, the flow rate exceeded 800 m^3/d. During most of the summer and fall months, flow was fairly constant at a rate of about 350 m^3/d. The specific conductance of discharge was also fairly constant over the period of investigation (Fig. 2b). However, some dilution of the discharge was associated with increased shallow groundwater inflow to the workings during winter thaws and the spring freshet. The pH of portal drainage was mildly alkaline with an average value of 8.7 (Fig. 2c). The highest pH values were observed in late winter.

4.1.2. Major dissolved species

Chemographs of major dissolved species (Fig. 3) are consistent with that of specific conductance, and reflect a relatively constant drainage composition over the study period except for some dilution (mainly in Na and sulfate) during the spring freshet. The Na content is derived mainly from the dissolution of albite in the host rocks whereas the sulfate content is derived from the oxidation of pyrite and arsenopyrite. The bicarbonate (alkalinity), Ca and Mg content of the drainage results from the dissolution of abundant carbonate minerals in the wall rocks. The K content (not shown) is mainly derived from sericite. It varies in the same fashion as the othercations and but averages only 0.1 meq/L. The chloride content of the drainage originates exclusively from the upwelling at the 55 Vein stope and reflects deep groundwater inflow to the flooded workings. Calculated saturation indices (SI) indicate that drainage waters are slightly supersaturated with respect to calcite ($1.05 < SI < 1.92$) and ferroan dolomite ($0.76 < SI < 1.89$) which suggests that these minerals are buffering pH. The supersaturation is consistent with the observed build-up of carbonate scale on the EC and temperature sensors deployed at the portal. Calculated saturation indices also indicate that drainage waters are in equilibrium with chalcedony ($-0.03 < SI < 0.09$) and under-saturated with respect to gypsum ($-1.29 < SI < -1.09$). X-ray diffraction analyses

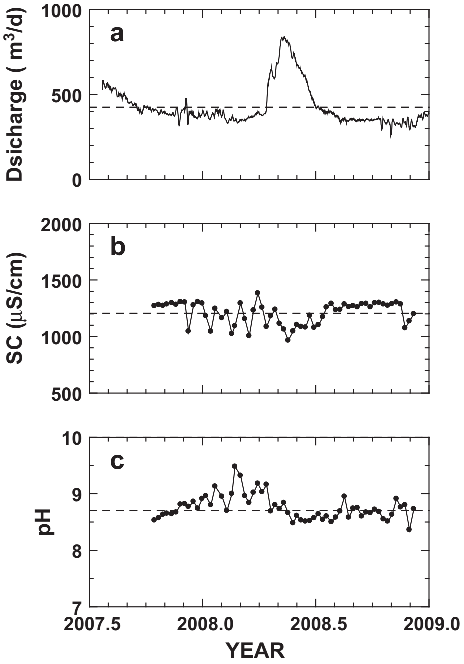

Fig. 2. Portal discharge rate and field parameters: (a) hydrograph of adit flow between July 23 2007 and December 31 2008. Dashed line indicates mean flow rate of 427 m^3/d during this period; (b) chemograph of specific conductance measurements made at the portal during sampling. Dashed line indicates mean values of 1200 μS/cm; (c) chemograph of pH measured at the portal during sampling. Dashed line indicates mean pH of 8.7.

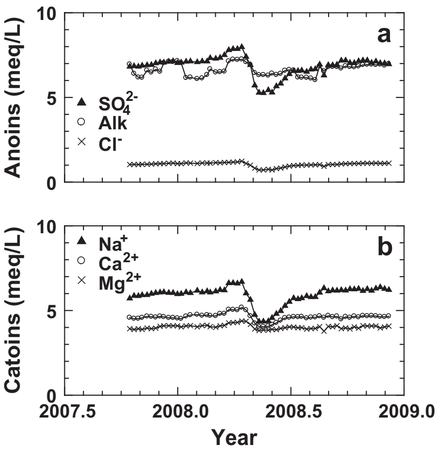

Fig. 3. Chemographs of (a) alkalinity and major anions; and (b) major cations in discharge from the 800-Level portal.

of precipitates in the adit (Parsons et al., 2012; Percival et al., 2009; Percival et al., manuscript in preparation) confirm the presence of calcite, dolomite and quartz.

4.1.3. Metals and metalloids

Total (unfiltered) concentrations of selected trace metals and metalloids in portal drainage are summarized in Fig. 4. Filtered (<0.45 μm) concentrations represent most of the totals for all species with the exception of Al and Fe. Arsenic, Fe, Mn and Al dominate the trace element chemistry of mine waters. Speciation modeling indicates that drainage waters are under-saturated with respect to gibbsite ($-1.5 < SI < -0.5$); in equilibrium ($-0.12 < SI < 0.30$) with rhodochrosite; and over-saturated ($1.7 < SI < 2.5$) with respect to amorphous ferric hydroxide ($Fe(OH)_3$). Drainage waters are strongly under-saturated with respect to scorodite ($-9.5 < SI < -6.3$) at the ambient mildly alkaline pH. They are also under-saturated with respect to all the Ca-arsenate phases considered. The least under-saturated Ca-arsenate was haidingerite ($-3.9 < SI < -3.3$).

Chemographs of As and Fe (Fig. 5) show that filtered (dissolved) concentrations are stable in portal drainage whereas total values vary erratically. Higher total concentrations of both species are associated with higher discharge rates and greater transport of fine suspended particulates within the 800-Level workings. Particulate concentrations are defined here as the difference between unfiltered (total) and filtered (dissolved) concentrations.

Chemographs of As and Fe loadings in portal drainage (Fig. 6) shows that most (76%) of the As is transported in the dissolved phase whereas most (98%) of the Fe is transported in the suspended particulate phase. Average total loadings of As and Fe during the study period are 1.34 kg/d and 0.903 kg/d, respectively.

4.2. Synoptic surveys

Synoptic surveys of water quality were performed on 800-Level by sampling drainage at 12 points (Fig. 1) between the portal and the "55 Vein Upwelling", on October 8–9, 2007, June 19 2008, and October 15, 2008 (Parsons et al., 2012). Drainage from the 800-Level portal originates from three sources, the Upper King Workings (UKW), the Upper Crown Workings (UCW) and the 55 Vein Upwelling. Knowing the portal discharge rate, it is possible to determine the flow contribution from each of these sources using a mass balance approach with chloride as a conservative tracer. During the October 2008 survey, contributions from UKW, UCW and the 55 Vein Upwelling represented 27%, 7% and 66% of portal discharge, respectively. Similar proportions were observed for the October 2007 survey. For the June 2008 survey, the corresponding proportions were 43%, 5% and 52%, respectively, reflecting greater inflows of shallow groundwater to the UKW during freshet conditions while flows from the 55 Vein Upwelling remained relatively constant. Geochemical profiles along the 800-Level adit were similar for the three synoptic surveys and only results from October 2008 are shown here unless otherwise indicated.

4.2.1. Field parameters

Mine waters at the upwelling point are circum-neutral (pH = 7.6), sub-oxic (DO = 0.3 mg/L) and quite warm (20 °C). However, as a result of CO_2 degassing, pH increases steadily downstream, reaching a value of 9 at the portal (Fig. 7). Dissolved oxygen levels increase concomitantly through aeration, reaching 10 mg/L at the portal. Temperature, meanwhile, decreases to 10 °C.

4.2.2. Major dissolved species

All major dissolved species exhibit conservative behavior between the upwelling point and the portal. Concentration profiles (not shown) are flat in between step drops marking the inflow of relatively dilute drainage from the UKW and the UCW.

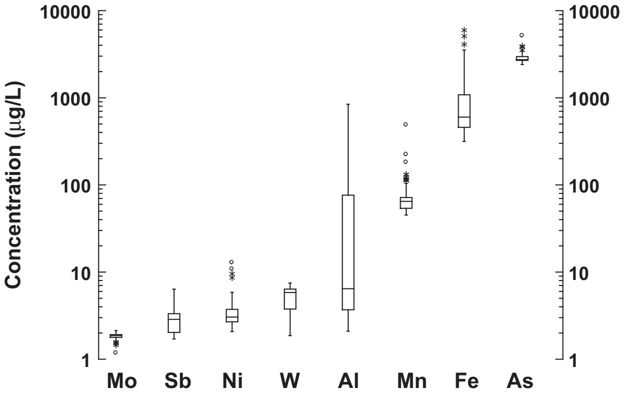

Fig. 4. Geochemical signature of drainage from the 800-Level portal: Box plots of total (unfiltered) concentrations for selected minor and trace metals and metal(loid)s. Two high outlier values of Fe (10,963 and 26,694 μg/L) were omitted for presentation purposes.

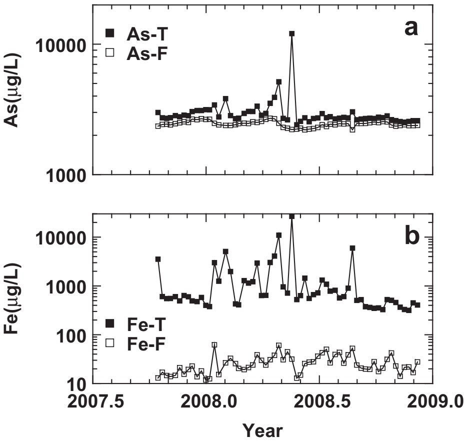

Fig. 5. Chemographs of total (*T*) and filtered (*F*) concentrations for (a) As and (b) Fe in portal discharge.

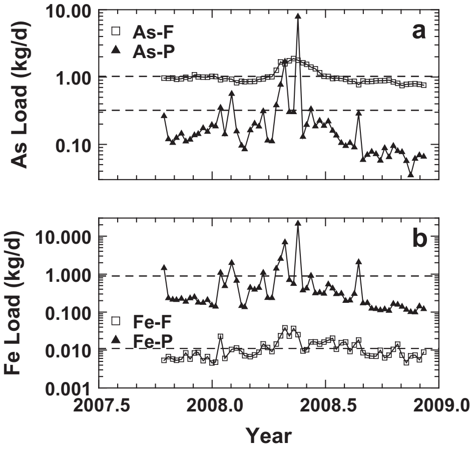

Fig. 6. Chemographs of filtered (*F*) and particulate (*P*) loads for (a) As and (b) Fe in portal discharge. Dashed lines indicated mean loads. Mean loads of filtered and particulate As are 1.02 and 0.32 kg/d, respectively. Mean loads of filtered and particulate Fe are 0.01 and 0.89 kg/d, respectively.

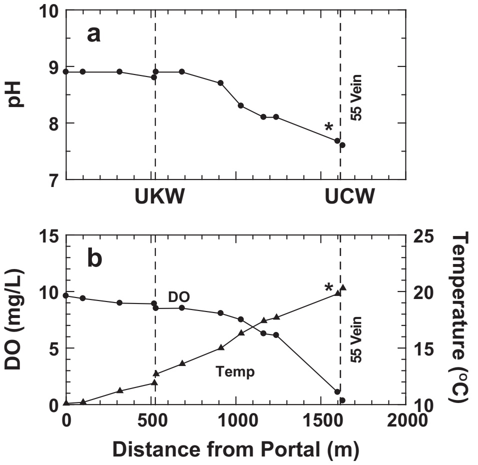

Fig. 7. Profiles of field parameters from the synoptic survey of 800-Level drainage on October 15, 2008: (a) pH; (b) dissolved oxygen and temperature. Dashed vertical lines indicate location of confluence between main drainage channel and tributaries from the Upper King Workings (UKW) and Upper Crown Workings (UCW). All parameter values at location marked by an asterisk (*) were calculated assuming conservative mixing between 55 Vein waters and drainage from the UCW.

4.2.3. Metals and metalloids

From a maximum of 3.35 mg/L at the upwelling point, total Fe concentrations decline to 0.37 mg/L at the portal (Fig. 8a). Dissolved Fe drops from 3.27 mg/L to less than 0.1 mg/L only 300 m downstream, reflecting the precipitation of hydrous ferric oxides (HFO) as DO and pH increase. Total As concentration at the upwelling point was 6.23 mg/L, virtually all in the dissolved phase and predominantly as As(III) (Fig. 8b). Total and dissolved As concentrations decrease downstream through sorption on, or co-precipitation with, HFO and through dilution with drainage from the UCW and the UKW. Through oxidation to As(V) and sorption to HFO, concentrations of As(III) decrease steadily along the flow path, becoming negligible 800 m downstream of the upwelling point.

The fate of transported Fe and As along the drainage flow path from the upwelling point is more clearly revealed by profiles of loadings (Fig. 9). Maximum total loads of Fe (0.75 kg/d) and As (1.38 kg/d) are observed at the confluence of upwelling mine waters and drainage from the UCW. Corresponding loads for total Fe and As at the portal (on the day of the survey) are 0.12 kg/d and 0.9 kg/d, respectively. These results suggest that Fe and As are accumulating in the 800-Level workings at rates of 0.63 kg/d and 0.48 kg/d, respectively.

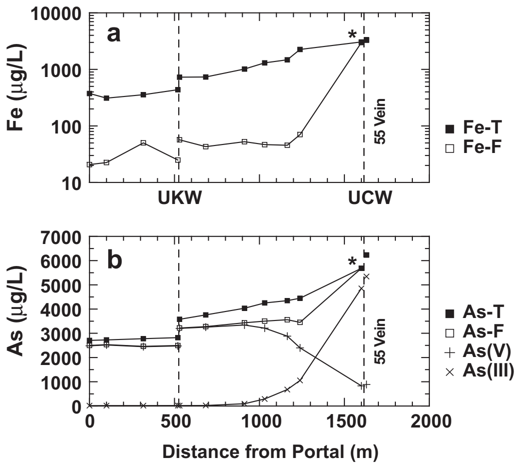

Fig. 8. Profiles of Fe and As concentrations from synoptic survey of 800-Level drainage on October 15, 2008: (a) total (*T*) and filtered (*F*) concentrations of Fe; (b) total (*T*) As, filtered (*F*) As and dissolved As species. Dashed vertical lines indicate location of confluence between main drainage channel and tributaries from the Upper King Workings (UKW) and Upper Crown Workings (UCW). All parameter values at location marked by an asterisk (*) were calculated assuming conservative mixing between 55 Vein waters and drainage from the UCW.

5. Analysis and discussion

5.1. Arsenic source

Analyses performed on surface stockpiles of waste rock and low-grade ore provide an indication of the *in-situ* abundance of arsenopyrite and pyrite (Table 1). Total sulfide concentrations are generally quite low and are usually less than 1 wt%. Arsenopyrite, with a median concentration of 0.48 wt%, is the dominant sulfide mineral although pyrite, with a median concentration of

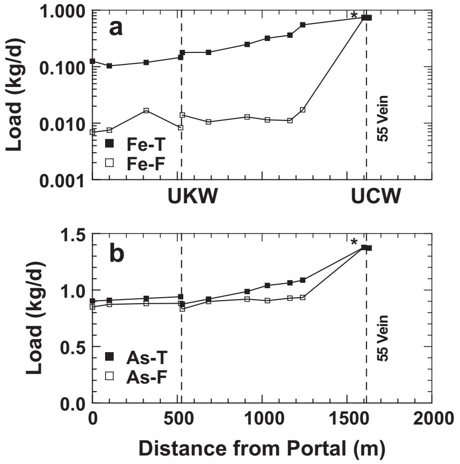

Fig. 9. Profiles of Fe and As loadings from synoptic survey of 800-Level drainage on October 15, 2008: (a) total (*T*) and filtered (*F*) loads of Fe; (b) total (*T*) and filtered (*F*) loads of As. Dashed vertical lines indicate location of confluence between main drainage channel and tributaries from the Upper King Workings (UKW) and Upper Crown Workings (UCW). All parameter values at location marked by an asterisk (*) were calculated assuming conservative mixing between 55 Vein waters and drainage from the UCW.

0.12 wt% may be equally abundant in waste rock. The corresponding median As content of the stockpiled material is 0.22 wt%. Considering only Fe from sulfides, the average As:Fe molar ratio in vein and wall rocks is approximately 0.75.

During mining operations (1932–1971), an initial mobilization of As occurred with the oxidation and dissolution of exposed arsenopyrite. Most of this As accumulated locally in the workings, co-precipitated or sorbed on HFO. However, with the subsequent flooding of the mine below 800-Level and the development of anoxic conditions, reduction of this HFO remobilized the As at depth (Strand, 2007). The average ($n = 3$) of total As concentrations measured at the 55 Vein Upwelling was 5898 μg/L. In the flooded Crown shaft, the average ($n = 6$) concentration was 6255 μg/L (Parsons et al., 2012). The Crown shaft and the 55 Vein stope (Fig. 1) are known to be hydraulically connected at depth and this is reflected in the overall similarity of their water chemistry (Parsons et al., 2012).

5.2. Arsenic attenuation and accumulation in mine workings

Mine water from the flooded workings decants to the 800-Level adit at the 55 Vein Upwelling whereupon it flows over 1600 m to the portal (Fig. 1). Along this path, dissolution of atmospheric O_2 and degassing of CO_2 alter the Eh and pH of the drainage (Fig. 7). In the sub-oxic and circum-neutral water at the upwelling, 86% of dissolved As occurs as As(III) whereas Fe(II) represents essentially all of the dissolved Fe (Fig. 8). Within 500 m of the discharge point, As(III) and dissolved Fe concentrations drop sharply while As(V) concentrations increase (Fig. 8). This reflects concomitant processes involving rapid precipitation of Fe oxyhydroxides with sorption or co-precipitation of As, as well as gradual oxidation of dissolved As(III) to As(V). The warm (20 °C) temperature of upwelling waters may enhance As and Fe oxidation rates as well as sorption of As on HFO. X-ray absorption near-edge structure (XANES) spectroscopy analyses from 800-Level (Percival et al., 2009; manuscript in preparation) indicate that the proportion of As(III) in precipitates downstream of the upwelling varies between 10 and 35 wt%, as pH climbs from 7.7 to 8.1. According to Raven et al. (1998) and Dixit and Hering (2003), As(III) sorbs to HFO and goethite as much or more than As(V) in this pH range.

Table 1
Sulfide chemistry of historical waste rock and low-grade ore stockpiles (data derived from Appendix E of Lorax, 2008). The 10 samples with the T3 prefix represent low-grade ore (80,000 tonnes). The remaining 11 samples represent waste material (100,000 tonnes).

Sample ID	Pyrite (moles/tonne)	Pyrite (wt%)	Arsenopyrite (moles/tonne)	Arsenopyrite (wt%)
T1-1	2.8	0.03	25.4	0.41
T1-2	68.0	0.82	81.0	1.32
T1-3	24.9	0.30	46.8	0.76
T1-4	6.6	0.08	24.9	0.41
T1-5	1.2	0.02	22.4	0.36
T1–C1	16.5	0.20	35.7	0.58
T1–C2	17.6	0.21	30.6	0.50
T3-1	0.0	0.00	38.6	0.63
T3-2	0.0	0.00	28.3	0.46
T3-3	0.0	0.00	28.5	0.46
T3-4	0.0	0.00	32.9	0.53
T3-5	0.0	0.00	36.0	0.59
T3-6	11.9	0.14	29.2	0.48
T3-7	16.5	0.20	26.0	0.42
T3-8	9.7	0.11	33.9	0.55
T3–C	2.0	0.02	33.6	0.55
T3–C2	5.1	0.06	27.5	0.45
WR-BGM-1	46.0	0.55	29.4	0.48
WR-BGM-2	38.3	0.46	20.4	0.33
WR-BGM-3	38.9	0.41	19.7	0.32
WR-BGM-4	52.3	0.63	9.4	0.15
Median	9.7	0.12	29.2	0.48

With increasing distance from the discharge point, as pH values approach 9 (Fig. 7), concentrations of dissolved As(III) are reduced to below detection limits while As(V) concentrations and loads stabilize (Figs. 8b and 9b). Indeed, along the last 500 m of the 800-Level flow path, between the UKW and the portal, filtered and total As concentrations behave conservatively. This is consistent with results from the literature indicating reduced sorption of As(V) at higher pH (Raven et al., 1998; Dixit and Hering, 2003). Competition for sorption sites by bicarbonate may be another factor limiting the sorption of As in adit drainage (Stollenwerk, 2002; Radu et al., 2005; Stachowicz et al., 2007; Saalfield and Bostick, 2010).

The results of the October 2008 synoptic survey indicate that Fe and As are accumulating in the 800-Level workings at rates of 0.63 kg/d and 0.48 kg/d, respectively. Analyses of Fe and As in sediments from the drainage channel (Table 2) show a decreasing trend in concentrations with distance from the discharge point. This is consistent with initial rapid precipitation of HFO and a more gradual settling of suspended HFO particulates along with their load of As (Fig. 9). Median concentrations of Fe and As in accumulated sediment amount to 3350 and 1137 mol/tonne, or 18.7 wt% and 8.5 wt%, respectively. The latter concentration represents a significant As enrichment compared to stockpiled waste rock and low-grade ore. The median As:Fe molar ratio in the sediment is approximately 0.3. Paktunc et al. (2003) used this ratio to discriminate between As sorbed on HFO, As co-precipitated with HFO, and secondary arsenate phases. A value of 0.3 falls within the range expected for As co-precipitated with HFO.

The possibility of As sequestration by precipitation of secondary Ca-arsenate phases was investigated by speciation modeling. Calculated saturation indices for haidingerite ($Ca(AsO_3OH):H_2O$) and pharmacolite ($Ca(HAsO_4):2H_2O$) at the 55 Vein Upwelling are −2.94 and −3.06, respectively. Saturation indices for other Ca-arsenates indicate even greater degrees of under-saturation. Sequestration of As by Ca-arsenates appears unlikely here. Bothe and Brown (1999a) found that significant immobilization of As by Ca-arsenates occurred only if pH > 11.

5.3. Arsenic sorption in portal discharge

While synoptic survey results (Fig. 9) indicate that approximately 35% of the original As load in mine waters remains sequestered within the workings, time study results indicate that a significant average load of 1.34 kg/d is discharged through the portal, nonetheless. Most of this load occurs in dissolved form (Fig. 6)

Table 2
Fe and As content of sediment samples from the 800-Level drift (data from Appendix B of Parsons et al., 2012).

Sample	Distance from 55 Vein Upwelling (m)	Fe (moles/tonne)	As (moles/tonne)	As:Fe Molar ratio
SS-43[a]	1530	1119	>113.5	>0.12
SS-39	1110	1379	233.6	0.17
SS-50	1100	2152	156.2	0.07
SS-41	946	2401	658.0	0.27
SS-44	718	4299	1616.3	0.37
SS-45	466	4415	1828.6	0.41
SS-42[a]	391	2088	>133.5	>0.06
SS-51	0	5200	1731.1	0.33
Median		3350	1137.2	0.30

[a] Insufficient sample material for As reanalysis. Datum excluded from median calculations.

as arsenate (Fig. 8). The partitioning of As between dissolved and particulate phases is investigated here in more detail.

Laboratory studies of As(III) and As(V) sorption on Fe oxyhydroxides (Pierce and Moore, 1982; Raven et al., 1998; Swedlund and Webster, 1999; Dixit and Hering, 2003) suggest that total Fe and As concentrations in solution, as well as pH, are important controlling factors. Observations at the portal show that pH is relatively constant, with a mean of 8.7 (Fig. 2). Concentrations of dissolved (filtered) As are also fairly stable (Fig. 5a). Total (unfiltered) concentrations of As and Fe, on the other hand, exhibit significant temporal variability (Fig. 5a and b). Indeed, the As:Fe molar ratio of total concentrations in portal discharge varies between 0.34 and 6.23 with a median of 3.42. Such ratios are considerably higher than those used in most laboratory investigations as summarized by Dixit and Hering (2003) although Pierce and Moore (1982) considered As:Fe ratios as high as 13. A plot of sorbed (total–filtered) As fraction versus sorbent (suspended particulate) Fe concentration reveals a well-defined trend (Fig. 10a). However, it is seen that high sorbed fractions are achieved only for lower As:Fe molar ratios (smaller plot symbols). For high molar As:Fe ratios, sorbed As fractions are below 20%. The relationship between sorbed As fraction and pH (Fig. 10b) is less clear. For lower As:Fe ratios (smaller symbols), higher sorbed fractions are associated with decreasing pH. However, for high As:Fe ratios, pH does not appear to affect the sorbed fraction.

In portal discharge waters, the As:Fe molar ratio of suspended particulate (total–filtered) concentrations varies between 0.10 and 0.99 with a median of 0.37. This latter value is close to the median molar ratio found in drainage sediments (Table 2). These sorption densities are much higher than maximum values observed in laboratory studies at similar pH (circa 8.7) but with lower total As:Fe ratios. Maximum sorption densities in the range of 0.14–0.17 are reported by Pierce and Moore (1982), Fuller et al. (1993) and Raven et al. (1998) for low total As:Fe molar ratios. However, for higher ratios, Pierce and Moore (1982) report sorption densities as high as 4. According to Dixit and Hering (2003), these latter results are inconsistent with sorption processes which are inherently limited by the availability of surface sites. Fuller et al. (1993), on the other hand, reported sorption densities as high as 0.7 in co-precipitation experiments. Based on the criteria of Paktunc et al. (2003) mentioned above, the observed sorption densities suggest that suspended particulates may consist of HFO with both sorbed and co-precipitated As.

There is a clear inverse relationship between As sorption density (expressed in m-mol/g Fe) and particulate Fe concentration (Fig. 10c). This relationship suggests that increasing sorbent concentrations (decreasing As:Fe ratios) are less efficient at scavenging As. Higher particulate Fe concentrations are usually associated with higher flows able to re-suspend larger particulates. Larger particle sizes with lower specific surface areas may explain the reduced As sorption capacity (Smith, 1999). Low sorbent concentrations, on the other hand, may be associated with smaller particulate sizes and exhibit much higher sorption densities.

The partitioning of As between sorbed and dissolved phases in portal discharge is illustrated in Fig. 10d, albeit for the narrow range of dissolved As concentrations and pH values observed here. No clear trend is apparent in this plot although Pierce and Moore (1982) reported a linear isotherm in this range of dissolved As concentrations. The plot does suggest, however, that more As is sorbed per gram of Fe at higher molar ratios of total As to Fe. The results of Fig. 10d can be used to estimate a field-based distribution coefficient (K_d) of 206 L/g Fe. Assuming a molecular weight of 88.8 g/mol for HFO, this value can also be expressed as 130 L/g for sorption of As(V) on HFO. This K_d corresponds to a median total As:Fe molar ratio of 3.42, a median dissolved As(V) concentration of 33 µmol/L and a median pH of 8.7. For comparable experimental conditions, Pierce and Moore (1982) reported a K_d for As(V) of 79 g/L in their Table 3. Experimental K_d values for As(V) at pH 7 compiled by Smedley and Kinniburgh (2002) vary between 8.1 and more than 1000 L/g HFO. The field results presented here appear more consistent with the laboratory results of Pierce and Moore (1982) and Raven et al. (1998) obtained for high (>0.6) total As:Fe molar ratios.

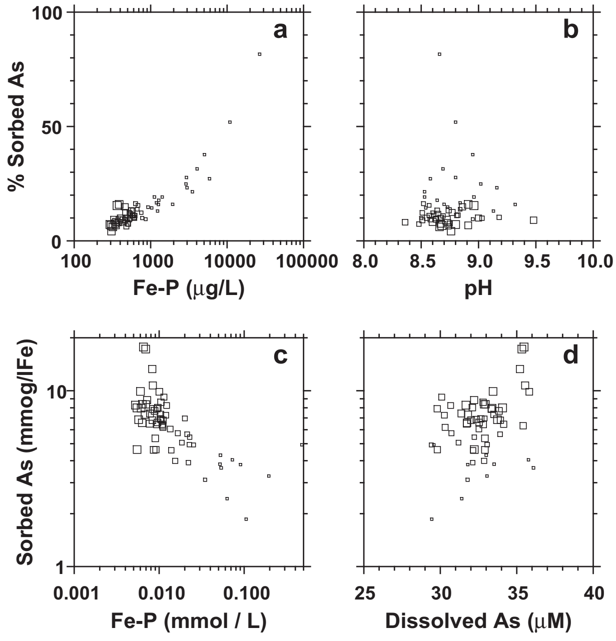

Fig. 10. Sorption of As on suspended Fe oxyhydroxides in portal discharge waters: (a) percentage of sorbed As versus particulate Fe; (b) percentage of sorbed As versus pH; (c) sorption density of As versus suspended particulate Fe; (d) sorption density of As versus dissolved As concentration in portal discharge waters. Symbol size is proportional to the molar ratio of total As to total Fe in the sample.

6. Summary and conclusions

The veins and wallrock of the Bralorne mine contain abundant carbonate minerals and relatively little sulfides, as is typical of orogenic lode gold deposits. Based on samples from stockpiled waste rock and low-grade ore, the in-situ total concentration of sulfide minerals is usually less than 1 wt%. The dominant sulfide minerals are arsenopyrite and pyrite. The median As content of host rocks is estimated at 0.22 wt%. Mobilization of this As in mine drainage is the main environmental concern associated with the deposit.

Most of the mine effluent originates 1600 m from the portal, at a point where flooded workings decant to the adit level. The upwelling water is sub-oxic, with circumneutral pH, an average dissolved Fe concentration of 3340 µg/L, and an average As concentration of 5898 µg/L mainly as As(III). The high As concentrations result from remobilization of sorbed As when accumulated HFO in the extensive workings underwent reductive dissolution as the mine flooded. As the upwelling water flows toward the portal, DO rises to 10 mg/L through aeration while pH rises to 9.0 through CO_2 degassing. Dissolved Fe is oxidized fairly rapidly whereas the oxidation of dissolved As proceeds more gradually. Near the upwelling point, both As(III) and As(V) sorb or co-precipitate with HFO. Further from the upwelling point, As(III) concentrations become negligible and sorption of remaining As(V) becomes less effective as pH increases and as the amount of available sorbent decreases through settling of particulate HFO. Nonetheless, approximately 35% of the original As load in mine drainage is sequestered in precipitates within the workings. The average As concentration of sediments in the adit is 8.5 wt% which represents a significant enrichment compared to the As concentration of host rocks.

An average of 1.34 kg/d of As is discharged from the adit portal at mean total and dissolved (filtered) concentrations of 3034 μg/L and 2444 μg/L, respectively. Partitioning of As in mine effluent between dissolved and particulate phases is characterized by an apparent sorption density of 0.37 mol As $(\text{mol Fe})^{-1}$ and by a field-based distribution coefficient (K_d) of 130 L/g HFO for a median pH of 8.7 and a median total As:Fe molar ratio of 3.42. A comparison of these results with those of controlled laboratory studies suggests that the strong partitioning of As to the solid phase may reflect a combination of adsorption and co-precipitation processes. Despite this partitioning of As to the solid phase, dissolved As concentrations in portal effluent are high, reflecting the Fe-limited nature of the drainage and its alkaline pH. Both these features are consequences of ore deposit mineralogy: an abundance of carbonates buffers mine drainage in a pH range unfavorable for the sorption of As(V) while a paucity of pyrite limits the amount of HFO sorbent available. Results of this study suggest that the As self-mitigating capacity of drainage from orogenic lode gold deposits may be poor in Fe-limited settings. Here, however, the situation may be exacerbated by the fact that As is being mobilized not only by the oxidation and dissolution of primary arsenopyrite but also by the release of a more concentrated source of sorbed As from the reductive dissolution of Fe oxyhydroxides that accumulated during mining operations in now flooded and anoxic workings.

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