Identification of acid rock drainage sources through mesotextural classification at abandoned mines of Croydon, Australia: Implications for the rehabilitation of waste rock repositories

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Abstract

Developing effective strategies to manage acid rock drainage (ARD) from historic and abandoned mine sites is a significant rehabilitation challenge. In Australia, there are more than 50,000 recorded abandoned mine sites, many of which have associated ARD and water quality issues. Traditional rehabilitation strategies focus on utilising a blanket approach to management. However, if sources of ARD were instead thoroughly characterised, cost-effective management strategies based on mineralogy could be formulated, potentially enhancing site rehabilitation and ensuring longer-term success.

A mesotextural method was developed to domain waste rocks into groups based on their mineralogical, textural and chemical similarities, using routine geological tools and field-based analytical instrumentation. This was tested at the abandoned mining operations at Croydon, North Queensland, from which uncapped sulphidic waste rock piles were sampled. Surface water and sediment samples collected from creeks up to 10 km downstream of the site showed elevated concentrations of As, Cd, Cu, Ni, Pb, S and Zn relative to local background levels, indicating the necessity for effective rehabilitation strategies to be implemented at these sites. Ten mesotextural waste rock groups (A to J) were identified in the piles across both mine sites and comprise of hydrothermally altered rhyolites, and massive sulphides. Three major sulphide-bearing groups were identified (G, H and J). Mineralogical and geochemical data indicated that group J (quartz–pyrite) was acid forming, with pyrite containing significant concentrations of As, Pb, Zn and Cu. Pyrite was in early weathering stages with some hydrous ferric oxides observed on grain rims and fractures. Group H (arsenopyrite–quartz–pyrite) was also acid forming; with scorodite extensively precipitated in fractures and rims, likely retarding arsenopyrite oxidation. Significant quantities of Zn and Cd were leached from Group G (quartz– sphalerite–galena) in first flush experiments, and were also measured downstream of the Glencoe site (at which the majority of group G material was identified). Microtextural analyses showed galena had partial weathering to anglesite, suggesting a potential Pb source. High concentrations of Fe and Cd (8.5 wt.% and 0.19 wt.% respectively) were measured in sphalerite, which likely encouraged oxidation, and subsequent release of Zn. Considering the diversity of the sulphide mineralogy and the associated weathering pathways, a rehabilitation strategy which focuses on segregating waste on the basis of mesotextural classification should be considered.

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1. Introduction

Effective management of acid rock drainage (ARD) is a significant rehabilitation challenge for abandoned mine sites. At these sites, the exposure of sulphides to water, air and microorganisms, leads to oxidation and ARD generation (Egiebor and Oni, 2007; Evangelou and Zhang, 1995). Under these acidic conditions, liberation of dissolved components including heavy metals (e.g., Cd, Co, Cu, Hg, Ni, Pb and Zn) and metalloids (e.g., As, Sb) is promoted (Ashley et al., 2004; Plumlee, 1999). Once metals enter streams, complex pH and redox dependant processes (including transformation, speciation and complexation) influence the transport and fate of metals and determine their concentrations in both surface and subsurface environments (Caruso and Bishop, 2009). Subsequently, aquatic and terrestrial ecosystems downstream of mine works are at risk of significant environmental degradation (David, 2003; Gray, 1997; Hudson-Edwards and Edwards, 2005; Luís et al., 2009).

In Australia, there are over 50,000 registered abandoned mines which range from isolated minor surface works, to large and complex sites (Franco et al., 2010; Unger et al., 2012). Features of these sites can include waste rock piles, tailings storage facilities, mineral...
processing wastes, and remains of mining infrastructure. Abandoned waste rock piles are significant sources of ARD (cf. Ashley et al., 2004; Aykol et al., 2003; Harris et al., 2003; Lottermoser et al., 2005; Marescotti et al., 2007; Mudd, 2005; Smuda et al., 2007; Tarras-Wahlberg and Nguyen, 2008). Current mining practices dictate that waste rock piles are engineered based on geochemical classifications, with waste rock classes or types defined by acid forming/neutralising characteristics (e.g., Andrina et al., 2006; Brown et al., 2009; Hutchison and Brett, 2006; Smith et al., 2009, Tran et al., 2003). However, at abandoned mine sites, waste rock piles were not constructed in this manner (Ashley et al., 2004; Harris et al., 2003; Hudson-Edwards and Edwards, 2005; Lottermoser et al., 1999), with costs of remediating associated ARD estimated at AUD$100,000 or more per hectare (Harries, 1997). Current rehabilitation strategies are responsive in their nature (i.e., only implemented if acid rock drainage occurs). Consequently, a “blanket approach” to management is adopted whereby techniques such as lime dosing and waste rock capping are implemented, but have mixed success (e.g., Edraki et al., 2009, 2012; Gasparon et al., 2007; Gore et al., 2007; Mudd and Patterson, 2010). Alternatively, undertaking detailed and effective predictive characterisation on an individual site basis may allow for the breakeup of source–pathway–receptor chains (Vik et al., 2001), and improve rehabilitation long-term.

The objective of this study was to develop a systematic approach to characterising waste rock pile materials and identifying ARD sources at abandoned mine sites. Therefore, a mesotextural classification method based on mineralogical and textural differences observed in hand specimens samples to define waste rock groups is proposed. The method was tested at the abandoned Croydon gold mines, north Queensland, Australia, from which ARD (pH < 4) is emanating as measured through a local geochemical study of sediments and surface waters. Following mesotextural grouping, samples were subjected to ARD predictive tests according to the geochemistry–mineralogy-texture (GMT) approach proposed in Parbhakar-Fox et al. (2011). This contribution demonstrates that through adopting a systematic mesotextural classification scheme, ARD sources are readily identified and can be prioritised for remediation as part of an effective long-term rehabilitation plan.

2. Croydon mining area

2.1. Mining history

The Croydon gold mining district is located approximately 15 km northeast of the Croydon Township and 400 km northeast of Mt. Isa, north Queensland (Fig. 1). Small-scale historic mining of reef gold was undertaken in the 1880 to 1890s, and modern open pit mines targeted 2.84 Mt of ore (3.4 g/t Au) from 1981 to 1991 at two main sites: Federation/La Perouse and Glencoe (Van Eck and Child, 1990). The mine workings and waste rock piles have remained undisturbed since 1991. Currently, the Department of Natural Resources and Mines is undertaking management of this site, with estimated rehabilitation liabilities of AUD $1.8 million for the waste rock piles alone (DME, 2008).

2.2. Physiography and climate

The region has a tropical savannah type climate with an average annual rainfall of 750 mm, much of which falls between December to March. The average annual temperature is 33.8 °C, with maximum temperatures experienced during November to January (Fig. S1; Bureau of Meteorology, 2013). Tabletop Creek and Deadhorse Creek drain the Federation/La Perouse and Glencoe sites respectively (Fig. 1). Deadhorse Creek is a tributary of Tabletop Creek, with the confluence approximately 10 km from the mining operations. Tabletop Creek is in turn a tributary of the Carron River, which flows into the Gulf of Carpentaria. Much of the Croydon district is used for grazing, including the immediate mine area (DME, 2008).

2.3. Geology and mineralisation

The geology of the Croydon district is dominated by the Mesoproterozoic rhylitic Croydon Volcanic Group (CVG) and Esmerelda Supersuite (Fig. 1). The Croydon lode gold deposits are hosted by the CVG, which is overlain by the Gilbert River Formation. The lodes consist of major quartz, potassium feldspar, muscovite, plagioclase, minor illite, kaolinite, sulphides (pyrite, arsenopyrite, sphalerite, galena), and traces of pyrrhotite and chalcopyrite (Van Eck and Child, 1990).

The CVG has been subjected to varying degrees of hydrothermal alteration, with evidence of silicification, kaolinisation and sericitisation observed in wall rock adjacent to the quartz veins (Van Eck and Child, 1990). In terms of acid forming potential, the host rocks to mineralisation have little potential for buffering acid produced from sulphide oxidation, as carbonates are notably absent. Effective silicate neutralising minerals (e.g., biotite, chlorite and serpentinite) as defined by Bowell et al. (2000) and Jambor et al. (2002) are also absent.

2.4. Site description

The Federation/La Perouse site consists of two pits (Federation: 320 m × 160 m × 35 m; and La Perouse: 270 m × 180 m × 40 m), two waste rock piles (Federation/La Perouse pile: 1.5 million m$^3$ and 35,000 m$^3$), one stockpile (25,000 m$^3$), heap leach pads (55,000 m$^3$), a catch dam (170 m × 65 m), a seepage collection pond (100 m × 30 m) and relict mining infrastructure including a crusher platform. The waste rock piles comprise materials ranging from boulder (>0.5 m diameter) through to coarse sand crushings (0.2–1 cm) and abundant fines (<0.2 cm). The entire waste rock piles comprise approximately 70% flow-banded rhyolite, 20% red-stained rhyolites and tuffs, and 10% quartz–sulphide vein material (DME, 2008). Most of this material displays...
dark to medium brownish-red Fe-staining, with metallic bluish black Mn-stains also observed.

Federation pit captures runoff and seepage from the main Federation/La Perouse waste rock pile. A catch dam was constructed below Federation pit for the purpose of containing seasonal overflow from the pit lake. A seepage pond was constructed below this to contain and pump back seepage to the catch dam. However, during the wet season, water overflows from the catch dam and seepage pond into Tabletop Creek. Consequently, the catch dam is acidic with an average pH of 2.9 (DME, 2008). There is also seepage from the waste rock pile directly into Federation and Tabletop Creeks during the wet season. Operations were smaller at Glencoe with one open pit (330 m × 60 m × 25 m) and a waste rock pile (483,000 m³). Seepage from this waste rock pile enters Deadhorse Creek. Field observations indicate that galena and sphalerite dominate the sulphide mineralogy of this pile.

Acid rock drainage has been established immediately downstream (<2 km) of the mine workings, with elevated concentrations of Cd (max. ~80 μg/L) and Zn (max. ~8000 μg/L) relative to the local baseline measured within 10 km of the operations. Remedial works were undertaken in November 2007 to improve the water quality in Federation pit, through addition of 140,000 t of lime (CaO) to raise pH. Lime was also sprayed on the pit walls and deposited on the surface of the Federation/La Perouse waste rock pile. Whilst initially pH values rose (pH 11 to 12), within two months pH values had declined to pH 3 to 4 (DME, 2008). Further remediation works (2009 to 2011) were conducted to reduce the volume of contaminated seepage waters entering Tabletop Creek, with the construction of the seepage pond described. Although these works have reduced the volumes of seepage entering Tabletop Creek, seepage water quality has not improved. Therefore, additional rehabilitation efforts are required and should instead focus on the identification and management of ARD sources rather than the treatment of ARD waters.

3. Materials and methods

3.1. Sampling and sample preparation

Field work was conducted in May 2008. Hand-specimen sized (c. 2 kg) waste rock samples (n = 53) were selected to provide a range of lithologies from four different locations across the waste rock piles. Samples were sawn, with one piece kept for textural studies, and the other jaw crushed to <5 cm (University of Tasmania (UTAS), Hobart, Australia). A split was taken, and the remaining material ground in a ring mill to <125 μm for mineralogical and geochemical characterisation.

Surface water samples (n = 29) were collected directly from Tabletop and Deadhorse Creeks, and at their confluence (Fig. 2). These samples were collected around the district to allow for comparison of water quality upstream and downstream of the mine operations. Only duplicate samples were obtained due to the limited amount of surface water available at most locations. Additionally, samples were obtained from the surfaces of Federation (35 m depth), La Perouse (40 m depth) and Glencoe (25 m depth) pit lakes. Water samples were collected for analysis of major cations and anions (unfiltered), and trace metals and metalloids (0.45 μm filtered) with samples preserved using 10% HNO3 at pH <1. Electrical conductivity (EC) and pH were measured in the field. Values of pH were measured using a TPS WP-81 meter, which was calibrated to pH 4 and 7 prior to each measurement. The EC was also measured using this instrument which was calibrated at the start of each sampling day using a 0.01 M KCl solution.

Stream sediment samples (n = 34) were also collected upstream and downstream of the Federation/La Perouse site, and represented background and ’mine-impacted’ materials. Samples were taken at, and downstream of Glencoe only. Duplicate sediment samples were collected from the middle of streams at a depth of 0 to 10 cm. Samples were dry sieved (using a stainless steel sieve) to <63 μm, with both the whole and the fine fraction (<63 μm) analysed for geochemical comparison. For water and sediment analyses, sampling equipment and HDPE sample bottles were cleaned prior to sampling by soaking them in HNO3 (trace metal grade) and rinsing in deionised (DI) water.

3.2. Mesotextural classification

Previously, only three lithological groups were identified in these waste rock piles (flow-banded rhyolite, red-stained rhyolites and tuffs, and quartz–sulphides; DME, 2008). However, when considering the styles of mineralisation and alteration, it is likely that additional groups exist. Therefore, a mesotextural classification method was developed as a means of identifying the major waste rock lithologies, and measuring their acid forming characteristics. Polished slices were prepared from each waste rock sample to facilitate the identification of primary and alteration minerals and textures, which was performed using a hand lens and a binocular microscope. Lithologies were described, with particular attention given to the texture (e.g., porphyritic, flow-banded), and estimating the modal mineralogy. As the groundmass of rhyolite samples was fine-grained, a portable short-wave infrared (SW-IR) mineral analyser (Terraspec) was used for mineral identification. In this analysis, three 30 mm² spots across each polished slab were analysed, with the spectra interpreted using The Spectral Geologist™ software. Pressed powder pellets were also prepared from each sample and analysed using a field-portable X-ray fluorescence instrument (InnovX X50). Based on the mineralogical and textural differences observed in hand-specimen, samples were categorised into mesotextural groups. Ten mesotextural groups were identified (A to J), with one representative sample from each group shown in Fig. 3.

One polished slice from each mesotextural group was evaluated by the acid rock drainage index (ARDI), whereby textural parameters known to influence acid formation were examined. As this is a site-
Fig. 3. Representative mesotextures (A to J) of the ten main lithologies observed at the Federation/La Perouse and Glencoe waste rock piles (scale bar = 1 cm). Stars indicate areas analysed by short-wave infrared, with the identified mineral phase given in italic. NB. Mineralogical descriptions of mesotextural groups are given in Table 1. Abbreviations: asp, arsenopyrite; chl, chlorite; Fe-ox, iron-oxide; gl, galena; ksp, potassium feldspar; msc, muscovite; py, pyrite; qtz, quartz; spl, sphalerite.
specific index, samples were screened prior to evaluation to define the ranking criteria. The ARDI evaluates sulphide content; sulphide alteration; sulphide morphology; neutralising mineral content; and sulphide mineral associations following the methodology described in Parbhakar-Fox et al. (2011). The first three parameters (A to C) are ranked from 0 to 10; and the latter two (D and E) — 5 to 10. Scores were averaged across each sample to calculate an overall ARDI value. To refine the ARDI value, evaluations were performed on a polished thin section made from the slab using a petrographic microscope. Values obtained from both hand-specimen and thin section analyses were averaged to obtain a final score. Samples scoring from 41 to 50 were classified as extremely acid forming (EAF); 41 to 40 as acid forming (AF); 21 to 30 as potentially acid forming (PAF); 11 to 20 as non-acid forming (NAF); 1–10 are NAF or have a potential neutralising capacity (NC); and — 10 to 0 have no acid neutralising capacity (ANC). These values are recommended for use alongside static geochemical data to enhance waste classification (Parbhakar-Fox et al., 2011).

3.3. Chemical and mineralogical analyses

The bulk elemental composition (major: Al₂O₃, CaO, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, PbO, SiO₂, TiO₂; trace: Ag, As, Bi, Cd, Cu, Ni, Pb, S, Sh, Zn, Zr) of all waste rock samples was assessed by X-ray fluorescence (XRF; Philips PW1480 X-ray Spectrometer, UTAS, Australia). In-house standards (TASGRAN, TASBAS, TASMONZ, TASYDOR, and a blank) were analysed during this run, in addition to standard reference materials (i.e., BCR-2, BHVO-2, RGM-1, W-2, WS-E, AC-E, CSP-2). These standards were run at the start of the analysis, and at the end with the relative standard deviation calculated as <1.5%. One sample from each mesotextural group was analysed for their mineralogical composition by quantitative XRD (Siemens D501 diffractometer, University of Ballarat, Australia).

One inch polished laser mounts (n = 15) were prepared from major sulphide bearing mesotextural groups (G, H, and J) and electron probe microanalysis (EPMA) performed ( Cameca SX100 electron microprobe; Central Science Laboratory (CSL), UTAS, Australia). Natural and synthetic materials were used as standards and included sphalerite-ast modified (S, Zn), marcasite (Fe), Cd–metal-UTAS4 (Cd), cuprivate–ast modified (Cu) and astimex. Spot analyses were performed operating with a 20 keV accelerating voltage, 15 nA beam current and a 2 μm beam diameter to measure concentrations of minor elements (e.g., Ag, As, Cd, Co, Ni) for comparison with Laser-Ablation ICP-MS (LA-ICPMS) data. In the case of sphalerite, Zn measurements were used as an internal standard. Both spot and mapping analyses were performed on these samples using LA-ICPMS (Agilent HP4500 Quadripole ICPMS; UTAS, Australia). Calibration was performed using an in-house standard (STDGL2b-2) comprising powdered sulphides doped with certified element solutions and fused to a lithium borate glass disc (Danyushhevsky et al., 2011). These analyses were performed to quantify trace elements in sulphides and observe their spatial distribution. Static acid base accounting (ABA) tests were performed on all waste rock samples (at both UTAS and University of Queensland (UQ), Brisbane, Australia), and included paste pH, Sobek, modified Sobek and a range of standard and advanced net acid generation (NAG) tests, following procedures given in White et al. (1999) and the AMIRA P387A Handbook (Smart et al., 2002). During paste pH testing, solutions were measured in triplicate (per sample) using a Eutech Instruments 510 pH meter. The pH probe was calibrated to pH 4 and 7 using standard buffer solutions (Merck Ltd.). After each sample measurement, Sample blanks (deionised water) were tested before and at the end of each sample batch. The EC was measured using a TPS WP-81 meter, with the probe calibrated prior to use with a 0.01 M KCl solution. During Sobek and modified Sobek testing, KZL-1 (sericitic schist) and NBM-1 (altered feldspar porphyry) standards (obtained from CANMET, Natural Resources, Ottawa, Canada) were used, with one sample of each tested for every five samples. Both reference materials are commonly used in ARD studies (e.g., Goodall, 2008; Paktunc, 2001). The relative standard deviation calculated between the standard measurements was <5%.

First flush experiments were performed on 2 kg samples (<10 mm and <4 mm) from mesotextural groups E (flow-banded rhyolite containing disseminated sulphide), G (quartz—sphalerite—galena), H (arsenopyrite — quartz — pyrite) and J (quartz — pyrite). Samples were loaded into a Buchner funnel with water added until the surface of the material was saturated. The pH and EC of leachates were measured after 24 h (using the same instruments as with paste pH testing, and following the same calibration methods). Selected trace elements (e.g., Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sh, Se, Zn) were determined using ICP-MS techniques (Agilent 4500 ICP-MS; UTAS, Australia). During ICP-MS analysis, three internal standards and a multi-element calibration standard (MISA29; Choice Analytical) were used before, and at the end of each sample run, in addition to two blank samples. The relative standard deviation for these data was <5%

3.4. Textural analyses

Samples from mesotextural groups C, E, G, H and J were selected for microtextural analysis (FEI Quanta 600 environmental scanning electron microscope (ESEM); Central Science Laboratory (CSL), UTAS, Australia). Relationships between primary sulphides and secondary minerals (e.g., scorodite, anglesite, rhomboclase which were identified by XRD; Table 1), were examined in this analysis. Additionally, inhomogeneties, which may influence trace element distribution (e.g. compositional zoning or mineral inclusions), were observed. Additionally, one sample from each of these groups (i.e., C, E, G, H and J) were subjected to textural mapping to examine sulphide mineral associations (FEI Quanta 600 mineral liberation analyser scanning electron microscope (MLA-SEM), CSL, UTAS, Australia). One inch polished tiles (3 cm x 3 cm) were prepared and analysed using the extended back scattered electron (XBS) technique as described by Fandrich et al. (2007). Data were processed in MLA Image Viewer and in-house Texture Viewer software to produce classified images for each sample based on a site-specific mineral library.

3.5. Sediment analyses

Selected sediments were analysed for their mineral composition by XRD powder diffraction (Bruker D8 Advance X-Ray diffractometer; UQ, Brisbane, Australia). Both the whole sediment and the fine-grained (<63 μm) sediment fraction were partially digested in hot aqua regia. The resulting extractants and the water samples collected from around the Croydon district were analysed for selected trace elements (e.g., Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sh, Se, Zn) using ICP-MS techniques (UQ, Brisbane, Australia). During ICP-MS analysis, two reference standards were used, a multi-element calibration standard-2A (Agilent Technologies) and an arsenic reference standard (Eawag aquatic research, Swiss Federal Institute of Aquatic Science and Technology). Both were analysed before and at the end of each sample run in addition to two blank samples. The relative standard deviation for these data was less than 10%.

Determination of the solid speciation of selected metals, was performed through a six-step sequential extraction analysis (Centre for Mined Land Rehabilitation (CMLR), UQ, Australia) on Fe-rich stream sediments (n = 6) collected at the Federation/La Perouse site only. The analytical procedure of Dold (2003) was followed, which differentiated between water soluble, ion exchangeable, Fe³⁺-oxyhydroxide, Fe³⁺ oxide, organic/sulphide and residual fractions. An additional step was added to include Mn oxides (20 mL 0.1 M Na₂O₃ – HCl; pH 2; shake 2 h).
Table 1

<table>
<thead>
<tr>
<th>Mesotextural group</th>
<th>Lithological description</th>
<th>Gangue minerals</th>
<th>Primary sulphides</th>
<th>Secondary sulphates and (hydro)oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Porphyritic pale-mid grey rhyolite with sub-cm muscovite pheno-crysts and mm-scale quartz veins</td>
<td>Major Quartz, Muscovite, K-feldspar</td>
<td>Minor Pyrite, Arsenopyrite</td>
<td>Minor Smolnokite, Goethite</td>
</tr>
<tr>
<td>B</td>
<td>Flow-banded blue-grey rhyolite with sub-rounded quartz phenocrysts and graphite clots</td>
<td>Major Quartz, Muscovite, K-feldspar</td>
<td>Minor Pyrite, Arsenopyrite</td>
<td>Major Goethite, Smolnokite</td>
</tr>
<tr>
<td>C</td>
<td>Porphyritic light-grey rhyolite-tuff with mm-scale quartz veins containing mm-scale pyrite</td>
<td>Major K-feldspar, Muscovite, Fluorite, Chlorite</td>
<td>Minor Pyrite, Arsenopyrite</td>
<td>Minor Smolnokite, Anglesite</td>
</tr>
<tr>
<td>D</td>
<td>Flow-banded beige-grey rhyolite containing mm-scale disseminated pyrite</td>
<td>Major K-feldspar, Muscovite, Fluorite, Chlorite</td>
<td>Minor Pyrite, Arsenopyrite</td>
<td>Minor Smolnokite, Rhombooclase</td>
</tr>
<tr>
<td>E</td>
<td>Porphyritic mid-grey-pink rhyolite-tuff with mm-scale quartz phenocrysts and cm-scale quartz veins</td>
<td>Major K-feldspar, Muscovite, Fluorite, Chlorite</td>
<td>Minor Pyrite, Arsenopyrite</td>
<td>Minor Smolnokite, Rhombooclase</td>
</tr>
<tr>
<td>F</td>
<td>Massive quartz with sub-cm-scale sphalerite and galena intergrowths and Mn mm-scale pyrite</td>
<td>Major Quartz, Muscovite, Albite, K-feldspar, Chlorite</td>
<td>Minor Galena, Sphalerite</td>
<td>Minor Smolnokite, Rhombooclase</td>
</tr>
<tr>
<td>G</td>
<td>Massive quartz with cm-scale arsenopyrite-pyrite intergrowths and mm-scale disseminated galena</td>
<td>Major Quartz, Muscovite, Albite</td>
<td>Minor Arsenopyrite, Pyrite, Sphalerite</td>
<td>Minor Smolnokite, Rhombooclase</td>
</tr>
<tr>
<td>H</td>
<td>Massive quartz containing cm-scale pyrite with cm-scale Fe-oxide weathering rind</td>
<td>Major Quartz, Microcline, Albite, Muscovite</td>
<td>Minor Pyrite, Galena</td>
<td>Minor Smolnokite, Rhombooclase</td>
</tr>
<tr>
<td>I</td>
<td>Porphyritic blue-grey rhyolite, silicified</td>
<td>Major Quartz, Microcline, Albite, Muscovite, Chlorite</td>
<td>Minor Pyrite, Galena</td>
<td>Minor Smolnokite, Anglesite</td>
</tr>
<tr>
<td>J</td>
<td>Massive quartz containing cm-scale pyrite with cm-scale Fe-oxide weathering rind</td>
<td>Major Quartz, Muscovite, Chlorite</td>
<td>Minor Pyrite, Galena</td>
<td>Minor Smolnokite, Rhombooclase</td>
</tr>
</tbody>
</table>

4. Results

4.1. Mineralogy and textural groups

The mineralogy of each mesotextural group is summarised in Table 1. From the ten mesotextural groups, four were porphyritic rhyolites (groups A, C, F and I), three were flow-banded rhyolites (groups B, D and E) and the remainder quartz–sulphides (groups G, H and J; Table 1). The porphyritic rhyolite groups differed in their component mineral proportions, presence/absence of quartz veins, phenocryst and alteration type. For example, in group C textural evaluations identified trace sulphides (≤ 1 wt.%) in both the groundmass and quartz veins. This consisted of euhedral–subhedral quartz-associated disseminated (<1 mm) pyrite and arsenopyrite, but similar sulphides were not observed in other porphyritic rhyolite groups. Additionally, whilst flow-banded rhyolite groups B and D are similar in appearance; group B had been more silicified, and group D weathered, so were classified differently.

Mesotextural group G, H and J differed significantly in terms of their sulphide mineralogy and texture (Fig. 4). Group G was dominated by sphalerite and galena (Fig. 4A), with minor pyrite also identified. In general, larger (>500 μm) sphalerite grains appeared more weathered than smaller grains, with secondary minerals pervasively developed within grains. Galena alteration was observed, with fine-grained anglesite identified as the alteration product (Fig. 4B). Sphalerite containing galena inclusions appeared more strongly weathered (Fig. 4C). This is likely the result of galvanic interactions between these sulphides, with sphalerite preferentially weathering due to its lower rest potential (~0.24 V) relative to galena (0.28 V; Kwong et al., 2003; Lottermoser, 2010).

Mesotextural group H displayed a massive arsenopyrite–quartz–pyrite texture with scorodite extensively precipitated at the interface of these minerals, and within fractures (Fig. 4D). Euhedral pyrite grains appeared relatively unweathered when encapsulated in scorodite. However, when intergrown with arsenopyrite, pyrite had weathered to a greater degree. Galena micro-inclusions were a common feature within pyrite (Fig. 4E). Smaller (~200 μm) quartz-associated arsenopyrite grains appear unfractured and unweathered. Scorodite layers within massive arsenopyrite had a relatively uniform thickness (c. 20 μm), but was occasionally observed as spherules (Fig. 4F). Weathering of scorodite to amorphous ferric arsenate phases rich in As, Cu, Fe and Pb was also recognised (cf. Murciego et al., 2011).

Pyrite was observed as both grains and very fine (<100 μm) veinlets in group J (Fig. 4G). Smaller, euhedral grains containing galena micro-inclusions (Fig. 4H) were less weathered than larger euhedral–subhedral pyrite grains which were highly fractured (Fig. 4I). Secondary products of pyrite oxidation (i.e., coatings) were not frequently observed.

4.2. Waste rock chemistry

4.2.1. Major and trace elements per group

All groups were dominated by SiO2 (55 to 87 wt.%) except in group H, where Fe2O3 dominated (36 wt.%) with values measured by XRF. The feldspar–biotite model (2[Ca + Na + K] / Zr vs. Al / Zr) of Downing and Madeisky (1997) was constructed to assess, based on whole rock chemistry, the buffering potential of each group (Fig. S2). This model allows for an assessment of alteration based on the stoichiometrically defined co-variation of the sum of the alkalis with Al in anorthite (CaAl2Si2O8), albite (NaAlSi3O8), orthoclase (KAlSi3O8) and biotite ([K(Fe,Mg)3]AlSiO10(OH)2). Unaltered rocks plot on the model line of slope 1, and altered rocks plot either above or below the model line, depending on whether they gained or lost alkalis during alteration processes (Downing and Madeisky, 1997). Group I was the least altered, plotting above the unaltered feldspar line. All other groups were altered, plotting below the model line indicating no significant buffering potential. The model suggests that groups C, H and J have undergone extreme...
Fig. 4. Classified mineral map of MLA tile (3 cm × 3 cm) and BSE images from mesotextural groups G, H and J: (A) Classified XBSE mineral map image of mesotextural group G material; (B) BSE image of altered reaction interface between galena and anglesite; (C) oxidised sphalerite grains (skeletal grain outlined) intergrown with galena; (D) classified XBSE mineral map image of mesotextural group H material; (E) massive arsenopyrite and pyrite; (F) scorodite microtextures (ribbons, spherules and masses) identified in pyrite; (G) classified XBSE mineral map image of mesotextural group J material; (H) unweathered pyrite with galena micro-inclusions; (I) highly fractured pyrite with galena micro-inclusions. Abbreviations: ang, anglesite; asp, arsenopyrite; gl, galena, msc, muscovite; py, pyrite; qtz, quartz, sc, scorodite; spl, sphalerite.

Fig. 5. Concentrations (ppm; measured by XRF) of As, Cu, Cd, Pb and Zn shown against S (wt.% for Croydon waste rock materials grouped by mesotextural characteristics (A to J).
acid leaching as several samples plotted along the X-axis (cf. Downing and Madeisky, 1997). Field evidence for this manifested as vuggy quartz–sulphide textures observed in waste rock materials belonging to these particular sulphide-dominated groups.

Concentrations of As, Cd, Cu, Pb and Zn (measured by XRF and given in ppm) were plotted against sulphur (wt.%) per mesotextural group (Fig. 5A–E) to demonstrate their concentration ranges within these groups. Average concentrations of Bi, Ni and Sb were < 100 ppm for all groups and are therefore not shown. Mesotextural groups A to F and I contained low concentrations of As, Cd, Cu, Pb, S and Zn. In relative terms, Cd, Pb and Zn measured high in group G, H and J, and Cu in groups G, H and J (Fig. 5C). One group J sample contained high Pb (~35,000 ppm), but relatively low S (maximum: 3164 ppm; average: 150 ppm; sd: 446 ppm) for the group, suggesting that the Pb is possibly hosted by a secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E). The greatest secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E). The greatest secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E). The greatest secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E). The greatest secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E). The greatest secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E). The greatest secondary hydrous ferric oxide (HFO) phase in this group. Zinc concentrations were relatively low in groups H and J (Fig. 5E).

4.2.2. Sulphide mineral chemistry

Sphalerite in group G is iron rich, with EPMA spot analyses (n = 58) measuring average contents of 8.4 wt.% Fe (sd: 1.28 wt.%) and 0.19 wt.% Cd (sd: 0.05 wt.%). The bulk chemical composition was calculated as \((Zn_{0.85}, Fe_{0.15})S\). These grains are likely to be relatively susceptible to weathering (compared to trace element poor sphalerite; cf. Weisener et al., 2004; Stanton et al., 2006). Distributions of Cd and Fe were homogeneous, with both pervasively distributed across the grain as shown by LA-ICPMS mapping, with an example shown in Fig. 6. This implies that Fe and Cd are in solid solution, as is typical for these elements (Cook et al., 2009). Sub-5 μm blebs of chalcopyrite (Fig. 6C) characteristic of chalcopyrite disease were recognised (cf. Barton and Bethke, 1987; Cook et al., 2009). Lead was present in veins (Fig. 6E) as galena intergrowths. A slight decrease in Zn concentration at the grain boundary was observed (Fig. 6G), implying the dissolution of sphalerite to form a Zn-deficient layer (Cook et al., 2009; Weisener et al., 2004). Galena present in group G (subjected to LA-ICPMS spot analysis; n = 61; data not shown) was identified as relatively enriched in Bi (maximum: 1508 ppm; average: 454 ppm; sd: 225 ppm) and Sb (maximum: 1026 ppm; average: 867 ppm; sd: 185 ppm), with similar element signatures reported in Diehl et al. (2008). Element mapping indicated no trace element zonation, and is therefore consistent with observations made by Bethke and Barton (1971) for lead sulphides associated with igneous activity, or heated after formation (i.e., orogenic areas).

Electron microprobe spot analyses of both larger arsenopyrite grains in mesotextural group H (n = 29) reported concentrations of Cd, Cu, Co, Ni, Pb, Sb and Zn below detection limit. However, LA-ICPMS analyses (spot: n = 11, mapping: n = 3) showed that in these grains Sb (maximum: 200 ppm; average: 140 ppm; sd: 31 ppm) is pervasively distributed, with minor Co (maximum: 27 ppm; average 10 ppm; sd: 5 ppm) and Ni (maximum: 5 ppm; average 1 ppm; sd 2 ppm) demonstrating a banded distribution (Fig. 7). Concentrations of Cd, Pb and Zn are relatively high in grain fractures and rims compared to arsenopyrite and quartz, potentially indicating adsorption of these elements to secondary scorodite (Fig. 7). Element distribution maps and spot analyses (n = 7 and n = 57 respectively; analysed by LA-ICPMS) were performed on pyrite grains in mesotextural group J, with a representative example shown in Fig. 8. The BSE images (Fig. 8A and B) and Fe-distribution map (Fig. 8F) show the grain outline, and the absence of fractures. Arsenic was relatively enriched in areas of the grain (Fig. 8C; maximum: 19,080 ppm; sd: 3800 ppm; sd: 5770 ppm), and showed an antithetic distribution to the metals. Pyrite (particularly towards the core) was rich in Cu (maximum: 1508 ppm; average: 454 ppm; sd: 225 ppm) and Pb (Fig. 8G; maximum: 3164 ppm; average: 150 ppm; sd: 446 ppm) and Zn (Fig. 8H; maximum: 4720 ppm; average: 820 ppm; sd: 1499 ppm). Galena micro-inclusions as shown in BSE images (Fig. 4H), were again observed with localised highs, and coincident distribution of Ag and Bi.

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**Fig. 6.** Relative element distribution (cps; analysed by LA-ICPMS) in a sphalerite grain (with galena intergrowths) from Croydon waste rock mesotextural group G: (A) Back scattered electron image of the original grain; (B) Cd; (C) Cu; (D) Fe; (E) Pb; (F) S; (G) Zn. Abbreviations: gl, galena; qtz, quartz; spl, sphalerite.
(<10 ppm). These Zn–Pb–Cu zones were rimmed by a fine band of Co (~10 ppm).

4.2.3. Static geochemical tests

A summary of static geochemical results are shown in Table 2. Average paste pH values were >pH 5.5 for all groups except G (pH 4.5); H (pH 5.09) and J (pH 3.76), classifying these as potentially acid forming (PAF). These three groups also returned relatively high average values for total-sulphur ($S_{\text{total}}$) of 1.21 wt.%; 14.10 wt.% and 10.5 wt.% respectively. The remainder of groups returned $S_{\text{total}}$ values below <0.25 wt.% Accordingly, groups G, H and J returned relatively high MPA values (approximate range 37 to 431 kg H$_2$SO$_4$/t; Table 2). Sobek ANC values were low for all groups (approximately ~4 to 5 kg H$_2$SO$_4$/t; Table 2), reflecting the absence of carbonates. Additionally, silicate

Fig. 7. Back scattered electron image (A), reflected light image (B) and photograph (C) of three arsenopyrite grains from Croydon waste rock mesotextural group H, with relative element distribution maps for Cu, Co, Ni, Sb and Zn shown (cps; analysed by LA-ICPMS). Abbreviations: asp; arsenopyrite; qtz, quartz.
minerals which may contribute to ANC (e.g., serpentine, chlorite, olivine; Jambor et al., 2002, 2007) were not identified in these samples. Average NAPP values > 20 kg H₂SO₄/t were calculated for groups G, H and J only, identifying these as PAF (Skousen et al., 2002), as confirmed in the NAPP against NAG plot shown in Fig. S3. Several samples from group C were identified as PAF (Fig. S3). However, ARDI assessments considered this group overall as NAF (Table 2). Several samples from group E plotted in the PAF field (Fig. S3), with the ARDI value for this group supporting this classification.

4.2.4. First-flush chemistry

Using the same cut-off criterion for paste pH (whereby leachates measuring > pH 5.5 are considered PAF) all samples from groups E, G, H and J were classified as PAF (Fig. 9A; range: pH 3.0 (group J, b4 mm) to 4.7 (group E, <4 mm)). This indicates the potency of pyrite to generate acid in the absence of neutralising minerals for this type of mine waste even when pyrite is present in very low concentrations i.e., group E where b0.5 wt.% was measured by QXRD. No significant differences between pH values from the finer (b4 mm) and browns.

Table 2

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<th>Group</th>
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<th>Total-S (%)</th>
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<th>Soebek ANC*</th>
<th>Net acid producing potential*</th>
<th>(M/NAG)*</th>
<th>NAG pH</th>
<th>ARD index (/50)</th>
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coarser (<10 mm) fractions were measured (Fig. 9A). However, a greater reactivity was expected from the coarser (<10 mm) fraction as a function of surface area (cf. Stomberg and Banwart, 1999), and this was observed in kinetic column leach experiments performed on these materials (Parbhakar-Fox et al., 2013). The lowest elemental concentrations (measured by ICP-MS) were from Group E, with the lowest quantities of Al, As, Cd, Cu, Fe, Pb and Zn measured (Fig. 9). Such a first-flush leachate signature was anticipated for this group when considering the low pyrite abundance, and its textural form (i.e., euhedral pyrite encapsulated in a quartz–muscovite groundmass). The highest values for Al and Zn were measured from the <4 mm fraction of group G (Fig. 9B; 3626 mg/L and 9 g; 26,260 mg/L respectively). High concentrations of Zn in first-flush leachate was anticipated when considering the presence of sphalerite in this material (Table 1). In group H the highest As concentrations were measured (~14,000 mg/L; Fig. 9C) corresponding to the high arsenopyrite and scorodite contents (Table 1). Generally, relatively similar element concentrations were measured between the two size fractions, however slightly higher As, Cd, Pb and Zn were measured from the <4 mm fraction (Fig. 9). High concentrations of Pb were measured from both size fractions, and were likely sourced from Pb micro-inclusions identified in pyrite intergrown with arsenopyrite (Fig. 4D).

For group J, the <4 mm fraction consistently measured highest values for each element, with the exception of Pb in sample 3 (Fig. 9G). Of the group J samples, J1 contained the highest As (<4 mm: ~210 mg/L; Fig. 9C), followed by group J3 (<4 mm: ~130 mg/L; Fig. 9C) and sample J2 the lowest (<10 mm: ~2 mg/L; Fig. 9C). These values increase with pyrite content, inferring As release during oxidation, and its consequent redistribution to soluble secondary minerals. The presence of significant sulphide sources of Cd (i.e., sphalerite) in this group was not inferred by this data (as confirmed by QXRD; Table 1). However, Cd concentrations ~120 mg/L were measured from the <4 mm fraction of sample J3 (Fig. 9D). This suggests that secondary minerals present in this group are Cd-bearing. Irwin et al. (1997) and Tauson et al. (2004) reported of Cd-bearing anglesite, therefore this is considered here a potential Cd source in material from this group. High concentrations of Cu were measured in leachate from samples J1 (<4 mm: ~2900 mg/L; Fig. 9E) and J3 (<4 mm: ~1500 mg/L; Fig. 9E), and likely relate to the presence of Cu in pyrite (Fig. 8E), furthermore, minor quantities of chalcopyrite were identified in SEM and MLA studies. The highest concentrations of Fe (range: ~133,780 to 997,800 mg/L; Fig. 9F) were measured in this group, specifically from the <4 mm fraction, and likely represents the dissolution of soluble secondary

<table>
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<th>Sample</th>
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<th>&lt; 10 mm</th>
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**Fig. 9.** First flush chemistry (mg/L; measured by ICP-MS) of leachates derived from material representative of Croydon waste-rock mesotextural groups E, G, H and J: (A) pH; (B) Al; (C) As; (D) Cd; (E) Cu; (F) Fe; (G) Pb and (H) Zn. Values for both the <10 mm and <4 mm size fractions are shown.
Fe-sulphates, which were identified by QXRD (Table 1). Measurements of Pb are linked to weathering of galena to anglesite with both measured the highest in sample J3 (Fig. 9G). Zinc is most likely sourced from pyrite and its alteration products rhombohedral anglesite, which were detected in minor quantities (Fig. 9H; Table 1; cf. Buckby et al., 2003; Giere et al., 2003; Nordstrom, 2004).

4.3. Stream sediments

Element contents of stream sediment samples (measured by ICP-MS) collected in the Croydon area were compared against Australian and New Zealand interim sediment quality guidelines (ISQGs). These empirical guidelines are derived from the North American effects database (ANZECC/ARMCanZ, 2000a; in Simpson et al., 2005). The guidelines contain two concentrations, the ISQG-Low concentration (or trigger value) and the ISQG-High concentration. The trigger value is a threshold concentration, and below this the frequency of biological effects is expected to be very low (Simpson et al., 2005). The ISQG-High concentration is intended to represent a concentration, above which adverse biological effects are expected to occur more frequently (Simpson et al., 2005).

The upstream (local baseline), on site, and downstream concentrations of selected metals and metalloids in both the total and fine (<63 µm) fractions are shown (for both mine sites) in Fig. 10 (measured by ICP-MS). Generally, background (upstream of mine operations) samples contain low concentrations of As (<20 mg/kg), Cd (<1.5 mg/kg), Cu (<65 mg/kg), Pb (<50 mg/kg), and Zn (<200 mg/kg). These values are within the ANZECC (2000) ISQG-High values. Several background samples with elevated As, Pb and Sb relative to ISQG-Low values (Fig. 10A, D and E) were measured and likely indicate the presence of

![Fig. 10. Trace element content (mg/kg; measured by ICP-MS) in stream sediments (total and <63 µm fractions shown) around the Croydon district. ANZECC (2000) ISQG-High and ISQG-Low values are shown for comparison: (A) As; (B) Cd; (C) Cu; (D) Pb; (E) Sb; (F) Zn. NB. Sample location numbers are shown at the top of each graph, and correlate to locations shown on Fig. 2.](image-url)
sulphide bearing lodes and mineralised rocks, causing localised element enrichment.

At the Federation/La Perouse site, elevated concentrations of As (total and 63 μm fractions), Cu (<63 μm), Cd (<63 μm), Pb (<63 μm) and Sb (<63 μm) relative to ISQG-Low values were measured. Only As was elevated relative to the ISQG-High value at the Glencoe site. The spatial distribution of sediment-associated metals downstream of both sites did not display a simple distance–metal concentration decay pattern. Downstream of Federation/La Perouse in Tabletop Creek, relative to the ISQG-High value, As remained generally in the <63 μm fraction to approximately 8 km (location 25; Fig. 10A). Cadmium was generally below the ISQG-Low value from approximately 3 km downstream of the Federation/La Perouse site (Fig. 10B) until the confluence (at approximately 10 km; location 27). Maximum concentrations of Cd (<63 μm) and Zn (<63 μm) exceeding ISQG-High values were measured in Deadhorse Creek approximately 0.9 km downstream of the Glencoe site (location 35; Fig. 10F and F). These concentrations fluctuated to the confluence, with occasional highs (e.g., location 30) again potentially indicating the presence of a mineralised sulphide body in proximity to the sampled location. Copper concentrations fluctuated downstream of the Glencoe site to the confluence (Fig. 10C). Lead concentrations also fluctuated for approximately 8 km downstream of the Glencoe site, after which it was measured below the ISQG-High value (Fig. 10D). At the confluence of Tabletop and Deadhorse Creek concentrations for As, Cu, Cd, Pb and Zn were measured below ISQG-High values. Monitoring (since 1998) of Tabletop Creek below the confluence (c. 17 and 30 km downstream of the Federation/La Perouse site) reported concentrations below ISQG-Low values for As, Cu, Cd, Pb and Zn (DME, 2008).

Sequential extraction results for six samples collected at the Federation/La Perouse site are presented in Table 1. Results show that Cu and Zn are dominantly associated with the Fe (III) oxyhydroxide (20%) and in the wet season the water bodies become linked.

4.4. Surface waters

The pH values measured across the Croydon district were compared against concentrations of As, Cd, Cu, Pb and Zn (Fig. 12). In Tabletop Creek upstream of the Federation/La Perouse site the pH range was 6.4 to 8.6, with low concentrations of Al (<67 μg/L), As (<6.1 μg/L), Cd (<2 μg/L), Cu (<3 μg/L), Pb (<1.1 μg/L), S (0.42 mg/L) and Zn (<9 μg/L) measured. Concentrations of Fe were elevated upstream of the mine operations (Fig. 12E). At the Federation/La Perouse site, pH values decreased to 3.7, with elevated concentrations of Al, As, Cd, Cu, Ni, Pb, S and Zn relative to local background/upstream value measured (Fig. 12). Downstream, pH values generally increased with a maximum of pH 7.6 recorded. Generally, concentrations of Cd, Cu, Pb and Zn decreased downstream.

At Glencoe, pH values were between 4.3 and 6.3 (Fig. 12), and elevated concentrations of As (20.4 μg/L), Cd (53 μg/L), Pb (14 μg/L) and Zn (7715 μg/L) relative to ANZECC (2000) drinking water guidelines (DWG) values were measured. In Deadhorse Creek adjacent to the site (location 36; Fig. 2), pH 3.95 was measured. However, by c. 1.7 km (location 33; Fig. 2), pH ~11 was measured. High dissolved Fe (2125 μg/L) was also measured at this location. At the confluence of Tabletop and Deadhorse Creeks, a near-neutral pH 6.7 was measured, with only Cu (13 μg/L), Ni (12 μg/L), S (18 mg/L) and Zn (137 μg/L) elevated relative to background/upstream concentrations (Fig. 12), but are not elevated in comparison to ANZECC (2000) DWG values. Element concentrations and pH values for Federation, La Perouse and Glencoe pit lakes are given in Table 3. Federation pit was the most acidic (pH 3.9) whilst La Perouse and Glencoe were only mildly acidic with measured values of pH 6.1 and 6.3, respectively. These values are similar to previous monitoring data collected by the DEEDI since 1998 (DME, 2008). The Federation Pit lake contained the highest concentrations of Cd (83.6 μg/L), Cu (989.6 μg/L), Ni (65.6 μg/L), Pb (71.3 μg/L) and Zn (1918 μg/L), and the highest As concentration was measured at Glencoe (20.4 μg/L). Elevated concentrations relative to ANZECC (2000) DWG values were detected for As (Glencoe) and Pb (Federation). Overall, La Perouse and Glencoe pit lakes have better water quality than Federation. Since the construction of the catch dam, water quality in Federation pit has deteriorated as in the dry season, water quality in the catch dam worsens due to evapo-concentration of solutes, and in the wet season the water bodies become linked.

5. Discussion

5.1. Acid forming groups and metal/metalloid sources

Detailed microtextural and chemical studies of the main sulphide-bearing groups revealed diversity of minerals and, in conjunction with geochemical data helped to identify the current ARD and metal/metalloid sources. Paste pH experiments indicate that material representative of group G (quartz–sphalerite–galena) is weakly acid forming, with the ARDI classifying them as PAF (Table 2). This group is a significant source of Cd, as indicated by first-flush experiments (Fig. 9). Specifically Cd is sourced from finer-grained sphalerite (~200 μm), which is undergoing oxidation at a greater rate than coarser-grained sphalerite (~200 μm) as a function of surface area, higher Fe-content and the presence of galena inclusions (cf. Lottermoser, 2010; Moncur et al., 2009; Stanton, 2005; Weisener et al., 2004). Zinc is also primarily sourced from sphalerite. Neither Zn nor Cd is retained surficially on sphalerite, indicating that on oxidation, metal deficient surface layers have formed (cf. Buckley et al., 1989). Chalcocyprite was not detected as a major sulphide mineral in any mesostructural group. However, it was observed in sphalerite as micro-inclusions. The presence of these micro-inclusions causes sphalerite lattice destabilisation, and enhancing oxidation (cf. Lottermoser, 2010, Urbano et al., 2007).
Galena in group G is rich in Ag, Bi and Sb increasing its potential for weathering and Pb release, with anglesite developed as a secondary product (cf. Diehl et al., 2003; Diehl et al., 2007; Savage et al., 2000). Finer-grained (<200 μm) galena appeared more weathered than coarser-grains, indicating that grain size poses a significant control on oxidation in accordance with Liu et al. (2008). Diehl et al. (2008) stated that anglesite does not function as a protective barrier against fluid infiltration because it is porous and fine-grained. However, Moncur et al. (2009) stated that anglesite rims slow oxidation progress. Observations from this study support Diehl et al. (2008).

Fig. 12. Trace element concentration (μg/L; measured by ICP-MS) versus pH in surface water samples collected from around the Croydon district: (A) Al; (B) As; (C) Cd; (D) Cu; (E) Fe; (F) Ni; (G) Pb; (H) S; (I) Zn.
Material representative of mesotextural group H (arsenopyrite–quartz–pyrite) was classified as extremely acid forming by geochemical tests and the ARDI. Highly fractured massive arsenopyrite dominated, and is in early stages of weathering, with scorodite dominating the secondary mineralogy. Scorodite behaves as a protective weathering barrier under acidic conditions as its dissolution is slow ($10^{-10}$ mol m$^{-2}$ s$^{-1}$; Harvey et al., 2006). Scorodite precipitates within arsenopyrite fractures and on grain boundaries as confined laminated layers of uniform thickness parallel to grain boundaries. Where scorodite growth is unconfined (e.g., in proximity to pyrite), a greater diversity of microtextures is observed, including spherules (DeSisto et al., 2011; Murciego et al., 2011) (e.g., in proximity to pyrite), a greater diversity of microtextures is observed, including spherules (DeSisto et al., 2011; Murciego et al., 2011). Paste pH results indicate that to an extent, scorodite is retard ing acid formation, as Craw et al. (2003) summarised that even at submicron-scale, this mineral offers protection. Mesotextural group J samples (quartz–pyrite) were consistently classified the most acid forming group at Croydon by all geochemical methods and the ARDI. General, larger pyrite grains were more oxidised as a result of extensive fracturing. Group J samples had the highest total concentration of metals (Cd, Cu, Ni, Pb and Zn). Arsenic in pyrite decreases resistance to oxidation (cf. Blanchard et al., 2007; Plumlee, 1999), here this has caused accelerated weathering of these cores, with weathering further enhanced by the presence of galena micro-inclusions ($<10$ μm diameter) straining the lattice (cf. Jambor, 1994; Kwong, 1995; Lottermoser, 2010; Plumlee, 1999). HFO have precipitated in pyrite fractures, and have adsorbed elements released on pyrite oxidation, particularly As (cf. Foster et al., 1998). In addition, szomolnokite and rhombooclase have precipitated and also represent a transient store of trace elements (Buckby et al., 2003; Lottermoser, 2010). Sediment loads of Cu, Cd and Zn declined downstream, with Cu sorbed onto Fe-bearing precipitates around neutral pH (Hudson-Edwards and Edwards, 2005). Cadmium and Zn concentrations correlate with Mn indicating coprecipitation of these elements with manganese oxides. At the confluence approximately 10 km downstream of both sites, neutral pH was measured, with metal (Al, Cd, Cu, Pb and Zn) concentrations similar to upstream values and below guideline values recommended by government authorities (e.g., ANZECC, 2000), indicating effective attenuation. However, at Croydon seasonal fluxes of metals may occur as a function of low flow conditions (low pH) or heavy rainfall events (high pH) causing desorption of elements (cf. Ashley et al., 2004; Harris et al., 2003; Nordstrom, 2009).

Generally water quality is similar in both creeks. Elevated Cd and Zn concentrations measured in Deadhorse Creek provide an indication that material representative of mesotextural group G dominates in the Glencoe waste rock pile. Consequently, there is a potential risk to cattle from ARD seepage at the site. However, these results suggest that Cd concentrations are relatively low from 1 km downstream of Glencoe. Instead, as the Croydon mine sites are currently designated grazing land, attention should be given to the presence of plant Calotropis (Calotropis procera) observed around the Croydon mines, as it is toxic if consumed (cf. Lottermoser, 2011).

5.3. Implications for site rehabilitation

Historic and abandoned sulphidic mine sites require rehabilitation. However, extensive ARD processes, limited capital and excessive costs associated with planning and remediation works mean that comprehensive site rehabilitation is rarely achievable. At these sites, rehabilitation is driven primarily by impacts on receiving environments i.e. soil and water quality (e.g., Alvarez and Ridolfi, 1999; Mudd and Patterson, 2010).

If water quality data alone is used to assess the requirement for rehabilitation at Croydon, the site would not be prioritised under Queensland’s Abandoned Mine Lands Program (AMLP). Our observations indicate that sulphidic mine wastes are in early weathering stages by the general mine waste paragenesis proposed by Moncur et al. (2009). However, first-flush data indicated that there would be significant discharge of metals and As after a heavy rainfall event. Thus, both Croydon sites studied are considered as long-term contamination sources posing serious environmental risk to the downstream environment.

Previous rehabilitation strategies at the site focused on raising pH in pit lakes and managing ARD seepage downstream. However, as shown in this study, this strategy can only have a temporary effect and a more sustainable long-term strategy should focus on the relocation of ARD sources into newly constructed impoundments, containing waste rock pile material domain ed into the ten mesotextural groups identified. Whilst upfront financial costs of adopting such a scheme may be considered high, a long-term cost saving is anticipated when considering that global liability costs associated with current and future ARD remediation is estimated at US $100 billion (Tremblay and Hogan, 2001 in...
Hudson-Edwards et al., 2011), indicating that a proactive rather than re-
 sponsive approach to ARD management is required.

Material representative of mesotextural group H is the dominant
 source of As, with its concentration in dissolved waters controlled in-
 part by scorodite formed in waste rock material. However, evidence of
 scorodite weathering was observed, indicating a likely temporal in-
 crease in dissolved As in waste pile leachates. Material representative
 of mesotextural group G contains significant quantities of Cd (and Zn)
 which is homogenously distributed in sphalerite grains and therefore
 identified as a long-term source of these elements. Whilst relatively
 low metal and As concentrations were measured from mesotextural
 group J in kinetic trials (Parbhakar-Fox et al., 2013), it is identified as a
 significant contamination source due to its high pyrite contents (i.e.,
generating low pH conditions). Considering these diverse chemical and
 mineralogical characteristics, consideration should be given to handling
 and managing mesotextural group G, H and J materials separately. Co-
disposal of these materials has potential to increase the environmental
 risk posed, through geochemical interactions. Such waste segregation
 practices are described in the GARD guide (2010). For example, sphalerite
 leaching is enhanced at low pH (2 to 4; Stanton et al., 2008), and first-
 flush pH measurements from group H were below 4. Therefore, co-
disposal may enhance sphalerite oxidation, releasing increased amounts
 of dissolved Cd and Zn.

As an alternative to impermeable covers, neutralisation strategies
could be implemented in the impoundments containing material repre-
sentative of mesotextural group G and J (and E, which can be co-
disposed with J) waste in order to raise pH and reduce heavy metal
and metalloid mobility (cf. Ashley et al., 2004). Alternatives to lime
should be sought as neutralising materials given the limited success
previously experienced (DME, 2008). As scorodite has extensively pre-
cipitated in mesotextural group H, the pH in the repository containing
it should be maintained in a range where it is relatively insoluble.
Bluteau and Demopoulos (2007) reported low solubility rates (0.35 mg/L−1)
of As at pH 5, with its dissolution from pH 5 to 9 similarly low. However,
Krause and Ettel (1988) reported that ~90 mg/L−1 As was leached
from scorodite at pH 5. Drahota and Filippi (2009) proposed that rea-
sions for these differences may be linked to the degree of scorodite
crystallinity used, with two types of scorodite texture observed in
here (spherules, and acicular grains). Therefore, prior to recommending
the geochemical conditions at which this material representative of this
mesotextural group should be maintained at, further work is required to
elucidate the crystallinity and stability of scorodite in this mesotextural

The mesotextural classification method developed in this study is
simple and cost-effective to perform at abandoned mine operations be-
cause it allows for the rapid assessment of large quantities of waste ma-
terials. Such a site-specific methodology should be designed primarily
by geologists (in conjunction with site managers), as an understanding
of the waste rock mineralogy is fundamental for scheme to be effective.
Based on the collection of real data (i.e., pXRF, SW-IR) and improved
mineralogical and textural assessments of waste materials, the selection
of the most appropriate samples for standard geochemical tests and in-
depth mineralogical evaluations is permitted. This allows for full ARD
characterisation i.e., identifying sulphide oxidation controls and under-
standing of ARD evolution on a mesotextural group basis. This method-