

Ephemeral acid mine drainage at the Montalbion silver mine, north Queensland

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Sulfide-rich materials comprising the waste at the abandoned Montalbion silver mine have undergone extensive oxidation prior to and after mining. Weathering has led to the development of an abundant and varied secondary mineral assemblage throughout the waste material. Post-mining minerals are dominantly metal and/or alkali (hydrous) sulfates, and generally occur as earthy encrustations or floury dustings on the surface of other mineral grains. The variable solubility of these efflorescences combined with the irregular rainfall controls the chemistry of seepage waters emanating from the waste dumps. Irregular rainfall events dissolve the soluble efflorescences that have built up during dry periods, resulting in 'first-flush' acid (pH 2.6–3.8) waters with elevated sulfate, Fe, Cu and Zn contents. Less-soluble efflorescences, such as anglesite and plumbojarosite, retain Pb in the waste dump. Metal-rich (Al, Cd, Co, Cu, Fe, Mn, Ni, Zn) acid mine drainage waters enter the local creek system. Oxygenation and hydrolysis of Fe lead to the formation of Fe-rich precipitates (schwertmannite, goethite, amorphous Fe compounds) that, through adsorption and coprecipitation, preferentially incorporate As, Sb and In. Furthermore, during dry periods, evaporative precipitation of hydrous alkali and metal sulfate efflorescences occurs on the perimeter of stagnant pools. Flushing of the streambed by neutral pH waters during heavy rainfall events dissolves the efflorescences resulting in remobilisation and transport of sulfate and metals (particularly Cd, Zn) downstream. Thus, in areas of seasonal or irregular rainfall, secondary efflorescent minerals present in waste materials or drainage channels have an important influence on the chemistry of surface waters.

KEY WORDS: acid mine drainage, efflorescence, ephemeral streams, heavy metals, oxidation, sulfides.

INTRODUCTION

Mining of metallic ore deposits can expose sulfide minerals to the atmosphere or oxygenated groundwater. As a consequence, the sulfides will oxidise to produce an acid water laden with sulfate, heavy metals and metalloids. In particular, the weathering of pyrite at mine sites causes the largest, and most testing, environmental problem facing the industry today—acid mine drainage (Evangelou 1995; Lottermoser 2003).

Acid mine drainage is known to occur under all climatic conditions, ranging from arctic to tropical. Much of the previous acid mine drainage research has focused on temperate regions in the northern hemisphere where sulfide oxidation in a wet climate produces a continuous supply of acid mine water. In contrast, vast regions of Australia are characterised by an arid or semiarid climate and here, acid mine drainage generation only occurs when seasonal or irregular rainfall favours the infiltration of water into sulfidic materials and drainage is possible from sulfidic materials. In the seasonally wet-dry climate of northern Australia, sulfidic materials are exposed to an irregular wet-dry cycle, which might lead to ephemeral acid mine drainage. At the onset of the wet season, sulfide oxidation and mineral-dissolution processes will generate acid mine drainage waters that might enter local surface waters and aquifers. Changing redox conditions commonly lead to the formation of Fe-rich precipitates (i.e. 'ochres' or

'yellow-boy'). Upon return to the dry season, acid mine drainage from the sulfidic material will cease. Evaporation causes the formation of mineral efflorescences (i.e. post-mining minerals that form due to evaporation as surface encrustations: Jambor *et al.* 2000) in pore spaces of sulfidic rocks, on stream beds and at seepage points and surfaces of waste-rock dumps, ore stockpiles and tailings repositories. In such environments, the nature and occurrence of the secondary minerals are important because soluble or metastable minerals might store metals, metalloids, sulfate and acidity until the next rainfall event (Alpers *et al.* 1994; Cravotta 1994; Keith *et al.* 1999; Nordstrom & Alpers 1999; Bigham & Nordstrom 2000; Jambor *et al.* 2000). Despite the knowledge that mineral efflorescences might impact on or even control the aqueous chemistry of acid mine drainage-affected streams, much of the previous work on acid mine drainage has focused on sulfide-oxidation processes (Evangelou 1995). In comparison, the characteristics and properties of ochres and mineral efflorescences are still poorly understood.

This paper documents the environmental geochemistry and mineralogy of the abandoned Montalbion silver mine, north Queensland (Figure 1). The mine site is located in a semiarid tropical environment and is characterised by ephemeral acid mine drainage. Particular emphasis is

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placed here on the varied and unusual efflorescent mineral assemblage as it has an important control on the aqueous mobility of elements from the Montalbion mine site.

MONTALBION MINING AREA

Physiography and climate

The Montalbion mine site is located in north Queensland, 100 km southwest of Cairns and 7 km west-northwest of

Irvinebank on the western slopes of the Atherton Tablelands at latitude 17°24.4'S, longitude 145°08.4'E. The mine site lies on an east–west-trending hill rising steeply above Oakey Creek, a tributary of the Walsh River (Figure 1). The region has a tropical savannah-type climate with an average annual rainfall of 756 mm, 80% of which falls between November and April (Dimbulah weather station, 30 km north of Montalbion) (Bureau Of Meteorology 2003). Rainfall tends to be irregular and patchy, characterised by local storms and rare cyclonic downpours.

Local geology

The Montalbion silver lodes are hosted by the Hodgkinson Province, a regionally extensive Early to Middle Palaeozoic succession comprised of turbiditic sedimentary rocks with generally subordinate interlayered chert, limestone and basic volcanic rocks (Bain & Draper 1997; Garrad & Bultitude 1999). At Montalbion, the mineralisation is enclosed by massive arenite with minor shale and siltstone which have been variably altered (Woodward 1976). Alteration consists of extensive silicification and kaolinisation with isolated intensive sericitisation. The mineralisation is contained within narrow, steeply dipping, lenticular and pipe-shaped quartz–sulfide veins. The ore lodes contain major amounts of argentiferous galena, argentiferous tetrahedrite, sphalerite, chalcopyrite and pyrite, traces of pyrrhotite and marcasite, and a gangue of quartz, dickite and illite with minor sericite and siderite (Woodward 1976). The mineralisation is also known for its elevated In concentrations. The lodes have been oxidised to a depth of at least 20 m, resulting in the widespread development of

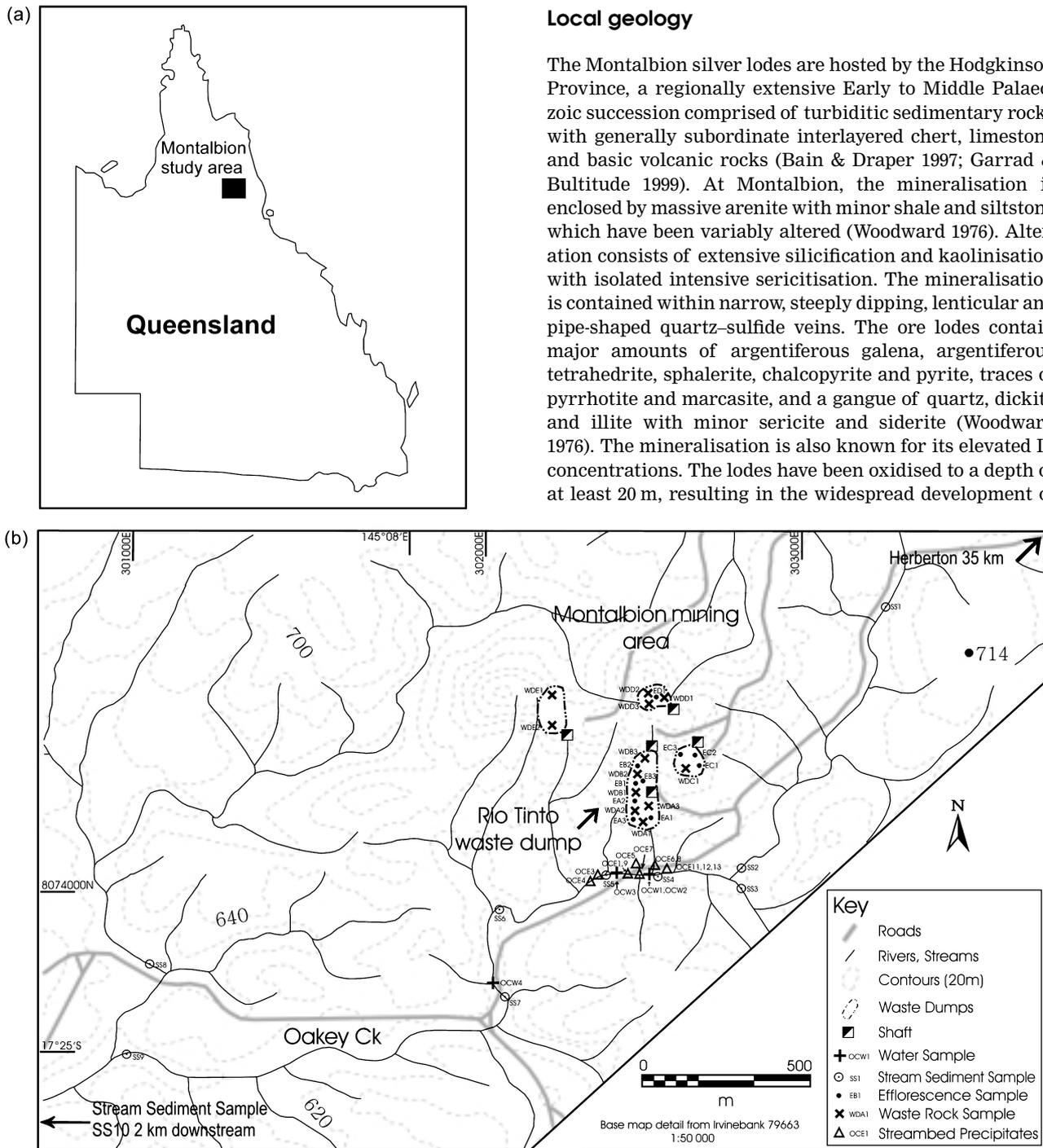


Figure 1 (a) Location of the study area. (b) Map of the Montalbion mining area showing sample localities.

secondary sulfides (chalcocite, covellite), (hydr)oxides (goethite, hematite) and sulfates (anglesite, chalcantite, goslarite, plumbojarosite) (Dash *et al.* 1991). The mineralisation style was interpreted by Woodward (1976) as epithermal, formed by hydrothermal solutions sourced from nearby mid- to Late Carboniferous granites of the O'Briens Creek Supersuite.

Mine history

The region contains historically significant areas of mineralisation for a range of metals (Sn, W, Mo, Ag, Au, Cu, Pb, Zn, Sb) and the Montalbion mine site is located in one of the most intensively mined areas of Queensland (Dash *et al.* 1991). The Montalbion silver-lead lodes were dis-

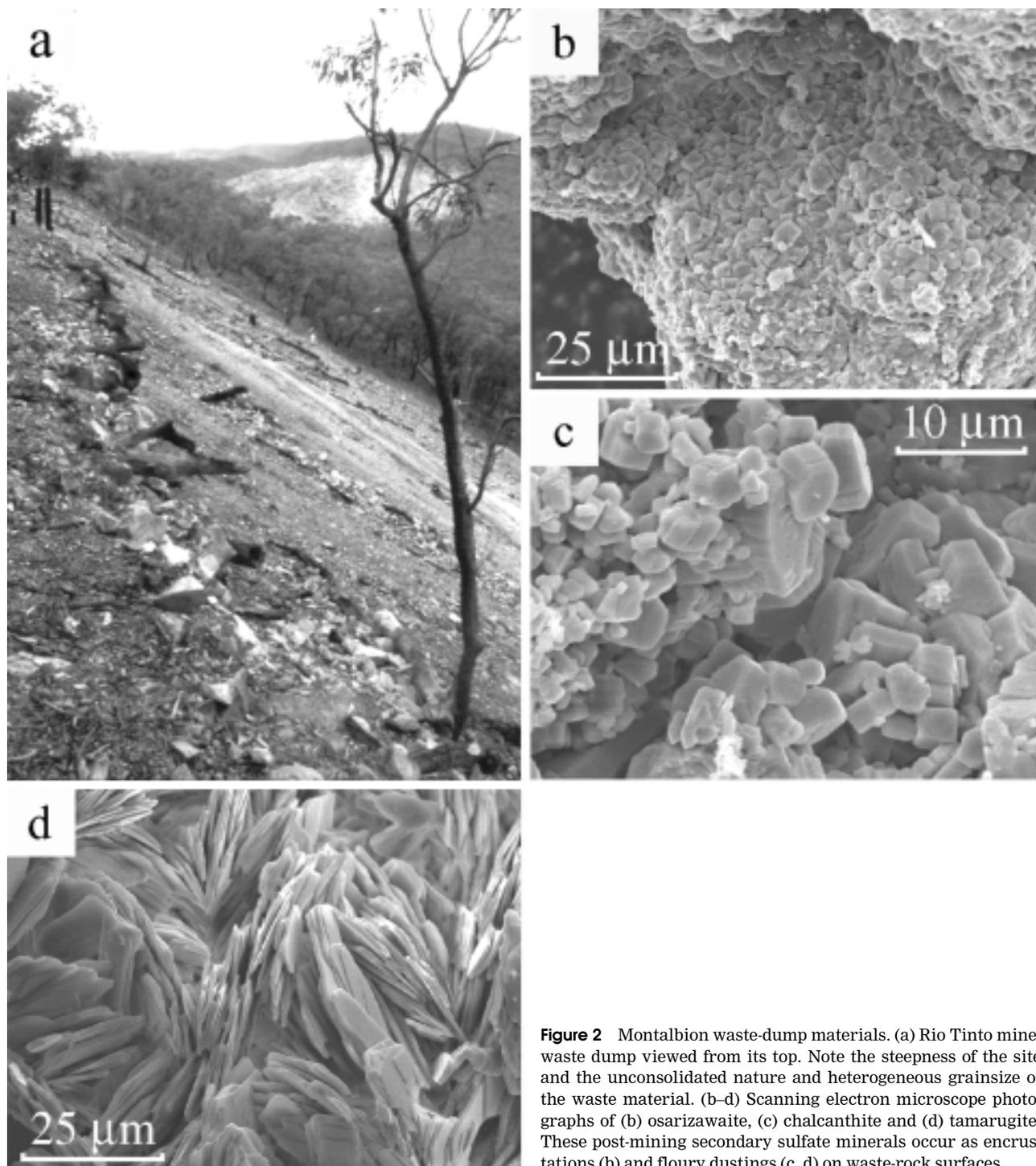


Figure 2 Montalbion waste-dump materials. (a) Rio Tinto mine-waste dump viewed from its top. Note the steepness of the site and the unconsolidated nature and heterogeneous grainsize of the waste material. (b–d) Scanning electron microscope photographs of (b) osarizawaite, (c) chalcantite and (d) tamarugite. These post-mining secondary sulfate minerals occur as encrustations (b) and floury dustings (c, d) on waste-rock surfaces.

covered in 1885 and were mined between 1885 and 1895 by opencut and underground methods, producing 49 258 kg Ag and 1038 t Pb from 39 799 t of sulfide ore (Dash *et al.* 1991; Garrad & Bultitude 1999). Intermittent small-scale mining of unknown production quantities occurred until 1922 and several small sulfidic waste-rock piles remain. The mine workings and waste dumps have remained undisturbed since 1922, with the exception of minor earthworks associated with mineral exploration in the 1970s (Woodward 1976).

Site description

The lodes occur in steep country, with slopes locally up to 30° and at altitudes between 620 and 800 m (Figure 2a). Ground disturbed by mining activities covers an area of approximately 0.25 km² and includes a series of shafts, adits, pits, access tracks and waste dumps scattered across an east-west-trending hill rising steeply above Oakey Creek. In the mined areas, waste materials were dumped on steep slopes resulting in masses of unconsolidated mine waste extending downslope. The Rio Tinto waste dump is the largest, covering 13 000 m² with a vertical extent of 80 m. Landsliding of the waste dumps continues especially during and after rainfall events. The actively eroding waste dumps are composed of diverse materials ranging from silty particles of <1 mm to boulders 0.5 m across. Constituents include metasedimentary material as well as minor sulfide fragments, pre- and post-mine oxidation minerals, and assorted mining waste. Uncontrolled, dynamic landsliding of the sulfidic material allows continuous oxidation of the waste. Little vegetation exists on the waste dumps, and gullies draining the mine site are devoid of vegetation. Ephemeral drainage from the mine site, particularly the Rio Tinto dump, runs into ephemeral

Oakey Creek, which has strong flow only after heavy rainfall and permanent waterholes during dry periods. During dry periods, drainage from the Rio Tinto dump appears to be the only source of surface water to Oakey Creek. Where acid mine drainage waters from the Rio Tinto dump enter Oakey Creek, the aquatic and bankside plant communities disappear. Moreover, there are abundant Fe-rich yellow-red-brown gelatinous precipitates coating the streambed and floating in shallow-water pools, and mineral-salt encrustations on the stream bank and bed. These visible effects of acid mine drainage pollution continue for ~800 m downstream where the stream progressively recovers to exhibit a more typical aquatic ecosystem with diverse plant species and near-neutral pH waters.

MATERIALS AND METHODS

Sampling and sample preparation

Field work was undertaken during June and September 2001 and April 2002. Over 60 stream sediment, water, Fe-rich precipitate, mineral efflorescence and mine-waste samples were collected in the Montalbion area. Local background stream sediments were taken upstream of the Montalbion mine site. All solid samples were air-dried. The stream sediment samples were sieved to <150 µm and <2 mm resulting in two size fractions (150 µm – 2 mm; <150 µm). The two size fractions were chosen to evaluate physical dispersion of metals from the Rio Tinto dump into Oakey Creek. Mine-waste samples (~5 kg) comprised random-grab sample composites and were taken from traverses across waste-dump faces. Iron-rich precipitates were collected as grab samples from the Oakey Creek streambed. Mineral efflorescences were scraped from

Table 1 Geochemistry of Montalbion mine waste (*n* = 12).

Element	Maximum	Minimum	Arithmetic mean	Median
Ag	780	30	293	235
As	6190	153	2230	1900
Bi	1250	<5	229	51
Cd	113	<5	39	21
Co	26	<5	13	11
Cu	35400	34	6920	1850
Fe	10.9	1.71	5.33	5.36
In	90	5	34	20
K	1.23	0.2	0.72	0.74
Mg	0.21	0.03	0.06	0.04
Mn	1670	31	197	51
Na	0.1	0.01	0.02	0.02
P	1860	143	656	526
Pb	69300	9700	29400	25450
S	3.71	1.01	2.23	2.18
Sb	7660	117	2200	768
Se	280	2.1	64	37
Sn	2450	28	457	254
W	80	<5	28	18
Zn	18600	360	6190	4040
Paste pH	6.1	2.7	4.2	4.5

All values with the exception of Fe, K, Mg, Na and S (wt%) are given in ppm dry weight.

Oakey Creek sediments, adit walls and loose rocks on the waste dumps. Mine-waste samples were crushed in a jaw crusher and ground in a chrome-steel mill, whereas mineral efflorescences and Fe-rich precipitates were ground with mortar and pestle in preparation for chemical and mineralogical analyses.

Mineralogical and geochemical analyses

Powders of stream sediments, Fe-rich precipitates and mine wastes were dissolved in a hot HF–HNO₃–HClO₄ acid mixture and analysed by inductively coupled (ICP) atomic emission spectrometry for Ag, As, Bi, Ca, Cd, Co, Cu, Fe, K,

Mg, Mn, Na, Ni, P, Pb, S, Sb, W and Zn, and by inductively coupled plasma mass spectrometry (ICP-MS) for Be, In, Se, Sn, Te, Tl and U at Australian Laboratory Services Chemex, Townsville. Duplicate samples and an aliquot of the geochemical reference material GXR-3 were used for data quality control.

Mineral identification of waste dump, stream sediment, Fe-rich precipitate and efflorescence samples was performed at the James Cook University, Townsville, Advanced Analytical Centre (JCU AAC) using X-ray diffraction and quantitative computational software (SIROQUANT, EVA). Scanning electron microscope observations and energy dispersive spectrometry measure-

Table 2 Minerals identified in the Montalbion mine wastes.

Paragenetic order	Name	Formula	
Primary ore mineral	Arsenopyrite	FeAsS	
	Bournonite	PbCuSbS ₃	
	Cassiterite	SnO ₂	
	Chalcopyrite	CuFeS ₂	
	Cobaltite	(Co,Fe)AsS	
	Galena	PbS	
	Pyrite	FeS ₂	
	Quartz	SiO ₂	
	Sphalerite	ZnS	
	Stannite	Cu ₂ FeSnS ₄	
	Sternbergite	AgFe ₂ S ₃	
	Stibnite	Sb ₂ S ₃	
	Tetrahedrite	Cu ₁₂ Sb ₄ S ₁₃	
	Wolframite	(Fe,Mn)WO ₄	
	Secondary pre-mining mineral	Chalcocite	Cu ₂ S
		Covellite	CuS
Cuprite		Cu ₂ O	
Dickite		Al ₂ Si ₂ O ₅ (OH) ₄	
Goethite		α-FeOOH	
Hematite		α-Fe ₂ O ₃	
Illite		KAl ₄ (Si ₇ AlO ₂₀)(OH) ₄	
Secondary post-mining mineral (highly soluble)		Chalcanthite	CuSO ₄ .5H ₂ O
		Gypsum	CaSO ₄ .2H ₂ O
		K-alum	KAl(SO ₄) ₂ .12H ₂ O
	Melanterite	Fe ²⁺ SO ₄ .7H ₂ O	
	Metavoltine	K ₄ Na ₄ (Fe ²⁺ ,Zn)Fe ³⁺ ₆ (SO ₄) ₁₂ O ₂ .20H ₂ O	
	Spangolite	Cu ₆ Al(SO ₄)(OH) ₁₂ Cl.3H ₂ O	
	Ramsbeckite	(Cu,Zn) ₁₅ (OH) ₂₂ (SO ₄) ₄ .6H ₂ O	
	Szomolnikite	Fe ²⁺ SO ₄ .H ₂ O	
	Tamarugite	NaAl(SO ₄) ₂ .6H ₂ O	
	Secondary post-mining mineral (relatively insoluble)	Anglesite	PbSO ₄
Antlerite		Cu ₃ (SO ₄)(OH) ₄	
Beaverite		PbCuFe ³⁺ ₂ (SO ₄) ₂ (OH) ₆	
Beudantite		PbFe ³⁺ ₃ (AsO ₄)(SO ₄)(OH) ₆	
Brochantite		Cu ₄ (SO ₄)(OH) ₆	
Goethite		α-FeOOH	
Jarosite		KFe ³⁺ ₃ (SO ₄) ₂ (OH) ₆	
Native sulfur		S	
Osarizawaite		PbCuAl ₂ (SO ₄) ₂ (OH) ₆	
Plumbojarosite		Pb _{0.5} Fe ³⁺ ₃ (SO ₄) ₂ (OH) ₆	
Scorodite		FeAsO ₄ .2H ₂ O	
Sideronatrite		Na ₂ Fe ³⁺ (SO ₄) ₂ (OH).3H ₂ O	
Wroewolfeite		Cu ₄ (SO ₄)(OH) ₆ .2H ₂ O	

Relative solubility in neutral pH water at ambient conditions is shown for secondary post-mining minerals according to Nordstrom and Alpers (1999), Bigham and Nordstrom (2000), Krause and Ettel (1988), Garvie (1999), Morris (1962) and D. K. Nordstrom (pers. comm. 2002).

ments were conducted on representative Fe-rich precipitates and efflorescences at JCU AAC. The qualitative mineral chemistry of selected sulfides was determined using a JEOL JXA840A electron microprobe (at JCU AAC). Microprobe analyses were performed on major mineral efflorescences present in Oakey Creek using a Cameca SX-100 (at Laval University, Quebec City, Canada). The microprobe analyses are regarded as semiquantitative because porous sample materials returned excessive total-element values compared to published halotrichite-dietrichite chemistries.

Water samples were collected for analysis of major cations and anions (waters unfiltered) and dissolved metals (waters filtered below 0.45 μm). Conductivity and pH were determined in the field. Chemical analyses were conducted by the James Cook University Australian Centre for Tropical Freshwater Research using argentometric titration (Cl^-), potentiometric titration (CO_3 , HCO_3), turbidometric spectrophotometry (SO_4), atomic absorption spectrometry for major cations (Ca, K, Mg, Na) and ICP-MS for dissolved trace elements (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, In, Mn, Mo, Ni, Pb, Sb, Se, Zn). The PHREEQC2 modelling program (Parkhurst & Appelo 1999) was used to establish the mineral phases in equilibrium with Oakey Creek and mine-drainage waters.

Laboratory experiments

Paste pH measurements were performed on powdered mine wastes following the procedure of Morin and Hutt (1997). In addition, three representative mine-waste materials from the Rio Tinto dump were subjected to short-term kinetic dissolution experiments. The experiment aimed to: (i) curtail sulfide oxidation in the waste samples; and (ii) establish whether the dissolution of secondary minerals influences the chemistry of 'first-flush' drainage waters emanating from the Rio Tinto waste dump. The waste samples (200 g of a 2–20 mm size fraction) were completely immersed in distilled water for a period of 1 day, 1 week and 1 month. All water was removed after 1 day and after 1 week. The mine wastes were then re-immersed in freshly distilled water. Conductivity and pH values of the leachates were measured at the conclusion of each time interval. The 1 day, 1 week and 1 month old leachates were submitted for chemical analysis using ICP-MS methods (Al, As, Ca, Cd, Cu, Fe, In, K, Mg, Mn, Na, Pb, S, Sb, Se, Zn; JCU AAC).

RESULTS

Waste dump material

PRIMARY MINERALOGY

Waste-dump materials are chemically and mineralogically heterogeneous. They display major (i.e. >1 wt%) median concentrations of Fe, Pb and S, minor (i.e. >100 ppm) As, Bi, Cu, Sb, Mn, Sn and Zn, and traces (i.e. <100 ppm) of Cd, Co, In, Se and W (Table 1). Such element distributions are consistent with the occurrence of relatively abundant sulfide minerals. Unweathered sulfide-bearing rocks are composed of major quartz (75–95 vol%), dickite (<1–

10 vol%), illite (<1–10 vol%), galena (<1–10 vol%), tetrahedrite (<1–8 vol%), sphalerite (<1–6 vol%), chalcopyrite (<1–5 vol%) and pyrite (<1–4 vol%) as well as minor to trace amounts (<1 vol%) of arsenopyrite, bournonite, cobaltite, stibnite, stannite, sternbergite, cassiterite and wolframite (Table 2). Some of the sulfide minerals contain variable amounts of trace elements, as indicated by qualitative electron microprobe analyses [tetrahedrite (Ag, As), galena (Ag, Se, W), sphalerite (Cd, In), wolframite (Se)].

SECONDARY MINERALOGY

Sulfidic dump materials are partly or completely oxidised with the development of secondary sulfides, oxides, hydroxides, arsenates and sulfates (Table 2). The Montalbion sulfide lodes were extensively weathered prior to mining, forming abundant secondary minerals (Dash *et al.* 1991). In addition, post-mining weathering processes have also resulted in the formation of secondary minerals. The distinction of pre- from post-mining secondary minerals is difficult to achieve because some minerals might have formed both prior to and after mining (Lottermoser 2003). However, post-mining minerals generally occur as mineral efflorescences coating the surfaces of other mineral grains.

At Montalbion, secondary sulfides and some of the sulfate phases (antlerite, brochantite) occur as pervasive replacements of primary sulfide disseminations and veins within the mine wastes. Moreover, some oxides (hematite, cuprite) are present as vein replacements and encrustations on rock surfaces, and minor goethite was identified as thin coatings on rock surfaces and vein replacements. The mineral coatings and efflorescences are regarded as post-mining reaction products, whereas pervasive replacements are thought to be pre-mining weathering phases (Table 2).

Most of the efflorescent minerals (with the exception of scorodite) are metal and/or alkali sulfates or hydrous sulfates (Table 2). Anglesite and plumbojarosite are the most abundant efflorescent minerals, with anglesite comprising up to 9 vol% and plumbojarosite up to ~3 vol% of the mine waste. An unknown Fe–Sb (oxy)hydroxide/oxide solid was observed as microscopic coating on quartz and tetrahedrite grains. This phase might represent either: (i) goethite with significant adsorbed Sb whereby the acidic pore waters caused the adsorption of anionic species such as SbO_3^- (Smith 1999); or (ii) an oxidation product of tetrahedrite such as senarmonite (Sb_2O_3), cervantite (Sb_2O_4) or tripuhyite (FeSb_2O_6) (Yakhontova *et al.* 1980), although no discreet Sb or Sb–Fe oxides could be identified.

The efflorescent minerals commonly occur close to their respective parent sulfides. For example, anglesite coats galena-rich mine wastes and chalcantite occurs on chalcopyrite-rich rocks. Rocks containing a polyminerally sulfide mineralogy are coated by polymetallic sulfates such as osarizawaite and beaverite. The efflorescences thereby display a wide range of habits, and the forms and faces of the efflorescences appear to be related to their solubility. Relatively insoluble minerals (e.g. anglesite, plumbojarosite, beaverite, osarizawaite) occur as subhedral granular masses that form earthy surface encrustations

(Figure 2b). In contrast, highly soluble efflorescences (e.g. melanterite, chalcantite, tamarugite) are present as euhedral grains in floury dustings on rock and adit surfaces (Figure 2c, d). This behaviour is likely attributed to the complete dissolution and removal of highly soluble minerals during rainfall events and reprecipitation of new crystals during dry periods.

LABORATORY EXPERIMENTS

Most waste-rock dump samples contain visible sulfides with modal amounts varying from <1 vol% to 20 vol%. It is therefore assumed that much of the total sulfur is present as sulfide S and to a lesser degree as sulfate S. Paste pH measurements of milled mine wastes confirm the fact that the waste is acid (average pH value of 4.2: Table 1). Hence, the net acid-producing potential of these materials is high. On the other hand, dump materials have a low acid-neutralisation capacity due to the lack of carbonate and the abundance of quartz, dickite and illite.

The immersion of mine wastes into distilled water for 1 day produced low pH, high conductivity leachates (pH 2.67–3.86, conductivity 384–990 $\mu\text{S}/\text{cm}$). Leachates collected after 1 week and 1 month generally had higher pH and lower conductivity concentrations (pH 2.89–4.66, conductivity 257–542 $\mu\text{S}/\text{cm}$). Furthermore, considerable concentrations of metals (Al, Cu, Fe, Pb, Zn), metalloids (As), alkalis (Ca, Mg, Na, K) and sulfur (presumably present as sulfate) were detected in the solutions. Metal values were as high as 108 mg/L Cu, 40 mg/L Zn, 25 mg/L Fe, 12.5 mg/L Pb, and 374 mg/L SO_4 . Generally, concentrations of most elements decreased with immersion time. Lead was a notable exception with leachate values increasing or remaining unchanged with immersion time. The abundance of soluble mineral efflorescences in the wastes and the relatively high concentrations of sulfate, metals and alkalis in the leachates suggest that the dissolution of sulfate efflorescences accounts for much of the detected leachate chemistry. A small amount of metal desorption from clay minerals and Fe (oxyhydr)oxides as well as

sulfide oxidation and consequent metal release might have occurred, particularly when the water was removed and replaced between experiment stages. However, the complete immersion of the waste in stagnant distilled water would not have allowed primary and secondary sulfide oxidation to proceed at a significant rate. Thus, the wetting of Montalbion mine wastes produces acidic 'first-flush waters' characterised by elevated sulfate and metal values (Cu, Zn, Fe). These element loads are due predominantly to the dissolution of secondary alkali and metal sulfate salts.

Stream sediments

Oakey Creek stream sediments in the Montalbion area range from very immature materials (gravel to cobble size) through sands to silts and muds deposited in low-energy settings. The sediments are dominantly composed of metasediment-derived detrital quartz with minor illite and rutile. Many stream sediments in the mine area and immediately downstream contain mineralised detritus (e.g. sulfidic vein material), Fe-rich precipitates (i.e. 'yellow-boy') and efflorescent salts.

Two stream-sediment samples collected upstream of the mine area are considered to represent background sample material and their fine-grained (<150 μm) and medium-grained (150 μm –2 mm) fractions have relatively low S and low metal and metalloid contents (Figure 3). Mining-influenced stream sediments contain distinctly higher element concentrations (Figure 3). Sulfur and metal-enriched sediments (i.e. median of four samples, <150 μm size fraction: As 34 ppm, Cu 289 ppm, Fe 2.9 wt%, In 1.5 ppm, Pb 169 ppm, S 789 ppm, Sb 20 ppm, Zn 306 ppm) particularly occur in the mining area up to 500 m downstream. The highest As, Cu, Fe, In, S, Sb and Zn concentrations occur in fine-grained sediments (<150 μm) 50 m downstream of the mine site. Moreover, the fine-grained (<150 μm) fraction of the stream-sediment population influenced by mining displays distinctly higher S, Cu and Zn concentrations than the medium-grained (150 μm –2 mm) fraction (Figure 3). In contrast, As, Pb and Sb concentrations are similar in both size fractions. This latter element distribution in the mining influenced population is interpreted as reflecting the importance of chemical dispersion of metalloids (As, Sb) in the Montalbion area. Furthermore, there are correlations of log-transformed data, in particular of Fe with As and Sb in the fine-grained (<150 μm) fraction and of S with Cu, In and Zn in the medium-grained (150 μm –2 mm) fraction. The Fe–As–Sb correlation is interpreted to represent the preferential adsorption/coprecipitation of dissolved As and Sb onto/with Fe-rich precipitates from acidic waters (Smith 1999). The correlation of S with In and Zn is interpreted to represent the association of In and Zn with sphalerite. The latter element distribution highlights the fact that active erosion of waste-dump materials leads to the physical dispersion of larger ore particles (e.g. sphalerite) into local stream sediments.

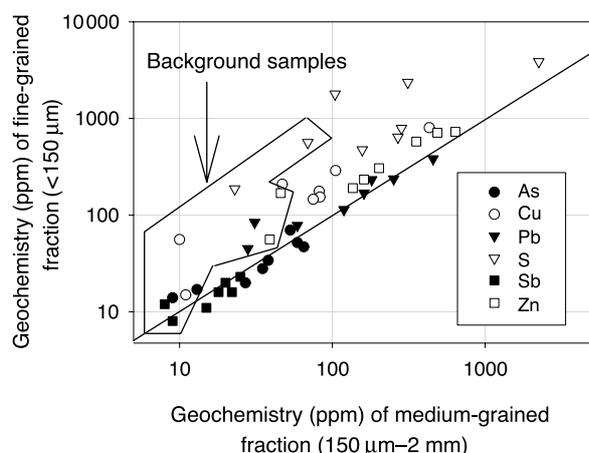


Figure 3 Geochemistry of Oakey Creek sediments. The concentrations of selected elements have been plotted for the fine- and medium-grained fractions of the background and mining-influenced populations. The line indicates equal concentrations of elements in both size fractions.

Waters

Surface waters in the Montalbion area show a range of element concentrations (Bartareau *et al.* 1998) (Table 3). Elements carried in solution in significant quantities

(>100 µg/L) are Al, Cd, Co, Cu, Fe, Mn, Ni and Zn. Drainage waters from the Rio Tinto waste dump and Oakey Creek surface waters immediately downstream of the acid mine drainage inflow have the lowest pH (3.3) and highest sulfate (596 000 µg/L) and metal values (Table 3).

During dry periods, the acidic waters of Oakey Creek are gradually neutralised, most likely due to buffering reactions with stream sediments. The waters reach a pH value of 4.8 approximately 0.5 km downstream of the mine site. Surface water at this location evaporates and/or enters the baseflow of the stream. Stream waters taken at distances up to 0.5 km from the mine site remain elevated in metal contents (Al, Cd, Co, Cu, Fe, Mn and Zn) (Table 3).

The lack of rainfall at the field site during 2001–2002 prevented the sampling of Oakey Creek during periods of flow. Background Oakey Creek water was collected upstream from the mine site during moderate flow by Bartareau *et al.* (1998). These waters have detectable Fe (1100 µg/L), Cu (150 µg/L) and Zn (90 µg/L) at a pH of 7.5. These waters are enriched in metals because the study area is part of the Herberton mineral province with over 3000 mineral occurrences and naturally high background metal concentrations. During moderate flow, drainage waters from the Rio Tinto waste dump add significant acid, metal-rich waters to Oakey Creek (pH 4.1, 77 000 µg/L Al,

700 µg/L Cd, 380 µg/L Co, 20 000 µg/L Cu, 8900 µg/L Fe, 14 000 µg/L Mn, 240 µg/L Ni, 300 µg/L Pb, 80 000 µg/L Zn) (Bartareau *et al.* 1998). During moderate flow, the stream waters are gradually neutralised, most likely due to buffering reactions with stream sediments and mixing with more alkaline waters. The waters reach a pH value of 6.4 approximately 1 km downstream of the mine site. Anomalous Zn concentrations (up to 1600 µg/L) are detectable in neutral pH waters up to 2 km downstream (Bartareau *et al.* 1998). After heavy rainfall coupled with extraordinary flow and dilution, Oakey Creek waters in the mining area display pH values (7.5) and Fe and Cu concentrations (400 µg/L and 150 µg/L, respectively) which are at or below background levels (Queensland Department of Natural Resources and Mines unpubl. data). However, Al (550 µg/L), Cd (3.1 µg/L) and Zn (560 µg/L) concentrations remain above background levels despite the dilution.

Computational modelling (PHREEQC2) was conducted on water samples collected during a period of no flow. The results indicate that the drainage waters emanating from the Rio Tinto waste dump are oversaturated with respect to alunite and barite. Oakey Creek waters taken distal to the drainage water input are oversaturated with alunite and barite as well as gibbsite, goethite and hematite, pointing to evaporation and mineral precipitation processes in the

Table 3 Water quality analyses of Oakey Creek (April 2002).

Parameter	Distance downstream from mine input		
	0 m	50 m	500 m
General			
pH	3.42	3.30	4.79
Conductivity (µS/cm)	1438	1294	859
Total dissolved solids (mg/L)	811	792	541
Hardness (mg/L as CaCO ₃)	374	211	308
Alkalinity (mg/L as CaCO ₃)	<0.1	<0.1	1.3
Major ions (mg/L)			
Na	9.8	8.6	28
K	7.3	8.3	7.5
Ca	92	45	69
Mg	35	24	33
SO ₄	525	596	362
Cl	10	8.3	7.5
HCO ₃	<0.1	<0.1	1.6
Trace metals (µg/L)			
Ag	0.5	0.5	0.5
Al	27 700	27 600	868
As	3	1	2
Ba	81	45	126
Be	8	8	<0.1
Cd	561	383	76
Co	273	222	59
Cr	<1	<0.1	<0.1
Cu	12 900	5430	288
Fe	12 100	11 200	372
In	0.4	0.4	0.3
Mn	18 500	11 900	9870
Mo	<0.1	<0.1	<0.1
Ni	172	133	25
Pb	52	67	36
Sb	0.2	0.1	2
Se	<1	<1	<1
Zn	60 700	45 600	13 100

streambed. However, such computational modelling provides only limited information on the chemical status of acid mine drainage waters due to the lack of thermodynamic data on phases typically found in acid mine drainage environments (e.g. sulfates, schwertmannite), inevitable disequilibrium within the waters and the effect of biotic processes on mineral precipitation.

Streambed precipitates

Mineral precipitates were observed in the Oakey Creek stream bed (Figure 4a) and include: (i) ochreous yellow-red-brown precipitates in stagnant water pools, between pool ripples, and on creek banks where acid mine drainage waters enter the stream; (ii) cream-green/blue, yellow and white efflorescent salts present at the edge of stagnant water pools; and (iii) metallic copper-coloured precipitates on a concrete pipe that subsequently proved to be mixtures of botryoidal tenorite and microcrystalline cuprite.

OCHRES

The ochreous precipitates occur as yellow-brown (Munsell colour value 7.5YR 5/8) honeycombed encrustations (i.e. schwertmannite and amorphous Fe-oxyhydroxides), dark red-brown (2.5YR 4/8) concretions (i.e. schwertmannite and goethite), and yellow-brown (10YR 6/6) flocculant precipitates (i.e. goethite). Schwertmannite displays two major habits: the characteristic 'pin-cushion' morphology of radiating fibrous crystals (Figure 3b) (Bigham *et al.* 1994), and hollow tubes of radiating crystals that produce the honeycomb appearance to the naked eye (Figure 4c). The latter texture might be due to the precipitation of schwertmannite onto plant roots that have since decayed. Goethite displays a subhedral rod-like morphology commonly observed in mine drainage precipitates (Bigham 1994).

Geochemical analyses of selected ochres show that the schwertmannite–amorphous Fe-oxyhydroxide and schwertmannite–goethite mixtures contain appreciable

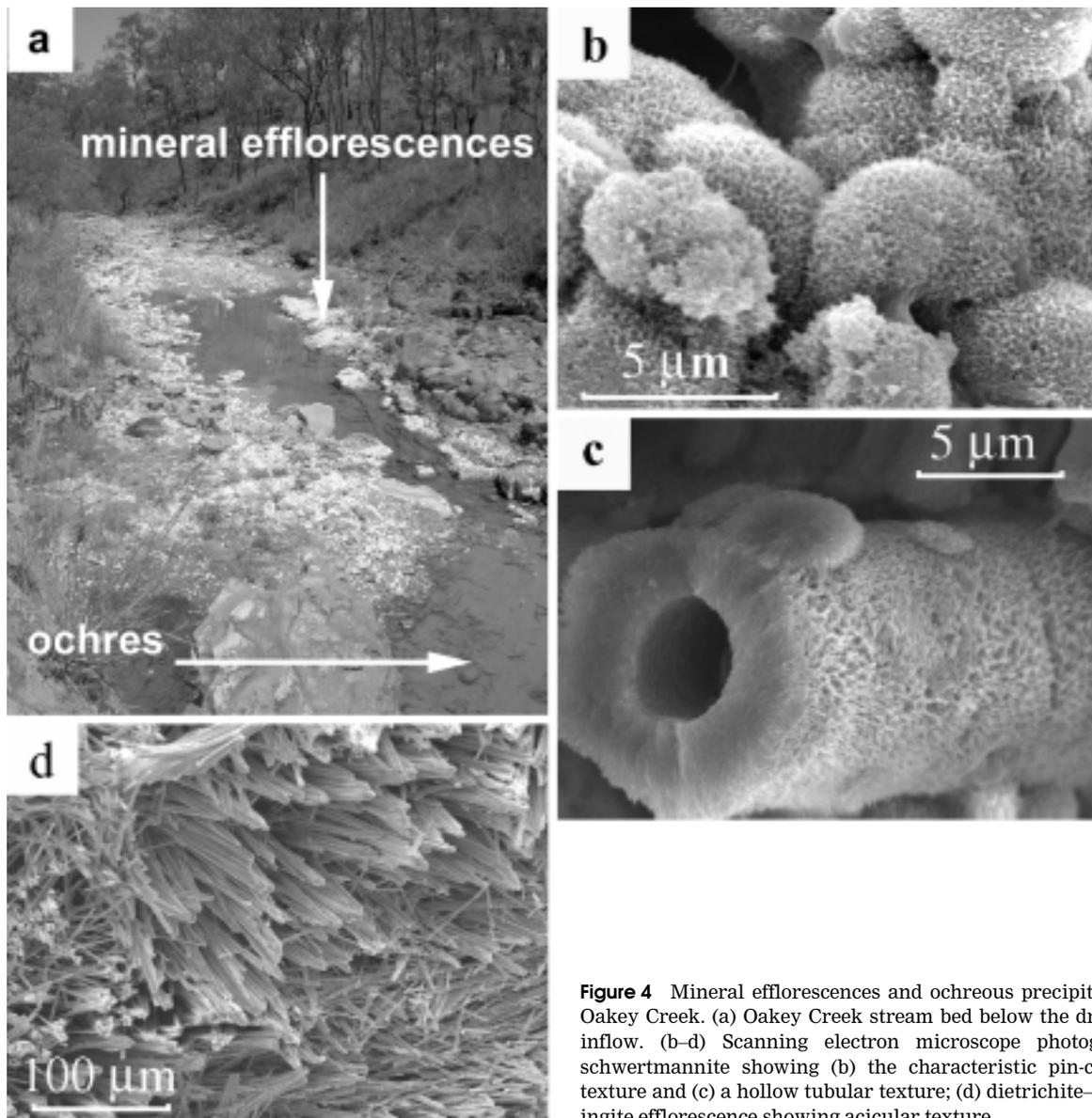


Figure 4 Mineral efflorescences and ochreous precipitates in Oakey Creek. (a) Oakey Creek stream bed below the drainage inflow. (b–d) Scanning electron microscope photographs: schwertmannite showing (b) the characteristic pin-cushion texture and (c) a hollow tubular texture; (d) diatrichite-pickeringite efflorescence showing acicular texture.

amounts of Al, As, Cu, In, Fe, Mn, S, Pb and Zn. Compared with Oakey Creek water collected from the same site, both types of ochreous precipitates show preferential enrichments in Fe, As and Sb (Figure 5). The schwertmannite–amorphous Fe-oxyhydroxide precipitates also show preferential enrichment in In (Figure 5). In contrast, surface waters are relatively enriched in Al, Cd, Cu, Mn and Zn. The preferential precipitation of As and Sb into the ochreous precipitates reflects coprecipitation and pH-dependent metal adsorption (Smith 1999), and is in agreement with concentration processes previously established from acid mine drainage environments (Fuge *et al.* 1994; Carlson *et al.* 2002; Ashley *et al.* 2003). In contrast, there is no previous knowledge on the behaviour of In in acid surface waters. However, the relative In enrichment detected in the ochreous precipitates suggests that the element is preferentially adsorbed to Fe oxyhydroxides and Fe hydroxysulfates under low pH conditions.

MINERAL EFFLORESCENCES

Efflorescent salts occur as globular aggregates comprising fine-grained acicular and prismatic crystals (Figure 4d). Identified efflorescences include hydrous alkali and metal sulfates (Table 4). Geochemical analyses of selected efflorescences reflect the chemistry of Oakey Creek water (Figure 5). X-ray diffraction patterns of the most abundant phase correspond to apjohnite ($\text{MnAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$; powder diffraction file no. 29–886). However, semiquantitative electron microprobe analyses of this abundant efflorescent salt returned elemental weight percentages ($\text{S} > \text{Al} > \text{Zn} > \text{Mg} > \text{Mn} > \text{Cu} > \text{Ca}$) that clearly do not match the apjohnite composition. Extensive solid solution is known to occur between halotrichite ($\text{FeAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), pickeringite ($\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), and apjohnite (Jambor *et al.* 2000). Hence, the efflorescent salt from Montalbion is likely a member of the dietrichite–pickeringite–apjohnite series rather than pure apjohnite. The apjohnite Joint Committee on Powder Diffraction Standards (JCPDS) powder-diffraction file is based on the work of Menchetti and Sabelli (1976), who provided only a partial mineral chemical analysis. This type of material might contain elements other than Mn and, therefore, the

JCPDS powder-diffraction file of apjohnite needs to be refined.

DISCUSSION

Acid mine drainage generation and first-flush waters

Much of the research into acid mine drainage development at mine sites has been related to the oxidation of sulfides. This previous research has shown that the oxidation of Fe-bearing sulfides, especially pyrite and pyrrhotite, leads to the production of acidic, metal-laden drainage waters. At Montalbion, the mine waste generally contains <1 vol% pyrite, yet the chemistry of mine-drainage waters and static and kinetic test data clearly indicate that the waste is acid-generating. Although the relatively low concentration of pyrite may still generate substantial acid, several other mineral reactions are also likely responsible for the acid production. First, Montalbion mine waste contains major amounts of chalcopyrite, Fe-bearing sphalerite and tetrahedrite and their oxidation also generates acid (Yakhontova *et al.* 1980; Jennings *et al.* 2000). Second, the waste contains abundant highly soluble efflorescences, some of which will generate acid on their oxidative dissolution. The Fe^{2+} -bearing minerals melanterite, metavoltine and szomolnikite and the Al^{3+} -bearing minerals K-alum, spangolite and tamarugite produce acidity on their dissolution due to the hydrolysis of Fe^{3+} and Al^{3+} , respectively (Cravotta 1994; Jambor 1994; White *et al.* 1999; Frau 2000; Jambor *et al.* 2000). For example, melanterite might dissolve as follows (Frau 2000):



Moreover, the release of Fe^{2+} into water and its oxidation to Fe^{3+} does not necessarily result in the precipitation of Fe-hydroxides. Available Fe^{3+} can also trigger more sulfide oxidation (Alpers & Nordstrom 1999; Keith *et al.* 1999; Plumlee 1999). Third, desorption of H^+ from the surfaces of secondary sulfates and clays might also contribute significant acidity to drainage waters. Finally, the lack of suitable acid-neutralising minerals in the Montalbion

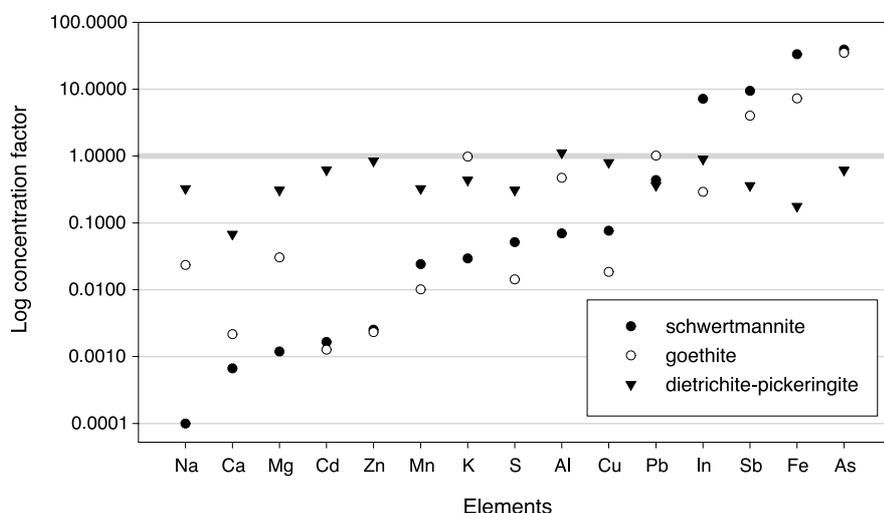


Figure 5 Concentration factors of mineral efflorescence (dietrichite–pickeringite) and ochreous precipitates (schwertmannite, goethite) from Oakey Creek. The concentration factor is the ratio of the element concentration in the solid to the element concentration in Oakey Creek water. The elements are ordered so that element concentration factors in the ochres increase from left to right in the diagram.

waste allows the unhindered production of acidic, metal-rich drainage waters. The abundance of illite and dickite is low, their reaction kinetics are slow and the minerals provide only limited acid neutralisation and buffering at a pH plateau of 3.5–4.1 (Plumlee 1999; Stromberg & Banwart 1999; Jambor *et al.* 2002). Thus, at Montalbion, pronounced acid mine drainage generation is due to the combination of sulfide oxidation, dissolution of acid-generating mineral efflorescences and limited buffering from gangue phases. Mineral efflorescences with low solubility (anglesite, plumbojarosite, scorodite, antlerite, brochantite) retain Pb and minor As and Cu in the waste dump, whereas readily soluble minerals (melanterite, chalcantite) release Fe, Zn and Cu to pore and drainage waters. Hence, during rainfall events, minerals with low solubilities become enriched on rock surfaces as the highly soluble minerals are removed. The mineral dissolution experiments also illustrate that first-flush drainage waters are enriched in Fe, Zn, Cu and sulfate, with these ions being derived from the dissolution of mineral efflorescences. Rapid depletion of the highly soluble efflorescences results in a decrease in metal and sulfate leachate concentrations with ongoing flushing.

The generation of drainage waters from sulfidic mine wastes in a seasonally wet climate is controlled by wetting and drying cycles (Perkins *et al.* 1997). Waste piles are intermittently wetted by meteoric water and runoff; they are dried by drainage and evaporation (Perkins *et al.* 1997). In the case of partly oxidised mine waste with high concentrations of secondary minerals like at Montalbion, intense wetting of these materials will release temporarily stored acidity and metals from soluble secondary minerals and produce first-flush waters of significant acidity, salinity and metal content. These mobilised elements and com-

pounds might become permanently or temporarily stored downstream from the waste in ochreous precipitates or evaporative mineral efflorescences coating local streambeds.

Acid mine drainage into receiving stream

At Montalbion, low pH (3.3–4.1) sulfate- and metal-rich waters emanate from the mine site and upon oxygenation precipitate Fe-rich ochres in the Oakey Creek bed. The prevalent pH and hydrochemical conditions favour the formation of schwertmannite and goethite (Bigham *et al.* 1996). Adsorption and coprecipitation processes account for the preferential As–Sb–In enrichment of secondary Fe minerals (Carlson *et al.* 2002; Ashley *et al.* 2003). Relative metal concentration factors of these ochres (Pb > Cu > Zn > Cd: Figure 5) agree well with the metal sorption curves of Smith (1999). The resulting water chemistry is characterised by elevated sulfate, alkali, Al, Zn, Cu, Mn, Fe and Cd concentrations. During the dry season, evaporative concentration of solutes occurs, resulting in the precipitation of efflorescences. During heavy rainfall events, flushing of the creek bed with neutral-pH water results in the dissolution of soluble efflorescent salts and consequent metal remobilisation and transport downstream, particularly of Zn and Cd.

Indium is a trace element of many sulfide ores and is commonly hosted by sphalerite (Schwarz-Schampera & Herzig 2002). Although many In-bearing sulfide ores are acid mine drainage generating, the behaviour of In in acidic surface waters is largely unknown. At Montalbion, waste rocks (In/Zn ratios: ~1/180) release In to acid mine drainage waters through the oxidative dissolution of sphalerite. The seepage waters enter Oakey Creek where In is preferentially incorporated into the ochreous streambed precipitates, leading to exceptionally low In/Zn ratios in Oakey Creek waters (~1/150 000). Thus, In adsorption onto and coprecipitation with Fe oxyhydroxides and hydroxy-sulfates cause In attenuation in acidic waters.

Table 4 Stream bed precipitates identified in the acid mine drainage-affected Oakey Creek.

Mineral	Formula
Major	
Schwertmannite	$\text{Fe}_8\text{O}_8(\text{SO}_4)(\text{OH})_6$
Goethite	$\text{Fe}(\text{OH})_3$
Dietrichite-pickeringite-apjohnite type phase	$(\text{Zn,Mg,Mn})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$
Kalinite	$\text{KAl}(\text{SO}_4)_2 \cdot 11\text{H}_2\text{O}$
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Minor	
Chalcantite	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$
Kroehnkite	$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$
Zaherite	$\text{Al}_{12}(\text{SO}_4)_5(\text{OH})_{26} \cdot 20\text{H}_2\text{O}$
Trace	
Aluminite	$\text{Al}_2\text{SO}_4(\text{OH})_4 \cdot 7\text{H}_2\text{O}$
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$
Bonattite	$\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$
Cuprite	Cu_2O
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Gunningite	$(\text{Zn,Mn})\text{SO}_4 \cdot \text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Pentahydrate	$\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$
Picromerite	$\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
Rostite	$\text{AlSO}_4(\text{OH,F}) \cdot 5\text{H}_2\text{O}$
Tenorite	CuO

CONCLUSIONS

The Montalbion mining area contains several waste dumps located on steep slopes that are actively eroding and are subject to dynamic landsliding. The waste dumps are mineralogically and geochemically heterogeneous with high concentrations of Fe, Pb and S, minor As, Bi, Cu, Mn, Sb, Sn and Zn, and traces of Cd, Co, In, Se and W. The unweathered waste-dump mineralogy consists of major quartz (75–95 vol%) with subordinate clay and sulfides (1–10 vol%) (galena, tetrahedrite, sphalerite, chalcopyrite, pyrite). Extensive weathering of the sulfide minerals, both prior to and post-mining, has resulted in the formation of abundant secondary metal and/or alkali (hydrated) sulfates. Post-mining efflorescences generally occur as thin encrustations or floury dustings on other mineral grains.

Ephemeral acid mine drainage from the Montalbion mining area runs into Oakey Creek resulting in acidic (pH 3.3–4.1) surface waters with elevated sulfate and Al, Cd, Co, Cu, Fe, Mn, Ni and Zn concentrations throughout the year,

except during periods of heavy rainfall and resulting extraordinary stream flow in Oakey Creek. The generation of acid mine drainage at Montalbion is probably caused by a combination of sulfide (chalcopyrite, sphalerite, tetrahedrite, pyrite) oxidation, the dissolution of Fe²⁺- and Al³⁺-bearing secondary sulfate efflorescences, the desorption of H⁺ from mineral surfaces, and a paucity of acid-neutralising minerals. Upon entering Oakey Creek, oxygenation of the acid mine drainage promotes Fe precipitation, resulting in extensive 'yellow-boy' formation (amorphous Fe, schwertmannite, goethite) on the streambed. Evaporation of Oakey Creek waters during dry periods leads to the precipitation of efflorescent hydrous metal and alkali sulfates. Geochemical analyses of the Fe-rich precipitates reveal preferential concentration of As, Sb and In into the ochres through adsorption/coprecipitation processes with Fe hydroxides and hydroxysulfates.

The wetting/drying cycle of the tropical climate has an important control on the chemistry of both the mine drainage and Oakey Creek waters. During dry periods, evaporation leads to the formation of soluble efflorescent mineral salts on the waste dump and on the edges of stagnant pools in Oakey Creek. Rainfall events dissolve the highly soluble efflorescences in the waste dump, resulting in acidic 'first-flush' drainage waters with elevated sulfate, Fe, Cu and Zn. Less-soluble efflorescent phases retain Pb and As in the waste rock. Continuing heavy rainfall flushes Oakey Creek with neutral pH waters dissolving the efflorescences on the streambed, remobilising sulfate, Al, Cd, Cu, Mn and Zn.

Chemical characteristics of ephemeral drainage waters from mine sites in tropical climates can vary greatly during different seasons. An important control on drainage-water chemistry is the speciation and solubility of secondary efflorescent minerals developed in mine-site environments.

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