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Mobility and microbially mediated mobilization of gold and arsenic in soils from two gold mines in semi-arid and tropical Australia

F. Reith *,[1], D.C. McPhail

Cooperative Research Centre for Landscape Environments and Mineral Exploration, Department of Earth and Marine Sciences, The Australian National University, Canberra, Australia

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Abstract

The mobility and microbially mediated solubilization of Au and As in regolith materials from two Au mines in Australia, i.e., the Peak Hill Gold Mine in semi-arid New South Wales and the Hit or Miss Gold Mine in tropical northern Queensland, was studied using a combination of geochemical and microbiological techniques. Gold is highly mobile in both environments, the mobility of Au increases with increasing degree of weathering of host materials, and the resident microbiota are capable of mediating its solubilization. The results of the microcosm experiments demonstrate that the activity of microorganisms needs to be taken into account when studying the mobility and solubilization of Au in the Australian regolith. In primary, unweathered mineralization material from the Hit or Miss mine 99 wt% of Au was extracted only in the strongest final step of the sequential extractions, in concentrated *aqua regia.* In alteration zone material from the Peak Hill Gold Mine 80 wt% of Au was associated with the operationally defined Mn and Fe oxides. In contrast, in auriferous soils overlying mineralization at both sites 90–95 wt% of Au was associated with the operationally defined exchangeable, clay-bound and organic fractions. Microcosm experiments were incubated biologically active and inactive (sterilized) in 1:4 (w/v) aqueous slurries at 25 °C in the dark for up to 95 days. In biologically active microcosms with soils from the Peak Hill- and the Hit or Miss Gold Mines approximately 55 wt% (907 ng g^{-1} d.w. soil) and 20 wt% (233 ng g^{-1} d.w. soil) of the total Au, respectively, was solubilized during the incubation. In contrast, no or significantly lower Au concentrations were observed in biologically inactive microcosms. The mobility and microbially mediated release of As was limited at both sites and appears to be mostly controlled by abiotic adsorption and desorption on Mn- and Fe-oxides. Arsenic has a low solubility in the more mobile fractions and is mostly associated with Mn- and Fe-oxides and the residual fraction. The release of As was not elevated in biologically active compared to inactive microcosms from the Peak Hill Gold Mine. In contrast, in biologically active microcosms with samples from the Hit or Miss Mine elevated concentrations of As were detected in solution compared to the biologically inactive experiments.

1. Introduction

The formation of lateritic Au deposits and anomalies in the regolith depends on the mobilization, transport and precipitation of Au in the weathering environment (Wilson, 1984). Sequential extractions have been used to study the association of Au and other trace elements with principle regolith fractions (Boyle, 1979; Lintern, 1989; Gray and Lintern, 1998; Xueqiu, 1998), and to infer element mobility. Other studies have shown that Au is mobile in the Australian regolith in and around mineralized zones (Mann, 1984; Gray and Lintern, 1998; Reith et al., 2005). For instance, at the Tomakin Park Gold Mine in south eastern New South Wales approximately 50 wt% of the total Au in the Ah-horizon overlying the mineralized zone was associated with the water-, ammonium-acetate-, sodium pyrophosphate- and hydroxylamine-hydrochloride-soluble fractions; in contrast, in the unweathered quartz-vein material more than 95 wt% of the Au was extractable only with concentrated *aqua regia* and appeared to be strongly bound in pyrite and arsenopyrite (Reith et al., 2005).

* Corresponding author. Fax: +61 8 8303 8350.
E-mail address: frank.reith@csiro.au (F. Reith).
[1] Present address: CSIRO Land and Water, PMB 2, Glen Osmond, 5064, South Australia, Australia.

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There is growing evidence that microbiota contribute to the biogeochemical cycling of Au in the Australian regolith (Reith and McPhail, 2006; Reith et al., 2006). A microcosm study conducted by Reith and McPhail (2006) with auriferous soils from the Tomakin Park Gold Mine has shown that the indigenous microbiota of these soils are capable of solubilizing up to 80 wt% of the finely disseminated Au adsorbed to the solid soil fractions as well as Au from the added Au pellets within 30–40 days of incubation, after which the solubilized Au was either adsorbed to the solid fractions or precipitated; in contrast, little to no Au was solubilized in biologically inactive (i.e., sterilized) microcosms. This behavior correlated with a change in the heterotrophic bacterial community structure in the microcosms from a dominantly carbohydrate- to an amino-acid utilizing population. They also found that the bacterial community in the early stages of the incubation produced amino acids, which may contribute to the solubilization of Au. Further evidence for this comes from in vitro studies with pure bacterial cultures, where it has been shown that microbially produced amino acids solubilize and form strong complexes with Au (Pares and Martinet, 1964; Lyalikova and Mockeicheva, 1969; Korobushkina et al., 1974; Korobushkina et al., 1983).

Arsenic is an important pathfinder element for Au and commonly used in mineral exploration, because of its generally wider halo around primary mineralization, which makes it easier to detect in geochemical surveys (Cavender, 1963; Boyle and Jonasson, 1973; Boyle, 1979; Yang and Blum, 1999). In primary mineralization As and Au are commonly associated with arsenopyrite (FeAsS; Boyle, 1979; King, 2002). Oxidation and subsequent breakdown of the mineral by iron- and sulfur oxidizing bacteria leads to the mobilization of As and Au (Nordstrom and Southam, 1997; Garcia-Sanchez and Alvarez-Ayuso, 2003; Papassiopi et al., 2003). The acidic and oxidizing conditions established by the bacteria not only create favorable conditions for indirect As and Au mobilization by dissolving the arsenopyrite, they also increase dissolved concentrations of these metals, and thus may contribute to their dispersion into the regolith (Bayard et al., 2006).

In the regolith the speciation of As is controlled by the pH and redox conditions, (Smedley and Kinniburgh, 2002; Oremland and Stolz, 2003); where arsenate species (i.e., As(V) as $H_2AsO_4^-$ and $HAsO_4^{2}$) dominate in oxic zones (Eh > 400 mV), and arsenite species (i.e., As(III) as $H_3AsO_3^0$ and $H_2AsO_3^-$) dominate in anoxic zones (Eh < 400 mV) at typical pH conditions between 4 and 8 (Smedley and Kinniburgh, 2002; Oremland and Stolz, 2003). The concentrations of dissolved arsenate and arsenite are controlled by surface complexation reactions on oxides and hydroxides of Al, Mn and especially Fe (Smedley and Kinniburgh, 2002; Oremland and Stolz, 2003). Arsenate is strongly adsorbed to Al-, Mn- and Fe-oxides under typical pH conditions, and as such unlikely to be mobile, whereas arsenite adsorbs less strongly and to fewer minerals and is the more mobile form (Smedley and Kinniburgh, 2002). Turnover of arsenate to arsenite and vice versa is used by a range of bacteria common in the regolith to gain metabolic energy, and thus resident microbiota may also contribute to the speciation and mobility of As in the regolith (Ahmann et al., 1997; Oremland and Stolz, 2003).

While these findings suggest that Au and As may be highly mobile in and around mineralized zones in the Australian regolith, a recent study using sequential extractions with samples from the Tomakin Park Gold Mine suggests that the mobility of As, in contrast to Au mobility, is limited (Reith et al., 2005). There also is a need to understand the influence of microbial processes on the solubilization of Au and As under a wider range of environmental conditions. Therefore, the aims of this study are to: (i) infer the mobility of Au and As in regolith samples from a semi-arid and a tropical site by determining their fractionation using sequential extractions on progressively weathered materials; and (ii) assess the microbially mediated solubilization of Au and As in the different regolith materials using microcosms. Samples of auriferous soils and deeper regolith materials overlying the deposits were obtained from the Peak Hill Gold Mine in semi-arid New South Wales, and the Hit or Miss Mine in the Palmer River Goldfields in tropical north eastern Queensland.

2. Study area description

2.1. The Hit or Miss Gold Mine

The geological, mineralogical, metallogenic, regolith, vegetational and climatic description of the Hit or Miss Gold Mine is summarized after Bultitude and Donchak (1992). The Hit or Miss Gold Mine is an abandoned mine located 3.4 km east of the abandoned township of Maytown in the Palmer River Goldfields in north eastern Queensland at 16°03′32″S and 144°19′09″E, as shown in Fig. 1. It was mined from 1878 to 1909 and produced approximately 4000 oz of Au. The deposit is set in the Hodgekinson Formation, which is part of the Hodgkinson Province. Gold occurs in quartz reefs in the Hodgkinson Formation of the Maytown district and in narrow quartz veins in the Dargalong Metamorphics in alluvial bars within the Palmer River. The dominant host lithiologies are greywacke, siltstone, mudstone and metamorphic phyllite, and the surrounding bedrock is highly weathered. The primary deposit consists of a 107 m by 0.3–0.5 m wide quartz Au vein hosted in phyllite, siltstone and greywacke, which strikes at 120–130° and dips 85–90° to the southwest. In the primary ore, Au occurs within the arsenopyrite and pyrite in solid solution or as small inclusions.

Extensive erosion since the Tertiary combined with steep dips and dominance of interlayered arenite and mudstone units have produced intensively dissected land surfaces. A typical regolith profile (thickness) consists of a 0.5–1 cm A-horizon, a 15–20 cm B-horizon, which are underlain by an intensely weathered saprock C-horizon. The soil texture

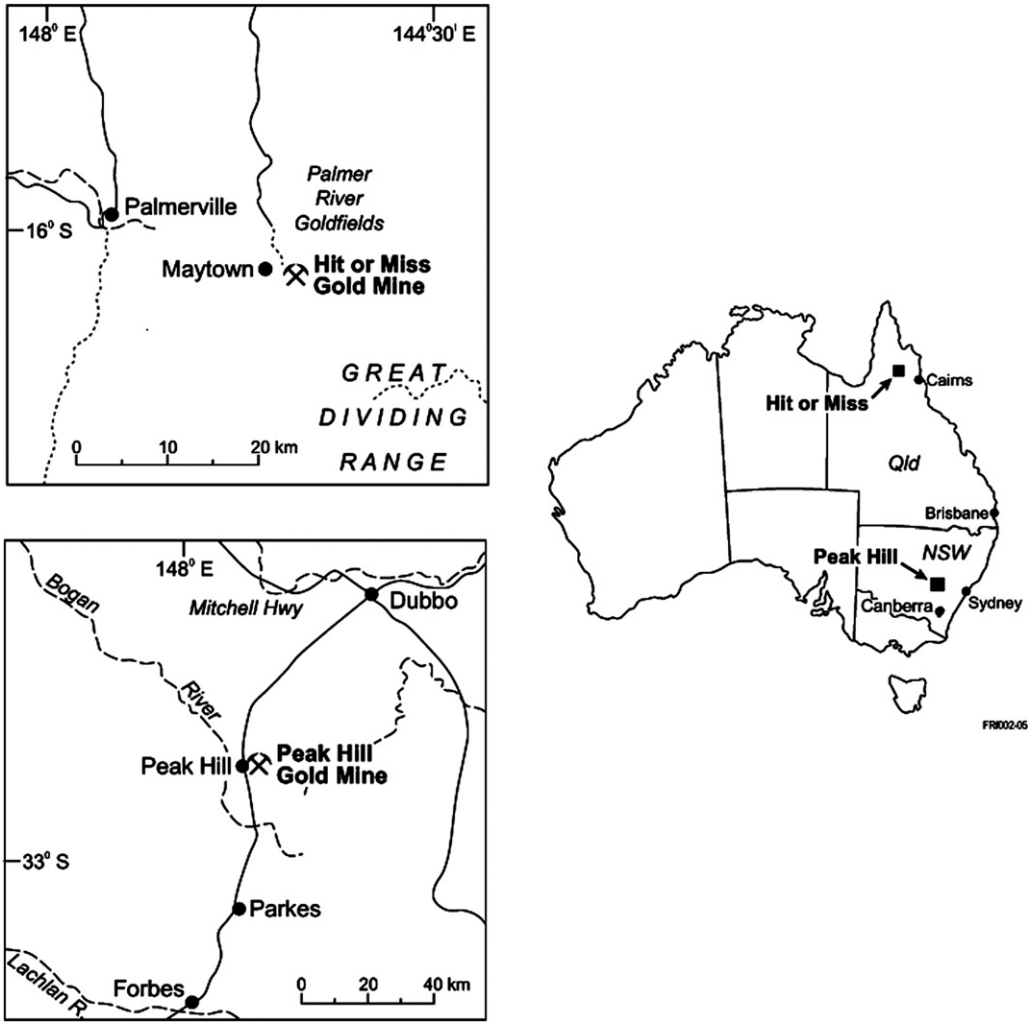


Fig. 1. Location map of the Hit or Miss Gold Mine in northeastern Queensland and the Peak Hill Gold Mine in New South Wales, Australia.

is silty loam with gravel content of up to 40 vol %, as determined in the field after McDonald et al. (1998), and the soil/regolith pH (1:5 w/v in H_2O; Rayment and Higginson, 1992) approximated 5.0 for the soil and quartz samples. The climate is tropical monsoonal with wet and dry seasons, an average annual rainfall of 1000 mm and mean temperatures ranging from 17 to 36 °C (Bureau of Meteorology, 1989, 2000). The vegetation in the region consists of savannah woodlands dominated by *Eucalyptus* sp. and *Acacia* sp. with an understorey of short- to medium-height grasses, which are dormant during the dry season. Ironbark (*Eucalyptus cullenii* and *Eucalyptus shirleyi*) are the most common tree species at the sampling site, and other trees are scattered throughout the area and include bloodwoods (*Eucalyptus dichromophloia* and *Eucalyptus polycarpa*).

2.2. The Peak Hill Gold Mine

The geological, mineralogical, metallogenic, regolith, vegetational and climatic description of the Peak Hill Gold Mine is summarized after Allibone (1998) and Chapman (2003). The Peak Hill Gold Mine is situated east of the township of Peak Hill in central western New South Wales, Australia, at 32°43′22″S and 148°11′42″E, as shown in Fig. 1. Alluvial Au was discovered in 1889 in drainage channels on the slopes of the Peak Hill and mining of the alluvial deposit and subsequently the oxide deposit, commenced in 1890. Over a 100-year history, the Peak Hill Gold Mine has produced over 200,000 oz of Au. The deposit is positioned on a prominent outcrop approximately 80 m above the surrounding residual soil and alluvial plain. Geologically, the deposit is located in the Lachlan Fold Belt in a high strain zone between the Parkes Thrust to the west and the Narromine Tumut Fault belt and is hosted in andesitic lavas and volcanogenic sediments of the Late Ordovician Goonumbla Volcanics. The central mineralization is marked by intense and pervasive alterations, which form an elongate zone of 3.3 km length and 0.6 km width where the textures of the host andesitic volcanic and volcanoclastic rocks have been completely altered. The alteration shows broad zonation features with an outer propyllitic chlorite–clay–hematite–pyrite assemblage and an inner complex of advanced argillic alteration consisting

of vuggy residual silica pyrophyllite–pyrite ± clay sericite that displays all of the characteristics of a high sulphidation style epithermal deposit. Gold mineralization is found throughout the alteration zone. The oxidized main ore body was approximately 300 m long, 50 m wide and extended from the surface down to 90 m. Gold exists mainly as sub-micrometer-sized particles in the pyrite; secondary Au grains have also been discovered in the ore body and indicate the mobilization and enrichment of Au in the supergene environment.

The regolith cover comprises mostly thin skeletal soil over saprolite and saprock. Distinguishing saprolite from soil is difficult, because of the complete destruction of original rock fabric due to hypogene alteration. The soil/regolith profile (thickness) at the sampling site consisted of a 1 cm A-horizon, a 15–20 cm B-horizon and an 80 cm saprolite horizon underlain by saprock. The soil texture is clay loam (after McDonald et al., 1998) and the pH (1:5 w/v in H_2O; Rayment and Higginson, 1992) is approximately 4.5 for the soil and saprolite samples and 5.0 for the oxidized material. The climate in the area is semi-arid with 550 mm annual rainfall distributed though the year but with a slight peak in summer, summer temperatures of 18–33 °C and winter temperatures of 5–15 °C (Bureau of Meteorology, 1989, 2000). Remnants of the natural vegetation are located on the hill and consist mostly of cypress pine (*Callitris* sp.) and ironbark (*Eucalyptus sideroxylon*) and other eucalyptus species (*Eucalyptus dwerii*; *Eucalyptus dealbata*), and scrubs consist mostly of cough bush (*Cassina laevis*).

3. Materials and methods

3.1. Sampling procedures and locations

Oxidized alteration zone material (OAZM) from the mine pit and samples of the soil overlying the mineralization were collected from the Peak Hill Gold Mine in January 2003. Soil and vein-quartz materials from the Hit or Miss Gold Mine were collected in May 2003. Samples for sequential extractions and microcosm experiments were collected using a flame-sterilized hammer, hand shovel and sieve. At the Peak Hill Gold Mine soil and saprolite samples were collected from 0 to 20 cm and 80 to 100 cm depth, respectively. Oxidized alteration zone materials were collected from the main pit wall from approximately 80 m below the natural ground surface. At the Hit or Miss Gold Mine soil samples were collected from depths of 0 to 10 cm and samples of the weathered phyllitic host rock were taken from 50 cm depth. Samples from the unweathered (QVMU), moderately (QVMW 1) and highly (QVMW 2) weathered quartz vein materials were taken from an outcrop close to the surface. Soil samples were sieved onsite to <2 mm size, stored in sterile plastic bags and transported over ice to the laboratory. Quartz-vein material and oxidized alteration zone material were hammered to rock chips onsite using the method described by Hirsch et al. (1995), ground under sterile conditions in the laboratory using a tungsten-carbide ring mill and sieved to <200 μm size.

3.2. Total and sequential extractions

Total Au concentrations of all materials were determined using *aqua regia* digests conducted in triplicate following a procedure developed by Reith et al. (2005). Five grams of sample were digested for 24 h in 30 ml concentrated *aqua regia* at 25 °C. The supernatant was filtered through a No. 4 Whatman paper filter and diluted with double deionized water to final HNO_3 and HCl concentrations of approximately 2 and 0.7 vol %, respectively. To assess the fractionation of Au and As in the solid regolith fractions and deduce changes in mobility of these elements with increased weathering of the host materials, sequential extractions were conducted. The sequential leaching procedure used in this study was developed by Reith et al. (2005) to study Au and As fractionation, and is based on methods used in previous studies (Chao, 1984; Hall et al., 1995, 1998; Xueqiu, 1998; Gray et al., 1999; Carbonell-Barrachina et al., 2004). The reagents and operationally defined fraction for each extraction were: (i) double deionized water for the water-soluble fraction, (ii) 1 M ammonium acetate (NH_4OAc) for the exchangeable, clay- and carbonate-bound fraction, (iii) 1% sodium pyrophosphate ($Na_4P_2O_7$) for the organic fraction, (iv) 0.25 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 0.25 M hydrochloric acid (HCl) for the amorphous Fe and Mn oxides fraction, (v) 4 M HCl for the crystalline Fe-oxide fraction, and (vi) conc. *aqua regia* for residual Fe oxides and silicates. The procedure for the first five extraction steps was: (1) 4 g of the sample were added to 50 ml Falcon tubes; (2) 40 ml of leaching solution were added; (3) the tubes were shaken for 6 h at 25 °C; (4) the tubes were centrifuged for 30 min at 4000 rpm after each extraction step; (5) the supernatant was decanted and filtered through Whatman No. 4 paper; (6) the residue was allowed to dry in air overnight at 60–70 °C; (7) the next leaching solution was added; and (8) steps (3) to (7) were repeated for each leaching step. The final *aqua regia* extraction was conducted with 20 ml conc. *aqua regia* for 24 h. All extract solutions were stored in the dark at −20 °C until analysis (Reith et al., 2005). Note that the extractions are operationally defined and may not necessarily reflect the fractions that are intended in any of these methods (Chao, 1984; Hall et al., 1995, 1998; Xueqiu, 1998; Gray et al., 1999). All selective extractions of were conducted in duplicate to assess the reproducibility, which was found to be within 10%.

3.3. Microcosm experiments

Batch-type microcosm experiments with soils, saprolitic- and vein-quartz materials were incubated as aqueous slurries on a rotary shaker at 25 °C for up to 95 days. Seventy-five

grams (dry weight) of solid material (biologically active or inactive—see below) plus 300 ml double deionized sterile water (1:4 w/v; chosen to allow up to ten 5 ml water samples per experiment) were placed under sterile conditions into 500 ml infusion bottles (Ochs, Bovenden-Lenglern, Germany). All microcosms were incubated under oxic conditions and specific conditions for all experiments are listed in Table 1. Microcosms were named according to a code based on the sampling sites, materials and experimental conditions used, for instance HM-S-a stands for a microcosm with Hit or Miss Gold Mine soil that was incubated biologically active. Microcosms were plugged with cotton wool to allow O_2 exchange with the atmosphere. Dissolved oxygen (DO) levels in the water were monitored in HM-S-a and in PH-S-a using a 1469-00 OX-2P dissolved-O_2 kit (Hach, Belgium) at day 10 and at the end of the incubation and ranged between 5.1 and 6.5 mg L^{-1}, similar to the results of Reith and McPhail (2006) and compared to DO = 7.9 mg L^{-1} in water saturated with atmospheric O_2 at 25 °C; other experiments were assumed to contain similar concentrations of oxygen. Five milliliters of aqueous samples were aseptically collected from all experiments using sterile one-way plastic syringes (Terumo, Tokyo, Japan), and centrifuged at 15,000 rpm for 20 min in a microfuge (Eppendorf, Germany). The supernatant was decanted, filtered through a Whatman No. 4 paper filter and analyzed for Au and As using inductively coupled plasma mass spectrometry (ICP-MS). Note that this method does not distinguish between dissolved and possible small particles of Au, and was chosen to measure how much of both forms of Au can be released from solid soil fractions under conditions that might represent what could happen in the field. In addition, the measured Au concentrations were too low to measure the speciation of Au reliably. Biologically active experiments contained field-fresh regolith materials and were commenced within 24 h of arrival in the laboratory. To assess if the effect of the resident microbiota on the solubilization of Au and As is reproducible, a number of microcosm experiments were conducted in replicate (Table 1). For biologically inactive microcosms (e.g., HM-S-i) the solid materials were generally sterilized by autoclaving up to three times at 125 °C and 1.1 atm for 1 h before sterile double deionized water was added (Trevors, 1996). Sterility was tested optically using phase contrast microscopy and by plating of 1:10 (v/v) soil dilutions on nutrient agar plates (Oxoid, Basingstoke, UK) after the 70 day incubation; only those experiments that had remained sterile were used for further evaluation.

3.4. Chemical analysis of samples

Major element analyses in homogenized soil and rock samples were determined at Geoscience Australia by XRF using a Philips PW2404 4 kW sequential X-ray spectrometer (detection limits in wt%): SiO_2 (0.006), TiO_2 (0.002), Al_2O_3 (0.001), Fe_2O_3 (0.002), MnO (0.001), MgO (0.004), CaO (0.002), Na_2O (0.004), K_2O (0.002), P_2O_5 (0.001), SO_3 (0.001); based on duplicate analyses, reproducibility was within 1 wt%. Minerals were identified and their abundances determined at Geoscience Australia using XRD on powdered samples using the SIROQUANT-software following the procedures outlined in Taylor (1991). Materials used for XRD and XRF analyses were: soil, phyllitic and unweathered quartz vein material (QVMU) from the Hit or Miss Gold Mine, and soil, saprolite and oxidized alteration zone material (OAZM) from the Peak Hill Gold Mine. Gold and As in the liquid samples were measured using an Agilent 7500S inductively coupled plasma mass spectrometer (ICP-MS) equipped with a concentric nebulizer and an automatic sampler at the Research School of Earth Sciences, Australian National University. The detection limits for Au and As were 2.8 and 3.7 ng L^{-1} and analytical precision lay within 5%. Total carbon, C_{tot}, and total nitrogen, N_{tot}, contents of the soil samples were measured using a Leco CNS 2000 element analyzer (Matejovic, 1997). pH was measured with an Activon pH electrode and meter, analytical precision lay within 0.1 pH unit (Rayment and Higginson, 1992).

Table 1
Incubation conditions for microcosm experiments conducted with soils, saprolite, and quartz-vein materials from the Hit or Miss Gold Mine and the Peak Hill Gold Mine

Microcosm	Sampling sites		Material	Biological activity	
	Hit or Miss (HM)	Peak Hill (PH)		Active (a)	Inactive (i)
HM-S-a[a]	X		Soil (S)	X	
HM-S-i[a]	X		Soil (S)		X
HM-Q-a[b]	X		Quartz (Q)	X	
HM-Q-i[b]	X		Quartz (Q)		X
PH-S-a		X	Soil (S)	X	
PH-S-i[a]		X	Soil (S)		X
PH-Sa-a		X	Saprolite (Sa)	X	
PH-Sa-i[a]		X	Saprolite (Sa)		X

[a] Conducted in duplicate.
[b] Conducted in triplicate.

4. Results and discussion

The results and discussion section consists of three subsections. In the first subsection the bulk geochemistry, the mineralogy of the regolith materials and the results of the sequential extraction for Au and As are presented. The second subsection focuses on the solubilization of Au and As in biologically active and inactive (sterilized) microcosms. In the third subsection the implications of these results for the mobility and mobilization of Au and As in the regolith are discussed.

4.1. Element composition, mineralogy and sequential extractions

The results of bulk geochemical analyses, the total As and Au contents, and mineralogy for major regolith components are given in Tables 2 and 3, respectively; the results of the sequential extractions are shown in Figs. 2 and 3. The total Au and As concentrations in samples from both sites as determined by *aqua regia* digests approximate the sums determined in the sequential extractions (Table 2; Figs. 2 and 3). In general, the results of the sequential extractions show that Au is present in more easily extractable fractions with increased weathering of the host material (Fractions 1–3; Figs. 2A and 3A), which indicates that Au is mobile in regolith environments in tropical and semi-arid areas, similarly to temperate areas (Reith et al., 2005). In contrast, As in all materials is mostly associated with the less extractable fractions (Fractions 4 to 6; Figs. 2B and 3B) indicating that As mobility is limited.

The total Au content of unweathered quartz vein material (QVMU) from the Hit or Miss Gold Mine is 47254 ± 1293 ng g^{-1} (d.w. material, Table 2). More than 99 wt% of this Au was only extractable in the last step of the selective extractions, i.e., with concentrated *aqua regia*, suggesting that Au is strongly bound within the pyrite or arsenopyrite detected in QVMU (Table 3). The Au content of moderately weathered quartz vein material (QVMW 1) is much lower, i.e., 265 ng g^{-1} (d.w. material; Fig. 2A). Gold is not associated with the residual fraction; approximately 70 wt% of the Au was extracted with the ammonium acetate leach indicating that it is exchangeable-bound, and thus highly mobile. In highly weathered quartz vein material (QVMW 2) no Au was detected, indicating the release of Au into the environment during weathering. The total concentration of Au in phyllite samples is 1844 ± 210 ng g^{-1} (d.w. material, Table 2), and most of the Au was detected in extraction 3 suggesting that Au is associated with the organic phase (Fig. 2A). Phyllite samples are highly weathered and contain 0.7 wt% of organic matter that is probably derived from decomposing roots (Table 2). Approximately equal concentrations of Au were detected in extractions 4 and 5, and approximately 30 wt% of Au was only extractable using *aqua regia* (Fig. 2A), suggesting it is bound in residual minerals. In soil approximately 80 wt% of the Au is bound in the operationally defined organic matter (extraction 3), with approximately 10 wt% associated with the amorphous Fe- and Mn-oxides and the residual phase (extractions 4 and 6, respectively; Fig. 2A). Replicate analyses showed that extraction patterns and total Au and As concentrations are reproducible.

Table 2
Major element oxide, Au, As, total carbon (C_{tot}) and nitrogen (N_{tot}) concentrations of regolith samples from the Peak Hill Gold Mine in central eastern New South Wales and the Hit or Miss Gold Mine in northern Queensland

	Peak Hill Gold Mine			Hit or Miss Gold Mine		
	Soil	Saprolite	OAZM[b]	QVMU[d]	Phyllite	Soil
Al_2O_3	9.7	9.2	4.9	3.5	15.7	15.2
CaO	0.06	0.03	0.01	n.d.	0.1	0.04
Fe_2O_3	8.4	8.9	13.4	1.7	4.5	4.8
K_2O	1.1	1.1	0.02	0.9	3.9	3.4
MgO	0.2	0.2	0.03	0.3	0.8	0.9
MLOI	10.8	5.5	4.2	1.2	3.5	4.8
MnO	0.01	0.01	0.01	n.d.	0.02	0.02
Na_2O	0.2	0.2	n.d.[c]	0.2	0.3	0.4
P_2O_5	0.2	0.2	0.3	0.01	0.04	0.06
SiO_2	68.0	73.6	74.9	91.2	70.7	70.1
SO_3	0.2	0.3	0.6	0.9	0.01	0.01
TiO_2	0.9	0.7	1.4	0.1	0.4	0.6
C_{tot}	3.8	0.7	n.d.	n.d.	0.7	1.6
N_{tot}	0.16	0.05	n.d.	n.d.	0.07	0.11
Total Au (ng g^{-1} d.w.)[a]	1632 ± 76	4398 ± 147	915 ± 89	47254 ± 1293	1844 ± 210	1216 ± 144
Total As (μg g^{-1}d.w.)[a]	28.7 ± 1.4	29.1 ± 1.2	56.4 ± 2.4	1457 ± 126	387 ± 31	25 ± 3

All values are results of replicate analyses in wt% unless otherwise indicated.
[a] Given are the averages ± standard deviation of 3 replicates.
[b] OAZM, oxidized alteration zone material.
[c] n.d., not detected.
[d] QVMU, quartz vein material unweathered.

Table 3
Mineralogy and mineral abundances of soil, other regolith and rock samples from the Peak Hill gold mine in central eastern New South Wales and the Hit and Miss Gold Mine in northern Queensland

Mineral	Peak Hill Gold Mine			Hit or Miss Gold Mine		
	Soil	Saprolite	OAZM[b]	QVMU[c]	Phyllite	Soil
Quartz	79	76	78	85	34	48
Albite	3	2	2	n.d.	n.d.	n.d.
Halloysite	<1	1	n.d.	n.d.	n.d.	n.d.
Illite	<1	<1	n.d.	12	45	36
Kaolin	1	1	1	2	19	10
Muscovite	4	1	<1	n.d.	n.d.	n.d.
Smectite	n.d.[a]	n.d.	n.d.	n.d.	n.d.	4
Pyrite	n.d.	n.d.	n.d.	1	n.d.	n.d.
Arsenopyrite	n.d.	n.d.	n.d.	1	n.d.	n.d.
Goethite	n.d.	n.d.	4	n.d.	1	1
Microcline	2	3	n.d.	n.d.	n.d.	n.d.
Rutile	1	1	2	<1	<1	1
Hematite	5	11	n.d.	n.d.	n.d.	n.d.
Pyrophyllite	4	6	12	n.d.	n.d.	n.d.
Diopside	n.d.	n.d.	<1	n.d.	n.d.	n.d.
Magnetite	1	n.d.	n.d.	n.d.	n.d.	n.d.

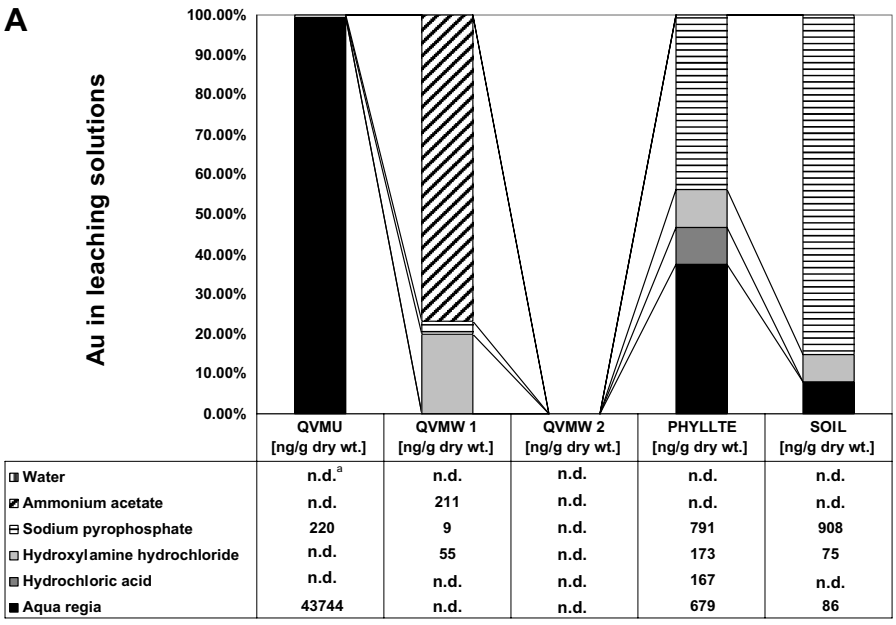
All values are averages of replicate analyses in %.
[a] n.d., not detected.
[b] OAZM, oxidized alteration zone material.
[c] QVMU, quartz vein material unweathered.

Gold in oxidized alteration zone material (OAZM) from the Peak Hill Mine is mostly associated with crystalline and amorphous Fe oxides and the Mn oxides (extractions 4 and 5, respectively; Fig. 3A). The highest observed total concentration of Au as established by total *aqua regia* digests to be 4398 ± 147 ng g^{-1} (d.w. material), was in saprolite (Table 2). Approximately 50 wt% of the Au in the saprolite was detected in extraction 2 indicating that it is exchangeable bound or associated with clay minerals (Fig. 3A). A further 45 wt% was bound in the operationally defined organic fraction. In the soil overlying the saprolite the total concentrations of Au approximated 1632 ± 76 ng g^{-1} (d.w. material). The general pattern of the sequential extractions in the soil was reproducible and similar to the pattern detected in the saprolite, indicating that Au is predominately bound to the operationally defined exchangeable, clay-bound and organic fractions.

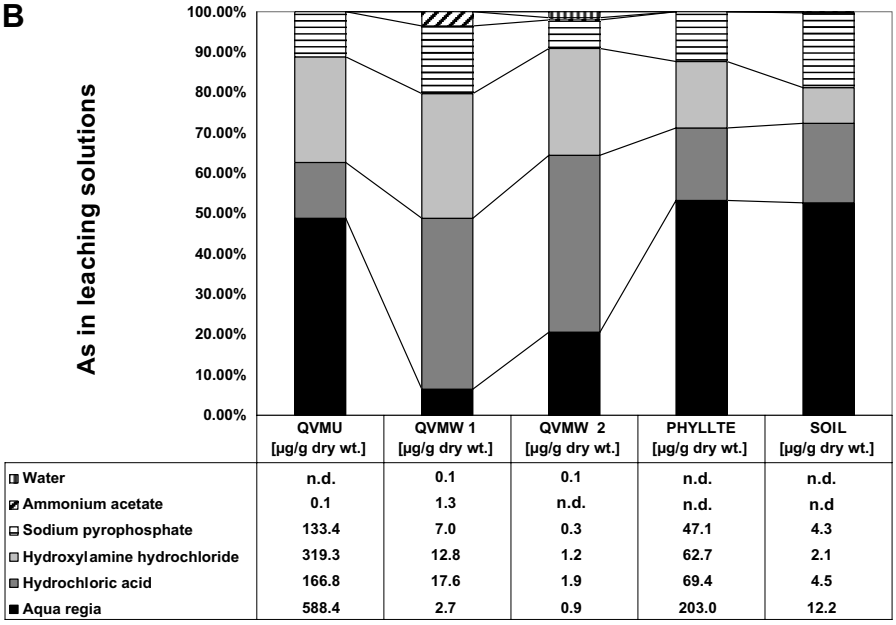
In contrast to the changing extraction patterns of Au in soils, weathered and unweathered materials from both sites, the extraction patterns of As displayed no principle shift with degree of weathering towards the more mobile fractions, i.e., the water-soluble, exchangeable, clay-bound, or organic fractions (Figs. 2B and 3B). In all materials from both sites 85–90 wt% of As is associated with residual and Fe- and Mn-oxide fractions. At the Hit or Miss Gold Mine the total concentrations of As in vein quartz materials ranged from 1457 ± 126 μg g^{-1} (d.w. material) in QVMU to approximately 4 μg g^{-1} (d.w. material) in QVMW 2 (Table 2). Because the extraction patterns show only minimal differences in As fractionation with increasing weathering of the host materials, the results may reflect varying concentrations of As in the different quartz-vein materials rather than As solubilization and release into the environment due to rock weathering. The distribution of As in the phyllite and soils samples supports this interpretation, because the extraction patterns of As in the sequential extractions are almost identical, yet the total concentrations were 387 compared to 25 μg g^{-1} (d.w. material) in phyllite and soil samples, respectively. At the Peak Hill Gold Mine, saprolite and soil samples displayed similar extraction patterns and similar concentrations of As (Table 2, Fig. 3B). Compared to the OAZM a shift in the concentration pattern from the residual fraction to the Fe- and Mn-oxide fraction is apparent (Fig. 3B). The results from both sites suggest that an increase in As mobility with increasing weathering of the host material is limited in tropical and semi-arid areas. Thus, they corroborate the results from earlier studies, which have also shown that As mobility is limited (Reith et al., 2005), and controlled by sorption to Mn and Fe oxides and oxyhydroxides (Smedley and Kinniburgh, 2002).

4.2. Solubilization of Au and As in microcosm experiments

In general, Au was detected in solution in all biologically active microcosms during the incubation (Figs. 4A and 5A), and was below detection in almost all biologically inactive (sterilized) microcosms, as was also found in Reith and McPhail (2006). The solubilization of As differed in microcosms conducted with materials from the two sites. In biologically active and inactive microcosms from the Peak Hill Gold Mine little difference in concentration or timing of As solubilization was detected (Fig. 4B). In biologically active soil and quartz vein microcosms from the Hit or Miss Gold Mine, the solubilization of As significantly increased during the incubation compared to the



	QVMU [ng/g dry wt.]	QVMW 1 [ng/g dry wt.]	QVMW 2 [ng/g dry wt.]	PHYLLTE [ng/g dry wt.]	SOIL [ng/g dry wt.]
Water	n.d.[a]	n.d.	n.d.	n.d.	n.d.
Ammonium acetate	n.d.	211	n.d.	n.d.	n.d.
Sodium pyrophosphate	220	9	n.d.	791	908
Hydroxylamine hydrochloride	n.d.	55	n.d.	173	75
Hydrochloric acid	n.d.	n.d.	n.d.	167	n.d.
Aqua regia	43744	n.d.	n.d.	679	86



	QVMU [µg/g dry wt.]	QVMW 1 [µg/g dry wt.]	QVMW 2 [µg/g dry wt.]	PHYLLTE [µg/g dry wt.]	SOIL [µg/g dry wt.]
Water	n.d.	0.1	0.1	n.d.	n.d.
Ammonium acetate	0.1	1.3	n.d.	n.d.	n.d
Sodium pyrophosphate	133.4	7.0	0.3	47.1	4.3
Hydroxylamine hydrochloride	319.3	12.8	1.2	62.7	2.1
Hydrochloric acid	166.8	17.6	1.9	69.4	4.5
Aqua regia	588.4	2.7	0.9	203.0	12.2

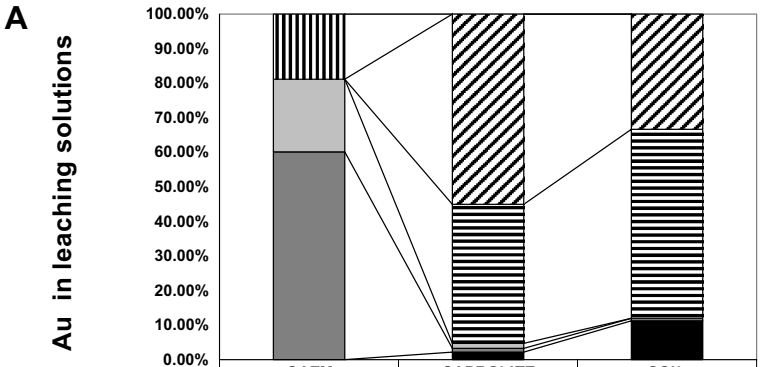
[a] n.d., not detected

Fig. 2. Fractionation determined by sequential extractions for Au (A) and As (B) in regolith materials from Hit or Miss Gold Mine in Queensland, Australia.

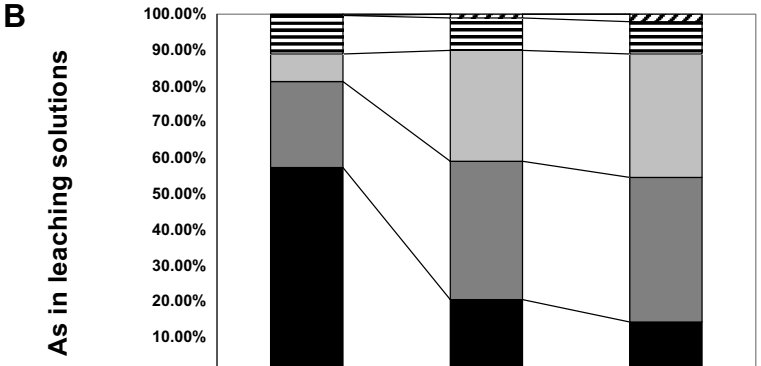
biologically inactive control experiments (Fig. 5B), indicating that resident microbiota may contribute to the limited As mobility in regolith materials at the Hit or Miss Gold Mine in tropical northern Queensland.

4.2.1. Solubilization of Au in microcosm experiments

Microcosms with soil samples from the Hit or Miss Gold Mine were conducted in duplicate under biologically active and inactive conditions, i.e., HM-S-a and HM-S-i, respectively. In the duplicate biologically active experiments the overall pattern of Au release and maximum concentrations of solubilized Au of approximately 220 ng g^{-1} (d.w. soil; Fig. 4A) was similar. Based on the *aqua regia* digests conducted with soils from HM-S-a, which yielded total Au concentrations of 1216 ± 144 ng g^{-1} (d.w. soil), this amounts to approximately 20 wt% of total Au contained in the soil being solubilized by the resident microbiota. The timing of Au release differed between the duplicates, indicating differences in the development of microbial communities during the incubation (Fig. 4A; Reith and McPhail, 2006). In contrast, in the biologically inactive soil microcosms Au was not detected in solution at any time during the incubation (Fig. 4A). The pH values were generally 0.5–1 unit lower in biologically inactive compared to active



	OAZM [ng/g dry wt.]	SAPROLITE [ng/g dry wt.]	SOIL [ng/g dry wt.]
Water	153	n.d.	n.d.
Ammonium acetate	n.d.[a]	2453	485
Sodium pyrophosphate	n.d.	1799	794
Hydroxylamine hydrochloride	173	56	n.d.
Hydrochloric acid	491	53	10
Aqua regia	n.d.	97	164



	OAZM [µg/g dry wt.]	SAPROLITE [µg/g dry wt.]	SOIL [µg/g dry wt.]
Water	0.1	n.d.	n.d.
Ammonium acetate	n.d.	0.3	0.6
Sodium pyrophosphate	6.0	2.6	2.5
Hydroxylamine hydrochloride	4.1	8.7	9.8
Hydrochloric acid	13.2	11.0	11.4
Aqua regia	31.7	5.8	4.1

[a] n.d., not detected.

Fig. 3. Fractionation determined by sequential extractions for Au (A) and As (B) in regolith materials from Peak Hill Gold Mine in New South Wales, Australia.

microcosms, which might be an effect of the autoclaving procedure used to sterilize the soils, but apparently the lower pH did not influence the dissolution of Au (Fig. 4C).

In the microcosms with soil and saprolite materials from the Peak Hill Gold Mine Au was solubilized in the biologically active experiments, i.e., PH-S-a and PH-Sa-a. Generally, Au was not detected or Au concentrations were significantly reduced in solution in the biologically inactive controls, i.e., PH-S-i and PH-Sa-i. In PH-S-a, 456 ng g^{-1} (d.w soil) of Au were detected in solution at day 22, after which the Au concentration in solution decreased to approximately 50 ng g^{-1} (d.w soil) and then increased to 907 ng g^{-1} (d.w soil) after day 42 (Fig. 5A). In contrast, in PH-S-i no Au was released during the first 44 days of incubation, after which the Au concentration in solution rose to 170 ng g^{-1} (d.w soil) at day 70 of the incubation (Fig. 5A). In PH-Sa-a, episodic release of Au into the solution was detected, i.e., between 80 and 160 ng g^{-1} (d.w soil) of Au at 8, 23 and 55 days. In contrast, in the sterilized equivalent experiment, PH-Sa-i, Au was not detected in solution during the 70 days of incubation (Fig. 5A). Based on the *aqua regia* digests conducted with soils and saprolite materials, which yielded total Au concentrations of 1632 ± 76 and 4398 ± 147 ng g^{-1} (d.w. material; Table 2), this amounts to approximately 55 and 4 wt% of total Au dissolved in PH-S-a and PH-Sa-a, respectively. The pH

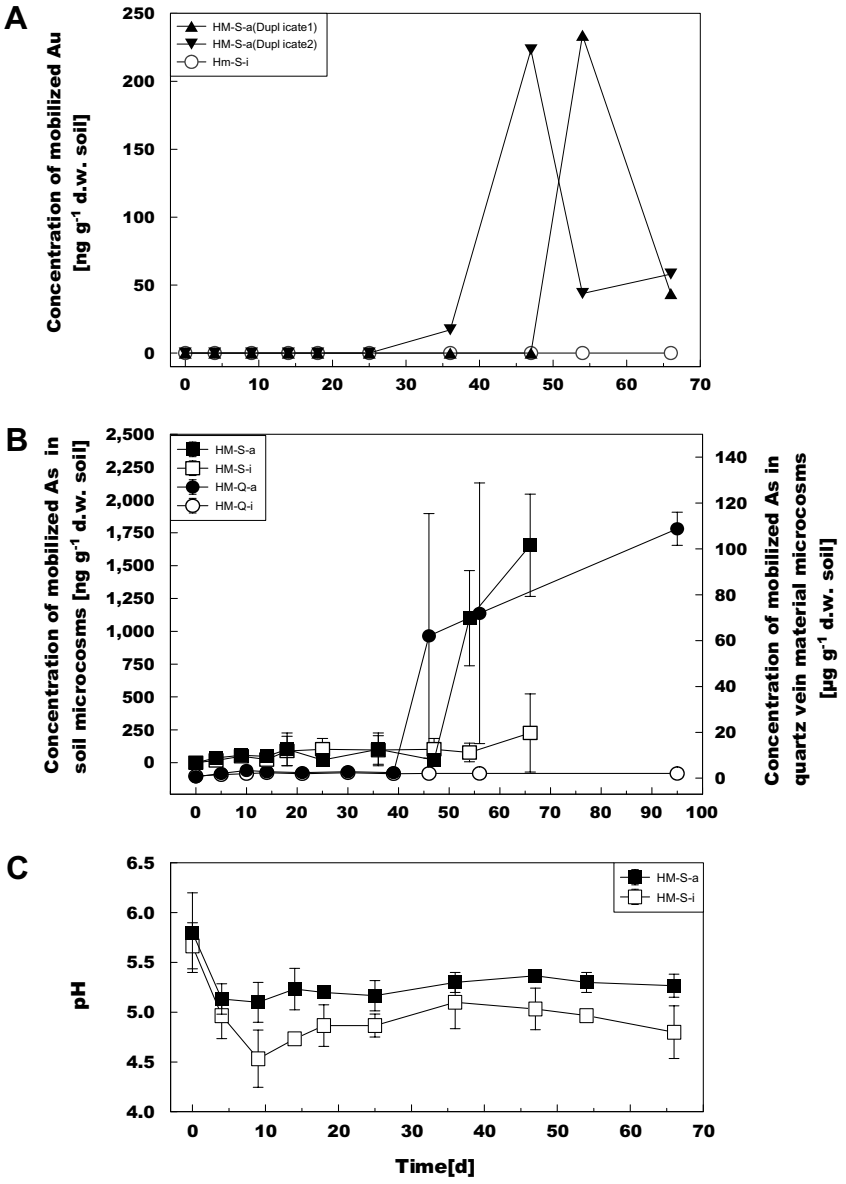


Fig. 4. Concentration of solubilized Au (A), As (B) and pH-values (C) in solution from microcosms incubated under oxic and biologically active or inactive conditions. Samples are from the Hit or Miss Gold Mine in northeastern Queensland.

values in both experiments lay between 4 and 5 during the incubation and did not differ between biologically active and inactive experiments (data not shown).

4.2.2. Solubilization of As in microcosm experiments

In microcosms with soil samples from the Hit or Miss Gold Mine (HM-S-a and HM-S-i) As release into solution ranged between 10 and 100 ng g^{-1} (d.w soil) during the first 47 days of incubation in the biologically active and inactive microcosms (Fig. 4B). After this As concentration increased to 1654 ng g^{-1} (d.w. soil) at day 66 in the HM-Q-a compared to a moderate increase to 226 ng g^{-1} (d.w. soil) in HM-Q-i. These results indicate that after 47 days of incubation the soil microbiota actively mediated the solubilization of As. A similar pattern of As release was detected for the biologically active and inactive quartz vein microcosms (Fig. 4B). The concentration of As in solution remained between 0.5 and 2.5 µg g^{-1} (d.w. material) for the first 40 days of incubation in biologically active and inactive microcosms with vein quartz materials, i.e., HM-Q-a and HM-Q-i. After this the concentration of As steadily increased to 108 ± 7.2 µg g^{-1} (d.w. material) in HM-Q-a, but remained at around 2.0 ± 0.5 µg g^{-1} (d.w. material) in the HM-Q-i. Based on the *aqua regia* digests conducted with soil and vein quartz material, which yielded total As concentrations of 25 and 1457 µg g^{-1} (d.w. soil), this amounts to approximately 7 wt% of As dissolved in both microcosms.

The solubilization of As in microcosms with soil and saprolite from the Peak Hill Gold Mine did not differ significantly between the biologically active and inactive incubations (PH-S-a, PH-S-i and PH-Sa-a, PH-Sa-I; Fig. 5B).

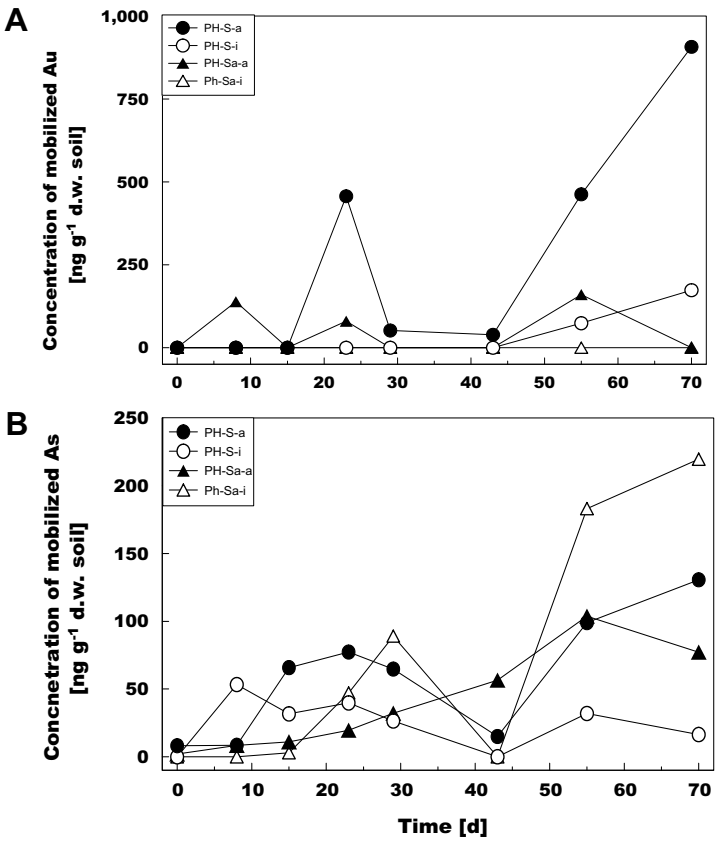


Fig. 5. Concentration of solubilized Au (A) and As (B) in soil and saprolite microcosms and incubated under oxic and biologically active or inactive (sterilized) conditions. Samples are from Peak Hill Gold Mine in New South Wales.

In all microcosms between 5 and 75 ng g^{-1} (d.w. soil) were detected in solution during the first 40 days of incubation, after which the concentration of As in solution appeared to decrease, and then rose again. Compared to the total concentration of As in the soil and saprolite (approximately 22,000 ng g^{-1} d.w. soil), less than 1 wt% of As was released into solution in any of the microcosms.

4.3. Implications for the mobility of Au and As in the regolith

The results of this study demonstrate that Au is mobile and that indigenous microbiota contribute to Au solubilization in regolith materials from tropical and semi-arid areas. The percentage of microbially mediated Au detected in solution differed in soils from tropical (20% of total Au disseminated in the soil) and semi-arid (up to 55% of total Au) sites, and also compared to an earlier study with samples from the Tomakin Park Gold Mine in moderate south eastern New South Wales, where up to 80 wt% of the total Au was released into solution (Reith and McPhail, 2006). The microbially mediated solubilization of Au was expected to be more rapid and the percentage of solubilized Au to be higher in the microcosms with samples from the tropical compared to the temperate or semi-arid sites, because microbial activity and universal weathering rates in tropical soils generally exceed those in temperate environments (Curtis, 1990; Macari and Hoyos, 1996). However, the observed lower rates of microbially mediated Au solubilization in Hit or Miss microcosms may be due to a microbial community that is limited in its capabilities to mediate the release of Au and/or to sorption of Au to the solid fractions or microorganisms.

One mechanisms that has been linked to the microbially mediated solubilization of Au is its dissolution and complexation by free amino acids produced and released by regolith microbiota (Korobushkina et al., 1983; Savvaidis et al., 1998; Reith and McPhail, 2006). This mechanisms depends the ability of the microbial community to release more amino acids to solution than are consumed. Under N-limited conditions the production and excretion of organic N containing compounds, such as amino acids, has been shown to be low and their consumption by microbiota and plants to be rapid (Falkengren-Grerup et al., 2000; Jones et al., 2002). Total organic carbon and nitrogen content (C_{tot} and N_{tot}) in the auriferous soils from the Hit or Miss Gold Mine were much lower than the soils from the Tomakin Park Gold Mine (this study; Reith and McPhail, 2006), which suggest that there are lower concentrations of amino acid in solution to dissolve and form complexes with Au. The results of the microcosms with soil and saprolite sample from the Peak Hill site support this suggestion. In soil that displayed a higher organic matter content than the saprolite a maximum of 55 wt% of Au was released into solution compared to only 4 wt% in the

saprolite; yet the general geochemistry, mineralogy and the fractionation of Au were similar in soil and saprolite.

Limited Au solubilization in Hit or Miss mine microcosms may be due to Au being strongly bound to the solid fractions, and thus be less accessible to the microbially mediated solubilization. The sequential extractions of the soil have shown that Au is strongly bound to the operationally defined organic matter, because Au is not detected in the water-soluble, exchangeable or clay-bound fractions. It is likely that Au was mostly bound to the part of the non-reactive organic material, because non-reactive organic matter, whose turnover rates is very slow and may be in the order of up to 100 years, forms a much larger fraction of the total soil organic matter in tropical soils compared to soils in temperate environments (Zech et al., 1997).

A further explanation for the observed behavior of Au may lie in the dominance of microbially mediated Au precipitation over solubilization. Common soil bacteria and fungi have also been shown to rapidly precipitate Au from solution and accumulate it extra- and intracellularly (Karamushka et al., 1990a,b; Ulberg et al., 1992; Southam and Beveridge, 1996; Savvaidis et al., 1998; Nakajima, 2003; Lengke and Southam, 2005; Reith et al., 2006). Evidence for processes leading to an authigenic formation of Au grains and nuggets mediated by microorganisms has been reported from the Palmer River Goldflieds (Bischoff, 1994, 1997; Reith et al., 2006), and supports the suggestion of the dominance of Au precipitation and nugget formation over solubilization at the site.

Arsenic is often used as a pathfinder element for Au in geochemical exploration in the regolith, because of the larger halos As forms around mineralization (Cavender, 1963; Boyle, 1979; Yang and Blum, 1999). The traditional interpretation of this behavior is that the mobility and dispersability of As in the regolith exceeds that of Au (Cavender, 1963; Boyle and Jonasson, 1973; Boyle, 1979). However, sequential extraction analyses and microcosm experiments with regolith samples from semi-arid, tropical and temperate climates indicate that the mobility of As compared to Au is limited (this study; Reith et al., 2005). Thus, it may be hypothesized that the larger As halos around mineralized zones form because of dilution of Au in the regolith to background levels. In contrast, because of the limited mobility and higher concentrations, As is less dilute with increased distance from the primary mineralization, and the As halo is picked further from the mineralization compared to the Au halo. This hypothesis requires further testing at the study sites.

5. Conclusions

The results of this study show that Au is mobile in regolith materials from tropical and semi-arid areas in Australia, similar to the results of Reith and McPhail (2006) for a temperate area in Australia, whereas As mobility appear limited. Using biologically active versus inactive microcosms, we have demonstrated an effect of the indigenous microbiota of auriferous soils from semi-arid and tropical sites on the solubilization of Au, and for As in regolith from the tropical site. Thus, this study and Reith and McPhail (2006) have demonstrated that the activity of microorganisms needs to be taken into account when studying the mobility, solubilization and transport of Au and As in a wide range of regolith environments in Australia. The study has also shown that the capacity of microbiota to solubilize Au and As, and the timing and total concentrations of Au released into solution varies greatly between samples from different sites. This indicates that environmental factors such as climate, soil geochemistry, substrate quality and availability influence the microbially mediated solubilization of Au and As by influencing the composition and activity of the indigenous soil microbiota. More research is necessary to elucidate the specific mechanisms of how and when microbiota interact with the Au and As. The species, or groups of bacteria and other microorganisms that are affecting Au and As mobility need to be identified more specifically using modern molecular microbial approaches such as fingerprinting and sequencing of community 16S rDNA (Reith et al., 2006). In addition, the speciation of Au, e.g., dissolved complexes, colloids, needs to be identified. By making such detailed measurements we will be able to learn more about the mechanisms as well as the kinetics of these processes. Ultimately, we may be able to incorporate appropriate data into numerical geochemical models to predict Au and As transport, which will be useful in developing successful gold exploration and ore-processing strategies.

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