



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Extreme environments in the critical zone: Linking acidification hazard of acid sulfate soils in mound spring discharge zones to groundwater evolution and mantle degassing

Paul Shand ^{a,b,*}, Travis Gotch ^c, Andrew Love ^b, Mark Raven ^a, Stacey Priestley ^b, Sonia Grocke ^a

^a CSIRO Land and Water, Private Bag 2, Glen Osmond, Adelaide, SA 5064, Australia

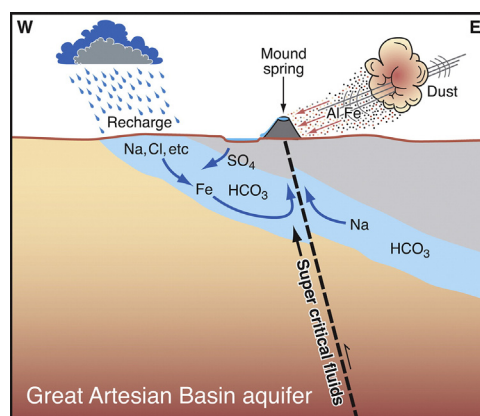
^b School of Environmental Sciences, Flinders University, Adelaide, SA 5042, Australia

^c Department of Environment, Water and Natural Resources, Roxby Downs, Australia

HIGHLIGHTS

- Critical zone biogeochemical cycles linked to mantle degassing and deep groundwater
- Fractionation of acidity and alkalinity in discharge zones forms acidification hazard.
- Rare hydroxysulfate efflorescences formed in extreme acidic environments.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form 20 May 2016

Accepted 20 May 2016

Available online xxx

Editor: D. Barcelo

Keywords:

Acid sulfate soil

Pyrite

Oxidation

Sulfate

Mineralogy

ABSTRACT

A decrease in flow from the iconic travertine mound springs of the Great Artesian Basin in South Australia has led to the oxidation of hypersulfidic soils and extreme soil acidification, impacting their unique groundwater dependent ecosystems. The build-up of pyrite in these systems occurred over millennia by the discharge of deep artesian sulfate-containing groundwaters through organic-rich subaqueous soils. Rare iron and aluminium hydroxysulfate minerals form thick efflorescences due to high evaporation rates in this arid zone environment, and the oxidised soils pose a significant risk to local aquatic and terrestrial ecosystems. The distribution of extreme acidification hazard is controlled by regional variations in the hydrochemistry of groundwater. Geochemical processes fractionate acidity and alkalinity into separate parts of the discharge zone allowing potentially extreme environments to form locally. Differences in groundwater chemistry in the aquifer along flow pathways towards the spring discharge zone are related to a range of processes including mineral dissolution and redox reactions, which in turn are strongly influenced by degassing of the mantle along deep crustal fractures. There is thus a connection between shallow critical zone ecosystems and deep crustal/mantle processes which ultimately control the formation of hypersulfidic soils and the potential for extreme geochemical environments.

© 2016 Elsevier B.V. All rights reserved.

* Corresponding author at: CSIRO Land and Water, Private Bag 2, Glen Osmond, Adelaide, SA 5064, Australia.

E-mail address: paul.shand@csiro.au (P. Shand).

1. Introduction

The critical zone, comprising the earth's surface from the zone of vegetation to the zone of groundwater (Brantley et al., 2006), forms a heterogeneous, dynamic system that incorporates the many coupled biogeochemical cycles that support life and shape the landscape over time. It is host to different types of geochemical barriers (Perel'man, 1986) often with strong chemical gradients and typically in a state of dynamic disequilibrium. The study of element cycling has largely focussed on the upper parts of the terrestrial environment including the atmosphere, surface waters and soils, with deeper groundwater systems often ignored or considered of limited impact. Yet, groundwater is an important component in sustaining river flows and wetland systems globally. The degree of coupling of biogeochemical cycles is being much better appreciated chemically (Falkowski et al., 2008; Finzi et al., 2011), although the incorporation of Fe, S and trace metals (Burgin et al., 2011), as well as changes across landscapes including wetlands requires much better understanding and integration. The impact of oxidation reactions involving Fe and S in generating acidification are well known from studies of acid mine drainage (AMD), but their significance is much broader in terrestrial (Shand et al., 2005; Rice & Herman, 2012) and planetary (Hurowitz et al., 2010) systems. In some legacy mines, acidification can be extreme e.g. with generation of high metal loadings and negative pH (Nordstrom et al., 2005).

The productivity of wetlands often far exceeds that of fertile farmland, forming foci of nutrient cycling. They also act as filters of landscapes (Madden et al., 2004; Hammer & Bastian, 1989), immobilising a range of natural and anthropogenic contaminants and protecting aquatic ecosystems. Inputs of metals, for example, can be removed by sorption onto oxyhydroxide mineral surfaces under oxidising conditions or incorporated into sulfide minerals under reducing conditions in wetland soils. However, changes in water balance may have a significant effect on this storage and build-up of contaminants if the geochemical environments in wetlands are modified. The complexities of coupled biogeochemical cycles in heterogeneous landscapes as well as the variety of water fluxes (rainfall, surface flows, interflow, groundwater) make it difficult to fully appreciate the role of groundwater as a source and control on nutrient and contaminant dynamics (De Nobili et al., 2002; Dupas et al., 2015).

The groundwater-fed carbonate Mound Springs of the western Great Artesian Basin (which covers 20% of the continent) are iconic symbols of the arid interior of Australia forming isolated ecological niches of cultural and ecological significance (Love et al., 2013). The springs form a major discharge zone for groundwater of the GAB, with waters sourced from westerly and northerly flowpaths. Discharge is focussed along a NW-SE to W-E zone close to the western and southern margin of Lake Eyre (Fig. 1). They typically form distinct travertine (calcium carbonate) mounds and platforms in the west, but change to more shallow features in the east without the development of travertine. Many of the larger mounds are now extinct due to declining flows as recharge decreased in central Australia due to natural climate change over the past 50,000 years. Of significance to the sustainability of spring flows and hydrodynamics of the western margin, is that recharge is now limited to episodic flows from river systems and diffuse recharge is effectively zero (Love et al., 2013). The age of many springs is not known, but luminescence dating of quartz grains in the carbonate of some springs has provided ages from 10 to 400 ka (Prescott & Habermahl, 2008). Similarly, U-series dating of carbonates gave ages from 6 to 460 ka, with age probability groupings suggesting periodicity in carbonate precipitation (Love et al., 2010). The spring zone thus represent a record of geological, hydrogeochemical and pedological processes occurring over millennia.

The springs are associated with old (Neoproterozoic), deep crustal fractures (the Torrens Hinge line and Tasman line) above a large transition in mantle velocity structure, thought to be the junction of a major terrane boundary (Karlstrom et al., 2013). There is also evidence for

mantle-derived ^3He and CO_2 in groundwater of the GAB (Crossey et al., 2013; Italiano et al., 2014), the latter playing a significant role in determining the geochemical evolution of groundwaters and the formation of travertine mounds. GAB spring fauna are extremely localised in their distribution and display a high genetic diversity and degree of endemism (Guzik & Murphy, 2013). The protection of such unique ecosystems is highly dependent on continued spring flows and good water quality, both of which are currently being impacted by groundwater abstraction.

This paper presents a study of these arid zone spring discharge zones in the western Great Artesian Basin (GAB), where spring flow is solely derived from a deep confined artesian aquifer system of Mesozoic age. Specifically, it aims to show how the redox cycling of Fe and S in acid sulfate soils (ASS) within carbonate-rich terranes can create extreme acidic environments, posing a risk to spring ecosystems as a result of climate change and groundwater abstraction. Furthermore, it explores the relationship between acid sulfate soil hazard and deep sub-surface processes, highlighting that influences on the critical zone can extend much deeper than commonly appreciated.

2. Experimental (materials and methods)

During a study of springs and groundwater as part of a national initiative in the western part of the GAB (NWC 2013), it was reported that one of the springs (Brinkley) had very low flow and yellow 'sulfur' crystals. A visit to the site confirmed the presence of thick mineral efflorescences varying in colour from white, bright yellow and brown to orange. During subsequent field campaigns, samples were collected from a number of different spring systems for further chemical and mineralogical analyses.

Soil samples were collected from a number of springs including 10 Mile Spring, 12 Mile Spring, Big Cadnaowie, Big Perry, Billa Kalina, Brinkley, Coodanoorina, Gosse, Hawker, Levi, Nilpinna, Outsider, Strangways, Vaughan, Wandallina and Warburton. At most springs, a shallow soil sample or surface mineral efflorescence was collected. More detailed sampling was undertaken at selected springs where sulfidic soils were observed or where strongly sulfuric ($\text{pH} < 4$) materials were identified. Soil pits were dug at these sites and samples collected in plastic bags and chip trays for mineral identification by x-ray diffraction (XRD) analysis. For saturated, reducing soils below a redox boundary, samples were kept refrigerated. Sub-samples were ground in an agate mortar and pestle before being lightly pressed onto silicon low background holders for x-ray diffraction analysis. XRD patterns were recorded with a PANalytical X'Pert Pro Multi-purpose Diffractometer using Fe filtered $\text{Co K}\alpha$ radiation, auto divergence slit, 2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded in steps of $0.016^\circ 2\theta$ with a 0.4 s counting time per step, and logged to data files for analysis. Qualitative analysis was performed on the XRD data using in-house XPLOT and commercial software HighScore Plus from PANalytical with the PDF4+ 2014 database from the International Centre for Diffraction Data (ICDD).

Soil pH measurements were made in water (approximately 1:1; pH_w) prior to and after being incubated for 16 weeks (pH_{INC}) to estimate natural oxidation (Creepers et al., 2012), and after treatment with a strong oxidising agent – hydrogen peroxide (pH_{OX}).

The nomenclature of acid sulfate soils has been modified recently and the following terms from Sullivan et al. (2010), now accepted in the Australian soils classification (Isbell, 2015), are used here:

- Sulfidic: soil materials containing detectable sulfide
 - o Hypersulfidic: Sulfidic soil material that is capable of severe acidification ($\text{pH} < 4$) as a result of oxidation of contained sulfides
 - o Hyposulfidic: Sulfidic soil material that is not capable of severe acidification ($\text{pH} < 4$) as a result of oxidation of contained sulfides
- Sulfuric: Soil material that has a $\text{pH} < 4$ (1:1 by weight in water, or in a minimum of water to permit measurement) when measured

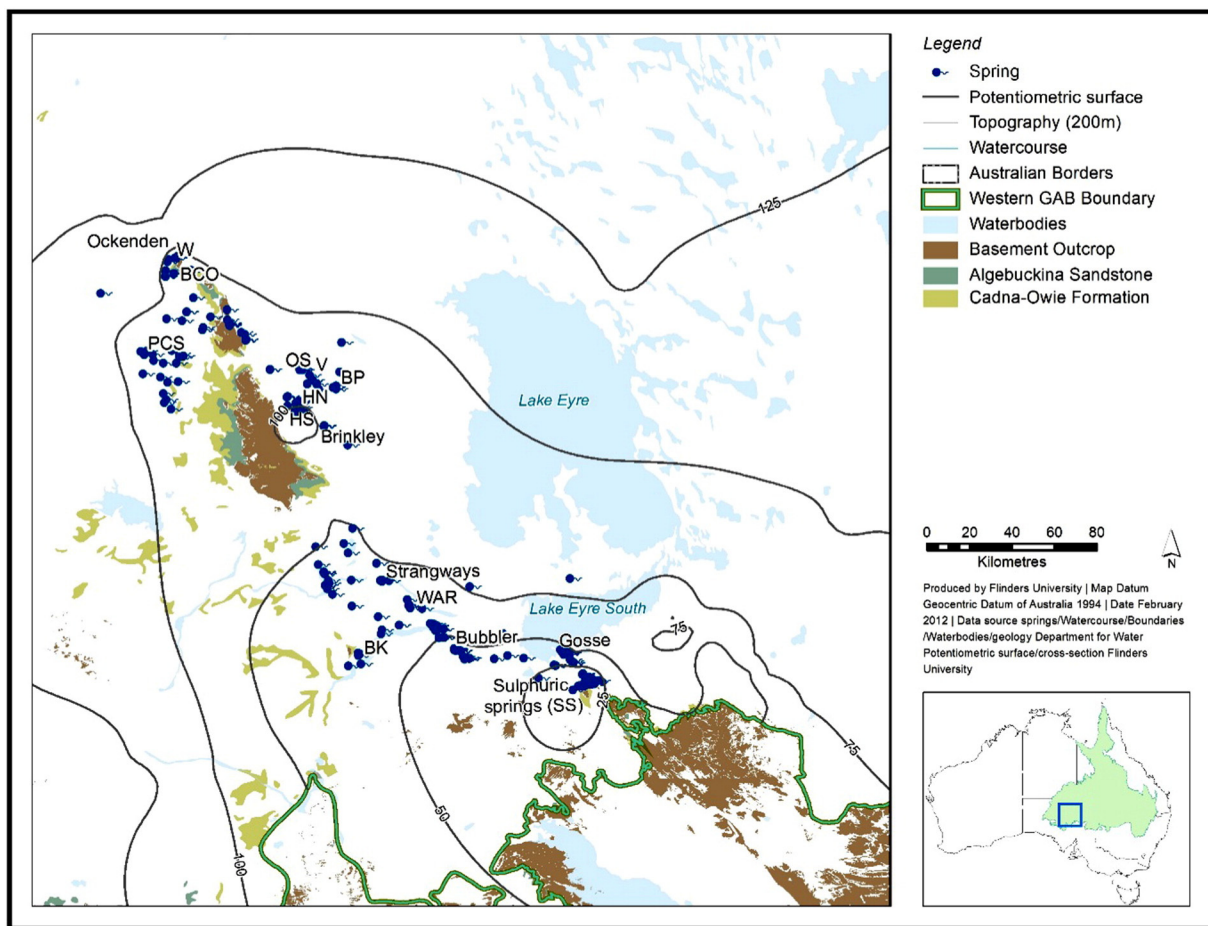


Fig. 1. Map showing the locations of springs in the Lake Eyre spring group of the western GAB. Spring sample codes are provided in Table 1.

in dry season conditions as a result of the oxidation of sulfidic materials

- Monosulfidic: Soil material containing $\geq 0.01\%$ acid volatile sulfide.

The total amount of reduced inorganic sulfur contained mainly within sulfide minerals (SCR), was determined by the Cr-reducible S technique for use in acid-base accounting (Ahern et al., 1998). The total amount of acid generated, assuming complete oxidation, is quantified in $\text{mol H}^+ \text{tonne}^{-1}$. As well as potential acidity in the pyrite, the amount of acidity already present in the soil was measured as titratable actual acidity (TAA). In sulfuric materials, retained acidity (RA: an operational term considered to be acidity stored in mineral phases such as jarosite) may form the major component of stored acidity. The sum of acidity generated by SCR, TAA and retained acidity represents the acid generating potential (AGP) of the sample. Acid-base accounting simply balances the total amount of acidity against the potential amount of neutralisation. The net acidity (NA) is calculated as the difference between AGP and acid neutralising capacity (ANC; typically using a factor to account for limited reaction of carbonate):

$$\text{NA} = (\text{TAA} + \text{SCR} + \text{RA}) - \text{ANC}/1.5$$

A positive value indicates an excess of acid and the likelihood of soil acidification when soil is disturbed and oxidised. Trigger values for coastal ASS vary according to texture, being 6 mol/tonne in clean sands to 62 mol/tonne for heavy clays (Dear et al., 2014).

Spring waters were collected from close to the discharge point. For bore waters, a minimum of 3 bore volumes were pumped, after checking that the field parameters pH, Eh and SEC were stable. Water samples were filtered on-site using Millipore 0.45 μm membrane filters and an aliquot for major and trace cations acidified to 1% v/v with nitric

acid. Alkalinity was measured by acid titration using a field HACH kit. Existing data were compiled into a project database including existing data for South Australia, Northern Territory and SW Queensland (Love et al., 2013). Major cations and sulfur were analysed on an ARL 3580B Inductively Coupled Plasma Optical Emission Spectrometer (ICP OES). For trace multi-element analysis, water samples were analysed by Inductively Coupled Plasma Mass Spectrometry (ICPMS) [APHA method 3125] on an Agilent 7500ce (Agilent Technologies, Tokyo, Japan). The samples were run using helium as a collision gas to remove oxide or doubly charged mass interferences and hydrogen as a reaction gas to remove Cl interferences on Se masses to be detected. Drift regulation was achieved using an internal standard with similar mass and first ionization potential to the elements to be analysed; ^{115}In , ^{103}Rh , ^{193}Ir and ^{209}Bi were used. Analyses were quantified by use of blanks and calibration standards. Nitrogen species, Cl and PO_4 were analysed by colorimetric analysis using an Auto Analyser, Br, F and SO_4 by ion chromatography and NPOC by a TOC Analyser.

3. Results

3.1. Field characteristics

The GAB springs varied in size, structure and flow (Fig. 2). They varied from small mounds devoid of travertine mounds (e.g. Gosse) to extensive travertine platforms in the central and western regions of the spring zone. Many of the larger travertine mounds and platforms had no flow or small satellite discharges, attesting to a lower piezometric surface than in the past. Mineral efflorescences were common around most springs, varying from pure white through brown and orange to bright yellow. These varied from fluffy white coatings to thick



Fig. 2. GAB spring photographs showing the variation in character from active to extinct travertine mounds and travertine-free discharges. Top left: extinct spring; top right: The Bubbler named because of the degassing of large bubbles; bottom left: extensive Fe-oxyhydroxysulfate efflorescences and dieback of *Phragmites* reeds at Big Perry spring; bottom right: dissolution features - undercutting of travertine mound by sulfuric materials at Strangways springs.

(> 10 cm) surface precipitates. The more brightly coloured precipitates were often found in spring zones displaying dissolution features (cavities, voids, cusped surfaces) in the travertine.

3.2. Mineralogy

There was a large diversity of mineral salt efflorescences identified around the vents, comprising mainly sulfate, hydroxysulfate, chloride,

carbonate and bicarbonate minerals in addition to the travertine mounds (Table 1). In the eastern sector, halite and gypsum were identified, along with the rarer sulfate minerals thenardite and eugsterite. The rare carbonates thermonatrite and trona were also found around discharge vents of Gosse Springs.

A range of rare Fe- and Al-bearing, acid generating hydroxysulfate efflorescence minerals were identified, especially in some of the north western springs where there was evidence of decreasing spring flow

Table 1
Mineral phases identified in the discharge zones of springs.

Minerals (by XRD)	Composition	Spring sources
Alunogen	$\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$	Brinkley, Vaughan
Blödite	$\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	Brinkley
Copiapite	$\text{Fe}^{2+}\text{Fe}^{3+}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$	Vaughan
D'Ansite	$\text{Na}_{21}\text{Mg}(\text{SO}_4)_{10}\text{Cl}_3$	Brinkley
Eugsterite	$\text{Na}_4\text{Ca}(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$	Little bubbler
Feldspar	$(\text{K}, \text{Na}, \text{Ca})(\text{Si}, \text{Al})_4\text{O}_8$	Brinkley
Ferrinatrite	$\text{Na}_3\text{Fe}^{3+}(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O}$	Brinkley
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Big Perry, Brinkley, Gosse, Hawker, Little Bubbler, Vaughan
Halite	NaCl	Big Perry, Brinkley, Gosse, Hawker, Little Bubbler, Vaughan
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	Big Perry, Hawker
Jurbanite	$\text{Al}(\text{SO}_4)(\text{OH}) \cdot \text{H}_2\text{O}$	Vaughan
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Brinkley, Hawker
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Big Perry
Metavoltine	$\text{K}_2\text{Na}_6\text{Fe}^{2+}\text{Fe}^{3+}_6(\text{SO}_4)_{12}\text{O}_2 \cdot 18\text{H}_2\text{O}$	Big Perry, Brinkley, Vaughan
Mica	$\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$	Brinkley
Natrojarosite	$\text{NaFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$	Big Perry, Brinkley, Hawker, Vaughan
Pyrite	FeS_2	Big Perry, Hawker
Rhombochase	$\text{HFe}^{3+}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	Big Perry
Sideronatrite	$\text{Na}_2\text{Fe}^{3+}(\text{SO}_4)_2\text{OH} \cdot 3\text{H}_2\text{O}$	Big Perry, Brinkley, Hawker, Vaughan
Smectite	$(\text{Ca}, \text{Na})_{0.3}(\text{Al}, \text{Mg}, \text{Fe})_{2-3}(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$	Brinkley
Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	Big Perry, Hawker
Tamarugite	$\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	Brinkley, Vaughan
Thenardite	NaSO_4	Brinkley, Little Bubbler
Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	Gosse
Trona	$\text{Na}_2(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$	Gosse
Tschermagite	$(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	Brinkley
Quartz	SiO_2	Big Perry, Brinkley, Gosse, Hawker, Little Bubbler, Vaughan
Unknownite	? (no known XRD pattern)	Vaughan

and intense evaporation; here the mineral efflorescences were up to 10 cm thick. These included the Al- and Fe-bearing hydroxysulfate minerals alunogen, tamarugite, sideronatrite and metavoltine as well as the first recorded occurrence of ferrinatrite in Australia. Many of these minerals are only stable under extremely acidic conditions. Some salts could not be identified as they did not match any spectra in current databases. The Fe hydroxysulfates varied in soil profiles with metavoltine, sideronatrite and ferrinatrite present at or near the surface, where the effects of evaporation led to concentration of H^+ , whilst natrojarosite and jarosite were present deeper in soil profiles where pH was higher. The deeper soils at Big Perry and Hawker comprised mainly pyrite with minor quartz and kaolinite (Table 1). Scanning electron micrographs are shown on Fig. 3, which displays the change from pyrite dominant at depth through jarosite above the redox front and sideronatrite and melanterite at the soil surface.

3.3. Soil/sediment pH and geochemistry

The pH of soils (1:1 soil:water) varied from pH < 0.1 to pH 10. In the most extremely acidic soils, sulfuric materials were present to depths of at least 80 cm (Fig. 4). The change in pH during incubation experiments also varied; many were already sulfuric but displayed potential to decrease even further, whilst others showed only a small decrease remaining circumneutral to alkaline due to acid buffering capacity due to high contents of ANC (mainly calcium carbonate). Even with peroxide treatment, some soils showed little change in pH (e.g. Warburton and Outside springs, Fig. 4) whilst others showed large decreases where sulfide concentrations were very high and ANC low.

3.4. Acid base accounting

Acid base accounting was undertaken on selected samples and profiles (Fig. 5). The concentrations of SCR varied from <0.01 to 42% (Table 2). At two spring sites (Hawker and Big Perry), a distinct redox boundary was noted by a change in colour to black or dark grey at the

present water table. The deepest profile at Brinkley was black but dry and non-sulfidic. The shallow soils were strongly sulfuric, consistent with the Fe- and Al-oxyhydroxysulfate minerals diagnostic of extreme acidity. Net acidities were extremely high at Brinkley (up to 7000 mol H^+ /tonne cf. the trigger value for coastal acid sulfate soils of 6–62 mol H^+ /tonne depending on soil texture). The upper soil layers were dominated by TAA, with RA more dominant deeper in the profile. Net acidities overall showed a wide range from –10,852 to > +20,000 mol H^+ /tonne. The highest values were from saturated soils at Big Perry and Hawker which contained the highest SCR concentrations yet recorded for an acid sulfate soil (33–42%).

3.5. Regional hydrochemistry (spring and regional groundwater)

The groundwaters and springs of the western GAB display a wide diversity of water types (Fig. 6), and they are indistinguishable chemically; most lie between Na- HCO_3 and Na-Cl type waters. In comparison with seawater composition, many of the Na-Cl type waters display much higher SO_4 relative to Cl, whilst the more Na- HCO_3 waters often have much lower ratios. The waters are dominantly circumneutral to alkaline (pH typically 7–9; median 7.70) and fresh to brackish (median SEC of 5497 $\mu S\ cm^{-1}$).

A distinction exists at a regional scale in terms of water type, with Na- HCO_3 to Na- HCO_3 -Cl types dominating flow paths from the north and Na-Cl- SO_4 and Na-Ca-Cl- SO_4 waters derived from the west and north-west. The northerly derived groundwaters are relatively fresh, with very low Ca and SO_4 , and very high alkalinity (up to 40 meq/L), whilst those derived from the western margin have relatively high Ca and SO_4 and lower (but still high) alkalinity (Fig. 7). Minor and trace element compositions are also variable, with some elements displaying large differences along the spring line e.g. F is much higher towards the east in the Na- HCO_3 waters and the Sr trend is similar to that for Ca. Apart from Fe and Mn which can be quite high in the groundwaters, trace metals and metalloids were generally very low reflecting limited

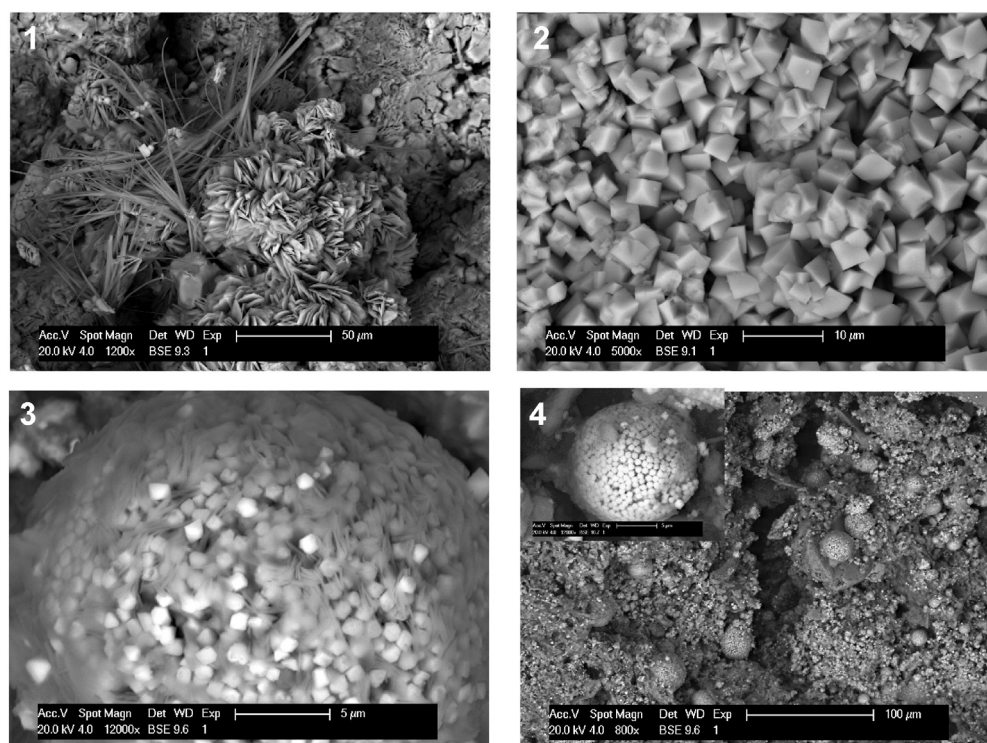


Fig. 3. Scanning electron micrographs of soils showing 1. Big Perry surface efflorescence comprising rosettes and acicular melanterite and sideronatrite; 2–4 Hawker springs: 2. Jarosite 15–40 cm; 3. Pyrite framboid with thin jarositic coating 46–60 cm; 4. Abundant pyrite framboids 60–80 cm.

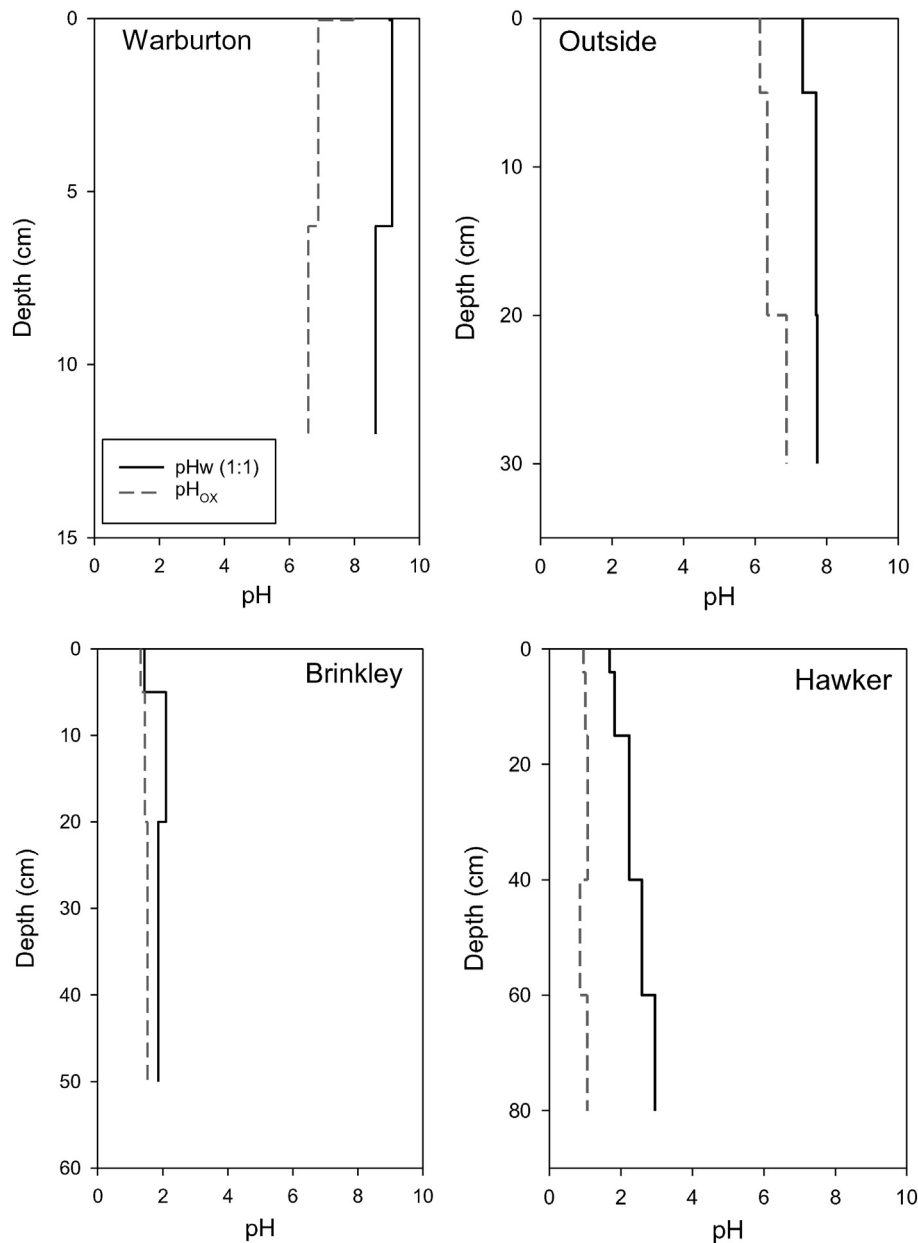


Fig. 4. Selected pH soil profiles for GAB spring soils, showing pH (1:1) and pH following peroxide treatment. The soils from Warburton and Outside springs are well buffered, whilst those from Brinkley and Hawker were sulfuric at the time of sampling and have potential to undergo even more acidification.

mobility in the neutral to high pH of groundwater and spring discharges.

4. Discussion

The presence of acid sulfate soils is a common feature of terrestrial wetland systems across Australia, and disturbance can have a significant impact on element cycling, nutrient dynamics and ecosystem diversity and resilience (Fitzpatrick & Shand, 2008; Mosley et al., 2014). Their occurrence within the discharge zones of the spring complexes is not surprising, but the severity of acidification in some areas, particularly as they are enclosed by extensive travertine mounds, was unexpected and greater than found in other inland and coastal wetland systems of Australia (Johnston et al., 2004; Macdonald et al., 2004; Lin et al., 1998; Fitzpatrick et al., 2009; Shand et al., 2010, 2012; Glover et al., 2011).

A decrease in the potentiometric surface in some areas of the Western GAB has resulted in the exposure of previously subaqueous soils and their subsequent oxidation. The most highly impacted spring sites contain some of the most extremely acidic in Australia and pose a potential risk to the unique spring ecosystems. A conceptual model is developed to explain the formation of highly sulfidic ASS, the geographical distribution of hypersulfidic and hyposulfidic ASS, and the role of deep groundwater processes in determining ASS hazard across this regional discharge zone.

4.1. Formation of highly sulfidic and sulfuric soil materials

The GAB springs are wholly dependent on groundwater. Their occurrence and the build-up of pyrite is controlled by the discharge of groundwater, which provides a source of SO_4 and Fe, and highly reducing organic-rich soils in the spring discharge vent. Sulfidic soils extend the beneath carbonate platforms as these areas are also saturated with

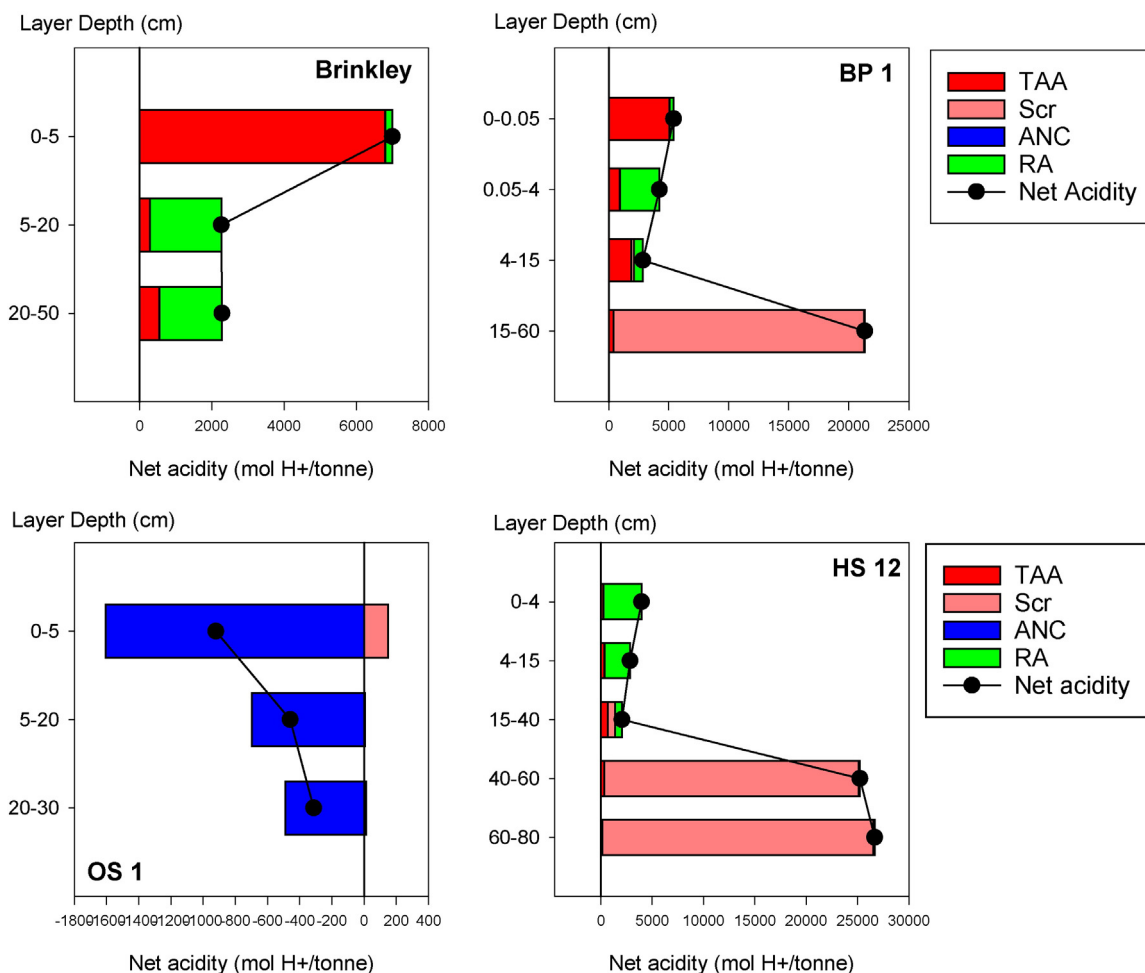
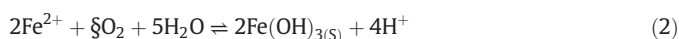


Fig. 5. Acid base accounting data for selected ASS profiles hypersulfidic: Brinkley, Big Perry (BP1) and Hawker South (HS 12) comprised sulfuric materials overlying were hypersulfidic layers and Outsider (OS 1) was hyposulfidic containing high calcite.

groundwater and reducing. The formation of pyrite occurs via a series of steps and there are different pathways, an overall reaction being:



The acidity of a water or soils is commonly represented by pH, however, potential or 'stored' acidity is present as dissolved reduced species that can generate protons through hydrolysis reactions e.g. the oxidation of Fe^{2+} :



This is one step during the multi-step process for the oxidation of pyrite. This process also occurs more generally e.g. moderately reducing Fe^{2+} -rich groundwaters with circumneutral pH may acidify to low pH when they are oxidised near the surface in areas unrelated to areas of pyrite oxidation. A better definition of acidity takes into account this additional 'stored' acidity (Kirby and Cravotta, 2005):

$$\text{Acidity} = 50 \left\{ 1000(10^{-\text{pH}}) + \left[2(\text{Fe}^{2+}) + 3(\text{Fe}^{3+}) \right] / 56 + 2(\text{Mn}) / 55 + 3(\text{Al}) / 27 \right\} \quad (3)$$

where concentrations are in mg/L

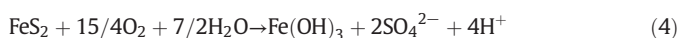
During the formation of the spring mounds, potential acidity and alkalinity are fractionated during mineral formation becoming spatially separated, especially pyrite and calcite. Pyrite is formed within the soils beneath the mound spring in highly reducing soils, and acidity is thus removed and stored within the soils and builds up over time, whilst dissolved alkalinity is largely transferred to the discharge zone and stored as calcite (note that where precipitation occurs in the vent soils, net acidity can be negative). This physical separation, therefore, provides for local hazards which may be a risk to ecosystems if a direct pathway exists for the transfer of oxidation products (protons and contaminants).

Some of the spring soils contain the highest recorded SCR (>40%) measured in acid sulfate soils, with pyrite being mainly in the form of framboids up to 30 μm diameter (Fig. 3). Net acidities in the deeper soil layers of >20,000 mol H^+ /tonne have not been observed in ASS systems previously. The presence of such high pyrite contents at some springs (equivalent to >90% pyrite in deeper soil layers) requires considerable amounts of time. This is consistent with the longevity of the springs over tens to hundreds of millennia (Prescott & Habermahl, 2008). It also suggests uninterrupted flow for long periods of time, since the soils would otherwise oxidise under lower flow conditions. There is anecdotal evidence that cattle stopped drinking water from Brinkley springs (previously considered very good quality stock water) some time before salt efflorescences began to form in the late 1960's (Bobby Hunter, Station Manager, Stuart Creek pers. Comm.), but sampling was not completed until a few decades after this time, hence the formation of very thick (>10 cm) hydroxysulfate mineral crusts. A number of springs have been extinct for some time as a

Table 2Selected acid base accounting data for soil samples. Note that RA is only completed on samples with $\text{pH}_{\text{KCl}} < 4$ and ANC on samples with $\text{pH}_{\text{KCl}} > 6.5$.

Spring group	Sample no.	AVS (% dry wt)	pH_{KCl}	TAA (mol H^+ /tonne)	SCR wt% as S	RA wt% as S	ANC wt%	Net acidity (mol H^+ /tonne)
Big Perry	BP 1.1		2.06	5070	0.04	0.69		5415
	BP 1.2		2.33	925	0.03	7.02		4226
	BP 1.3	0.035	1.89	1878	0.39	1.55		2844
	BP 1.4	0.020	2.60	429	33.41	0.14		21,333
Vaughan	V 4.1		2.26	2859	0.02	1.86		3740
	V 7.1		2.30	2838	0.04	0.41		3055
	V 14.1		3.02	137	0.02	2.26		1209
	V 15.1		3.38	126	0.01	4.40		2192
	V 17.1		4.49	95	0.01	3.64		1805
	OS 1.1	0.087	7.64	0	0.24		8.04	−921
Outsider	OS 1.2	0.030	8.19	0	0.01		3.50	−460
	OS 1.3	0.014	8.53	0	0.02		2.45	−314
	OS 4		8.44	0	0.02		14.25	−1886
	HN 1.2	0.042	3.05	264	4.76	1.54		3953
Hawker North	HN 1.3	0.065	4.02	146	9.99	0.21		6475
	HS 2.1		2.21	2983	0.06	3.34		4585
	HS 11.2		3.56	94	0.74	6.24		3476
Hawker South	HS 12.1		2.75	219	0.05	7.97		3978
	HS 12.2		2.67	310	0.07	5.33		2849
	HS 12.3	0.056	2.50	667	1.15	1.46		2065
	HS 12.4	0.020	3.01	310	39.75	0.29		25,238
	HS 12.5	0.024	3.56	156	42.28	0.33		26,680
	BCO 4		3.13	205	1.66	1.72		2044
Big Cadnaowie	BCO 5	0.056	8.03	0	4.30		11.28	1179
	BCO 6		8.41	0	0.01		0.25	−27
	W 1	0.086	7.96	0	0.92		0.45	514
Wandallina	ON 5	0.697	7.72	0	1.36		0.92	726
10 mile spring	10 M 2.2		8.91	0	0.21		17.72	−2229
Coodanoorina	PCS 001a		2.21	3719	0.02	1.18		4285
	PCS 001b		2.10	6530	0.01	0.30		6678
	PCS 001c		3.81	602	0.02	3.55		2276
Brinkley	pool		3.47	95	0.06	6.91		3366
	discharge		7.72	0	0.35		38.32	−4885
	BK 3.1		2.10	6799	<0.01	0.41		6998
	BK 3.2		2.83	290	<0.01	4.21		2265
	BK 3.3		2.57	548	0.01	3.69		2283
Billa Kalina	BK 1		8.78	0	2.27		24.29	−1823
	BK 2		9.15	0	0.18		28.73	−3713
	BK 3		8.60	0	2.09		34.39	−3278
Gosse	GOSSE 5		8.03	0	<0.01		3.37	−445
Warburton	WAR 2.1		9.62	0	0.01		45.34	−6033
	WAR 2.2		9.52	0	0.21		49.29	−6436
	WAR 3.1		9.30	0	0.27		82.75	−10,852
	WAR 3.2		9.66	0	0.05		19.26	−2532
	WAR 3.3		8.53	0	<0.01		50.39	−6709

consequence of reduced recharge over the past few millennia as a drier climate has been established and have not flowed in living memory. However, many springs showed evidence of a relatively recent decrease in flow e.g. the presence of stone water culverts which are now dry, and geochemical indicators of drying such as mineral efflorescences and oxidation fronts close to the current vent. At one of the springs where discharge was still active (and alkaline), dissolution features in the carbonate mound also suggest that older acidification events have occurred in the past. The oxidation of pyrite is one of the most acid generating reactions in nature. It takes place by a series of steps (some acid generating, some acid neutralising), which may be separated in space, hence the impacts may vary depending on transport processes. The overall reaction is:



Most of the oxidation occurs in the unsaturated zone where oxygen replenishment by diffusion and advection is high. The formation of secondary hydroxysulfate minerals, especially in semi-arid and arid environments (Figs. 2 and 3) may store some of the acidity, but can release this at a later date when the soils are re-wetted or saturated.

The springs which showed evidence of extreme acidification were mainly located in the central and western part of the spring line from Ockenden to Strangways (Fig. 1). Where the springs had dried completely (e.g. most springs at Brinkley), or dried out on the

margins of saturated areas (Fig. 2), soil pH was very low (minimum of pH 0.1). The pH of flowing spring waters was mainly slightly acidic to slightly alkaline (pH 6–9) as these areas are continuously saturated, but pulses of acidity occur during rainfall events. At Brinkley, ponded water at the margin of the channel had acidified strongly (pH 2.5; acidity 16 meq/L) and contained high concentrations of Al (61 mg/L) and Fe (68 mg/L). Most transition metals were present only at low concentrations at Brinkley, suggesting a limited source, the exceptions including slightly elevated Zn (170 $\mu\text{g/L}$) and high Be (223 $\mu\text{g/L}$). At Strangways, endemic species became confined to the discharge point during acidic pulses during rainfall events, returning to spring tails only after several months. The combination of exposure of hypersulfidic soils to oxygen and high evaporation rates has generated thick hydroxysulfate salt efflorescences, and these have been largely preserved by the lack of surface flow systems. The oxidation process in many springs is relatively recent and many of the risks from acidification are yet to be realised. The oxidation front has permeated to at least 50 cm at some sites (Fig. 5). Net acidities are generally lower in the upper parts of the profile (BP1 and HS 12 on Fig. 5) suggesting losses of acidity, during sulfide oxidation (only part of the acidity is left in secondary hydroxysulfates) or following rainfall events. Jarosite and natrojarosite (Fig. 3) were present above the redox front giving rise to high retained acidity (Fig. 5). Jarosite and natrojarosite are typically stable in the range $\text{pH} < \text{ca. } 2\text{--}4$ under oxidising conditions, but the pH of the upper soils were much more

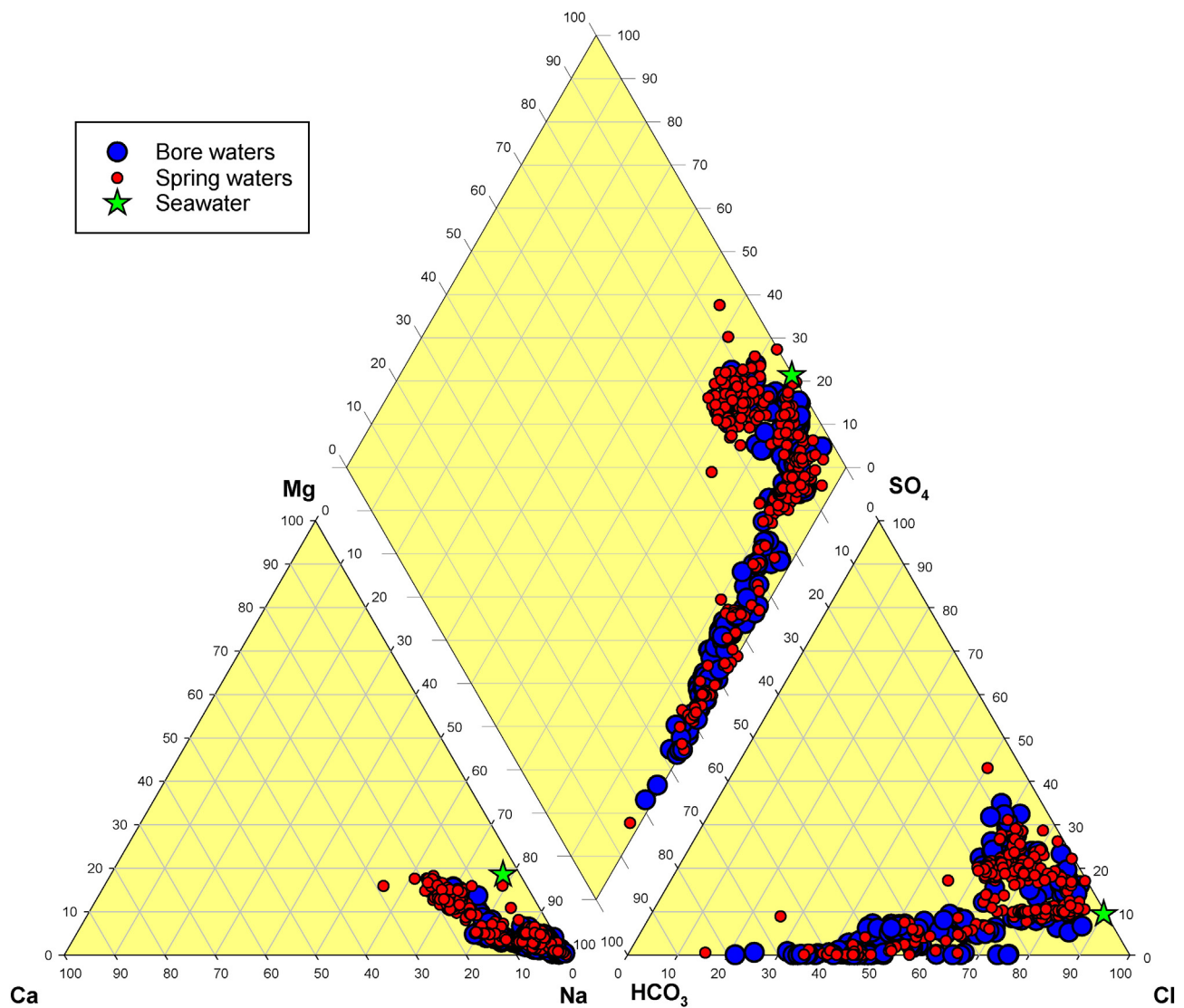


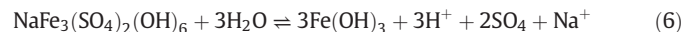
Fig. 6. Piper plot showing the variations in groundwater and spring discharges along the spring line.

acidic, due to high evaporation rates increasing proton activity. The very rare minerals metavoltine, sideronatrite and ferrinatrite (and in some cases melanterite) were the dominant hydroxysulfate minerals in the surface soil layers, having formed as oxidation products of pyrite under more extreme conditions e.g. for sideronatrite:



Chemical Acid base accounting analyses (Fig. 5) show that these minerals do not come under the operational definition of retained acidity, but are released under the titratable actual acidity step. The kinetics of dissolution and solubility of these acidic salts is, therefore, very different from that of the jarosite group, being easily mobilised and rapid. This should be taken into account in any risk assessment. As the oxidation front moves down the profile the effect of evaporation is likely to decrease, with an increase in pH by buffering with soil minerals such as clays, leading to differences in hydroxysulfate mineral assemblages. The paragenesis of hydroxysulfate minerals is likely to be from sideronatrite/metavoltine/ferrinatrite to jarosite/natrojarosite, with specific forms depending on local mineralogy and the availability of leached major cations (Na, K, Mg, Ca). The mineralogy is generally different to many AMD suites which are dominated by Fe sulfates (Jerz & Rimstidt, 2003), probably due to more intimate relationships between

pyrite and clays in the soil environment providing cations. The Fe-hydroxysulfate minerals melanterite and copiapite were, however, found in a few surface samples where acid-clay interactions were locally limited (Table 1). The formation of the hydroxysulfate salts represents a significant hazard because they act as stores of acidity, dissolving and releasing protons through hydrolysis reactions such as:



They may also release high concentrations of contaminants, as these mineral phases have a number of structural sites (Papike et al., 2006) that can incorporate a range of co-precipitated contaminants. Preliminary water leaching experiments (Shand et al., 2014) have shown that a range of contaminants including Al, As, Fe, Tl and V can be mobilised from these salt efflorescences.

Most spring waters visited in the south of the area showed no sign of acidification, the exception being 'Sulphuric Spring'. The chemistry of this spring, including S isotope data, suggest that the S in this spring is sourced from nearby Pre-Cambrian basement. A number of white mineral efflorescences were sampled around the more easterly vents. These were identified by XRD as the common minerals halite and gypsum, and the rarer minerals thenardite and eugsterite, the latter two minerals being sulfates typically associated with oxidised ASS in well buffered

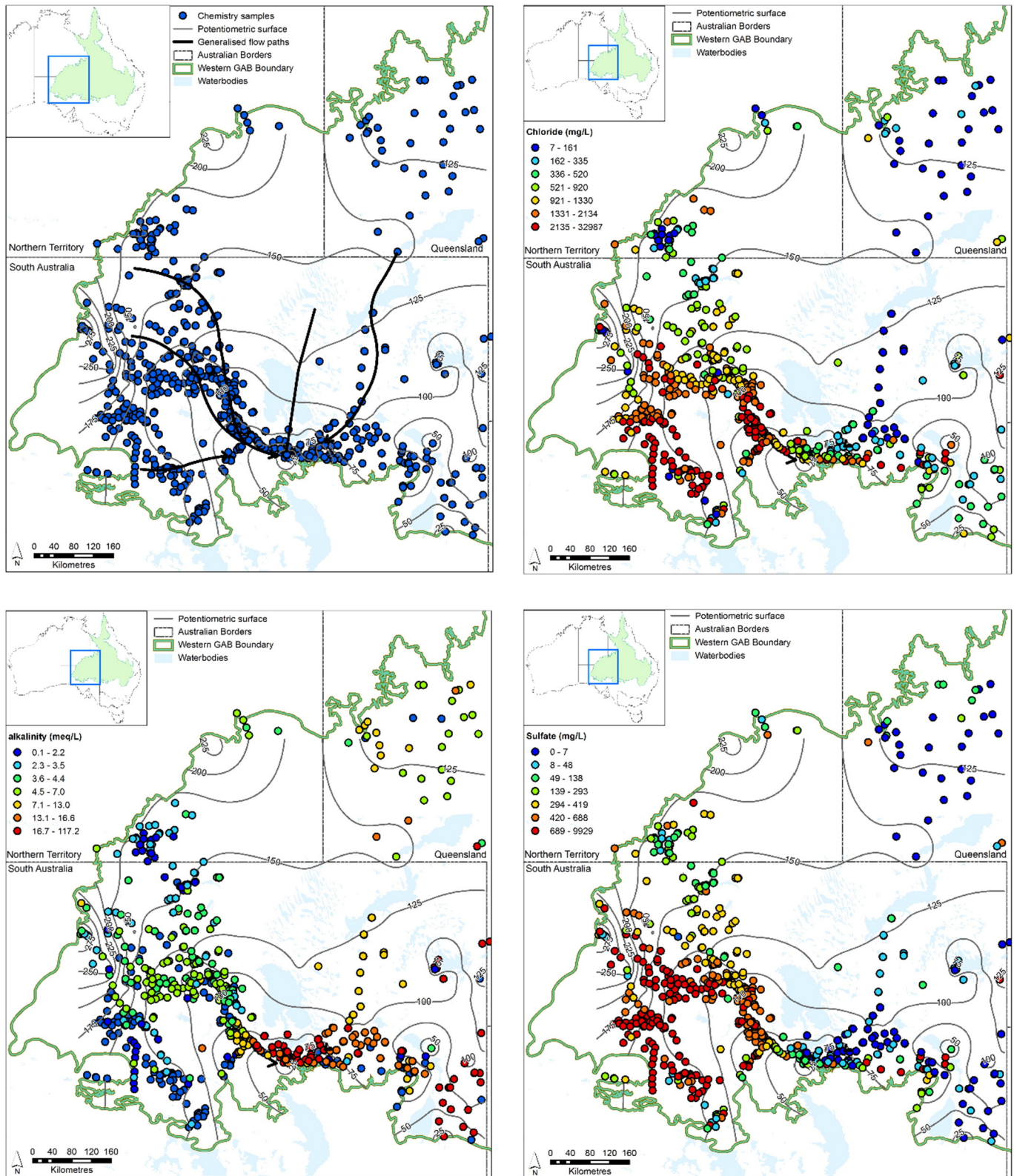


Fig. 7. Spatial maps showing (a) locations of samples with piezometric surface and generalised flow directions, and concentrations of (b) Cl (c) alkalinity and (d) SO_4 .

environments. At Gosse Spring, the Na-carbonate/bicarbonate minerals thermonatrite and trona were found around discharge zones. These minerals are uncommon, and Earman et al. (2005) noted that they are typically confined to young volcanic areas, and that the addition of excess CO_2 is an important condition for their formation. There is no evidence in the study area of recent volcanism, however, the Na-HCO_3

type waters in these springs along with exogenic CO_2 from deep mantle de-gassing (Love et al., 2009) has led to similar water compositions (with high alkalinity: Ca) which upon evaporation can explain the presence of these minerals from low temperature GAB springs. Their occurrence may thus be useful as an indicator of deep CO_2 -rich fluids from within the Earth's crust and mantle.

Most of the springs in this remote region of Australia have not been assessed for the occurrence of ASS, and their distribution is not known in detail. However, all of the sites which are being impacted by soil acidification were in areas where travertine mounds were present. The presence of abundant travertine and surrounding calcareous soils at these sites makes extensive soil acidification unlikely. However, the impact on the rare ecosystems, many with endemic species, within spring pools and tails may be severe and the potential hazards from oxidation of acid sulfate soils need to form part of any risk assessment of the springs. Towards the central part of the spring line, travertine mounds were present, but net acidities were negative in the few samples collected. In many of the eastern springs, carbonate mounds were absent and alkalinities very high in the groundwater and soils. Consideration is now given to the groundwater as a potential control on the occurrence of ASS hazard and on Fe and S cycling in the spring discharge zones.

4.2. Linking hazardous ASS to groundwater hydrochemistry

The regional variations in groundwater chemistry in the western GAB are, in detail, not simple, with compositions being a function of recharge processes (e.g. climate variability controlling salinity), geochemical pathways through the aquifer and inter-aquifer leakage. Nevertheless, there are some broad features which are relevant to the formation of ASS and provide a clue as to why some discharge zones contain high net acidities whilst others have highly negative net acidities (high alkalinities). The fractionation of acidity (forming sulfidic sub-aqueous soils) from alkalinity (forming carbonate caps) has already been alluded to in the previous section and shows how net acidity can be focussed in specific areas of the critical zone, but this cannot explain why it happens in some systems and not others.

The springs represent the discharge from deep aquifers, and it is not yet clear to what degree inter-aquifer mixing and geochemical reactions

are occurring as the artesian waters make their way to the surface. However, the spring waters display similar concentrations and spatial variations to the local groundwater sourced from the underlying Jurassic-Cretaceous aquifer, and it is likely that this dominates the source of spring discharge. A detailed geochemical interpretation of groundwater evolution is beyond the scope of this study, but the spring data display chemical trends (Fig. 8) along the spring zone from Ockenden to Gosse (Fig. 1). Some scatter exists due to the effects of evaporation, especially in low discharge pools (confirmed by heavy stable $\delta^{18}\text{O}$ isotope signals). The transect can be subdivided into at least three sections (Fig. 8):

- North-west – from 0 to ca. 90 km
- Central – from ca. 90 km to ca. 200 km
- Eastern – from ca. 200 km to ca. 350 km.

The north-western section is characterised by relatively high SO_4 , moderate Ca and alkalinity, along with high SO_4/Cl ratios (higher than the seawater ratio of 0.142), the latter indicating an additional source of SO_4 from recharged rainfall. A significant increase in SEC occurred in Section 2, where the spring waters have higher Ca (and other major elements), SO_4 and increasing alkalinity and decreasing SO_4/Cl towards the east. The eastern sector, where Na- HCO_3 type waters dominate, displayed very high alkalinity along with low SO_4 , Ca and SO_4/Cl ratios. Sulfate was often below detection limit and SO_4/Cl ratios much lower than seawater, indicating removal of SO_4 from solution. Although sulfate reduction can explain a trend between SO_4 and HCO_3 , alkalinities are too high for the inorganic C to be derived solely by this process alone. The spatial variations in spring discharge chemistry are consistent with different mixtures of groundwater sources which have evolved differently along regional flow pathways (Fig. 7). The north-

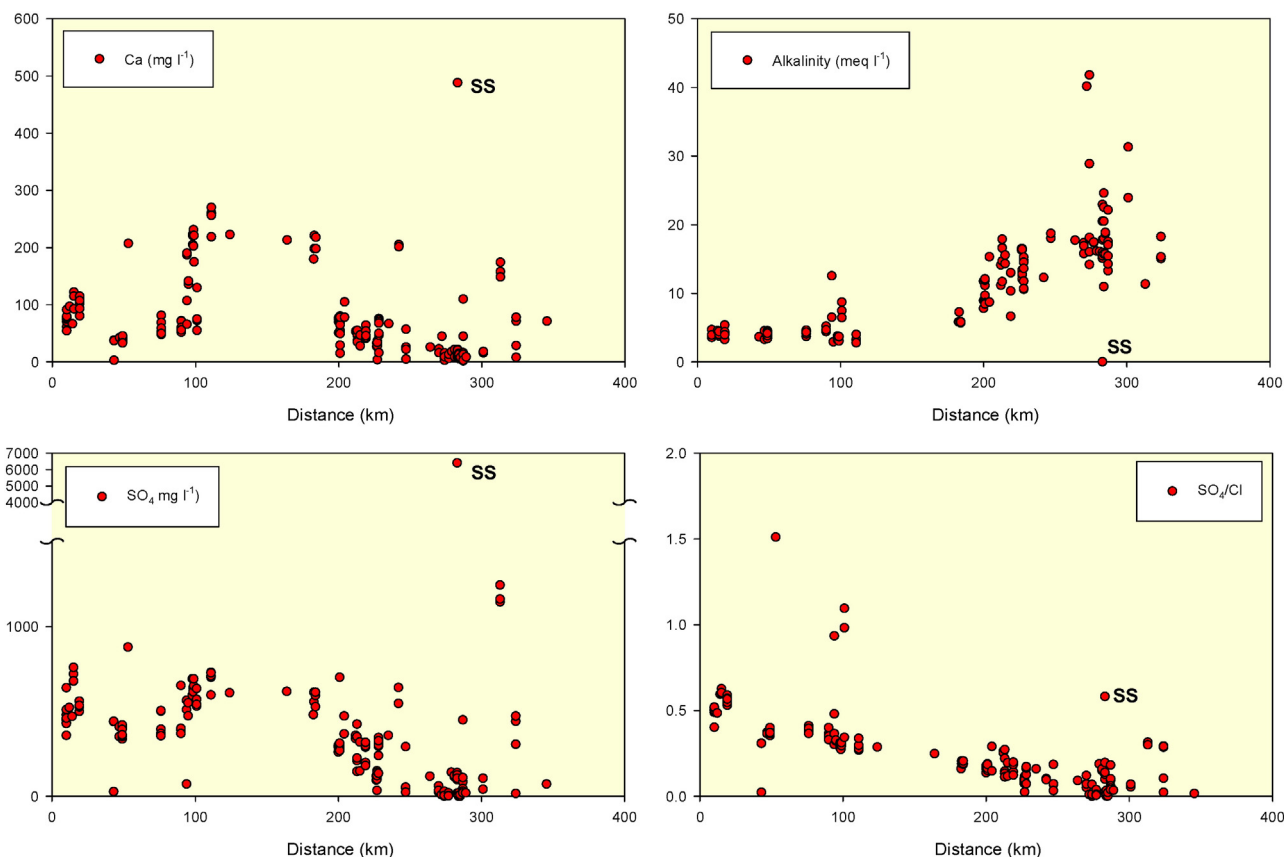


Fig. 8. Hydrochemical variations in spring waters along the spring transect from the north-west to southeast (see Fig. 1 for spring zone).

west springs are dominantly sourced from northern South Australia and Northern Territory where modern recharge is currently dominated by episodic river recharge e.g. from the Finke River (Love et al., 2013); the central section springs have a much greater influence from the western margin where salinity, including SO_4 is very high; and the eastern sector comprises waters dominantly from Queensland which are low in SO_4 and high in alkalinity. Most of the severely impacted springs occur in regions where groundwater Ca and SO_4 are high, the latter providing S for the formation of pyrite. Iron concentrations in these areas are variable in the spring waters as much of the Fe is removed to form sulfide during flow through the reducing subaqueous soils or as Fe oxyhydroxides as the spring waters discharge in contact with the

atmosphere. The eastern spring waters typically contain low SO_4 combined with high alkalinity, hence much more limited opportunity to form sulfide-rich and hypersulfidic soils over time. Therefore, there appears to be a strong link to groundwater chemistry in terms of acidification hazard and risk.

4.3. Controlling factors on the acidification potential of springs in the critical zone: linking hazardous ASS to groundwater evolution and mantle dynamics beneath the Australian craton

The build-up of hypersulfidic sub-aqueous soil materials occurs in the very shallow critical zone, where a major geochemical barrier exists

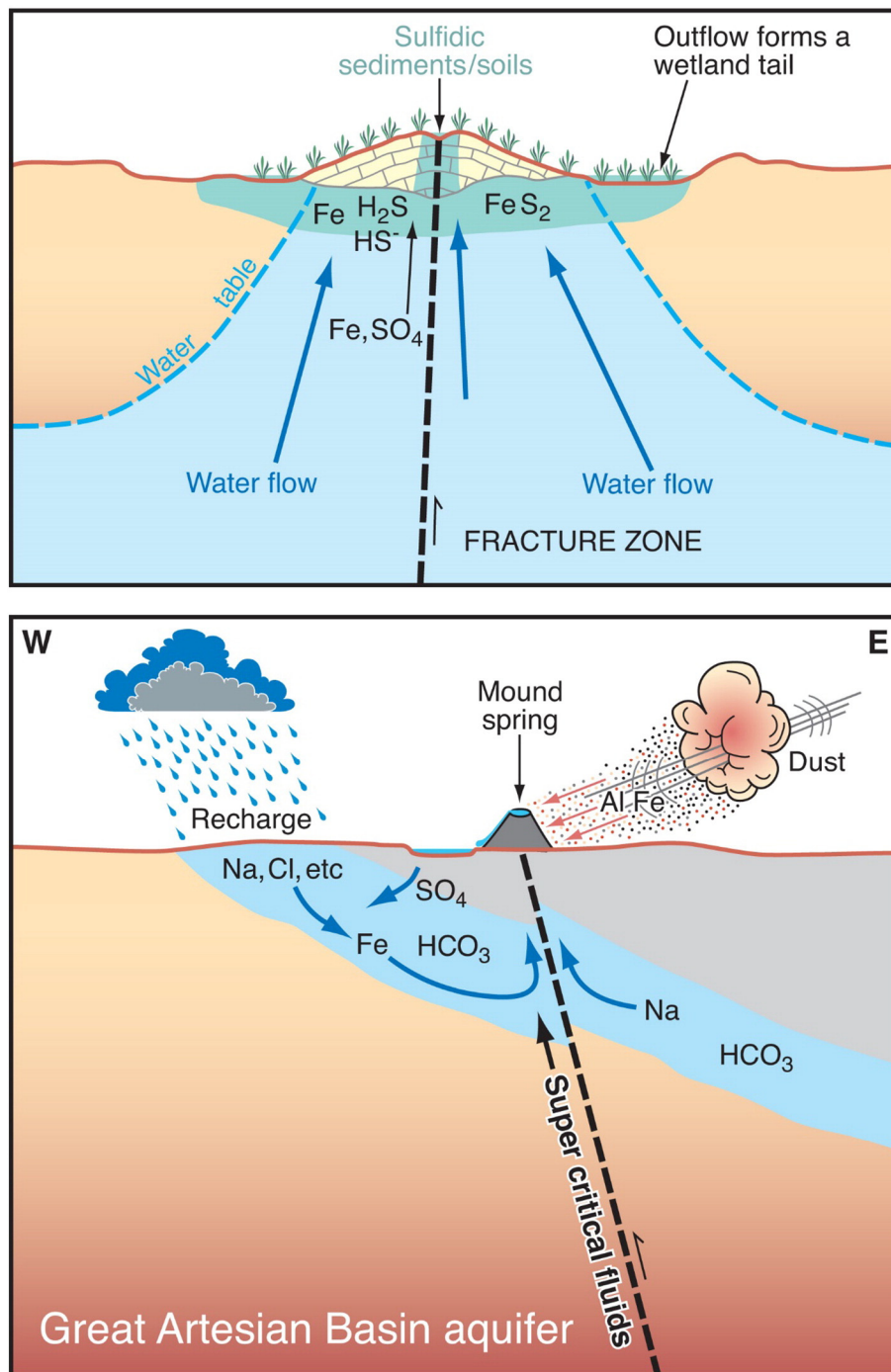


Fig. 9. Top: schematic of a spring vent in the north-western area of springs showing the local environment where pyrite forms in saturated reducing soils within and beneath the travertine mound; bottom: schematic of the relationship between regional groundwater evolution and mound springs highlighting the different sources of components which control ASS hazard.

to remove Fe and SO₄ from deep moderately reducing groundwaters. At a local scale (Fig. 9), the discharge zone can be considered as a series of evolving geochemical compartments as the groundwater moves firstly through sub-aqueous soils containing sufficient organic matter to reduce SO₄ and Fe to ultimately form pyrite. Limited degassing of CO₂ (the main control on reaching calcite saturation) beneath the carbonate mounds means that most of the alkalinity is not removed from the groundwater in this part of the system and net acidity becomes positive and increases with time. The build-up of pyrite is a function of time and history of groundwater flow, with perennial flow and long timescales needed to build up high contents of pyrite and net acidity. Some precipitation of carbonate may occur within the vent, but typically oversaturation with respect to calcite (by CO₂ degassing) is needed for the travertine to form, and precipitation is mostly separated from the zone of sulfidization. This separation of acidity and alkalinity derived from the groundwater, and potential pathways of contaminants to surface flow and the adjacent aquatic and terrestrial ecosystems are the main controls on risk. The C and S cycles essentially become decoupled within the discharge zones due to transport processes. In detail, the form and geochemical environments of each spring system are unique, being a function of landscape position, underlying geology and groundwater composition, hence, a detailed study is required to determine the risk at each site.

A much better understanding of the location of hazards across the spring discharge is, therefore, gained through detailed knowledge of regional groundwater flow patterns and chemistry. The correlation of extreme acidity with travertine mounds may seem counter intuitive, but the conceptual model developed above explains the formation of hypersulfidic soil and correlation of acidification hazard with travertine. A similar geochemical correlation of acidic drains in Western Australia and calcareous soils (Shand et al., 2008) may well be due to a similar process. The lack of both sulfidic systems and travertine mounds in most of the eastern springs despite very high alkalinity is due to the nature of the groundwaters: Na-HCO₃ water types with very low concentrations of Ca and SO₄. A key feature of the GAB groundwaters is the high alkalinities in general, and these play a key part in the conceptual model developed above. The addition of CO₂ from deep mantle and/or crustal fluids to groundwaters can have a profound effect on water chemistry (Wexsteen et al., 1988; Shand et al., 2004). For the northerly-derived groundwaters in the east of the spring zone, the excess CO₂ has been

buffered by reactions with aquifer minerals generating high bicarbonate and carbonate alkalinity and well buffered pH. This has suppressed any potential increase in Ca due to the common ion effect, and Ca is too low for the formation of travertine deposits. High net alkalinities combined with loss of SO₄ due to sulfate reduction in the aquifer, means that these springs pose very little risk of acidification. The high HCO₃/Ca ratios have led to the formation of rare Na bicarbonate and carbonate mineral efflorescences as a key indicator of excess CO₂ and loci of deep earth degassing.

The north western and western-derived groundwaters are much higher in the base cations Ca and Mg. Although alkalinities are lower than those in the east, they are still high enough to form large travertine mounds on de-gassing of excess CO₂ as the groundwaters equilibrate with the atmosphere (lower partial pressure of CO₂), causing an increase in pH and consequent supersaturation with respect to calcite. Combined with the formation of pyrite over time, this has allowed the formation of strongly hypersulfidic soils beneath the mounds and a severe hazard to develop. Extensive dissolution occurs where the hypersulfidic soils are in intimate contact with travertine e.g. note the undercutting of travertine on Fig. 2 (lower right).

The GAB spring environments highlight an important geochemical connection between the mantle/deep crust and the critical zone that has been active for millennia to millions of years (Fig. 10). The development of ancient crustal scale fractures form important pathways for the flux of supercritical fluids from deep within the earth, incorporation into deep and shallow groundwater circulation systems, geochemical evolution of groundwater and controls on shallow critical zone biogeochemical cycles which have a significant effect on water quality and groundwater dependent ecosystems.

The influence of deep groundwater systems on the critical zone the and connections between deep and shallow fluids in the earth are often difficult to ascertain due to the diversity of internal hydrological flow systems on and within the earth. The artesian arid zone GAB springs, located in internally draining basins where surface flows do not influence discharge, have helped to highlight these controls, including the role of deep fractures as conduits for discharge. However, the details of how other deep multi-layer aquifer systems interact with fluids along complex structures and their role in biogeochemical cycling, ecosystem diversity and endemism currently and in the past remain key challenges to critical zone scientists.

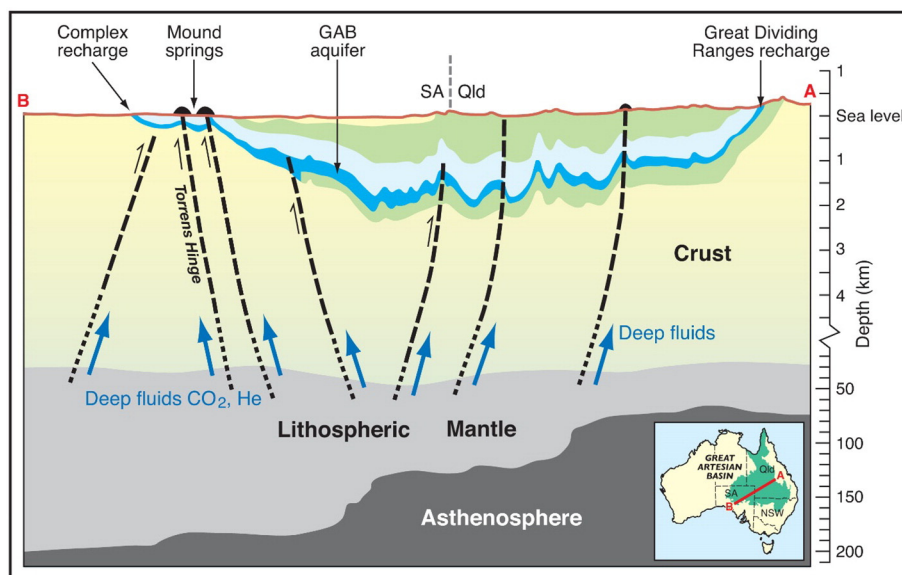


Fig. 10. Schematic of the GAB showing the zone of influence of the critical zone extending down to the mantle via. ascent of deep fluids which interact with regional groundwater, thereby controlling geochemical processes in the shallow critical zone.

5. Conclusions

Hypersulfidic soils with extremely high net acidities appear to be a common feature of travertine mound springs in the western GAB discharge zone. Their presence is controlled by the discharge of deep artesian flow from underlying aquifers through organic-rich soils and formation of pyrite within and beneath the carbonate mounds. With decreasing flow conditions, exposure of the soils is leading in some cases to extremely acidic soil, often with $\text{pH} < 1$, and potentially devastating effects on local ecosystems. A range of very rare iron and aluminium hydroxysulfates have formed in these highly acidic environments due to oxidation under high evaporation conditions in the arid zone. The presence of locally high net acidities is considered to be a result of the effective fractionation of acidity from alkalinity in the groundwater: stored acidity is built up in the reducing soils by the precipitation of pyrite, whilst alkalinity (from artesian groundwater as well as sulfate reduction) is transported to the surface to form travertine mounds upon degassing of CO_2 .

The distribution of ASS hazard is linked to groundwater chemistry. The areas of acidification correlate with the presence of carbonate mounds formed from water with moderately high Ca and SO_4 as well as excess CO_2 derived, at least in part, from mantle degassing. Spring discharges in the eastern part of the study area do not have travertine mounds as the groundwaters are of Na-HCO_3 type with very low concentrations of Ca and SO_4 . In the arid environment evaporation has led to the formation of rare Na carbonates and bicarbonates as a result of very high HCO_3 :Ca ratios. These mineral phases may be a useful guide to areas of degassing along buried deep crustal lineaments.

The spring environments highlight a deep sub-surface connection to the critical zone that has been active in some cases for millions of years: controlling the flux of dissolved components and gases in fluids from deep sedimentary basins and concentration within and above highly reducing sediments at the discharge zone. This coupling of flow systems to shallow biogeochemical cycles has been strongly influenced by geochemical evolution in deep aquifer systems and the incorporation of even deeper endogenic mantle-derived gases particularly CO_2 . This study demonstrates the influence of sub-surface processes and linkages between deep and shallow fluids, sometimes down to hundreds of km, on biogeochemical cycling in the critical zone, and the need to consider the earth in a much more holistic way.

References

- Ahern, C.R., Ahern, M.R., Powell, B., 1998. Guidelines for Sampling and Analysis of Lowland Acid Sulfate Soils (ASS) in Queensland 1998. QASSIT, Department of Natural Resources, Resource Sciences Centre, Indooroopilly, Queensland, Australia.
- Brantley, S.L., White, T.S., White, A.F., Sparks, D., Richter, D., Pregitzer, K., Derry, L., Chorover, J., Chadwick, O., April, R., Anderson, S., Amundson, R., 2006. Frontiers in Exploration of the Critical Zone: Report of a Workshop Sponsored by the National Science Foundation (NSF), October 24–26, 2005, Newark, DE (30p).
- Burgin, A.J., Yang, W.H., Hamilton, S.K., Silver, W.L., 2011. Beyond carbon and nitrogen: how the microbial energy economy couples elemental cycles in diverse ecosystems. *Front. Ecol. Environ.* 9 (1), 44–52.
- Creeper, N.L., Fitzpatrick, R.W., Shand, P., 2012. A simplified incubation method incorporating the use of chip-trays as incubation vessels to identify sulfidic materials in acid sulfate soils. *Soil Use Manag.* 28, 401–408.
- Crossey, L., Priestley, S., Shand, P., Karlstrom, K., Love, A.J., Keppel, M., 2013. Source and origin of western GAB spring water. In: Love, A.J., et al. (Eds.), *Allocating Water and Maintaining Springs in the Great Artesian Basin*, Volume II: Groundwater Discharge of the Western Great Artesian Basin. National Water Commission, Canberra, pp. 10–33.
- Dear, S.-E., Ahern, C.R., O'Brien, L.E., Dobos, S.K., McElnea, A.E., Moore, N.G., Watling, K.M., 2014. Queensland Acid Sulfate Soil Technical Manual: Soil Management Guidelines. Department of Science, Information Technology, Innovation and the Arts, Queensland Government, Brisbane.
- De Nobili, M., Francaviglia, R., Sequi, P., 2002. Retention and mobility of chemicals in soil. *Dev. Soil Sci.* 28A, 171–196.
- Dupas, R., Gruau, G., Gu, S., Humbert, G., Jaffrezic, A., Gascuel-Oudou, C., 2015. Groundwater control of biogeochemical processes causing phosphorous release from riparian wetlands. *Water Res.* 84, 307–314.
- Earman, S., Phillips, F.M., McPherson, B.J.O.L., 2005. The role of “excess” CO_2 in the formation of trona deposits. *Appl. Geochem.* 20, 2217–2232.
- Falkowski, P.G., Fenchel, T., Delong, E.F., 2008. The microbial engines that drive earth's biogeochemical cycles. *Science* 320, 1034–1039.
- Finzi, A.C., Cole, J.J., Doney, S.C., Holland, E.A., Jackson, R.B., 2011. Research frontiers in the analysis of coupled biogeochemical cycles. *Front. Ecol. Environ.* 9 (1), 74–80.
- Fitzpatrick, R.W., Shand, P., 2008. Inland Acid Sulfate Soil Systems Across Australia: Covering: Distribution, Properties, Significance and Biogeochemical Processes of Inland Acid Sulfate Soils (ASS) across Australia and overseas. CRC LEME Open File Report No. 249 (Thematic Volume) CRC LEME, Perth, Australia. CRC LEME, Perth, Western Australia (305 pp. ISBN 1329-4768).
- Fitzpatrick, R.W., Shand, P., Merry, R.H., 2009. Acid sulfate soils. In: Jennings, J.T. (Ed.), *Natural History of the Riverland and Murraylands*. Royal Society of South Australia (Inc.), Adelaide, South Australia, pp. 65–111.
- Glover, F., Whistworth, K.L., Kappen, P., Baldwin, D.S., Rees, G.N., Webb, J.A., Silvester, E., 2011. Acidification and buffering mechanisms in acid sulfate soil wetlands of the Murray-Darling Basin, Australia. *Environ. Sci. Technol.* 45 (7), 2591–2597.
- Guzik, M., Murphy, N., 2013. Fauna of the GAB springs: comparative phylogeography of GAB spring invertebrates. In: Gotch, T. (Ed.), *Allocating Water and Maintaining Springs in the Great Artesian Basin*, Volume V, Groundwater-dependent Ecosystems of the Western Great Artesian Basin. National Water Commission, Canberra, pp. 27–41.
- Hammer, D.A., Bastian, R.N., 1989. Wetlands ecosystems: natural water purifiers. In: Hammer, D.A. (Ed.), *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial and Agricultural*. CRC Press.
- Hurowitz, J.A., Fischer, W.W., Tosca, N.J., Milliken, R.E., 2010. Origin of acidic surface waters and the evolution of atmospheric chemistry on early Mars. *Nat. Geosci.* 3, 323–326.
- Isbell, 2015. Australian Soil Classification. second ed. CSIRO Publishing.
- Italiano, F., Yuze, G., Uysal, I.T., Gasparon, M., Morelli, G., 2014. Insights into mantle-type volatiles contribution from dissolved gases in artesian waters of the Great Artesian Basin, Australia. *Chem. Geol.* 378–379, 75–88.
- Jerz, J.K., Rimstidt, J.D., 2003. Efflorescent iron sulfate minerals: paragenesis, relative stability, and environmental impact. *Am. Mineral.* 88, 1919–1932.
- Johnston, S.G., Slavich, P., Hirst, P., 2004. The acid flux dynamics of two artificial drains in acid sulfate soil backswamps on the Clarence River floodplain, Australia. *Soil Res.* 42 (6), 623–637.
- Karlstrom, K., Keppel, M., Crossey, L., Love, A.J., Boreham, C., 2013. Structural and tectonic history. In: Keppel, M., et al. (Eds.), *Allocating Water and Maintaining Springs in the Great Artesian Basin*, Volume I: Hydrogeological framework of the western Great Artesian Basin. National Water Commission, Canberra, pp. 45–65.
- Kirby, C.S., Cravotta, C.A., 2005. Net alkalinity and net acidity 1: theoretical considerations. *Appl. Geochem.* 20, 1920–1940.
- Lin, C., Melville, M.D., Islam, M.M., Yang, X., van Oploo, P., 1998. Chemical controls on acid discharges from acid sulfate soils under sugarcane cropping in an eastern Australian estuarine floodplain. *Environ. Pollut.* 103 (2–3), 269–276.
- Love, A., Crossey, L., Karlstrom, K., Hilton, D.R., Wolaver, B.D., Rousseau-Gueutin, P., 2009. Toward a new paradigm for the Great Artesian Basin: hydrologic mixing, partitioned sub basins, and mantle influences on groundwater quality. *Geol. Soc. Am. Abstr. Programs* 41 (7), 28.
- Love, A.J., Karlstrom, K., Crossey, L., Rousseau-Gueutin, P., Priestley, S., Shand, P., Fluin, J., 2010. Geochemical and neo-tectonic data provides a new understanding of the hydrogeology of the Great Artesian Basin. International Conference “Transboundary Aquifers: Challenges and New Directions” (ISARM2010).
- Love, A., Shand, P., Crossey, L., Harrington, G., Rousseau-Gueutin, P., 2013. Groundwater Discharge of the Western Margin of the Great Artesian Basin, Australia. National Water Commission, Canberra (147 pp).
- Macdonald, B.C.T., Smith, J., Keene, A.F., Tunks, M., Kinsela, A., Whsit, L., 2004. Impacts of runoff from sulfuric soils on sediment chemistry in an estuarine lake. *Sci. Total Environ.* 329 (1–3), 115–130.
- Madden, M.E.E., Badnar, R.J., Rimstidt, J.D., 2004. Jarosite as an indicator of water limited chemical weathering on Mars. *Nature* 431, 821–823.
- Mosley, L.M., Fitzpatrick, R.W., Palmer, D., Leyden, E., Shand, P., 2014. Changes in acidity and metal geochemistry in soils, groundwater, drain and river water in the Lower Murray River after a severe drought. *Sci. Total Environ.* 485–486, 281–291.
- Nordstrom, D.K., Alpers, C.N., Ptacek, C.J., Blowes, D.W., 2005. Negative pH and extremely acidic mine waters from Iron Mountain, California. *Environ. Sci. Technol.* 34, 254–258.
- NWC, 2013. *Allocating Water and Maintaining Springs in the Great Artesian Basin*. Volumes I–VI. National Water Commission, Canberra.
- Papike, J.J., Karner, J.M., Shearer, C.K., 2006. Comparative planetary mineralogy: implications of martian and terrestrial jarosite. A crystal chemical perspective. *Geochim. Cosmochim. Acta* 70, 1309–1321.
- Perel'man, A.I., 1986. Geochemical barriers: theory and practical applications. *Appl. Geochem.* 1, 669–680.
- Prescott, J.R., Habermahl, M.A., 2008. Luminescence dating of spring mound deposits in the southwestern Great Artesian Basin, northern South Australia. *Aust. J. Earth Sci.* 55, 167–181.
- Rice, K.C., Herman, J.S., 2012. Acidification of earth: an assessment across mechanisms and scales. *Appl. Geochem.* 27 (1), 1–14.
- Shand, P., Degens, B., Rogers, S., 2008. The geochemistry of acid-saline waters and drainage sediments in the Avon Catchment, Western Australian Wheatbelt. *Explore* 140, 1–11.
- Shand, P., Fitzpatrick, R.W., Thomas, M., Merry, R.H., Grocke, S., Thomas, B., Creeper, N., Hollis, B., Marsland, K., Fogg, M., Turner, R., Goode, J., 2010. Mobilisation of metals and acidity during re-flooding of a wetland containing acid sulfate soils. In: Birkle, P., Torres-Alvarado, I.S. (Eds.), *Water-Rock Interaction 13*. Balkema, Rotterdam, pp. 303–306.
- Shand, P., Grocke, S., Kirby, J., Baker, A.K., 2012. The characterisation of metal and metalloid contaminants in re-flooded Acid Sulfate Soils of Lake Alexandrina, South Australia. Water for a Healthy Country Flagship Report Series (ISSN: 1835-095X 58pp).

- Shand, P., Haria, A.H., Neal, C., Griffiths, K.J., Goody, D.C., Dixon, A.J., Hill, T., Buckley, D.K., Cunningham, J.E., 2005. Hydrochemical heterogeneity in an upland catchment: further characterisation of the spatial, temporal and depth variations in soils, streams and groundwaters of the Plynlimon forested catchment, Wales. *Hydrol. Earth Syst. Sci.* 9 (6), 621–644.
- Shand, P., Johannesson, K.J., Chudaev, O.V., Chudaeva, V.A., Edmunds, W.M., 2004. Rare earth element contents of high pCO₂ groundwaters of Primorye, Russia: mineral stability and complexation controls. In: Johannesson, K. (Ed.), *Rare Earth Elements in Groundwater Systems*. Springer-Verlag, pp. 161–187.
- Shand, P., Love, A., Gotch, T., Raven, M., Grocke, S., Kirby, J., Scheiderich, K., 2014. Extreme geochemical environments in mound springs of the Great Artesian Basin, Australia. *Goldschmidt 2014 Abstracts* 2260.
- Sullivan, L.A., Fitzpatrick, R.W., Bush, R.T., Burton, E.D., Shand, P., Ward, N.J., 2010. The classification of acid sulfate soil materials: further modifications. Southern Cross Geo Science Technical Report No. 310. Southern Cross University, Lismore, NSW, Australia.
- Wexsteen, P., Jaffé, F.C., Mazor, E., 1988. Geochemistry of cold CO₂-rich springs of the Scuol-Tarasp region, Lower Engadine, Swiss Alps. *J. Hydrol.* 104, 77–92.