

Hydrogeochemistry applied to mineral exploration under cover in the Curnamona Province



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Introduction

The Curnamona Province hosts a supergiant Pb–Zn–Ag orebody at Broken Hill, and numerous smaller deposits (Pb–Zn–Ag, Cu–Au, Sn, W, U, etc.), that mostly occur in the limited outcrop regions of the Palaeo- to Mesoproterozoic basement rocks (Fig. 1). The basement includes metasedimentary and metavolcanic rocks of the Willyama Supergroup, that host the world-class Broken Hill deposit (Willis et al., 1983; Conor, 2000; Burt et al., 2004). The areas of exposed basement have undergone mineral exploration for over a century, yet additional significant mineral discoveries have been limited. However, ~90% of the Curnamona Province basement is concealed by variable thicknesses of cover, including Neoproterozoic (meta)sediments, Cambrian, Mesozoic and Cainozoic sedimentary sequences. Thus, the high mineral potential of this province for Broken Hill and FeO–Cu–Au style mineralisation is likely to be realised under regolith cover. Traditional mineral exploration methods used in areas of outcrop face challenges when applied to areas of transported cover, especially where this cover is greater than a few metres thick. Thus, novel or modified exploration tools are needed.

Groundwater is a geochemical sampling medium that moves through the subsurface (basement and regolith cover), is easily collected, and can be analysed with great accuracy and sensitivity. It may have interacted with mineralisation and retained a chemical or isotopic ‘memory’ or fingerprint of such an encounter. Can such fingerprints be detected in groundwater collected from existing pastoral and exploration bores? Can groundwater be used in exploratory drilling in areas of transported cover? Can the groundwater’s chemical and isotopic composition help rank geophysical anomalies? These are some of the questions this study in the Curnamona Province attempts to answer.

Methods

Over 350 groundwater samples were collected from existing boreholes in the southern Curnamona Province, both in areas of outcrop in the ranges and in areas of cover in the surrounding basins (Fig. 2). The aim of this scientific investigation was to test whether this medium could be helpful in the search for hidden mineral deposits in the province. Major, minor and trace element concentrations of the groundwaters were determined by ion chromatography, inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry, ion specific electrode, spectrophotometry and titration. Selected samples were analysed for their isotopic compositions of hydrogen, oxygen (in water and in sulfate), carbon, chloride, sulfur, strontium and lead by mass spectrometry after various preparation methods. Several rain and surface water samples were analysed to better constrain the starting points of the evolution of the groundwaters.

Results and discussion

The results indicate that the present composition of the groundwater is affected by a number of processes: evaporation, evapotranspiration, mixing, precipitation–dissolution and oxidation–reduction. These processes take place during an often complex and, in many instances, long evolution. The impact of each of these major processes is teased out using ‘conservative’ tracers (chloride, bromide), isotopes and geochemical modelling. To develop hydrogeochemistry into a useful tool for exploration

requires a number of steps in the analysis of the data.

First, an index of ‘sulfur excess’ is calculated to gain knowledge of which samples contain more sulfur than can be accounted for by evaporation or mixing. This exercise shows that many groundwater samples in the Curnamona Province contain ‘anomalous’ sulfur, which is not surprising given the abundance of sub-economic sulfide mineralisation in the area.

The sulfur isotopic composition of dissolved sulfate enables discrimination between the samples containing sulfur of meteoric origin (average $\delta^{34}\text{S} +12.5$ to $+15\%$ V-CDT; Caritat et al., 2005) and sulfur from Broken Hill-type sulfide mineralisation (average $\delta^{34}\text{S} \sim 0\%$ V-CDT; Bierlein et al., 1996). A number of groundwater samples, mainly from the ranges and including several from marginal and basinal areas, have both high sulfur excess (>0.0 molar ratio) and

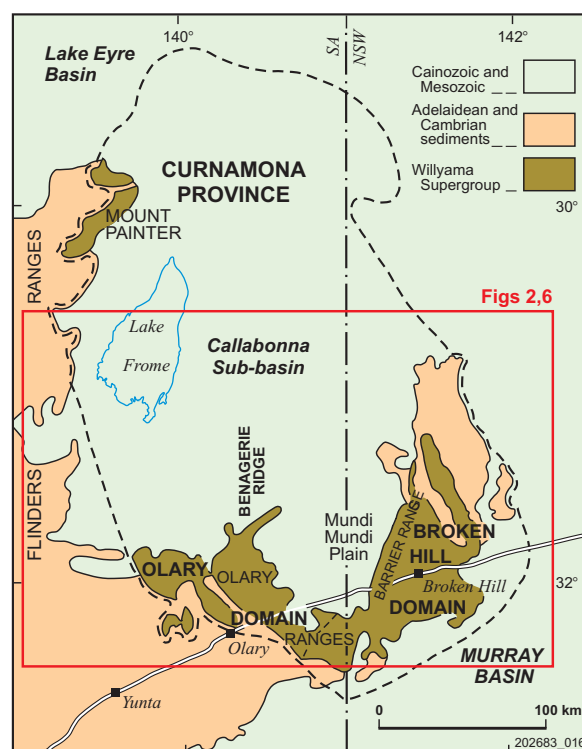


Fig. 1 Location of the study area in the southern Curnamona Province.

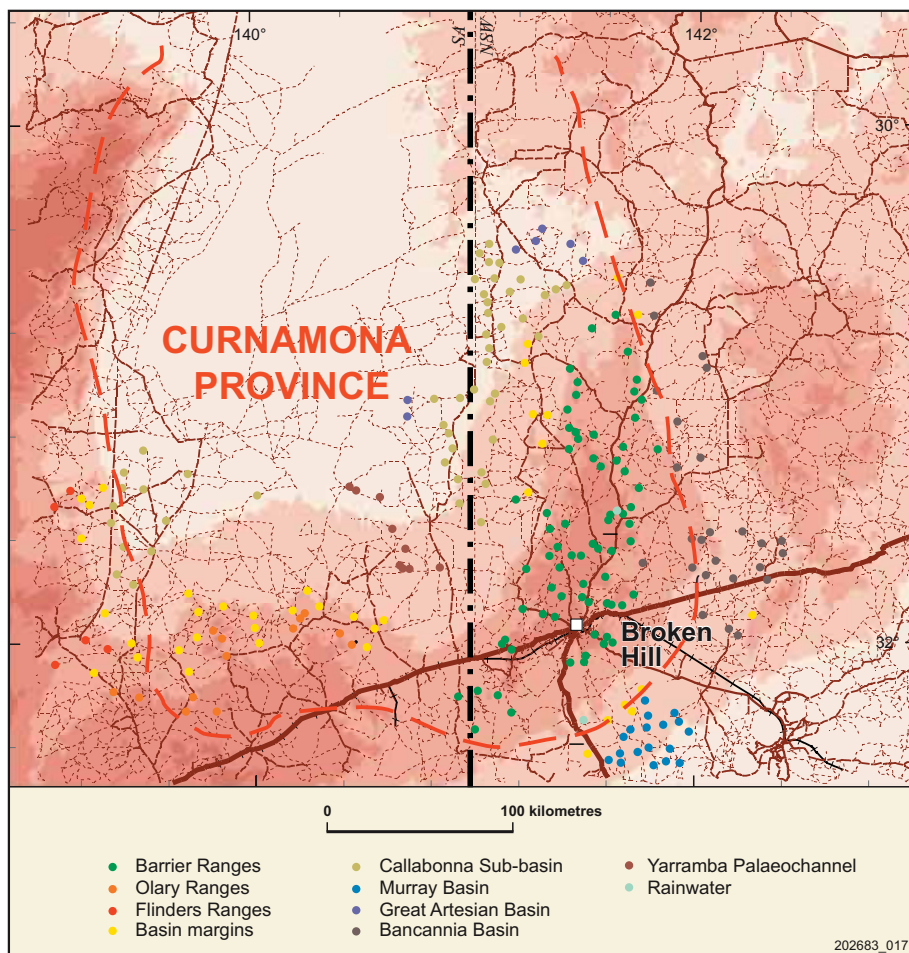


Fig. 2 Sample locations and symbols key on digital elevation model of the southern Curnamona Province.

low $\delta^{34}\text{S}$ ($<+12.5\%$) values (Fig. 3). The $\delta^{34}\text{S}$ versus sulfur excess diagram shows that rainwater can evolve along three different paths representing:

- (1) dissolution of gypsum (G), a common component of the shallow regolith here
- (2) oxidation of Broken Hill-type sulfide mineralisation (M)
- (3) oxidation of diagenetic–sedimentary pyrite (S) characterised by negative $\delta^{34}\text{S}$ values (Chivas et al., 1991).

The bulk of the data falls between the trends of oxidation of Broken Hill-type sulfide mineralisation and dissolution of regolith gypsum.

Further, the oxygen isotopic composition of dissolved sulfate can shed light on where sulfide oxidation occurred within the hydrogeological system. Samples cluster along different trends in a $\delta^{18}\text{O}_{(\text{SO}_4)}$ versus $\delta^{34}\text{S}_{(\text{SO}_4)}$ space depending on whether the oxygen used for sulfide oxidation came from the atmosphere (dissolved oxygen) or

the water molecule itself (Kirste et al., 2003).

The oxidation of sulfide minerals (e.g. galena, sphalerite, chalcopyrite) will result in increased concentrations of sulfate, lead, zinc and copper (and other trace elements) in solution in the groundwater at the oxidation site. Reaction-path modelling reveals that the initial concentration levels and ratios are strongly influenced by the reaction pathway and progress (Fig. 4). These initially elevated concentrations then progressively decrease along the flowpath as dispersion, adsorption and ion exchange take place in hydrological conditions (head gradient, hydraulic conductivity) typical for the region (Kirste et al., 2004).

Three dimensional reactive-transport modelling is used to quantify this ‘decay’ in concentrations of compounds released by oxidation of sulfides as water moves through an aquifer containing clay minerals and iron oxyhydroxides

(Fig. 5). The basic initial assumptions in the model are:

- there is a regional flux of groundwater, which initially has a composition typical of background (non-mineralised) sites within the region
- the injected fluid is the same typical groundwater after equilibration with galena, sphalerite and chalcopyrite, with no secondary mineral precipitation allowing for a maximum metal content in the groundwater
- the flow path has ion exchange sites and adsorption sites, which are initially equilibrated with the unreacted groundwater
- flow and transport occur (from left to right in the model) under a hydraulic gradient of 0.002 m/m and an hydraulic conductivity of 13.7 m/yr for 10 000 years.

This modelling provides insight into how far from a sulfide body sulfate or trace element concentrations of a given level may be expected to persist, and thus gives an indication of the footprint size of the hydrogeochemical anomalies in a given environment.

The results show that elevated dissolved zinc and copper concentrations extend to ~100 m down the flowpath, while lead concentrations are strongly attenuated within ~50 m of mineralisation.

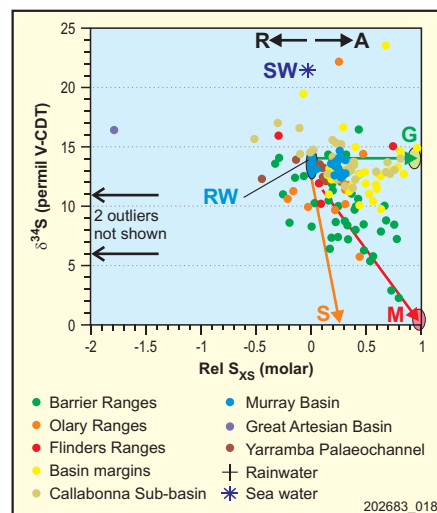


Fig. 3 Diagrams of $\delta^{34}\text{S}$ versus relative sulfur excess (see text) for the groundwaters from the southern Curnamona Province. Trends are A: addition of SO_4^{2-} ; R: removal of SO_4^{2-} (e.g. bacterial sulfate reduction). End-members are SW: sea water; RW: rainwater (Caritat et al., 2005); G: gypsum; M: Broken Hill-type mineralisation; S: sedimentary pyrite. See Figure 2 for location of samples.

Perhaps the most important outcome of this exercise is to illustrate that trace metals do not travel far in such groundwater systems and that zinc and copper have a greater mobility than lead. High metal contents are therefore not expected at any great distance from the deposits; conversely, where relatively higher concentrations of specific metals are found, this may indicate proximity to mineralisation, depending on aquifer mineralogy and hydrogeology. However, other groundwater constituents such as dissolved sulfate, with its diagnostic

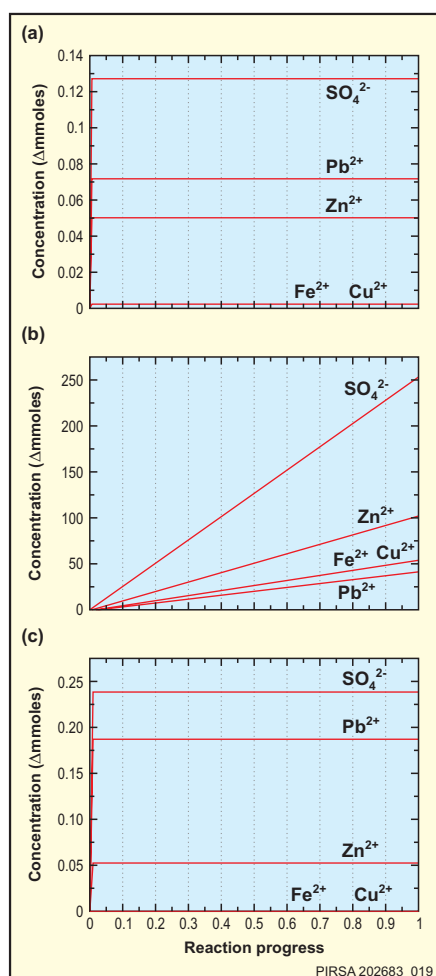


Fig. 4 Batch type geochemical reaction-path modelling results showing changes in SO₄²⁻, Fe²⁺, Cu²⁺, Zn²⁺ and Pb²⁺ during oxidation of galena, sphalerite and chalcopyrite. Differences in concentrations and ratios of products reflect the oxidation pathway and reaction progress. (a) Oxygen as oxidant with concentration equal to that of water saturated with respect to the atmosphere. (b) Oxygen as oxidant but with a fixed oxygen fugacity. (c) Trivalent iron as oxidant. Cases (a) and (c) show initial concentration increases during oxidation followed by fixed contents when oxidant supply is exhausted, whereas case (b) has a continuous supply of oxidant.

isotopic fingerprint, may present a much larger footprint of a blind deposit.

The strontium isotopic composition of the groundwater can be used to recognise the broad types of bedrock that it has been interacting with. For instance, this study recognises evidence of interaction with less radiogenic Adelaidean rocks (and minerals) in the west of the study area ranging up to highly radiogenic Willyama Supergroup rocks (and minerals) in the east (groundwater ⁸⁷Sr/⁸⁶Sr ratio up to 0.737). This shows that groundwater can be used to ascribe broad geological types to concealed bedrock (Caritat et al., 2005).

The lead isotope compositions, obtained for a small selection of samples, are useful to evaluate the specific mineralisation type (Broken Hill-type, Thackaringa-type, etc) that is compatible with the ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb ratios in the groundwater or to make inferences regarding mixing of mineralisation lead with background lead (Caritat et al., 2005).

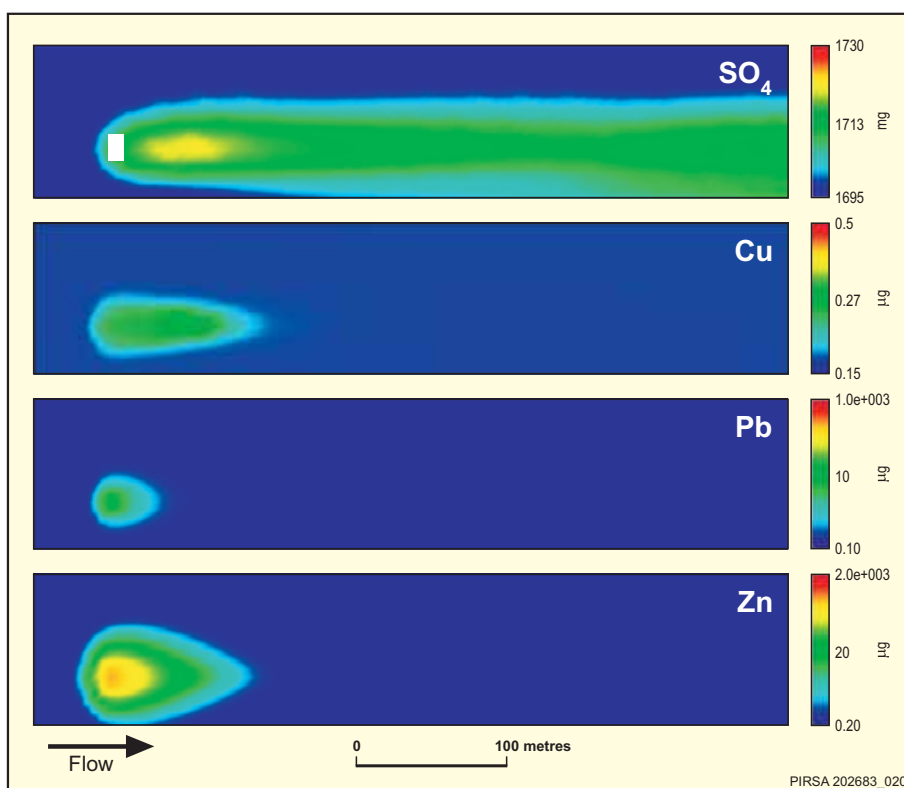


Fig. 5 Plan view of 3D reactive-transport model outputs showing distributions of SO₄²⁻, Cu²⁺, Pb²⁺ and Zn²⁺ after 10 000 years of reactive-transport. The white rectangle in the top diagram represents the mineralised zone. Conditions: 3D model size = 100 x 500 x 10 m (20 x 100 x 2 cells), hydraulic conductivity K = 13.7 m/yr, dispersion Dx = 0.81, Dy = 0.081, Dz = 0.0036, porosity Φ = 0.22, head gradient dh/dl = 0.002, time = 10 000 yr, ion exchange site density X = 0.2 mol/kg H₂O, adsorption site density Hfow = 0.11 'weak' sites per kg H₂O, Hfos = 0.003 'strong' sites per kg H₂O.

Does it work?

In order to test the hydrogeochemical approach outlined here, a small area with abundant mineralisation was selected to see if the indicators developed above would confirm proximity, or otherwise, to known mineralisation. The area chosen was the southern Barrier Ranges, where Broken Hill and many other mineral occurrences are located. Of 23 real groundwater samples taken in this sub-area, 16 (70%) yielded positive indicators, namely:

- positive sulfur excess
- δ³⁴S lower than the estimated precipitation value
- elevated copper and/or zinc concentrations.

Close inspection of Figure 6a overall suggests that samples unrelated to known mineralisation have a background sulfur isotopic composition, but the ones that are closer to mineralisation have a diagnostic (lower) sulfur isotopic composition. The samples that are closest to 'targets'

additionally have elevated zinc and/or copper concentrations, as the modelling in this study predicts.

Subsequently, the same methodology was applied to the complete data set over the southern Curnamona Province. This confirms proximity to mineralisation in the few exploration boreholes sampled in the basins but, more importantly, highlights several new locations under sedimentary cover where those same indicators suggest relatively proximal interaction with yet unknown mineralisation (Fig. 6b; Caritat et al., 2005).

Conclusions

Hydrogeochemistry is one of the novel tools needed to assist mineral exploration under regolith cover, now and into the future. It has potential to fingerprint groundwater–mineralisation interaction through the application of major and trace element concentrations, stable and radiogenic isotope signatures, and reaction-path and reactive-transport modelling. This approach leads to significant cost-savings for the minerals exploration industry by helping to:

- delineate areas of interest for subsequent detailed exploration under regolith cover (area selection)
- rank geophysical anomalies
- vector towards mineralisation.

Hydrogeochemistry is a very useful tool and should be part of any multi-disciplinary mineral exploration campaign. During initial, regional stages of exploration, groundwater geochemistry can assist in selecting areas more likely to contain mineralisation (e.g. sulfate ‘plumes’ with potentially anomalous isotopic compositions). At the tenement scale, trace element concentrations and relative ratios can help vector towards the site where sulfide oxidation is taking place. By using the bore water supply infrastructure, where it exists, mineral explorers can save substantial amounts of operational capital, and resort to expensive drilling only in smaller, carefully targeted areas.

Acknowledgements

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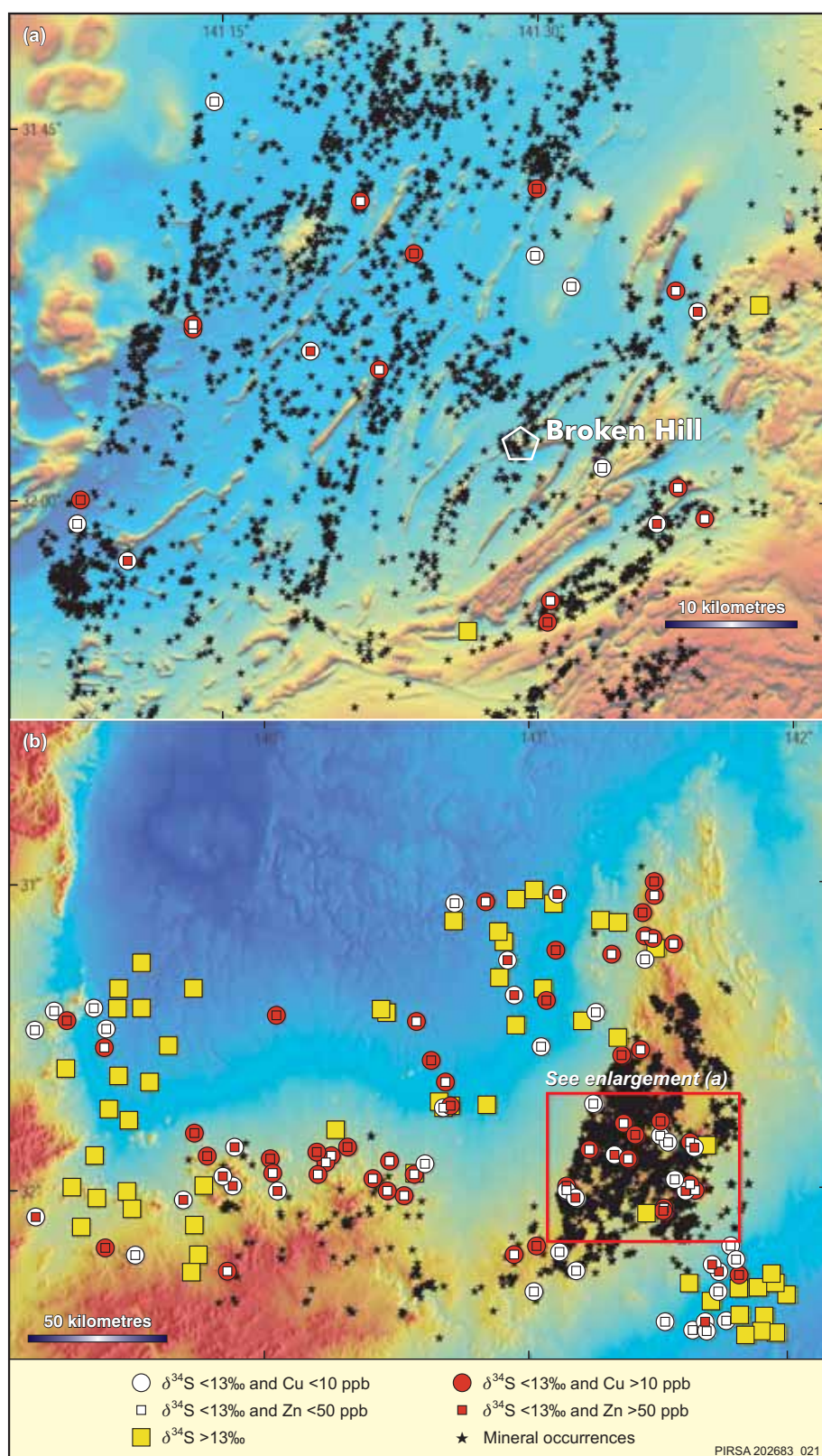


Fig. 6 Distribution of groundwater samples in the southern Broken Hill Domain on an airborne electromagnetic background (a), and in the southern Curnamona Province on a digital elevation model background (b); the location of (a) is shown as yellow rectangle. Symbols show groundwaters that have ‘high’ sulfur isotopic compositions as yellow squares, and ‘low’ sulfur isotopic compositions as circles; the latter are coloured red if copper concentrations are greater than 10 parts per billion, or contain a red square if zinc concentrations are greater than 50 parts per billion. These symbols represent a gradation from probably unrelated to any mineralisation (yellow square), to distal (>~2 km) to potential mineralisation (white circle), to more proximal to potential mineralisation (red circle and/or square).

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Review of 1997 to mid-2003 open file company exploration data from CURNAMONA 1:250 000 map area, Olary Domain

Open file company exploration information, released since the previous exploration review of the CURNAMONA 1:250 000 map area (McCallum, 1998), is summarised in a report now released by PIRSA. The most significant exploration was by Rio Tinto Exploration Pty Ltd (now held by Southern Cross Resources Australia Pty Ltd), which focused on the southeastern portions of the map area in regions of moderately shallow basement. The exploration was for all metals, with a number of anomalous zones of Cu, Zn, Pb, Au, U, W and Bi defined by a combination of surface geochemical sampling, ground EM, magnetics, gravity and drilling.

BHP Minerals Ltd, with Lynch Mining Ltd, concentrated on the eastern portion of the map area in regions of more limited previous exploration and of moderately deep cover. The models targeted included mineralisation in the 'Bimba Formation' identified as being comparable to parts of the Mount Isa Block Western Succession, large-scale structures reflecting primary growth faults, FeO–Cu–Au (Olympic Dam style), Cambrian carbonate-hosted mineralisation (Mississippi Valley Type), stratiform Pb–Zn–Ag (Broken Hill, Mt Isa), porphyry Cu–Mo–Au and endo-skarn style mineralisation. Anomalous values were returned for most targets.

Exploration for sedimentary 'roll front' style uranium contributed to a considerable portion of the exploration on the CURNAMONA map area. The most significant work released during the reported period was by Paladin Resources NL. This included the re-evaluation of all existing drilling that led to a new interpretation of palaeochannel locations as well as an evaluation of their prospectivity for sedimentary uranium throughout the map area. Of particular interest was the definition of the Oban, Oban North and Lake Charles prospects. The Oban prospect was shown to have near-economic grade and tonnage, although closer spaced drilling was deemed necessary to accurately assess the economic potential. The uranium potential of the Lake Charles, Erudina, Wyambana and Stickhole palaeochannels was highlighted.

Copies of the report on the CURNAMONA 1:250 000 map area can be purchased from PIRSA Customer Services, Ground Floor, 101 Grenfell Street Adelaide SA 5001 (ph. 08 8463 3000, e-mail pirsa.customerservices@saugov.sa.gov.au).