HYDROGEOCHEMISTRY
—clues to hidden mineralisation

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Can groundwater collected from existing pastoral and exploration bores provide evidence of buried mineralisation? Can groundwater assays be used to guide exploratory drilling in areas of transported cover? Can the groundwater's chemical and isotopic composition help rank geophysical anomalies? Our study in the Curnamona Province attempts to answer these and other questions.

This region hosts a supergiant lead–zinc–silver ore body at Broken Hill and numerous smaller deposits (including lead–zinc–silver, copper–gold, tin, tungsten and uranium), which mostly occur in the limited outcrop regions of the Paleo- to Mesoproterozoic basement rocks. The basement includes the metasedimentary and metavolcanic Willyama Supergroup, which contains the Broken Hill mineralisation (Burtt et al 2004). However, approximately 90 per cent of the Curnamona Province basement is concealed by variable thicknesses of Neoproterozoic (meta) sediments, Cambrian and/or Mesozoic sediments, overlain by the Cainozoic sedimentary sequence of the Callabonna Sub-basin and soils.

The areas of exposed basement have undergone mineral exploration for over a century, yet few significant new mineral discoveries have been made. Thus, the province's high potential for Broken Hill style and iron-oxide/copper–gold mineralisation is more likely to be fulfilled under cover.

Traditional mineral exploration methods used in regions of outcrop face challenges when applied to areas of transported cover, especially where this cover is greater than a few metres thick. Different exploration tools are needed to explore effectively in this environment. Groundwater is a geochemical sampling medium that moves through the subsurface, is easily collected and can be analysed with great accuracy and sensitivity. It may have flowed near mineralisation and retained a chemical 'memory' or fingerprint of such an encounter.

Sampling and analysis

We have collected about 350 groundwater samples 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 (figure 1). The aim of this scientific investigation was to test whether groundwater could be helpful in the search for hidden mineral deposits in the Broken Hill region. We determined the major, minor and trace element concentrations of the groundwaters. On selected samples, we also determined the isotopic composition of hydrogen, oxygen (in water and in dissolved sulfate), carbon, chloride, sulfur, strontium and lead.

The results indicate that the groundwater's present composition is affected by a number of processes: evaporation, evapotranspiration, mixing, precipitation/ dissolution and oxidation/reduction. These occur during an often complex and—in many instances—long evolution. The impact of each of these major processes is teased out using 'conservative' tracers such as chloride or bromide, isotopes and geochemical modelling. To develop hydrogeochemistry into a useful tool for exploration, we have followed a number of steps in the analysis of the data:

1. Calculation of a 'sulfur excess' index to gain knowledge of which samples contain more sulfur than can be accounted for by evaporation or mixing.
2. Determination of the sulfur isotopic composition of dissolved sulfate to identify samples that may have experienced an addition of Broken Hill type (i.e. isotopically light; Bierlein et al 1996) sulfur. Consideration of the oxygen isotopic composition of dissolved sulfate in conjunction with its sulfur isotopic composition can shed light on where sulfide oxidation occurred with respect to the groundwater table (Kirste et al 2003).
3. Evaluation of the specific mineralisation types (Broken Hill type, Thackaringa type etc.) that are compatible with the lead isotope ratios of the groundwater or imply mixing with background lead.

▲ **Figure 1.** Sampling groundwater from a windmill-driven pastoral bore in the southern Curnamona Province.

4. Geochemical reaction-path modelling of oxidation of sulfide minerals (e.g. chalcopyrite, sphalerite, galena) and reactive-transport modelling of the dispersion of reaction products along the groundwater flow path (Kirste et al 2004).

We tested this methodology in the southern Barrier Ranges region, where Broken Hill and a series of minor mineral deposits are located. Of the 23 groundwater samples collected in this mineralised subprovince, 16 (70 per cent) suggest proximity to mineralisation: they have positive sulfur excess, 'low' sulfur isotopic composition and 'elevated' copper and/or zinc concentrations. Inspection of figure 2a shows that most of the 'positive' samples are indeed located within two kilometres of known mineralisation. We subsequently applied the same procedure to the full regional dataset. This revealed several locations under sedimentary cover where our vectors suggest proximity to sulfide mineralisation (figure 2b). More details of the methods and results of this study can be found in Caritat et al (2005).

(a)

(b)

▲ **Figure 2.** Distribution of groundwater samples in the southern Broken Hill Domain on airborne electromagnetic background (a) and in the southern Curnamona Province on digital elevation model background (b; location of (a) 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. Thus background sites (unrelated to mineralisation) are repesented by yellow squares, those related to - but distant from - mineralisation are symbolised by white circles, and those close to (> ~2 km) potential Broken Hill type mineralisation are depicted by red circle and/or squares.

Conclusion

We concluded that hydrogeochemistry may well be one of the novel tools needed to assist mineral exploration under cover. We have demonstrated its potential to fingerprint groundwater–mineralisation interaction through analysing major and trace element concentrations, establishing stable and radiogenic isotope signatures, and modelling geochemical reactions and transport. There are indications that this approach can help delineate areas of interest for subsequent mineral exploration under sedimentary cover, to rank geophysical anomalies and to vector towards mineralisation.

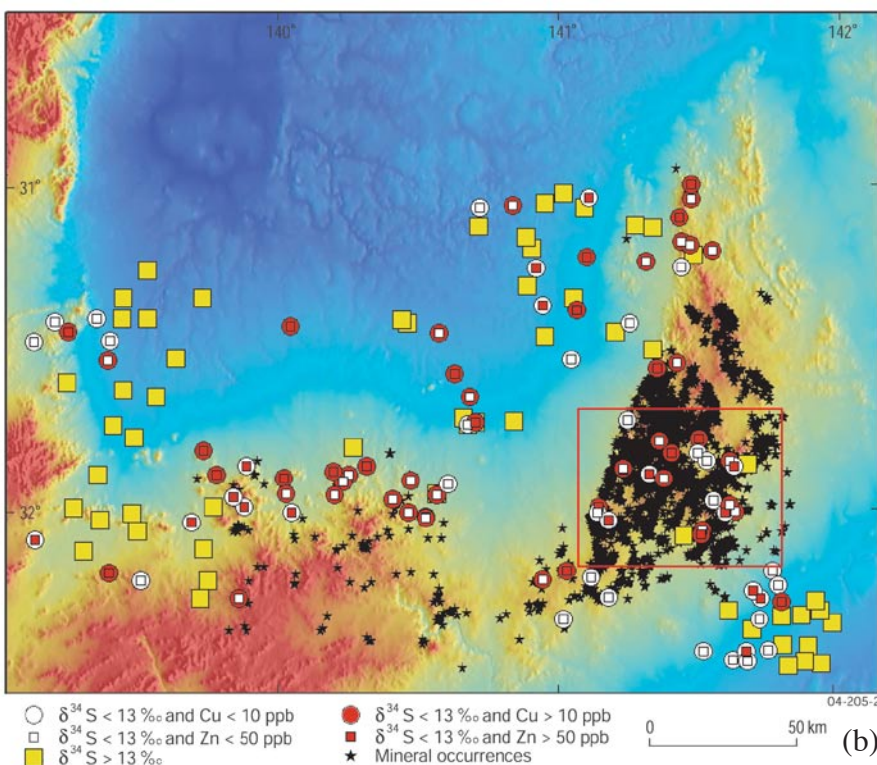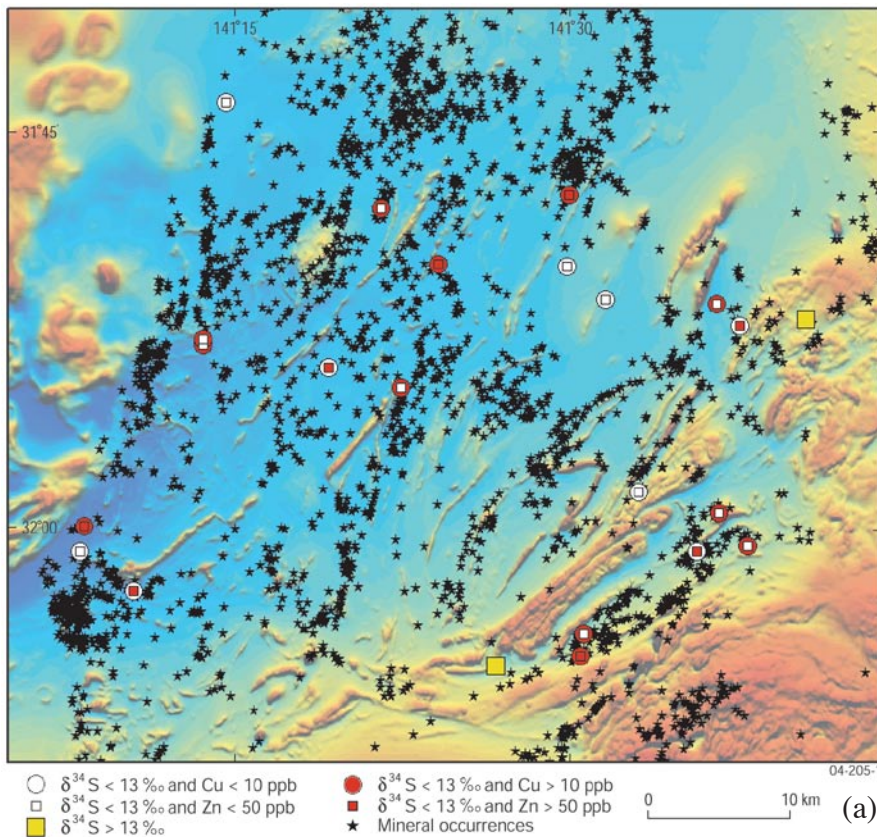Hydrogeochemistry is a very useful tool and should be part of any multidisciplinary mineral exploration campaign.

References
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