



Groundwater geochemistry as an exploration tool through cover

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SUMMARY

Groundwater chemistry is influenced by its contact with host rocks and reveals information on lithology, alteration, and potential mineralisation. It is a prospective exploration tool that samples a derivative of the subterranean geochemistry, with the effectiveness for mineral exploration depending on: (a) the availability of boreholes and borehole density; (b) boreholes with appropriate depth of penetration; (c) hydrologic connectivity of the country rocks; and (d) the availability of a regional hydrogeochemical baseline, to define chemical anomalism.

Minerals react with groundwater and the metal solutes can be transported considerable distances from their sourcing ore bodies. Solubility depends on the physiochemical conditions of aquifer, with solutes typically in very low concentrations at levels of parts-per-billion or even parts-per-trillion for precious metals. The highest concentrations of ore-related trace elements tend to be restricted to within 2–5 km of a metal source and tail off with distance from the source, although their distribution is modified by groundwater flow. Isotopic analyses for $\delta^{18}\text{O}$, $\delta^2\text{H}$ and Pb isotopes are useful for determining source region, with the latter applied to fingerprinting a source region, e.g., Proterozoic mineralisation.

Hydrogeochemical interpretation applies a variety of techniques: (a) the direct statistical analysis of a single element concentration is employed for metal prospectivity for Cu, Pb, Zn, Ni, Co, Pt, Au, Ag, etc., by comparing the element concentration to its regional-background value; (b) assessment based on a combination of elements (also known as Specific Mineralisation Index), a robust technique that uses prior knowledge of known mineralisation models to predict mineralisation types, e.g., Ni-Co-Pt for NiS systems; Zn-Cu-Pt-Ag for VMS deposits; and Au, Ag, As, Mo, Sb for lode-Au deposits; and (c) interpretation of undercover geology using multi-element indices: Higher Cr and V concentrations are indicative of mafic rocks; higher U, of granitic rocks; and B/Na ratios used to differentiate between metamorphic and sedimentary terranes.

Key words: Hydrogeochemistry, exploration, mineral indices, isotopes

INTRODUCTION

Groundwater boreholes can be regarded as subterranean probes that penetrate to depths which conventional surface geochemistry exploration techniques are unable to reach. Pore waters react with lithology and sulfide minerals, and the water chemistry assimilates some of the geochemical signatures of host formation. The area of influence from a bore depends on the porosity and permeability, groundwater flow, reactivity of rock and the hydrostatic conditions at the time of sampling. CSIRO pilot studies (Noble and Gray, 2010) demonstrated that sampling boreholes spaced from 10 m to >5 km can provide sufficient chemical indicators to decipher the underlying geology, hydrothermal alteration and highlight areas of interest to mineral exploration.

Case studies have demonstrated that groundwaters have the capacity to transport metal solutes considerable distances from ore bodies, and metal contents increase towards sulfide sources enabling a chemical gradient to be used for mineral exploration (Eppinger *et al.*, 2009; Leybourne and Cameron, 2010; Gray *et al.*, 2016; Hannan *et al.*, 2018). Sulfur, oxygen, hydrogen, and lead isotopic signatures are effective tools to determine water and metal sources (e.g., Caritat *et al.*, 2005; Reid *et al.*, 2021) and copper isotopes are indicative of sulfide source and related weathering processes (Mathur *et al.*, in prep).

Learnings from exploration-focused trials in the Yilgarn Craton, Capricorn Orogen and under cover areas to the east of the Mount Isa Inlier showed that advanced geochemical processing of single or a combination of elemental chemistries (e.g., Mineral Saturation Indices and Specific Mineralisation Indices) can identify chemical anomalism (Gray *et al.*, 2009, 2014, 2016, Thorne *et al.*, 2018, Reid *et al.*, 2021). In the Mt Isa Inlier, As-Sb-Mo-W haloes are used to model chalcophile association, Au-Ag-As-Mo-Sb for lode Au, and W-As-Co-PGEs for base metals targeting. Uranium saturation index is used to predict primary and secondary alteration styles. For lithochemical mapping, Cr, V, U, Ba,

Na and Si contents are useful elements to map under cover lithology, e.g., high Si and U are indicative of granitic rocks whereas high V and Cr suggest mafic rocks.

Metal isotopes have increasingly been used to understand metal sources or sulfide weathering. For example, Pb isotopes in the Mount Isa region are used to predict Proterozoic Pb mineralisation in areas that has limited surface geochemical expression (Reid *et al.*, 2021).

CORE SECTIONS OF DOCUMENT

Designing a hydrogeochemical exploration program

Unlike conventional geochemical exploration where the sampling array can be customised according to the intended target size, hydrogeochemical exploration is regarded as opportunistic sampling that capitalises on the fixed existing borehole infrastructure of an area. It is a low impact method that uses water collected from existing bores as the sample medium to provide subterranean multielement chemistry at ultra-low concentrations. Hydrogeochemical exploration is ideal for many parts of Australia where there is a good coverage of farm and mineral exploration boreholes (Figure 1) that penetrate close to the base of the post-mineralised cover sequence or into the basement rocks. Most state and territories in Australia have good borehole registration systems that provide the basic information such as location, depth of boreholes, drill hole logs and screen depth, which are essential information for borehole selection.

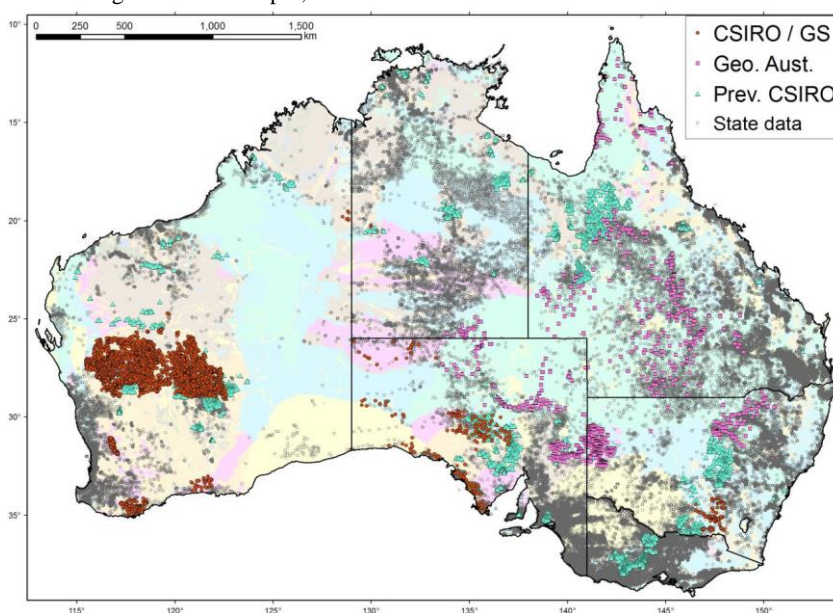


Figure 1: Distribution of ground water bores in Australia. Data source from CSIRO and Geological Surveys (Forbes *et al.*, 2013; Giblin, 2001; Gray *et al.*, 2012, 2014, 2015, 2016, Reid *et al.*, 2021), Geoscience Australia (Caritat *et al.*, 2005), Great Artesian Basin (GAB) project (Radke *et al.*, 2000), State borehole and sample registers (Bardwell and Gray, 2016a,b,c; Gray and Bardwell, 2016a,b,c,d,e; DOR, 2022).

The design of a hydrogeochemical exploration program must consider appropriate sample density that depends on borehole availability and local fracture density, in addition to bore suitability parameters guided by the depth of borehole and the absence of contaminations at each sample site. For the Mount Isa project, fracture analysis over the outcropping area was undertaken to confirm that rocks are highly fractured to ensure good hydrological connectivity. It is assumed that under covered areas surrounding the Mount Isa Inlier has similar structural deformation for groundwater exploration.

Data appraisal by Hannan *et al.*, (2018) and Reid *et al.*, (2021) demonstrated that geochemical signatures of known deposits in the Mount Isa area extend to approximately 5 km. Data from the Ernest Henry mine shows that the geochemical halo extend as far as 2 km distally from ore body but up to 3km in the downflow direction. Recent work within under cover areas of eastern Mount Isa showed that mineralisation signals are not detected at distance of more than 5 km from known mineral occurrences, hence effectively limits the spacing between borehole spacing to ~10 km. Sample density is important when designing the hydrogeochemical exploration to ensure cost-effectiveness as well as not under sampling an area.

An important component of the exploration program is the choice of reliable analytical laboratory that is capable of analysing hydrogeochemistry at very low concentrations. The sensitivity of analysis must ideally be in part-per-billion

to ensure that the subtle geochemical changes can be detected. It is always important to adopt the same laboratory and analytical method through an entire program to ensure consistency of results.

Interpreting and using hydrogeochemical data

Hydrogeochemistry differs from conventional geochemistry (e.g. soil or rock) as water from a bore is subjected to evapotranspiration, dilution from rainfall, changes in groundwater flow and seasonal or diurnal physiochemical changes that resulted in ionic concentrations changes. Elements/compounds form ions in water and ionic solubility fluctuates with changes in redox potential, temperature, pH, chemical saturation, and ionic balance from competing elements. All groundwater samples must be accompanied by time reference and field observations to ensure that data processing can incorporate these timely differences.

CSIRO has collated and QA/QC (quality assured/quality controlled) a nationwide hydrogeochemical dataset for all states and territories (Bardwell and Gray, 2016a,b,c; Gray, 2016; Gray and Bradwell, 2016a,b,c,d,e) and this regional data are essential to establish the baseline geochemistry for geochemical anomaly recognition. All curated data met the stringent QA criteria. Erroneous data such as samples with pH values below 1.9, electrical balance outside the -0.05 and 0.05 range, or concentrations above solubility concentration threshold e.g. > 62 mg/L for Si, have been removed. This robust groundwater dataset can be combined with other datasets across Australia. The two main hydrogeochemical data processing methods are by i) single or combination of multiple single element results, and ii) combining multi element chemistry either as sum, multiples, ratio, mineralisation or mineral saturation indices, or thermodynamic calculations.

Single element analysis

High concentrations of the metal in water is interpreted as an indicator of proximal metal sources. Prospectivity analysis requires a reliable regional-background dataset whereby the water chemistry is statistically compared to or normalised against the background value. Single element prospectivity analysis is applicable to ore-based elements such as Cu, Pb, Zn, Ni, Co, Pt, Au, Ag, As and S, which commonly concentrate in mineral deposits. The backgrounds of such metals in country rocks are normally very low and any chemical anomalies are commonly the result of localised mineralisation.

Combining several single element plots provides a better prospectivity analysis where overlapping anomalies at a common location is indicative of a mineral system or mineralisation style. For example, anomalies for As, Sb, Mo and W are characteristic of chalcophile associations; Au, Ag, As, Mo and Sb for lode Au; Zn, Cu, Pt and Ag for VMS deposits; Ni, Co and Pt for NiS systems, and W, As, Co and PGEs are diagnostic for base metals. Figure 2 shows geochemical anomalies of As and Au in eastern Mount Isa. Individually, As and Au plots merely highlight locations of respective anomalies whereas the combination of both elements has identified an area for hydrothermal Au-As mineralisation.

Major rock forming elements (Si, Al, Fe, Mg, Ca) and element such as Cr, V, Ba and U are strongly controlled by lithology and hydrothermal alteration. Although major multielement indices are preferred for such analysis, the combination of single element plots can also differentiate rock chemistry from mineralisation related anomalism. Higher dissolved concentrations of Cr and V can indicate greenstones and higher Si, U and F can indicate granites.

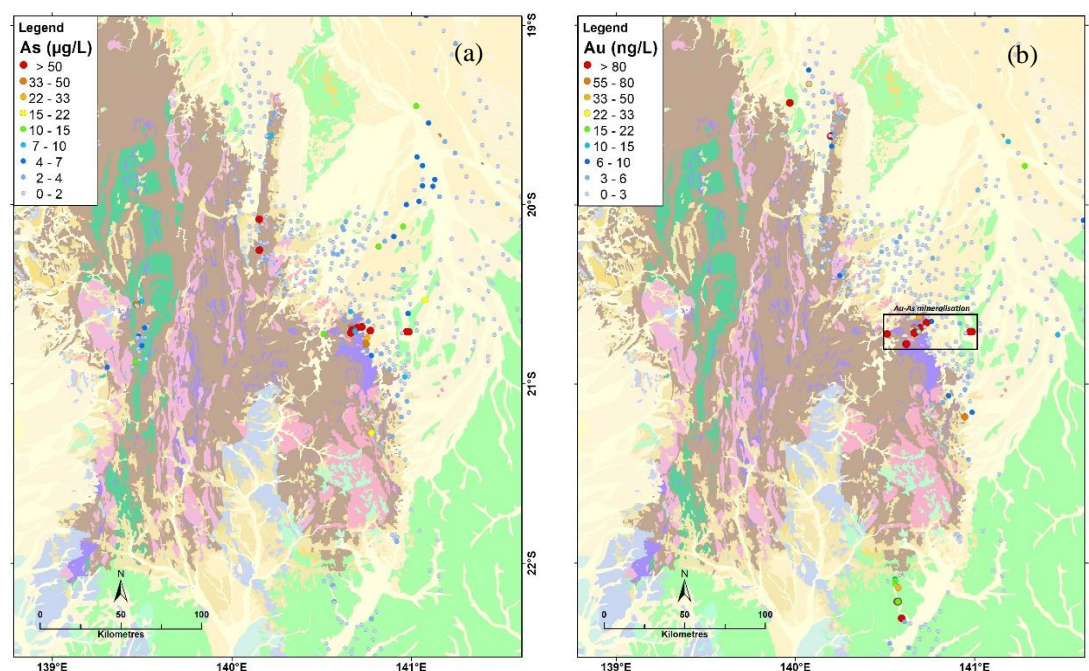


Figure 2: Geochemical concentrations in groundwater of the eastern Mount Isa highlighting anomalous values (red symbol) for (a) As, and (b) Au. Overlapping As-Au anomalies is interpreted as an Au-As hydrothermal system.

Multielement data analysis

Multielement geochemistry provides a robust way of analysing complex geochemistry whereby a combination of elements is used in a single computational. The elemental association requires prior chemical knowledge of known mineralisation, lithology, and weathering. There are various ways of using multielement data that include arithmetic sum, elemental ratio, and in established equations and thermodynamic calculations. Table 1 summarises the specific mineralisation indices established from previous learnings in Queensland, Western Australia, South Australia and Northern Territory (Reid *et al.*, 2021). Geochemical index formula is not a fixed entity and can always be modified suit local mineralising environment.

Label	Type/target	Formula
FeS	Weathering of barren sulfides	pH+Eh+Fe+Mn
AcidS	Attack on wall-rocks from acid produced from sulfides	Mo+Ba+Li+Al
Ni Min	Mineralised sulfides	Ni+Co+W+Pt
Au Min	Regional Au targets	Au+Ag+As
Au MinC	Capricorn Au	2*Au+Ag+Sb+As
Litho1	Lithology mapping/Mafics	V+Cr-2*U
SEND1	Sulfate enrichment/nitrate depletion	2*SO4ClSW-NO3

Table 1: Specific mineralisation indices based on prior knowledge of known mineralisation systems.

Groundwater chemistry fluctuates with dilution from meteoric water, or from evapotranspiration enrichment where ions are concentrated with the removal of water. Changing chemistry from the same water bore sampled at different times makes statistical analysis of multi-batch geochemistry challenging. Despite varying elemental concentrations, element ratio pairs such as Na/K remains stable with dilution, or salination from evaporation. Ion excess and depletion calculations (Reid *et al.*, 2021) identifies chemical deviation from an ideal sea water evaporation line for the ionic pair, and divergence from the trend can be attributed to alteration process, lithology, or crystallisation. For mineralisation related processes, the ability to identify sulfate excess (relative to Cl) is important to determine the presence of weathered sulfide ores or gypsum (Gray and Noble, 2006).

Mineral saturation indices based on mineral stoichiometry and thermodynamics (Parkhurst *et al.*, 1980) calculates the mineral saturation of minerals. If the saturation index is below the zero, the solution is under-saturated with respect to that mineral and may indicate an environment favourable for dissolution of that mineral phase, whereas values above zero represents over-saturation leading to potential precipitation from solution. High SO₄:Cl correlates with waters at or near gypsum saturation suggests SO₄ could derive from gypsum or from the oxidation of sulfides. Saline waters with low SO₄:Cl near gypsum saturation could result from gypsum precipitation from evaporation. Mineral saturation indices are also used in mineral exploration e.g., carnotite saturation for uranium exploration.

Isotope hydrogeochemistry

Isotope chemistries are mainly used to fingerprinting the groundwater source regions and identifying mixtures of different waters. Oxygen and hydrogen isotopes can differentiate meteoric water from formation and hydrothermal sources. Metal isotopic ratios (e.g., $^{65}\text{Cu}/^{63}\text{Cu}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$) are largely unaffected by the dilution or concentration factors and therefore can be used as a robust geological exploration tool that defines source characteristics and weathering processes related to the sources. A pioneering case study using Cu isotopes in the Jericho area (eastern Mount Isa) has confidently identified buried copper orebodies at considerable depth.

Lead isotopic evolution of the Proterozoic aged mineralisation in the Mount Isa region is well-documented (e.g., Hannan *et al.*, 2018) and this isotopic system can be used to interpret the groundwater source region and mineralisation potential of host rocks. Lead isotopes from a Cannington mine monitoring bore, a Dugald River mine bore and a farm bore at Toolebuc have similar isotopic signatures to the Proterozoic aged mineralisation. Based on the recognition of a Pb-Pb evolution trend for mineralisation in the Mount Isa region, a prominent Pb evolution trend has been identified from the Dugald River mine to the Queen Sally exploration hole that includes the Blackard and Little Eva deposits. Towards the south, a strong Proterozoic Pb signature is identified within a bore on Hillside Station while a borehole on Coolullah station could represent a distal northern extension of this trend. Another Pb evolution trend is also identified from Cloncurry through the Ernest Henry mine (not sampled) and north towards Clonagh Station. A third Pb evolution trend is recognised from south of the Eloise-Altia prospects on Levuka Station.

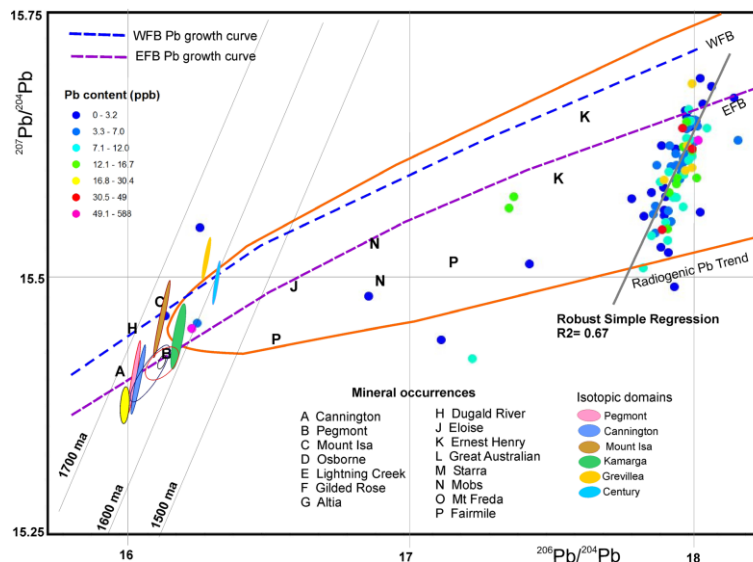


Figure 3. Pb-Pb graph shows the isotopic trends in groundwater of the eastern Mount Isa Block. Borewater that coincides with the radiogenic Pb growth trend are considered for Proterozoic mineralisation, whereas the tangential trend that evolved from this Mount Isa trend is regarded as non-mineral prospective (Reid *et al.*, 2021).

Prospectivity mapping

Hydrogeochemical interpretation is applied for undercover metal prospectivity assessment in the Mount Isa region using single element, multielement, specific mineralisation index and isotopic geochemistry. Although individual element concentrations may not be anomalous for mineralisation, the combination of multielements, stable and radiogenic isotopes are able to define prospective area for mineral exploration (Figure 4). Thirteen area of interest have been identified using geochemistry for polymetallic exploration and 4 areas have been identified using Pb isotopes to have potential for Proterozoic aged mineralisation.

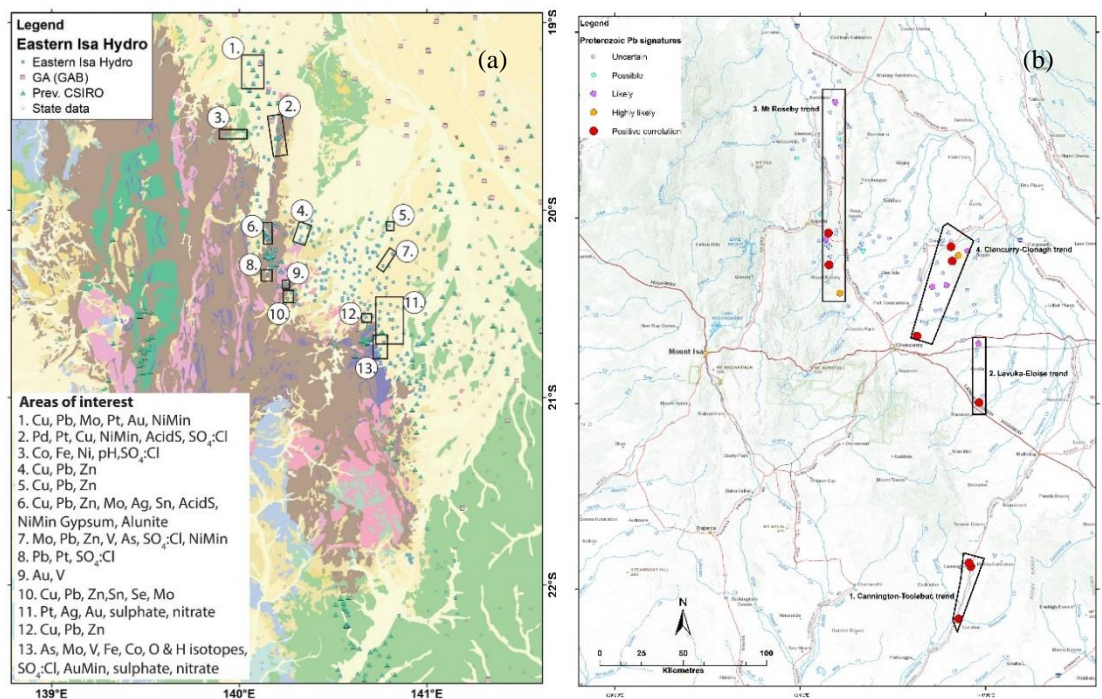


Figure 4: Prospective areas for mineral exploration in the Mount Isa region based on hydrogeochemical data interpretation (adapted from Reid *et al.*, 2021). (a) is based on geochemical interpretations using specific mineral indices whereas (b) is based on Pb isotopic ratios.

CONCLUSIONS

Groundwater geochemistry is an ideal tool to explore through sediment cover where geochemical signals from deep seated deposits failed to reach surface. The technique requires a good borehole coverage and availability of regional data for baseline levelling. Groundwater chemistry has very low concentrations, which is subjected to dilution and evaporation processes, and hence the data processing and data interpretation requires expert knowledge.

Effective data processing methodologies are:

- Ranking metals and pathfinders concentration to define geochemical anomalies and water quality assessment, and vectoring the anomalies towards potential deposit sources.
- Applying specific chemical indices which enable the identification of different mineralisation styles.
- Applying Mineral Saturation Indices for exploration e.g. carnotite saturation for uranium exploration.
- Applying isotopic geochemistry in source recognition.

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