GROUNDWATER ISOTOPIC GEOCHEMISTRY

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Groundwater chemical and isotopic composition: a mineral exploration tool for areas of regolith cover – Lessons from the Curnamona Province

EXTENDED ABSTRACT

The Curnamona Province is endowed with the supergiant Pb-Zn-Ag Broken Hill orebody and numerous minor mineral deposits (Pb-Zn-Ag, Cu-Au, Sn, W, U, etc.). These occur mostly within the limited outcrop of the Proterozoic Willyama Supergroup. Yet, the vast majority of this Province is concealed by transported regolith, hampering the success of exploration based on conventional strategies.

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. Can one detect such fingerprint in groundwater collected from existing pastoral and exploration bores? Can it be used to target exploratory drilling in areas of transported cover? These are some of the questions our study in the Curnamona Province attempts to answer.

We have collected about 300 groundwater samples to test whether this medium 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 (by ion chromatography, inductively coupled plasma-atomic emission and inductively coupled plasma-mass spectrometry, ion specific electrode, photospectrometry and titration) as well as the isotope compositions of H, O (of H_2O and SO_4^{2-}), C, Cl^-, S, Sr and Pb (by mass spectrometry after various preparation methods). We also analysed several rain and surface water samples to better constrain the starting point of the evolution of the groundwater.

The groundwaters have undergone a range of processes; their present-day composition is the end product of a complex and, in many instances, long evolution. Using hydrogeochemical principles and modelling, we have been able to identify and, in some cases, quantify these processes. Thus, we have been able to recognise that a number of the groundwaters have a sulfur excess (S_{XS}), ie an amount of S that can be ascribed neither to evaporation nor to mixing. Many of these samples have a low $\delta^{34}S$ composition, which possibly results from oxidation of sulfides with a Broken Hill type $\delta^{34}S$ signature (average ~0 ‰ V-CDT). Further, the $\delta^{18}O$ composition of the SO_4^{2-} helps discriminate whether sulfide oxidation occurred near the groundwater table or in deeper settings. Sr isotopes identify the broad types of bedrock that the groundwater has been interacting with, from less radiogenic Adelaidean rocks (and minerals) in the west to highly radiogenic Willyama Supergroup in the east (groundwater $^{87}Sr/^{86}Sr$ ratio up to 0.737). The groundwaters have $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios comparable to, or intermediate between, various mineralisation types recognised in the area (Broken Hill, Rupee, Thackaringa, etc. types).

The oxidation of any sulfide mineralisation will result in increased concentrations of Cu, Pb and Zn (and other trace elements) in solution in the groundwater. To predict the behaviour of these trace metals during transport along a flow path, we have generated a 1-D reactive transport model. The basic initial assumptions in the model are:

- the transporting fluid is a typical groundwater equilibrated with galena, chalcopyrite and sphalerite, 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, and
- flow and transport occur at 1 m/yr for 4,000 years.

The results show that elevated Cu and Zn concentrations extend to ~150 m down the flowpath, while Pb values are attenuated already within ~50 m of the deposit. Perhaps the most important outcome of this exercise is to illustrate that trace metals do not travel far in such groundwater systems and that Zn and Cu have a higher mobility than Pb. We cannot expect high metal contents at any great distance from the deposits, but where we have higher amounts of specific metals it may indicate proximity to mineralisation, depending on the aquifer mineralogy and the hydrogeology. However, other groundwater constituents (such as SO_4^{2-}) may present a much larger footprint of a buried deposit.

Of the 23 real groundwater samples taken in the vicinity of known mineralisation in the Curnamona Province, 21 yield positive indicators, that is:
- positive S_{XS},
- low $\delta^{34}S$,
- $^{87}Sr/^{86}Sr$ signature consistent with bedrock type,
- Pb isotope fingerprinting consistent with mineralisation type, and
- elevated Zn and/or Cu concentrations.

This study also highlights several new locations under sedimentary cover where our vectors suggest interaction with mineralisation. We conclude that hydrogeochemistry is a very useful tool in the search for mineralisation under cover, particularly at the regional scale for area selection or target ranking, and should be part of any multi-disciplinary mineral exploration campaign.

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