## DOMINANT CONTROLS ON GROUNDWATER COMPOSITION IN THE BASINS SURROUNDING THE BROKEN HILL SILVER-LEAD-ZINC DEPOSIT: IMPLICATIONS FOR MINERAL EXPLORATION UNDER COVER

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We have collected and analysed over 200 groundwater samples from the region surrounding Broken Hill, including the Callabonna Sub-basin and the Murray Basin, in order to develop methodologies for using groundwater as a mineral exploration tool in regolith-dominated terrains, particularly in areas of thick sedimentary cover. Groundwater interacts with the minerals that form or line the aquifer system through which it flows, and thus it has the potential to be a direct sampling medium representative of the subsurface. The concentrations of target elements such as Zn and Pb tend to be very low in natural waters and geochemical maps based on these can be noisy and unreliable in terms of 'go-maps'. Therefore, one has to look for other clues in the geochemistry of the groundwater in order to detect the presence of concealed mineralisation.

A robust methodology needs to be developed starting from sensible field sampling procedures, followed by a comprehensive analytical protocol and a reliable QA/QC program. Once a methodology (recipe) is proposed and tested, means need to be found to make its uptake by industry as cost-effective as possible. Thus, we have concentrated our efforts on sampling *fresh* groundwater from the aquifers, analysing for an *extensive* suite of major and trace species (IC, ICP-AES, ICP-MS, ISE) and isotopes (MS, MC-ICP-MS) in order to find the most promising ways to vector toward mineralisation using groundwater.

Many physical, chemical and biological processes influence groundwater composition in the near-surface environment. One has to be able to 'remove' quantitatively the effects of the most dominant of these processes in order to tease out the often more subtle influence of, say, a body of sulfide mineralisation encountered some distance up-gradient from the sampling point. Thus, we need to understand the processes that control dispersion of elements from ore bodies. The aim of this presentation is to review the dominant controls on groundwater composition, so that we can subsequently suggest ways to quantify their impact on the final water chemistry, and propose a methodology to identify the signature of a buried ore deposit using groundwater.

The processes that most significantly change the composition of water as it falls on the landscape as rain and infiltrates the upper layers of the regolith on its way to the aquifer(s) in the Broken Hill region are *evaporation* and *transpiration*. These processes are particularly active in the uplands (recharge) areas of the Barrier, Olary and Flinders ranges. They result in the up-concentration of species contained in the rainwater, commonly by a factor of 100 to 1,000. Some of the Callabonna basin waters show evidence for a *mixing* with Na-Cl-SO<sub>4</sub> water, in addition to the evapotranspiration effects. Other processes that we recognise in the Broken Hill groundwaters include mineral *precipitation* and *dissolution* (including of primary, radiogenic minerals and gangue mineral fluorite), *redox reactions, cation exchange* and *adsorption* onto Feoryhydroxides and clay minerals. These processes affect the groundwater composition in ways that can be recognised and assessed quantitatively. Knowledge of the physical and chemical controls on the water chemistry enables us to determine even the very subtle effects on the water composition that interaction with mineralisation can cause.

One result that holds significant promise relates to the sulphur in the groundwater. A few basin waters and a larger number of the recharge waters show an addition of SO<sub>4</sub> over and above what can be attributed to evaporation and mixing. This is potentially attributable to the *oxidation* of sulfide minerals along the flowpath. We investigated this further by performing  $\delta^{34}$ S and  $\delta^{18}$ O analyses of the dissolved SO<sub>4</sub>, which showed a promising broad correlation between the 'excess' SO<sub>4</sub> and lower (closer to ore values)  $\delta^{34}$ S values. Further, this method also gave insights into the location of the sulfides in a hydrogeological context.