New horizons for groundwater geochemistry in uranium exploration

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SUMMARY

Groundwater geochemistry assists in determining the character of deep geological or geophysical targets from a limited number of boreholes, refining location, size and orientation of host target zones, or directly demonstrating presence of alteration or mineralisation. By themselves, uranium analyses can be very misleading in applying groundwater to U exploration. Detailed analyses of multi-element data is required to properly interpret water data, sorting false from significant indicators. Examples from a range of Australian areas reinforce these comments and show that, sometimes, the U indicator is a mineral assemblage, not a U concentration. Ready availability of modelling software and chemical databases allow exploration implications from groundwater data to be easily accomplished.

Key words: uranium, exploration, groundwater, palaeochannel

INTRODUCTION

Groundwater is a chemically reactive medium. With its dissolved gases (O_2 and CO_2) it contributes to the break down of rocks and minerals and production of the regolith. At depth, groundwater can transport ore and host rock elements both laterally and vertically. Groundwater therefore constitutes an important geochemical exploration sample medium in regions where thick cover caps targets such that they are invisible to surface geochemical or geophysical exploration techniques. Further, a water sample reflects an area that is far greater in extent then the core or chips removed from the bore or drill hole from which it was collected. Hence, groundwater compositions assist in determining the character of deep geological or geophysical targets from a limited number of boreholes, refining location, size and orientation of host target zones, or directly demonstrating the presence of alteration or mineralisation. For deep mineralisation the cost savings may be significant.
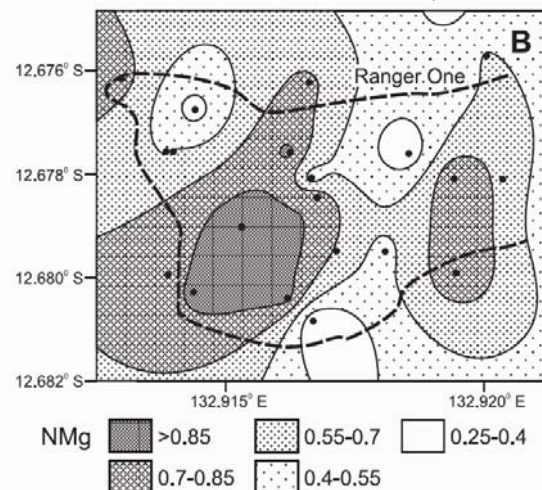
WHY USE GROUNDWATERS FOR U EXPLORATION

The use of groundwater for uranium exploration has a long but not altogether a happy history. Searching for "anomalies" of just U in waters can be futile given the ubiquitous distribution of U in many rocks and the ability of this U to be released into surface and groundwaters. The highest U concentration we know of in an Australian groundwater is 16 ppm and this was not related to a U deposit but rather to the easy dissolution of U previously exsolved from biotite networks into chloritised rims within a monzonitic granite

(pers com Moutier, 1982). Clearly, water data needs to be handled in a holistic way to reveal fully the nature of the rock and water system.

In this paper we review the progress of over 30 years of research and look at methods for optimizing outcomes from exploration investment in groundwater studies Groundwaters associated with each of the U ore deposits on which the currently active 3 U mines in Australia are based were studied and groundwater geochemical exploration indicators identified. In the Pine Creek Geosyncline, U deposits are reflected in groundwater by combined extreme enhancements in Mg and U. Associated Mg enrichments are leached from chloritic schists that host the U deposits. Figure 1 shows the elevated Mg depicted as NMg (the proportion of total cations that is Mg) contours across the Ranger One, No. 3 orebody in the Pine Creek Geosyncline in the Northern Territory. (Giblin, 2005)

The unique Olympic Dam Cu-U-Au deposit in South Australia is reflected in associated groundwaters collected from exploration drill holes and local water bores, as coincident enrichments of U, rare earth elements, fluorine, phosphorus and copper (Giblin, 2001).

Also in South Australia, U concentrations in Tertiary palaeochannel sediments are distinguished from their sub-economic or non-mineralised surroundings by characteristics which include neutral pH, equilibrium with carbonate minerals and a high degree of decomposition and wide distribution of associated carbonaceous matter (Giblin, 1987).


Figure 1: Contoured distribution of NMg in groundwaters across the Ranger One, No, 3 orebody.

DATA AVAILABILITY

Generally, there is little data available in state water databases that is of use for U exploration. However,, although uranium ceased being an exploration target during the 1980s, CSIRO at North Ryde continued to research groundwater geochemical applications for mineral exploration for other commodities. This resulted in an Australia wide database of ~5500 groundwater samples (Figure 2) that included U values for many locations where they now can be applied to exploration targets as they are identified. Experience gained over the 20+ years of this CSIRO project has also resulted in recommended field procedures for sample collection, data interpretation and techniques for laboratory analyses. (Giblin, 2001).

The database also includes major and other trace elements that can relate to the identification of rock types that have potential as uranium ore deposit hosts.
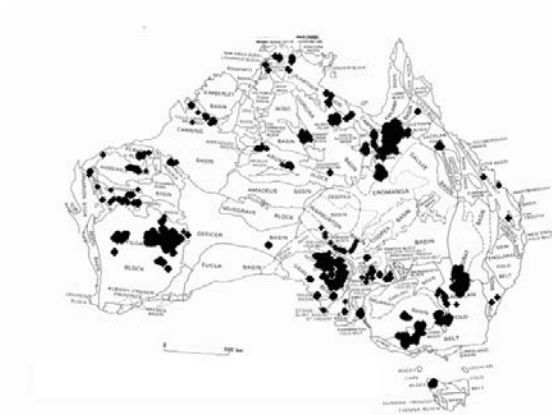
**Figure 2: Locations where exploration potential has been assessed using groundwater geochemistry**

Groundwater data of relevance to U exploration may be held by other agencies. For example, in a study of U in waters of the Murray Basin (Dickson and Giblin, unpublished results) data was found in records of CSIRO, BRS, University of Melbourne, PIRSA, etc. There is recognition amongst some state and federal bodies (GA, DIPNR, Vic and PIRSA in South Australia) of the value of groundwater data to exploration, resulting in ongoing efforts to compile existing data into accessible databases. Other states, which currently charge for access to their water databases, will hopefully follow suit.

It should be noted that pre-1980's data may be of questionable reliability. Since the cessation of most U exploration in the mid 1980's, the most important advancement for using groundwater as a uranium geochemical exploration sample is the introduction of ICPMS that provides a low (1 ppb) reliable detection limit. This makes the technique available to any exploration company and does not rely on specialist equipment in a research laboratory.

SAMPLING CONSIDERATIONS

As has been the case since geochemical exploration techniques were first introduced, in all geochemical exploration programs orientation studies are necessary to determine the required sample properties such as depth and spacing. For groundwaters this requires some understanding of groundwater pathways and flow directions. At the beginning of a groundwater sampling program it is rare for such detailed groundwater flow patterns and spatial distribution of aquifers to be known.

Regional controls on rate and direction of groundwater flow are physical parameters that result from measurements of hydraulic gradient, heterogeneity and relative transmissivity of aquifer rocks. Regional measurements of these are unlikely to be economically feasible within the economic constraints of exploration budgets. However, groundwater geochemistry does provide its own clues. Figure 3 illustrates the conformation of contours of groundwater hydraulic head with contours of Na concentrations of groundwaters in the same exploration area. This conformation is based on the relationship between groundwater flow rates and groundwater salinity. The slower the flow, the greater the degree of evaporative concentration of a groundwater.
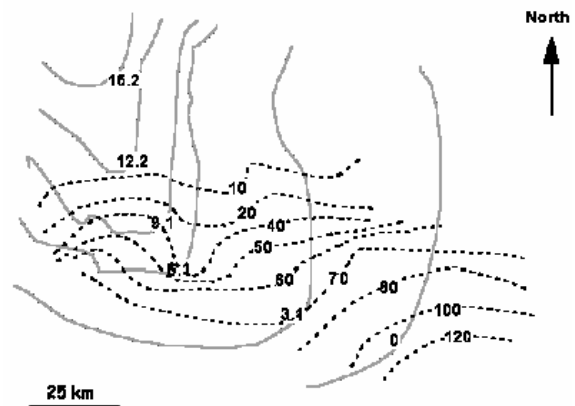
Figure 3: Illustration of coincidence of decreasing groundwater hydraulic head (denoted by solid grey lines) with increasing groundwater salinity expressed as Na concentrations (denoted by dashed black lines). This coincidence provides a means for inferring directions of groundwater flow from groundwater chemistry. (after Wood, 1981).

Alternatively, in locations where data in the CSIRO database were based on planned sample locations, studies can be made of the requisite sample spacing to identify potential anomalies e.g. samples from an orientation study north of Parkes, NSW, where groundwaters were sampled from drill holes in a deliberately spaced grid.

Exploration indicators in groundwaters are not restricted to the ore elements. In addition to variations in targeted ore element concentrations, changes in groundwater major and other trace constituents across a region can reflect changes in country rock type, alteration, or interaction of the groundwater with a body of mineralisation. Strategic elements include both major

constituents (Ca, Mg, Na, K, Cl, S and carbonate species) and trace elements that occur at low concentrations such as U, F, Cr, Ni, Rb and Mo that may be useful lithological indicators to targeted host rocks. Comprehensive field and laboratory chemical analyses are made on groundwater samples collected using standardised procedures from widely spaced drill holes or existing water bores. Field measurements include pH, salinity, temperature and reduced Fe; major and trace element analyses are undertaken in the laboratory.

GROUNDWATER GEOCHEMICAL REACTION MODELLING

One of the reasons groundwater geochemistry has been underutilised as an exploration tool in covered terrains is the lack of understanding of the basic methods of data interpretation. Effective interpretation normally requires an understanding of relatively simple solution chemistry.

Interpretation of exploration geochemical anomalism from stream, rock or soil analyses is normally based on the relative abundances of target commodity elements. With groundwaters however, this approach is only appropriate if the commodity element is rare, or poorly reactive with low temperature groundwaters; for example gold.

For elements that are less rare and exhibit higher degrees of reactivity with groundwaters and whose solubility varies with the groundwater composition (including changes in pH, redox and salinity conditions), anomaly identification is not simply based on absolute abundance. It is necessary to take into account whether prevailing conditions favour or reduce the element's solubility. Because these conditions might vary across an exploration project area, the relative solubility of an element in any individual groundwater sample has to be considered separately from other samples to take into account any local differences in the groundwater geochemistry.

Major recent advances in application of groundwaters to mineral exploration are the improvements and widespread availability of efficient computer hardware and geochemical reaction modeling programs such as "The Geochemist's Workbench" (Bethke, 1998). These now allow routine application of solution chemical models to identify potential ore deposits from their interacting groundwaters. In addition, the intense international interest in environmental implications of uranium waste disposal has resulted in new thermodynamic data for a wide range of aqueous uranium species. Together these should make the direct application of solution chemical models for uranium exploration much more effective.

Where the explorer knows the rock unit that is the expected host rock for targeted ore minerals, solution chemical modeling of major groundwater constituents can determine whether or not the sampled groundwater could or could not be in contact with that host rock. If a groundwater is equilibrated with its aquifer minerals, these minerals may be identified from the solution activities of relevant dissolved species. In environments where ore grade minerals have been preserved for long periods of time, it is reasonable to assume that either the groundwater-aquifer rock system is at equilibrium, or that rates of chemical reactions are so slow that a steady state, or locally equilibrated state exists. Figure 4 demonstrates that if variation in Si content of groundwaters is removed from consideration, and quartz is assumed to be present and saturated, groundwaters collected in 1980 during the exploration drilling for mineralised locations at the Olympic

Dam U deposit, plot predominantly in the phengite and muscovite fields. Interestingly, early exploration stage electron microprobe analyses indicated that the "sericite" associated with mineralisation at Olympic dam was in fact phengite. (Roberts and Hudson, 1983,)
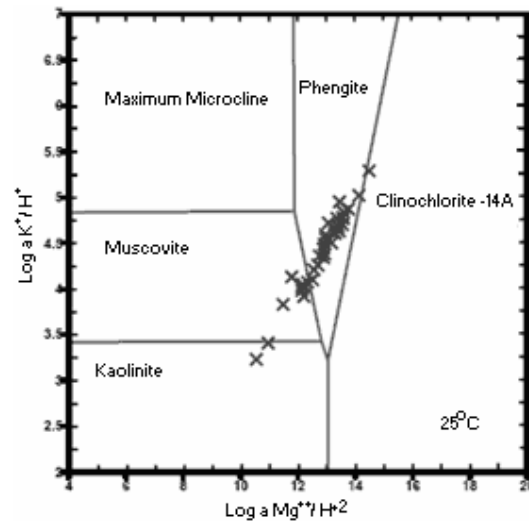
Figure 4: Olympic Dam groundwater compositions plotted against muscovite and chlorite stability fields when quartz is fixed as saturated (from Giblin, 2001).

Single variable and multivariate statistical procedures can also be applied to groundwater constituents to identify groupings which may relate to an identified uranium deposit. For example weathering processes release U in the oxidized U(VI) state and groundwater anions such as carbonate and phosphate form stable soluble complexes with U(VI). Thus in granitic terrain, such as Northern Victoria, elevated U in groundwaters is not uncommon. But, U in such groundwaters can be distinguished from uranium from an ore mineral source by the U concentration in the groundwater having a single variable relationship with F leached from the same granitic source.

CONCLUSIONS

Groundwater geochemistry can assist in locating uranium prospects but, by themselves, uranium analyses can be very misleading. Detailed analyses of multi-element data is required to properly interpret water data, sorting false from significant indicators. Sometimes, mineralogy predicted from other groundwater constituents can be as useful an indicator. Ready availability of modelling software and chemical databases has made such detailed interpretation of groundwater data far easier than was previously the case.

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