# GEOCHEMISTRY OF GROUNDWATERS AT TUNKILLIA: SIMILARITIES AND DIFFERENCES TO YILGARN CRATON GROUNDWATERS.

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#### SITE DESCRIPTION

The Tunkillia gold deposit is located within the central part of the Gawler Craton along the western margin of the Gawler Range Volcanic Province. Basement rocks are intensely weathered with a thin veneer of sediments. Calcrete sampling has identified a surface Au anomaly with an area of approximately 25 km<sup>2</sup>, with Au greater than 10 ppb, over a background of 1-2 ppb. The main resource is located in Area 223 (Figure 1), with Area 191 also identified as prospective (Anon 2003). Mineralisation at Area 223 comprises a broad, flat-lying supergene blanket at 50 metres depth overlying a series of steeply dipping, primary ore shoots trending sub-parallel to the regional shear trend. Recent resource estimation (Anon 2004) indicates Area 223 to contain 10.5 Mt at 2.2 g/t Au (1.0 g/t cut-off) and 5.6 g/t Ag, for approximately 730,000 oz Au and 1,900,000 oz Ag.



**Figure 1:** Drilling, calcrete Au distribution and mineralisation for Area 223 (from Anon 2003). Inner blue box represents the hydrogeochemical sampling area (Figure 2).

#### SALINITY AND MAJOR IONS

As part of the CRCLEME Tunkillia project (Worrall 2003), 94 groundwaters were sampled in May 2003 and analysed as per normal protocols (Gray 2001). Most of the Tunkillia groundwaters have salinities (Figure 3) close to or slightly below sea water (salinity of 3.5%) and Na, Cl, Br and SO<sub>4</sub> are correlated with total salinity and are close to the sea water dilution/evaporation line. With the exception of a few fresher samples (possibly representing fresher water from rainfall or perched aquifers), the variation in salinity is low relative to other sites (Figure 3). However, unlike other sites, there is a marked enrichment in Ca (Figure 3) and Sr, correlated with a K depletion. This Ca enrichment/K depletion shows a weak trend with pH (being greater at higher pH), indicating that the common reason for K depletion in the southern Yilgarn, alunite precipitation in acid Al-rich waters (Gray 2001), is unlikely to be the cause here. One possible cause is the hydrolysis of feldspars to secondary clay minerals:

 $4\text{CaAl}_{2}\text{Si}_{2}\text{O}_{8} + 2\text{SiO}_{2} + 1\frac{1}{2}\text{H}_{2}\text{O} + 7\text{H}^{+} + \text{K}^{+} \rightarrow$ (Anorthite) (Quartz)

In contrast to these previously identified Eh/pH groupings (Gray 2001), some of the groundwaters in the mineralized zone at Area 223 (i.e., 223 central in Figure 2) appear to be different from other Tunkillia (and indeed other Western and South Australian; Figure 3) groundwaters. The high Eh even at neutral pH indicates a higher  $O_2$  fugacity than for other waters (Figure 3).

#### GOLD HYDROGEOCHEMISTRY

The high salinity of the Tunkillia groundwaters means that the dominant mechanism for the mobilization of Au in the southern Yilgarn, namely as the chloride complex (AuCl<sub>2</sub><sup>-</sup>):

is expected to be significant for those groundwaters that are acid and oxidizing. Thermodynamically, the neutral and oxidising groundwaters in the main mineralised zone at Area 223 should also be effective at dissolving Au. However, these groundwaters have surprisingly low Au concentrations (Figure 4),

suggesting kinetic barriers to Au dissolution for

 $\begin{array}{ll} 2K_{0.5}Al_{2.5}Si_{3.5}O_{10}(OH)_2 + 1\frac{1}{2}Al_2Si_2O_5(OH)_4 + 4Ca^{2+}\\ (Illite) & (Kaolinite) \end{array}$ 



**Figure 2:** Location of water samples, overlain on conductance map (Lane & Worrall 2002).

these unusual groundwaters. Highest Au solubilities were observed for the 191 north area (Figure 4), with only moderate Eh (Figure 4). These Au-rich groundwaters also had observable dissolved Fe (Figure 5), despite the fact that dissolved Fe will reduce  $AuCl_2^-$  at these Eh levels:

$$\operatorname{AuCl}_2 + \operatorname{Fe}^{2+} + \operatorname{3H}_2O \Longrightarrow \operatorname{Au}(S) + \operatorname{Fe}(OH)_3 + 2\operatorname{Cl}^2 + \operatorname{3H}^2$$

Possible Au complexes that would not be reduced by Fe are with thiosulfate  $[Au(S_2O_3)_2^{3-}]$ , although this is unlikely to be stable at the pH values of these Au-rich groundwaters (< 4.2). The iodide complex  $(AuI_2^{-})$ , would be expected to be stable, although there is little evidence for high I concentrations in Area 191. Further research is needed to identify the form of dissolved Au in these groundwaters.

Although not fully understood, the differing properties of these groundwaters appear to cause a subdued dissolved Au response around mineralisation in Area 223 and enhanced dissolved Au in Area 191.

## CONCLUSIONS

Although Gawler Craton groundwaters have many features in common with Yilgarn groundwaters, this research demonstrates subtle differences, which may be important for the processes of Au dispersion. There appears to be little variation in salinity for Tunkillia, despite the large area of sampling and changes in geomorphology. This may reflect very old groundwaters, with low flow and little density driven groundwater movement. There are reactions not observed in eastern Yilgarn groundwaters, such as Ca-enrichment.

Differing Eh conditions at Tunkillia may affect processes of Au dissolution, and indeed dissolved Au concentrations are not readily explainable, using models developed in the Yilgarn Craton. It remains to be seen how these differences affect supergene Au dispersion and the formation of extensive surface Au anomalies.



Figure 3: Dissolved Ca versus TDS for ground-waters from Tunkillia and other sites.

Figure 4: Eh versus pH for Tunkillia groundwaters, differentiated by area (Figure 2). The dashed line is the lower Eh limit for a Au solubility of  $0.2 \mu g/L$  relative to Au metal.



Figure 5: Eh versus pH for Tunkillia and other Figure 6: Dissolved Au versus Eh for Tunkillia Australian groundwaters. In addition to the usual water stability line  $[P(O_2)=1 \text{ atm}]$ , lines for  $P(O_2) =$  $10^{-5}$  and  $10^{-10}$  are also shown.

groundwaters, differentiated by area (Figure 2).



Figure 7: Dissolved Au versus Fe for Tunkillia groundwaters.

## REFERENCES

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