

## RECENT ADVANCES IN HYDROGEOCHEMISTRY

David J. Gray and Ryan R.P. Noble

CSIRO Exploration and Mining, ARRC, 26 Dick Perry Ave, Kensington, WA 6151

### INTRODUCTION

This abstract describes some activities of the hydrogeochemistry group at ARRC over the previous year. Our goal is to develop useful regional vectoring techniques to mineralisation using groundwater chemistry, with particular emphasis on the Yilgarn Craton and surrounds. In order to do this effectively requires developing a model of groundwater evolution, consistent and realizable sampling/analytical techniques and, ultimately, straight-forward interpretation procedures.

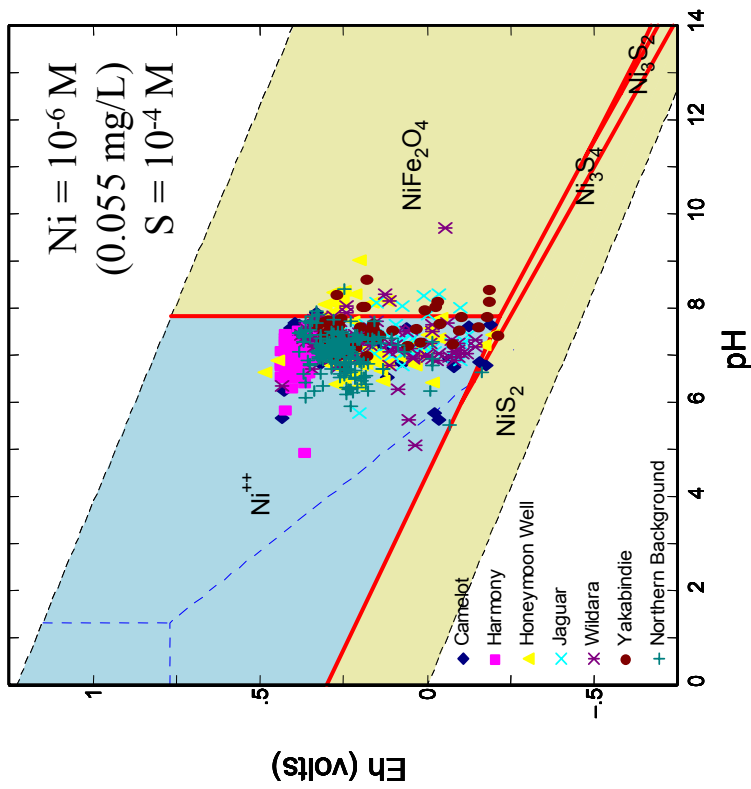
### EXPLORATION FOR NICKEL SULPHIDE AND OTHER SULPHIDE-RICH DEPOSITS

Over the previous year, our research has concentrated on the development of reliable regional and smaller-scale hydrogeochemical vectors to Ni sulfide (NiS) mineralisation in the NE Yilgarn Craton. To achieve this it is critical to understand controls on groundwater expression of NiS mineralisation (*e.g.*, Figure 1), evaluate larger scale variation in element concentrations, test different collection, sample treatment and analytical protocols to develop cost-effective recommendations for hydrogeochemical exploration, and understand groundwater-induced dispersion processes in this environment. We have sampled 265 relevant groundwaters from Wildara/Weebo/Waterloo, Camelot, Yakabindie, and Honeymoon Well Ni prospects, combined with previous results from Lawlers/Agnew, Harmony Ni deposit and various background areas.

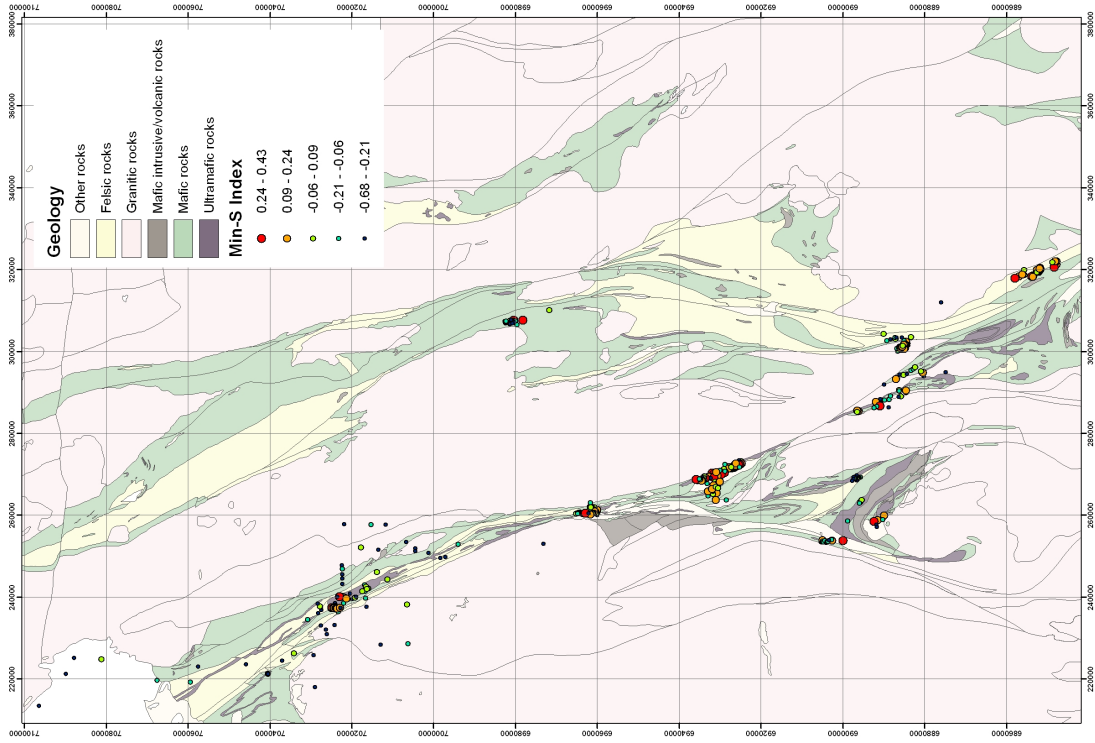
The hydrogeochemistry of the region is dominantly fresh and neutral, with increases in groundwater salinity in the base of palaeochannels or with close proximity to salt lakes. Groundwaters have relatively low dissolved concentrations of metals compared with groundwaters from the central and southern Yilgarn. Hydrogeochemical sampling for NiS in the NE Yilgarn Craton of W.A. has significant potential for close (10's m) to medium (100's m) scale exploration. The findings may also prove beneficial for smaller scale investigation of anomalous samples that could represent near-miss drilling in under-explored, brownfield regions, as well as investigations in hydrogeochemically analogous greenfield regions. The geochemical halo around the Ni deposits is sporadic with regard to false negatives, however, the results do not show many false positives. Most high concentrations of metals associated with the Ni hydrogeochemical signature are indicative of sulfides and mineralisation. Chromium is the best indicator element for ultramafic rocks, while the single elements of Ni and W are the best individual pathfinders for Ni sulfide mineralisation.

Hydrogeochemical differentiation and targeting is improved by using the Box-Cox transformation (Box and Cox, 1964) to derive indices from the multielement data. The indices, consistent with the model for groundwater evolution around weathering sulfides, delineate the sulfide signature independent of the type of water *i.e.* whether the major parameters of Eh and pH are different. The better performing indices for mineralisation targeting is the Miner-S and Miner-FeS that use the mineralised signature (Ni+Co+W+Pt) and take away the groundwater signatures of weathering, acid producing sulfides (Mo+Ba+Li+Al) and Fe-rich sulfides (pH-Eh+Fe+Mn) (*e.g.*, Figure 2). The single element indices of Ni and W were also useful vectors to mineralisation. The mineral saturation indices were not beneficial to exploration, as nearly all samples were under saturated with respect to most ore minerals. A few exceptions included those minerals associated with U mineralisation. Preliminary results would indicate that hydrogeochemistry would be an effective tool for U exploration in the NE Yilgarn.

Method developments implemented in this study are discussed in more detail by Noble and Gray (this Volume). In particular, adsorption from unfiltered waters onto activated carbons is easy to use, enables analysis for Au, Ag and PGE, with semi-quantitative analysis for some other important elements such as W and Mo, and may be more applicable to the mining and exploration industry.



**Figure 1:** Selected NE Yilgarn groundwater samples plotted on the Eh pH diagram for Ni speciation. Clearly most of the samples occur in a range of conditions where Ni<sup>2+</sup> is soluble.



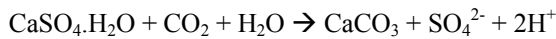
**Figure 2:** Groundwater Mineralised-S Index distribution for the NE Yilgarn Craton.

**MAJOR ELEMENT RATIOS – EXTRACTING MORE FROM WATER DATABASES?**

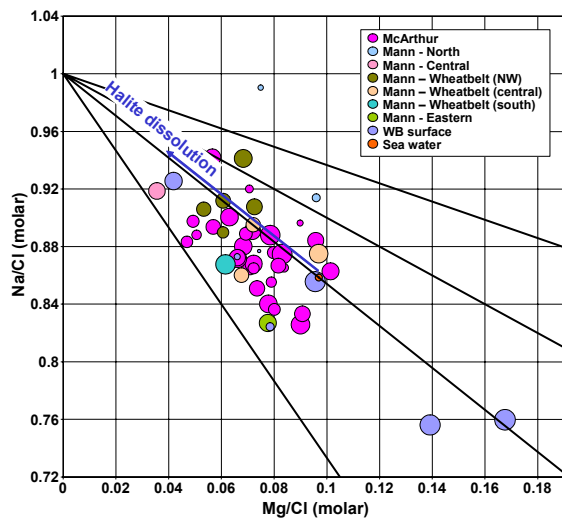
Although saline groundwaters in southern WA and SA, SW NSW and NW Victoria commonly show similar major element ratios to sea water, consistent with an origin of the salt from sea water incursion or salt aerosol, there appear to be various processes occurring. The most likely groundwater reactions potentially include:

1. halite precipitation or dissolution
2. gypsum precipitation in groundwater
3. alteration of wind-blown gypsum to calcite in soils
4. precipitation of alunite
5. oxidation of bromide to Br<sub>2</sub> and loss through volatilization
6. Increase dissolved S due to sulfide oxidation

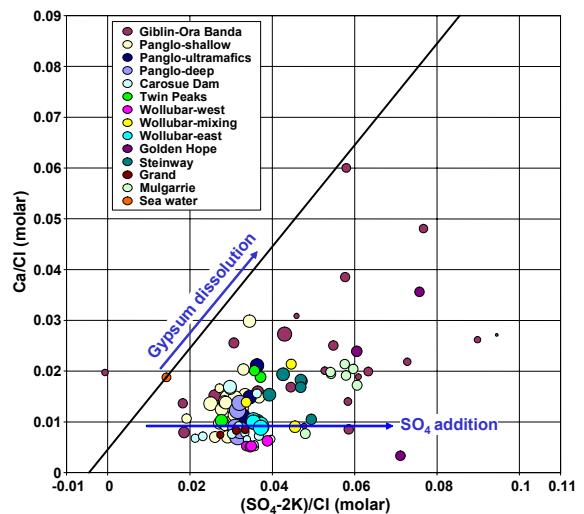
Understanding the magnitude of the first five processes is of value in understanding groundwater evolution whereas identifying process six would have exploration utility. With the exception of alunite, simple ion/TDS ratios are not adequate to identify these effects. Modifications of Pearce and General Element ratios have been used to differentiate a number of groundwater processes, e.g., halite chemistry (**Figure 3**). Areas around SE Yilgarn, Kalgoorlie, and north to Lake Carey show considerable enrichment in dissolved SO<sub>4</sub>, even when the effects of equilibration with alunite and gypsum are accounted for (**Figure 4**). The pervasiveness and geographic control suggest that it is not due to mineralogical effects such as sulfide dissolution. Alteration of wind-blown gypsum to calcite in soils:



could explain the enrichment in dissolved SO<sub>4</sub>, as well as the common acidity in these areas. As the above mechanism would generally not occur in an abiotic environment, it is postulated that a sequence of transformations, probably biologically mediated are important.



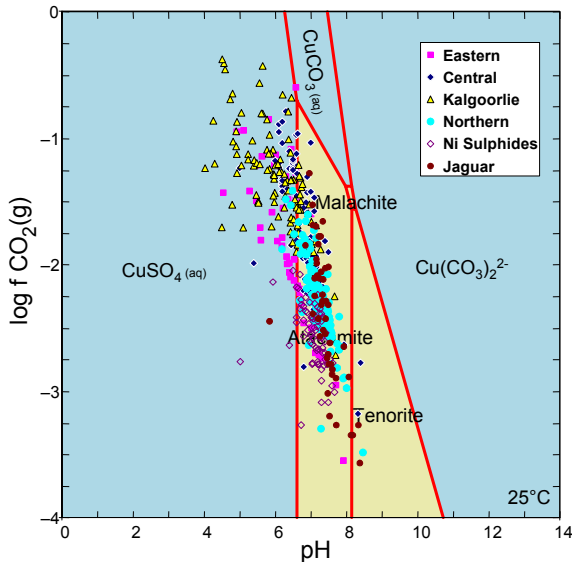
**Figure 3.** Molar Na/Cl vs Mg/Cl for playa waters, sized by salinity, indicates most waters are dissolving halite.



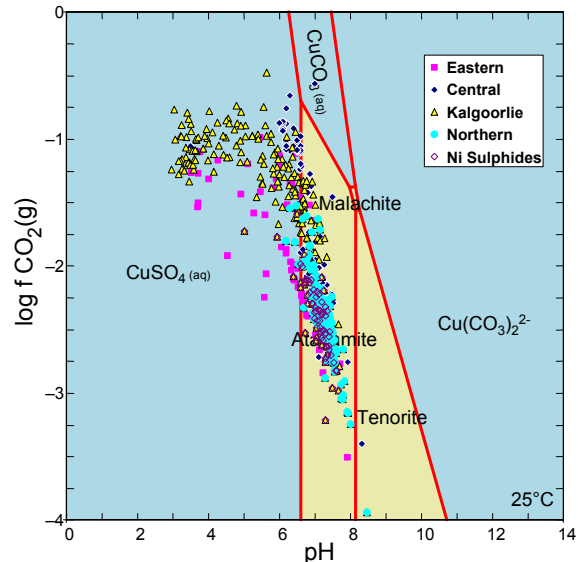
**Figure 4.** Molar Ca/Cl vs (SO<sub>4</sub>-2K)/Cl for Kalgoorlie groundwaters, sized by salinity. Almost all these groundwaters contain much more dissolved SO<sub>4</sub> than expected, even when the effects for alunite and gypsum are accounted for.

**SAMPLING AND INITIAL ANALYSIS – MAXIMUM RESULTS FOR TIME EFFECTIVE INPUT**

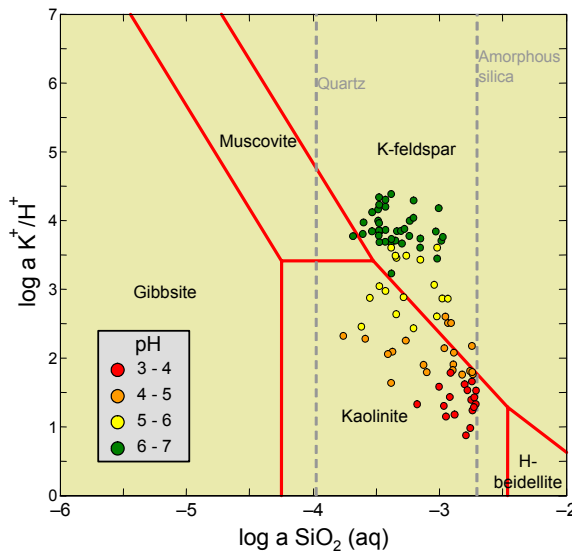
Alkalinity is a critical variable for a number of analyses of groundwater data, but field determination adds to time of sampling. We discuss potential for estimation of  $\text{HCO}_3^-$  and  $\text{PCO}_2$ , and potential for equilibrium activity diagrams. For example, comparison of plots using  $\text{PCO}_2$  calculated by PHREEQE (Figure 5) and estimated from pH, Eh and elemental data (TDS, Ca, Mg,  $\text{SO}_4$ ) only (Figure 6) shows very good agreement above pH 5.5. If time allows we will discuss use and mis-use of such diagrams in regolith environments. Examples are given in Figure 7 and Figure 8.



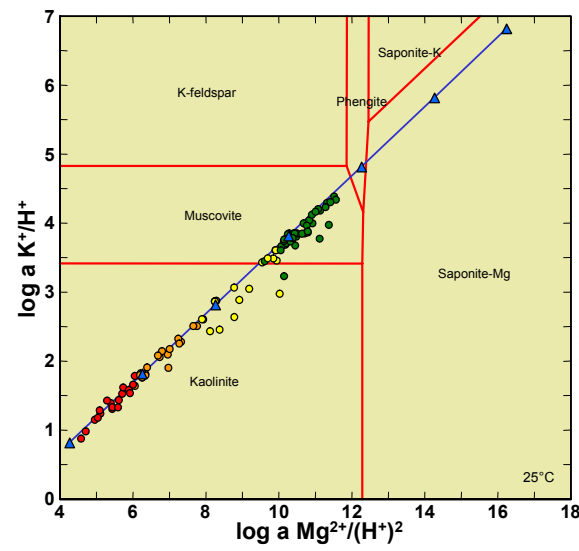
**Figure 5.**  $\text{CO}_2$ :pH Equilibrium Activity diagram (Geochemist's Workbench®; thermo.com.v8.r6+.dat), for  $[\text{Cu}^{2+}] = 10^{-5}$  M,  $[\text{Cl}^-] = 1$  M,  $[\text{SO}_4^{2-}] = 0.1$  M. pH and  $\text{PCO}_2$  data for WA groundwaters is overlain.



**Figure 6.**  $\text{CO}_2$ :pH Equilibrium Activity diagram (Geochemist's Workbench®; thermo.com.v8.r6+.dat), for  $[\text{Cu}^{2+}] = 10^{-5}$  M,  $[\text{Cl}^-] = 1$  M,  $[\text{SO}_4^{2-}] = 0.1$  M. pH and derived  $\text{PCO}_2$  data for WA groundwaters is overlain.



**Figure 7.** K:Si Activity diagram – Al speciation (Geochemist's Workbench®; thermo.dat) for Tunkillia groundwaters, pyrophyllite suppressed, indicating amorphous silica control at low pH, and that K-feldspar will be soluble in deeper neutral regolith.



**Figure 8.** K:Mg Activity diagram – Al speciation (Geochemist's Workbench®; thermo.dat) for Tunkillia groundwaters. Blue triangles and line are sea water at varying pH. Thus the linear groundwater trend reflects acidification and not mineralogical control!

**REFERENCES**

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 NOBLE R.R.P. & GRAY, D.J. 2006. Comparison of hydrogeochemical methods in exploration groundwater sampling. This Volume