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HYDROGEOCHEMISTRY IN THE YILGARN CRATON

D.J. Gray

CRC LEME OPEN FILE REPORT 99

May 2001

(CSIRO Division of Exploration and Mining Report 312R, 1996.
2nd Impression 2001.)

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RESEARCH ARISING FROM CSIRO/AMIRA YILGARN REGOLITH GEOCHEMISTRY PROJECTS 1987-1996

In 1987, CSIRO commenced a series of multi-client research projects in regolith geology and geochemistry which were sponsored by companies in the Australian mining industry, through the Australian Mineral Industries Research Association Limited (AMIRA). The initial research program, "Exploration for concealed gold deposits, Yilgarn Block, Western Australia" had the aim of developing improved geological, geochemical and geophysical methods for mineral exploration that would facilitate the location of blind, buried or deeply weathered gold deposits. The program commenced with the following projects:

P240: Laterite geochemistry for detecting concealed mineral deposits (1987-1991). Leader: Dr R.E. Smith.

Its scope was development of methods for sampling and interpretation of multi-element laterite geochemistry data and application of multi-element techniques to gold and polymetallic mineral exploration in weathered terrain. The project emphasised viewing laterite geochemical dispersion patterns in their regolith-landform context at local and district scales. It was supported by 30 companies.

P241: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1987-1991). Leader: Dr C.R.M. Butt.

The project investigated the distribution of ore and indicator elements in the regolith. It included studies of the mineralogical and geochemical characteristics of weathered ore deposits and wall rocks, and the chemical controls on element dispersion and concentration during regolith evolution. This was to increase the effectiveness of geochemical exploration in weathered terrain through improved understanding of weathering processes. It was supported by 26 companies.

These projects represented 'an opportunity for the mineral industry to participate in a multi-disciplinary program of geoscience research aimed at developing new geological, geochemical and geophysical methods for exploration in deeply weathered Archaean terrains'. This initiative recognised the unique opportunities, created by exploration and open-cut mining, to conduct detailed studies of the weathered zone, with particular emphasis on the near-surface expression of gold mineralisation. The skills of existing and specially recruited research staff from the Floreat Park and North Ryde laboratories (of the then Divisions of Minerals and Geochemistry, and Mineral Physics and Mineralogy, subsequently Exploration Geoscience and later Exploration and Mining) were integrated to form a task force with expertise in geology, mineralogy, geochemistry and geophysics. Several staff participated in more than one project. Following completion of the original projects, two continuation projects were developed.

P240A: Geochemical exploration in complex lateritic environments of the Yilgarn Craton, Western Australia (1991-1993). Leaders: Drs R.E. Smith and R.R. Anand.

The approach of viewing geochemical dispersion within a well-controlled and well-understood regolith-landform and bedrock framework at detailed and district scales continued. In this extension, focus was particularly on areas of transported cover and on more complex lateritic environments typified by the Kalgoorlie regional study. This was supported by 17 companies.

P241A: Gold and associated elements in the regolith - dispersion processes and implications for exploration (1991-1993). Leader: Dr. C.R.M. Butt.

The significance of gold mobilisation under present-day conditions, particularly the important relationship with pedogenic carbonate, was investigated further. In addition, attention was focussed on the recognition of primary lithologies from their weathered equivalents. This project was supported by 14 companies.

Most reports related to the above research projects were published as CRC LEME Open File Reports Series (Nos 1-74), with an index (Report 75), by June 1999. Publication now continues with release of reports from further projects.

P252: Geochemical exploration for platinum group elements in weathered terrain. Leader: Dr C.R.M. Butt.

This project was designed to gather information on the geochemical behaviour of the platinum group elements under weathering conditions using both laboratory and field studies, to determine their dispersion in the regolith and to apply this to concepts for use in exploration. The research was commenced in 1988 by CSIRO Exploration Geoscience and the University of Wales (Cardiff). The Final Report was completed in December 1992. It was supported by 9 companies.

P409: Geochemical exploration in areas of transported overburden, Yilgarn Craton and environs, WA.

Leaders: Drs C.R.M. Butt and R.E. Smith.

About 50% or more of prospective terrain in the Yilgarn is obscured by substantial thicknesses of transported overburden that varies in age from Permian to Recent. Some of this cover has undergone substantial weathering. Exploration problems in these covered areas were the focus of Project 409. The research was commenced in June 1993 by CSIRO Exploration and Mining but was subsequently incorporated into the activities of CRC LEME in July 1995 and was concluded in July 1996. It was supported by 22 companies.

Although the confidentiality periods of Projects P252 and P409 expired in 1994 and 1998, respectively, the reports have not been released previously. CRC LEME acknowledges the Australian Mineral Industries Research Association and CSIRO Division of Exploration and Mining for authority to publish these reports. It is intended that publication of the reports will be a substantial additional factor in transferring technology to aid the Australian mineral industry.

This report (CRC LEME Open File Report 99) is a second impression (second printing) of CSIRO, Division of Exploration and Mining Restricted Report 312R, first issued in 1996, which formed part of the CSIRO/AMIRA Project P409.

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PREFACE

The CRC LEME-AMIRA Project "Exploration in Areas of Transported Overburden, Yilgarn Craton and Environs" (Project 409) has, as its principal objective, development of geochemical methods for mineral exploration in areas with substantial transported overburden, through investigations of the processes of geochemical dispersion from concealed mineralization. The Project has two main themes. One of these, *'Surface and subsurface expression of concealed mineral deposits'* is addressed by this report, which focuses on the hydrogeochemistry of a number of sites in the Yilgarn Craton and margins.

Hydrogeochemistry has long been considered as having considerable potential in exploration, on the premise that groundwaters are a pervasive medium by which ore-associated elements may be widely dispersed and thus present a broader target than the mineralization itself. This target may be relatively localized, indicating mineralization just missed by drilling, or be of district or regional scale. Prospective zones of high reactivity, such as shears and faults, may also have distinct hydrogeochemical signatures, though the rocks themselves may have unremarkable compositions. In addition, hydrogeochemical studies may provide information on currently active processes of weathering. Despite its potential, however, hydrogeochemical exploration has proved difficult to apply, largely due to the complex element interactions and the strong influence of the local environment on salinity, pH, composition and hydrology of the groundwater.

The data compiled here demonstrates that different regions of the Yilgarn Craton have significantly different groundwater characteristics. These differences have major implications for the use of groundwater as an exploration medium, and to our understanding of the timing and extent of supergene mobilization of ore elements, particularly Au. In addition, different pathfinder elements may be useful for Au exploration in different regions.

C.R.M. Butt and R.E. Smith
Project Leaders
September 1996

ABSTRACT

This Report is a compilation of work done to date within CRC LEME on the hydrogeochemistry of the Yilgarn Craton and its margins. The various sites can be grouped into three distinct regions: the Kalgoorlie region, which has acid and saline to hypersaline groundwaters; the Central region, at and immediately N of the Menzies line, which has variably saline and neutral groundwater; and the Northern region, which has neutral and mostly fresh groundwaters. These differences are reflected in trace element geochemistries, with Kalgoorlie groundwaters having high dissolved Au, base metals, REE and U but low oxy-anions (*e.g.*, As, Sb, Mo, W, Tl, Bi), Central groundwaters having moderate dissolved Au and high oxy-anion concentrations, and Northern groundwaters having low Au, moderate oxy-anions and high V and P. Exploration strategies resulting from these observations are discussed, as are effects of transported overburden.

Gold dissolution is hypothesized to be mainly as a result of halide (chloride and/or iodide) complexation of Au. This only occurs in saline/acid/oxidizing conditions, which do occur regularly in the Kalgoorlie region and to a lesser extent in the Central region. This is reflected in the Au concentrations observed for the three regions. The presence of dissolved Mn is hypothesized to be important for the generation of sufficiently high oxidation potentials for Au dissolution, whereas dissolved Fe appears to precipitate Au. As the primary source for dissolved Fe is from depth, this is consistent with leaching of Au in the upper part of the water table and Au precipitation at depth where the oxidized Au contacts dissolved Fe.

As well as exploration for Au, a number of pathfinder elements may be useful for lithological discrimination. This includes base metals for distinguishing various lithologies, particularly in acid groundwaters, and Cr, which appears to reliably distinguish ultramafic rocks, in all groundwater types, regardless of the degree of weathering.

Although the hydrogeochemistry of further sites should be investigated, particularly in the south-west Yilgarn, data accumulated to this point does indicate consistent hydrogeochemical behaviours within each of the three regions given here, thus allowing a consistent use of groundwater data in each region, for Au exploration, lithological discrimination or enhancing our understanding of weathering and dispersion processes.

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1. INTRODUCTION

This Report is a summary of hydrogeochemical investigations undertaken in CRC LEME-AMIRA Project 409 and earlier projects, which include 14 different sites across the Yilgarn Craton and its margins. Research work in Australia and elsewhere (Morris, 1982; Hamilton *et al.*, 1983; Giblin and Snelling, 1984; Runnells, 1984; Dissanayake and Weerasooriya, 1986; Hall *et al.*, 1986; McHugh, 1988; Bergeron and Choinière, 1989; Dekkers *et al.*, 1989; Cidu and Edmunds, 1990) has suggested that hydrogeochemistry may be useful for exploration for Au and other metals. Groundwater anomalies may be broader and more regular than the mineralization and secondary dispersion halo in the regolith, thus enhancing the exploration signature. In addition, areas of high reactivity (*e.g.*, faults and shear zones) may have distinct hydrogeochemical signatures even where they are unremarkable in terms of elemental abundances, and where petrographic study is difficult.

Hydrogeochemical studies also provide information on how various materials are weathering. This enhances understanding of active dispersion processes and assists in the development of weathering and geochemical models, which are essential for effective exploration in regolith-dominated terrain. Particular emphasis has been placed on the hydrogeochemistry of Au, both in terms of site selection and on laboratory investigations that assist in interpretation of the data. It is intended that this enhanced understanding of the hydrogeochemistry of Au will be valuable in predicting the form and degree of supergene mobilization of Au in the regolith.

The aims of the hydrogeochemical studies were, therefore:

- (i) to provide information on whether groundwater can be used successfully as an exploration medium in the Yilgarn Craton adjoining belts;
- (ii) to yield data on geochemical dispersion processes;
- (iii) to create a groundwater database on the characteristics of groundwaters at various sites, and to enhance our understanding of groundwater processes in mineralized zones;
- (iv) development of techniques for analysis of groundwater data from mineralized areas.

In general, a hydrogeochemical site study will include the effect of underlying lithology on the observed water chemistry, thermodynamic modelling, mapping of the data and comparison with results from other sites. This Report will summarize the important observations from these investigations, as well as developing a regional scope for modelling of groundwater characteristics.

2. STUDY SITES

Fourteen different sites have been used for hydrogeochemical investigations in CSIRO/AMIRA Project 409 and earlier projects (Figure 1). They are grouped by geography and chemistry as follows:

- (i) *Northern groundwaters* (N Yilgarn and margins) -

Baxter (Gray, 1995): 90 km N of Meekatharra, in early Proterozoic belt developed on the northern margins of the Yilgarn Craton, primarily mafic and ultramafic volcanics;

Lawlers (Gray, 1994): 30 km SW of Leinster, primarily mafic and ultramafic volcanics with sedimentary sequences of sandstone, siltstone, shales, conglomerates, and cherts to the N, and outcropping granitoid rocks in the SW of the study area.

Groundwaters in these areas are fresh and neutral, trending more saline in the valley floors.

- (ii) *Central groundwaters* (close to and north of the Menzies line) -

Granny Smith (Gray 1993a): 25 km S of Laverton, characterized by siltstone and shale, capped by BIF and subordinate tuff in the south and quartz-rich greywacke and lithic wacke in the N of the study area;

Golden Delicious (Bristow *et al.*, 1996): 50 km S of Laverton, Archaean granitoids that intrude mafic volcanic and volcanoclastic greenschist rocks 5 km E of Lake Carey;
 Mt Gibson (Gray, 1991): 100 km NE of Dalwallinu, with interlayered volcanoclastic and epiclastic metasediments, felsic and mafic volcanic rocks, cherts and porphyries;
 Boags (Gray, 1992a): Bottle Creek, 210 km NNW of Kalgoorlie, basaltic volcanics intruded by quartz porphyry, with the presence of massive sulfides weathered to form a gossan.

Groundwaters are neutral and brackish (commonly < 1% TDS) to saline (about 3% TDS), trending to hypersaline (10 - 30% TDS) at the salt lakes, with common increases in salinity with depth.

(iii) *Kalgoorlie groundwaters -*

Golden Hope (Gray, 1993b): near New Celebration mine, some 40 km SE of Kalgoorlie, containing chloritic schist and ultramafic rocks;

Wollubar (Gray, 1993b): major palaeochannel system 40 km SE of Kalgoorlie, which crosses mafic, ultramafic and felsic rocks ;

Panglo (Gray, 1990a): 30 km N of Kalgoorlie, with 40 m of leached saprolite overlying mineralization hosted by interlayered mafics, ultramafics and shales;

Baseline: adjacent to Panglo, up to 20m of transported material;

Mulgarrie (Gray, 1992b): minor palaeochannel overlying ultramafic rocks, 40 km N of Kalgoorlie;

Steinway (Lintern and Gray, 1995a): a minor palaeochannel system over mafic andesites with trachytes, porphyritic tuff and black shales, 15 km W of New Celebration.

Argo (Lintern and Gray, 1995b): reduced palaeochannel system over high-Mg basalts and dolerite, 25 km S of Kambalda;

These groundwaters are commonly acid (pH 3 - 5) and saline within the top part of the groundwater mass, except where buffered by extremely alkaline materials (*e.g.*, ultramafic rocks), trending to more neutral (pH 5 - 7) and hypersaline at depth and when within a few km of various salt lakes in the region.

(iv) *Officer Basin -*

Mulga Rock (Douglas *et al.*, 1993): a highly reduced palaeodrainage system, over a sequence of predominantly unmineralized quartzites, cherts, shales and dolomites in the Officer Basin, about 240 km NE of Kalgoorlie.

Groundwaters are saline to hypersaline and neutral to acid. The major ion chemistry is similar to that of the Kalgoorlie region, but the dissolved concentration of many other ions is low, due to the presence of lignites in the channel sediments

Results for all these sites are grouped into the regions and elemental data plotted in Appendix 1, Figures A1.1 - A1.54. This report will give a discussion and summary of critical observations of this research. For site-specific results the reader should consult the site reports.

Investigations of these sites have led to the hypothesis that the concentrations of major and minor elements are controlled by particular mechanisms, related either to hydrological phenomena, lithological effects, groundwater controls (*e.g.*, pH, Eh) and, in the case of Au, presence or absence of ligands (*e.g.*, chloride, iodide, thiosulfate) and or interfering ions (*e.g.*, Fe). In addition, the different regions have distinct major and minor element compositions. This has major significance for the mobility of Au and other pathfinders, the processes of supergene depletion and enrichment and for the use of groundwater as an exploration medium. Information on these controls, and on general groundwater characteristics, have contributed to the assessment and development of hydrogeochemistry as an exploration technique and enhanced understanding of regolith geochemistry.

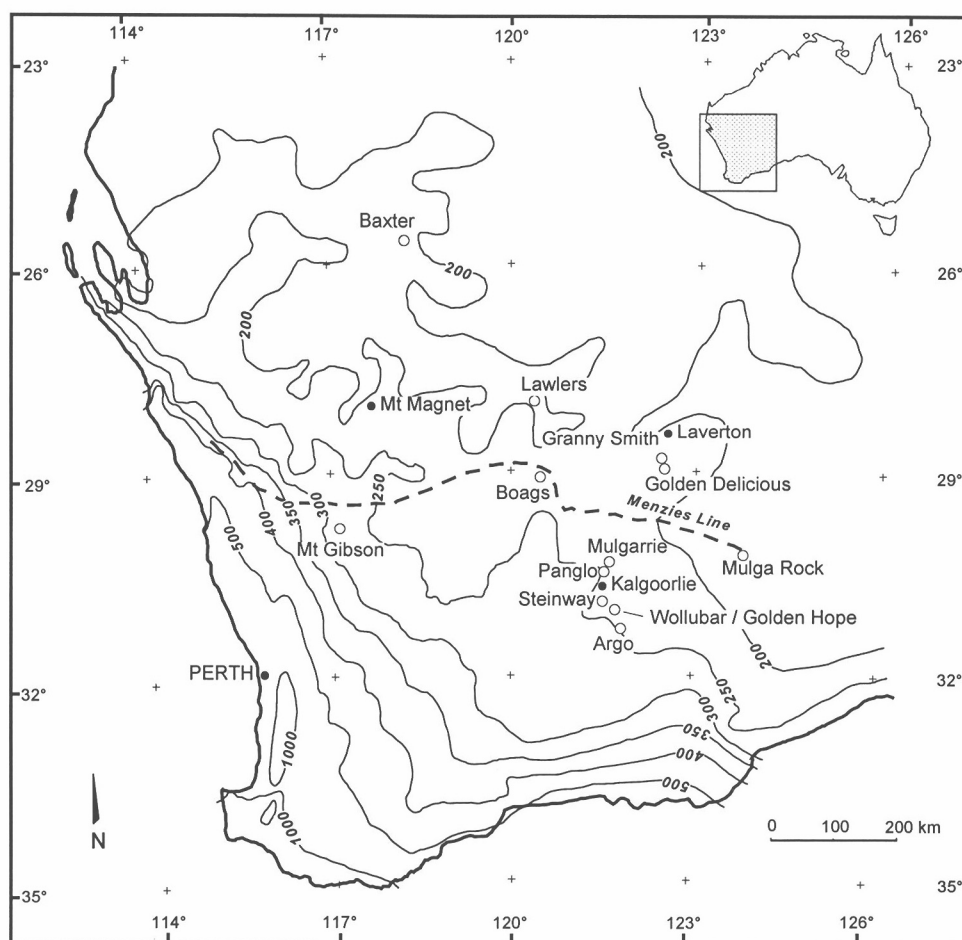


Figure 1: Location map of groundwater investigation sites.

3. SAMPLING, ANALYTICAL AND INTERPRETATIONAL METHODS

Due to the difficulty in obtaining properly drilled and cased bore holes for pumping, groundwaters are commonly collected using direct collection within drill holes, preferably 5 m or more below the water-table. Waters are treated in the field and analysed in the laboratory using a general regime, as detailed in any of the site reports (Section 2). In particular, a one litre sub-sample of the filtered water is shaken with one gram sachet of activated carbon in a saline/acid medium and the carbon analysed for Au and other elements. This pre-concentration system permits successful quantitative analysis of waters for Au to $< 0.005 \mu\text{g/L}$ and qualitative analyses for As, Mo, W, U, La, Ce and Sm.

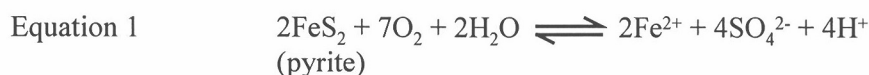
Additional understanding of groundwater processes is obtained by computing the solution species of many of the major and trace elements and degree of mineral saturation from solution compositions, using the program PHREEQE (Parkhurst *et al.*, 1980; described in detail in Gray, 1990a and Gray, 1991). To obtain highly accurate speciation data on a limited suite of the major elements (Na, K, Mg, Ca, Cl, HCO_3 , SO_4 , Sr and Ba) for highly saline solutions, the specific ion interaction model known as the Pitzer equations is applied, using the program PHRQPITZ (courtesy USGS).

These programs are used to calculate the solubility indices (SI) for a number of mineral phases for each water sample, which are compiled in Appendix 2. If the SI for a mineral equals zero, the water is in equilibrium with that particular solid phase, under the conditions specified. Where the SI is less than zero, the solution is under-saturated with respect to the phase, so that, if present, the phase may

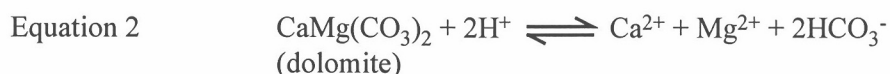
dissolve. If the SI is greater than zero the solution is over-saturated with respect to this phase and the phase can precipitate. In Figures A2.1 - A2.34 the shaded area around SI = 0 represents the degree of uncertainty in the calculation, which will vary from a narrow band for well characterized minerals such as calcite (Figure A2.5), to a very broad band for minerals of minor elements with less well characterized thermodynamics (*e.g.*, iodyrite; Figure A2.22). Thus, any point within the shaded area may represent a groundwater at equilibrium with that phase, though care should be taken to distinguish merely accidental occurrences of SI = 0 (*e.g.*, eskolaite, for which SI goes from -11 to 12, depending on pH; Figure A2.24), from elements which are consistently controlled by mineral equilibration [*e.g.*, Ba - for which most Central and Northern groundwaters are equilibrated with barite (Figure A2.4), which is reflected by the reduction in Ba concentration with higher salinity (due to higher SO₄ causing barite precipitation; Figure A1.12)].

4. EFFECT OF SAMPLE DEPTH ON SALINITY, EH AND PH

Deep groundwaters in contact with mineralization commonly have high concentrations of dissolved Fe and other chalcophile elements, probably derived from the first stage of the oxidation of pyrite and other sulfides:

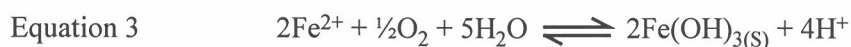


At depth, such acid production is buffered by minerals such as carbonates or feldspar:



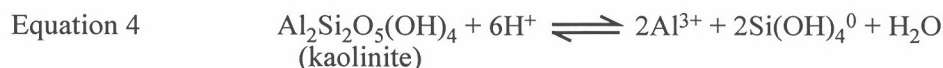
Thus, these groundwaters contain significant dissolved Fe (>0.1 mg/L) and are neutral and reduced [filled in symbols in the neutral region (6 < pH < 8) in Figure 2]. They commonly have Eh values of 200 mV or less.

Closer to the surface, conditions are more oxidizing, and soluble Fe²⁺ will oxidize to Fe³⁺, which then precipitates as an oxide/hydroxide, generating acidity (Equation 3). As this occurs higher in the profile, and (unlike the initial phase of sulfide weathering; Equation 1) buffering minerals are commonly absent, highly acid conditions can ensue. This critical groundwater Eh/pH control is known as the "ferrolysis" reaction (Brinkman, 1977).



Because the reaction is governed by both Eh and pH, the ferrolysis control is an angled line on an Eh/pH diagram (denoted by the Fe line in Figure 2). All groundwaters with significant Fe concentrations (> 0.1 mg/L; solid symbols in Figure 2) congregate around this line.

Under most weathering conditions, there is an absolute groundwater pH limit of 3, because such acid conditions cause aluminosilicates such as kaolinite to dissolve and reduce acidity:



maintaining the solution pH at about 3.2. This control is Eh independent (the Al line in Figure 2). In the more acid groundwaters, dissolved Si concentrations are high, and reach saturation with amorphous silica (Figure A2.8). Thus, Al and Si dissolved from kaolinite appear to be equilibrating with phases that have fast precipitation/dissolution reactions, namely jurbanite:

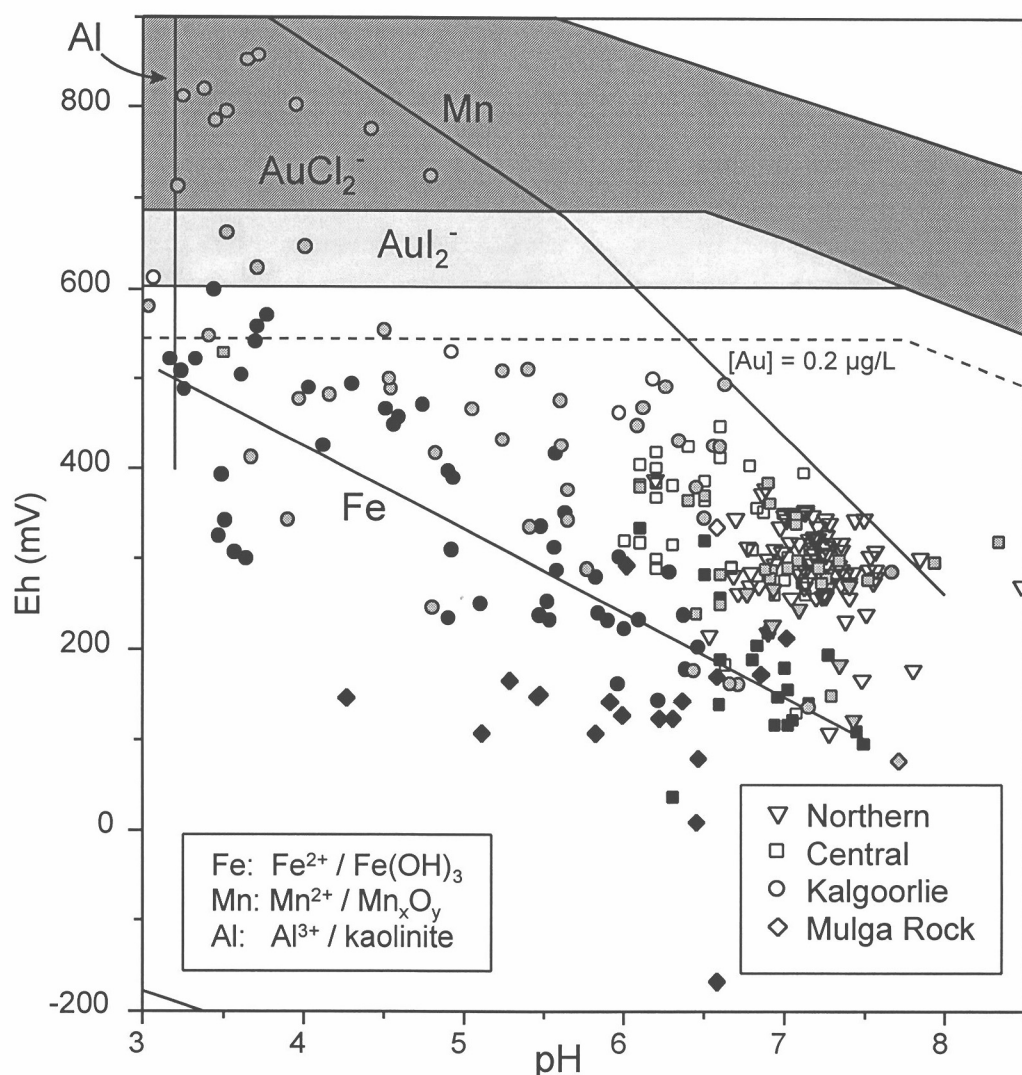
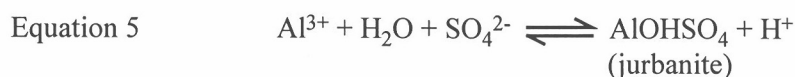
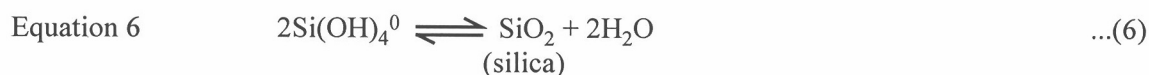


Figure 2: Eh vs. pH in groundwaters from WA research sites: solid symbols indicate samples with $[\text{Fe}] > 0.1 \text{ mg/L}$ (ppm); grey-filled symbols have $[\text{Fe}] < 0.1 \text{ mg/L}$ and $[\text{Mn}] > 0.1 \text{ mg/L}$; open symbols have $[\text{Fe}]$ and $[\text{Mn}] < 0.1 \text{ mg/L}$. The Mn line is derived using data from Moussard *et al.* (1974), assuming $[\text{Mn}] = 10^{-4} \text{ M}$ (5.5 mg/L). Hatched area is zone where $[\text{Au}] > 2 \text{ µg/L}$ (ppb) in 1 M (5.7%) NaCl solution, with stippled area showing the decrease in Eh required to dissolve 2 µg/L Au from the presence of 10^{-5} M (1.3 ppm) I^- . Dashed line is lower Eh limit for $[\text{Au}] = 0.2 \text{ µg/L}$ in $10^{-5} \text{ M I}^- / 1 \text{ M NaCl}$ solution.



and amorphous silica:



Many of the acidic groundwaters contain significant Mn, which can then stabilize groundwaters at very high Eh values (up to 850 mV; denoted by the Mn line in Figure 2) in the Mn analog to ferrollysis. As will be discussed later (Section 7.2), this control is critical to the mobility of Au in the Kalgoorlie and, possibly, Central regions.

The final type of groundwater observed in the study areas is that containing neither significant Fe or Mn (open symbols in Figure 2). These waters almost exclusively have neutral pH (6 - 8.5), include virtually all of the Northern, some Central and few Kalgoorlie groundwaters, and are denoted as the HO group. Although there are redox couples within the range measured for these waters (the most probable being $\text{H}_2\text{O}_2/\text{O}_2$; Sato, 1960), they have slow kinetics and the solution Eh will be weakly controlled. This group is the least chemically active of the waters, being neither strongly reducing (neutral group Fe waters), strongly acid (group Al) or strongly oxidizing (group Mn).

These four Eh/pH controls appear adequate to model the Eh/pH data from all Yilgarn sites investigated to date. The Eh/pH characteristics vary from neutral to moderately acid and reducing at Mulga Rock (probably a site specific characteristic), neutral to highly acid and oxidizing in Kalgoorlie, and neutral in the Central and Northern Regions (Table 1).

5. MAJOR ELEMENT HYDROGEOCHEMISTRY

The major elements are classified as those primarily controlled by salinity effects (*i.e.*, Na, K, Mg, Ca, Cl, SO_4 , Br; Figures A1.1 - A1.7) as well as HCO_3^- , Si, Al and Fe (Figures A1.18, A1.23, A1.24 and A1.30). There are major salinity differences between the four groundwater regions: the Kalgoorlie region is highly saline (median salinity over 2x sea water), whereas Central and Mulga Rock groundwaters are less saline, and show major reductions in salinity away from the salt lake zones; the Northern groundwaters are fresh. In all but the Northern region, salinities show major increases with depth, probably due to back-flow at depth from salt lakes (Figure 3).

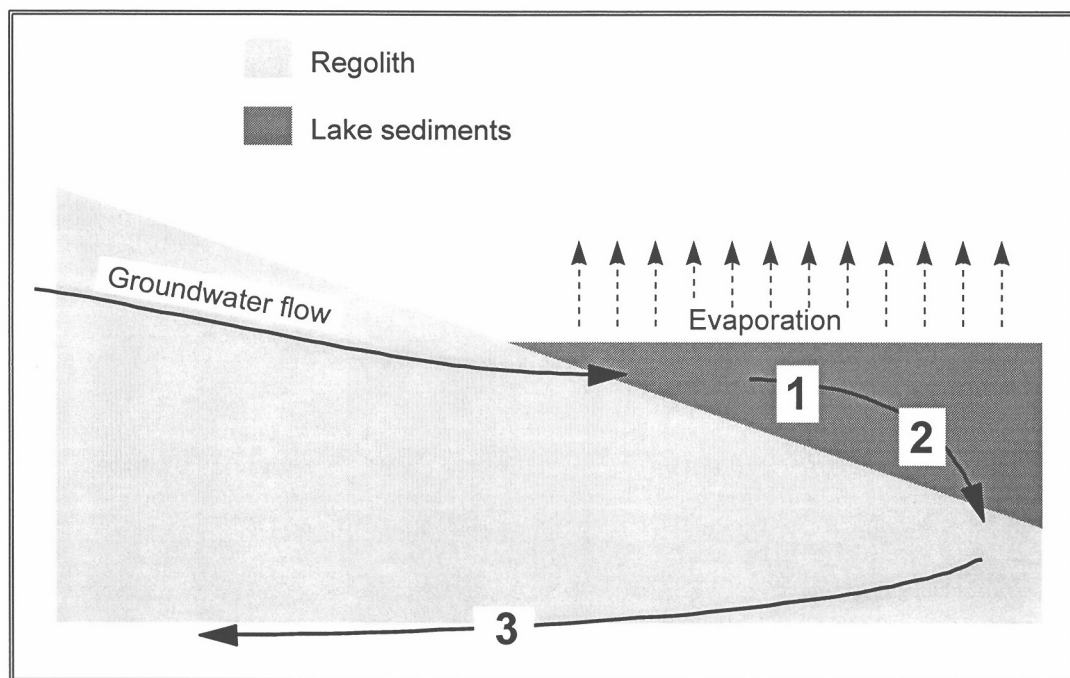


Figure 3: Diagrammatic representation of groundwater evaporation and flow at salt lakes:

1. Evaporation, leading to saline and dense groundwater;
2. Downward flow of dense groundwater;
3. Back-flow of saline waters, leading to higher salinity at depth.

Ion ratios for the Central, Kalgoorlie and Mulga Rock sites suggest a sea water norm, possibly due to a previous sea water incursion or deposition of sea water as aerosol. The modifications (Table 1) observed are:

- (i) the Central groundwaters appear to have a minor enrichment in Na and SO₄ (Figures A1.1 and A1.6);
- (ii) the Mulga Rock groundwaters have minor Ca and SO₄ (Figures A1.4 and A1.6) enrichments, possibly due to dissolution of diagenetic carbonates and sulfides;
- (iii) Kalgoorlie groundwaters are moderately reduced in SO₄ (Figure A1.6) and dramatically reduced in K (Figure A1.2), which appears to reflect pervasive precipitation of alunite [KAl₃(SO₄)₂OH₆], as a by-product of the dissolution of kaolinite and other alumino-silicates in these acid systems (Equation 4). In addition, there is a significant depletion of Br in the Kalgoorlie region (and for Mulga Rock and Granny Smith; Figure A1.7), which could be due to oxidation of Br⁻ to Br₂. Such a mechanism for Br loss via volatilization, rather than by precipitation of salts, is supported by the observation that Br/TDS is never significantly greater than for sea water. If Br volatilization is occurring, it would be expected to be slow, even for the oxidized Kalgoorlie groundwaters, and would suggest them to be very old. Volatilization would be likely to be even more significant for I (which oxidises more readily than Br), with important consequences for Au hydrogeochemistry (Section 7.2)

Table 1: Median pH, Eh and major element compositions of groundwaters in Western Australian study sites (with number of samples in brackets).

	Seawater	Northern (90)	Central (89)	Kalgoorlie (102)	Mulga Rock (20)
pH		7.2 ± 0.3	6.8 ± 0.6	4.9 ± 1.2	6.3 ± 0.8
Eh (mV)		290 ± 50	290 ± 90	430 ± 170	140 ± 100
TDS (%)	3.5	0.05 ± 0.05	2.0 ± 3.2	7.4 ± 3.8	2.6 ± 2.3
Na/TDS	0.307	0.196 ± 0.034	0.331 ± 0.021	0.315 ± 0.016	0.300 ± 0.012
Mg/TDS	0.037	0.061 ± 0.020	0.026 ± 0.007	0.037 ± 0.010	0.033 ± 0.003
Ca/TDS	0.012	0.105 ± 0.034	0.009 ± 0.009	0.007 ± 0.004	0.020 ± 0.010
K/TDS	0.011	0.031 ± 0.012	0.010 ± 0.003	0.001 ± 0.002	0.010 ± 0.002
Cl/TDS	0.552	0.300 ± 0.047	0.527 ± 0.042	0.577 ± 0.020	0.530 ± 0.013
SO ₄ /TDS	0.077	0.155 ± 0.051	0.084 ± 0.032	0.060 ± 0.020	0.105 ± 0.025
Br/TDS	0.0019	0.0020 ± 0.0002	0.0017 ± 0.0007	0.0005 ± 0.0005	0.0006 ± 0.0003
HCO ₃ (mg/L)	140	90 ± 50	170 ± 180	10 ± 150	100 ± 280

In contrast, the Northern groundwaters are distinctly different from sea water (Table 1), although both sites have very similar ion ratios. This may reflect a general groundwater characteristic for dissolution of a suite of mafic/ultramafic and granitic rocks.

These differences between sites are clearly demonstrated in a plot of pH vs. TDS (Figure 4), for which the Northern, Central and Kalgoorlie groundwaters plot in distinct domains: Northern groundwaters are neutral and fresh; Central groundwaters are neutral and fresh close to groundwater divides but highly saline adjacent to salt lakes; Kalgoorlie groundwaters vary from saline and acid close to the surface to hyper-saline and neutral at depth and close to salt lakes. The few Kalgoorlie groundwaters that are neutral and saline (rather than hyper-saline) are shallow groundwaters in contact with weathered ultramafic rocks.

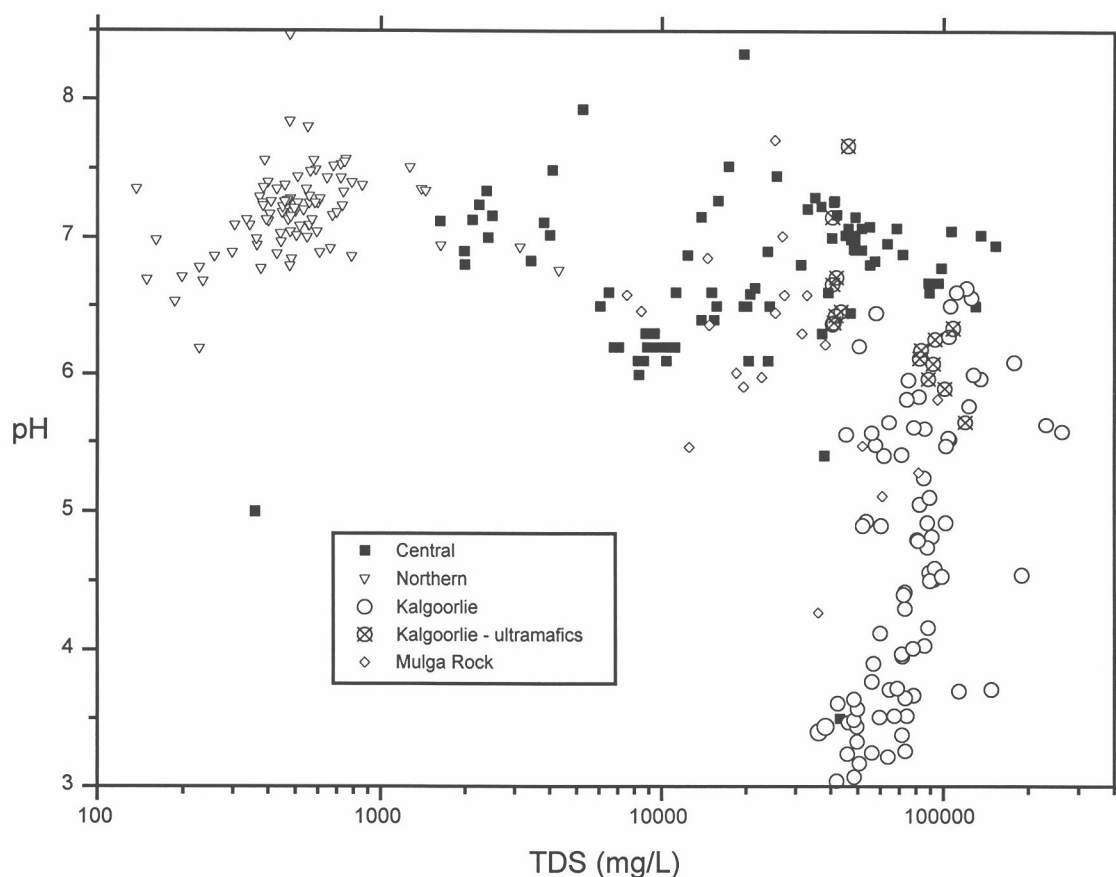


Figure 4: pH vs. TDS for groundwaters in Western Australian study areas.

The concentrations of most of the major elements in groundwater are controlled by mineral equilibria in some circumstances:

- (i) in highly saline environments, such as within the salt lakes, groundwaters are sufficiently saline ($> 30\%$ TDS) to reach equilibrium with halite (Figure A2.1);
- (ii) K appears to be precipitated as alunite in acid environments. However, SI calculations indicate that the groundwaters tend to be over-saturated with respect to alunite and, instead, equilibrate with a postulated phase - jurbanite (AlOHSO_4 ; Figures A2.11 and A2.12), even though this mineral has not been recorded within the regolith. This may reflect the presence of a jurbanite-like phase as a coating on the alunite. Similar effects have been noted in acid soils (Gray, 1990a, and references given within);
- (iii) in moderately to highly saline environments, Ca is in equilibrium with gypsum (Figure A2.2);
- (iv) HCO_3^- , Ca and Mg are equilibrated with calcite, magnesite and sepiolite [$\text{Mg}_2\text{Si}_3\text{O}_{7.5}(\text{OH}) \cdot 3\text{H}_2\text{O}$] at neutral pH (Figures A2.5, A2.7 and A2.9). This is particularly marked for the Central region, which has moderate salinity and neutral conditions. There is a poor degree of equilibration with dolomite (Figure A2.6), as reflected by the significant number of groundwaters over-saturated with respect to this mineral.
- (v) Si concentrations are higher than for equilibration with quartz (Figure A2.8), indicating equilibration with more amorphous forms of silica, particularly at low pH, and with sepiolite (see above) in neutral/saline conditions;
- (vi) Al concentrations are very low in neutral conditions (Figure A1.23), and increase to $> 100 \text{ mg/L}$ below pH 4, presumably due to the solubility of kaolinite (Figure A2.10) and

other alumino-silicates under these conditions. Much of this Al is reprecipitated as alunite, though possibly via a highly soluble jurbanite intermediate (see above).

Where ratios differ from the regional trend, this may relate to mineralization or other sources that contrast with the surrounding country rock. In particular, localized enrichments in SO_4 , as observed for the Golden Hope (Kalgoorlie; $\text{SO}_4/\text{TDS} = 0.13$) and Boags (Central; $\text{SO}_4/\text{TDS} = 0.17$) pit areas, and in groundwaters in overburden above Four Corners mineralization at Lawlers (North; Figure 5), may indicate oxidation of major sulfide bodies.

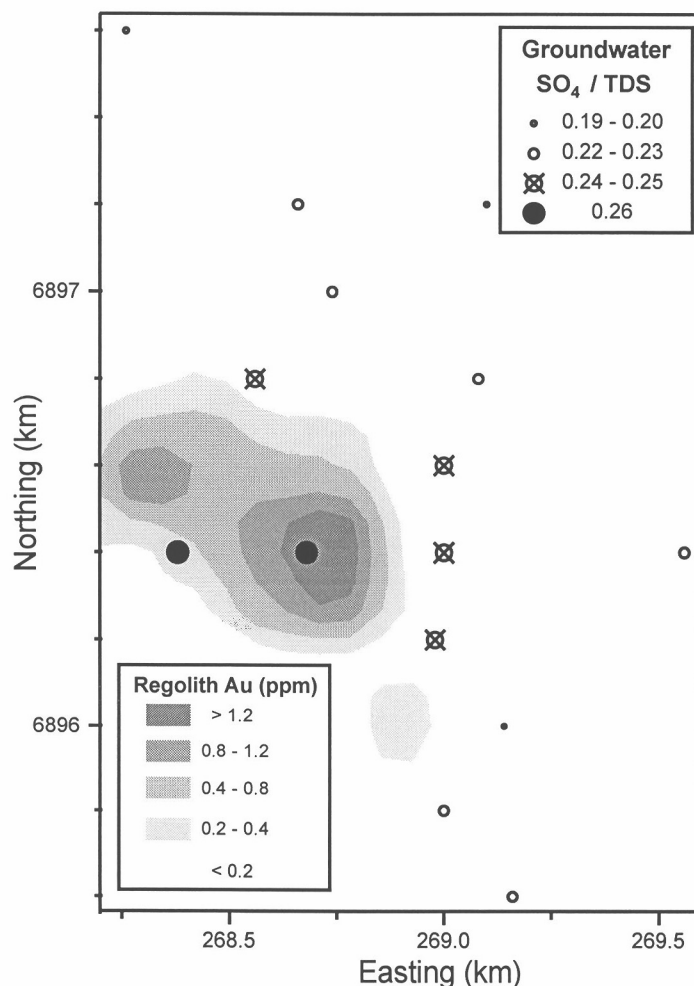


Figure 5: SO_4/TDS distribution in groundwaters at Four Corners, Lawlers study area, Western Australian.

6. MINOR ELEMENT HYDROGEOCHEMISTRY

6.1 General features

Median minor element concentrations in Yilgarn groundwaters are listed in Table 2. The last column gives the postulated control on groundwater concentration. Thus, for example, Y and REE concentration is primarily controlled by pH, whereas Co concentration is high in waters in contact with mafic or ultramafic rocks, with further enhancement in acid groundwaters. Elements whose concentration is controlled by equilibrium with specific secondary minerals are generally not very useful for exploration, whereas other elements may give useful information as to lithology and/or presence of sulfides.

Table 2: Median minor element compositions of groundwaters.

	Seawater	Northern	Central	Kalgoorlie	Mulga Rock	Controls
Iodide	nd	nd	0.1 ± 0.8	0.3 ± 0.6	0.52 ± 0.25	
I	0.06	0.2 ± 0.3	5 ± 4	5.8 ± 1.9	0.32 ± 0.22	S/Sal ?
P	0.06	0.013 ± 0.07	0.013 ± 0.012	0.010 ± 0.015	0.1 ± 1.6	?
Li	0.18	<0.005	<0.005	0.9 ± 0.6	nd	Ac ?
Be	0.000006	<0.002	<0.005	0.003 ± 0.008	nd	?
Rb	0.12	0.013 ± 0.006	0.051 ± 0.013	0.032 ± 0.028	nd	Min ?
Sr	7.9	0.31 ± 0.18	2.7 ± 2.8	6 ± 4	6 ± 3	Sal/Eq
Cs	0.0003	<0.0002	0.0013 ± 0.0030	0.006 ± 0.016	0.010 ± 0.008	?
Ba	0.013	0.04 ± 0.03	0.02 ± 0.04	0.04 ± 0.04	0.03 ± 0.04	Eq/Min
B	4.4	0.6 ± 0.4	4.3 ± 0.7	4.9 ± 2.6	nd	Sal
Al	0.002	0.003 ± 0.022	0.0 ± 1.5	1 ± 25	0.0 ± 0.5	Ac
Si	2.2	24 ± 9	26 ± 11	7 ± 13	5 ± 7	Ac/Eq
Sc	0.0000006	0.009 ± 0.008	0.017 ± 0.004	0.019 ± 0.017	nd	Ac/Min
Ti	0.001	<0.002	<0.002	<0.005	nd	?
V	0.0025	0.007 ± 0.009	<0.005	<0.005	nd	Eq
Cr	0.0003	0.01 ± 0.05	<0.005	0.003 ± 0.07	0.002 ± 0.017	Um
Mn	0.0002	0.01 ± 0.09	0.1 ± 2.3	2 ± 7	0.3 ± 0.8	Mf/Um/Ac
Fe	0.002	0.003 ± 0.010	0.05 ± 7	0.1 ± 21	1 ± 18	S
Co	0.00002	<0.0005	0.002 ± 0.030	0.16 ± 0.23	<0.002	Um/Mf/Ac
Ni	0.00056	0.002 ± 0.008	0.001 ± 0.04	0.26 ± 0.30	0.020 ± 0.023	Ac/Mf/Um
Cu	0.00025	0.003 ± 0.002	0.003 ± 0.033	0.05 ± 0.09	0.00 ± 0.09	Ac/Mf
Zn	0.0049	0.006 ± 0.008	0.01 ± 0.10	0.05 ± 0.6	0.04 ± 0.08	Ac/Mf
Ga	0.00003	0.002 ± 0.002	<0.005	0.006 ± 0.017	nd	S
Ge	0.00005	<0.0005	<0.005	0.018 ± 0.012	nd	Ac ?
As	0.0037	<0.0002	0.09 ± 0.09	<0.02	<0.02	S
Y	0.000013	<0.0002	0.0005 ± 0.0003	0.21 ± 0.20	0.004 ± 0.002	Ac
Zr	0.00003	<0.0001	<0.001	<0.001	nd	?
Mo	0.01	0.001 ± 0.002	0.009 ± 0.020	<0.01	nd	S
Ag	0.00004	<0.001	0.0005 ± 0.0008	0.001 ± 0.002	nd	?
Cd	0.00011	<0.002	0.001 ± 0.002	<0.002	<0.001	?
Sn	0.000004	<0.0002	0.001 ± 0.024	<0.001	<0.001	?
Sb	0.00024	<0.0003	0.001 ± 0.050	<0.001	<0.0004	S
REE	0.000013	<0.002	<0.008	0.8 ± 1.9	0.013 ± 0.005	Ac
W	0.0001	<0.0002	0.001 ± 0.003	0.001 ± 0.027	nd	S
Au	0.004	0.004 ± 5.9	0.03 ± 0.19	0.05 ± 0.46	0.001 ± 0.006	Min
Hg	0.00003	<0.0002	<0.001	0.002 ± 0.013	<0.001	S
Tl	0.000019	<0.0002	0.001 ± 0.008	<0.002	0.0005 ± 0.0002	S
Pb	0.00003	<0.001	0.001 ± 0.17	0.06 ± 0.32	0.012 ± 0.014	Ac/Min
Bi	0.00002	<0.0002	0.001 ± 0.006	<0.001	<0.002	S ?
Th	0.000001	<0.0002	<0.001	<0.002	<0.001	?
U	0.0032	0.0003 ± 0.0017	0.002 ± 0.017	0.004 ± 0.06	<0.002	Ac

All concentrations in mg/L (ppm), except Au in µg/L (ppb)

nd: not determined

Eq mineral equilibrium

S enriched in waters contacting weathering sulfides

Ac enriched in acid groundwaters

Min enriched in waters contacting Au mineralization

Um enriched in waters contacting ultramafic rocks

Sal enriched in saline groundwaters

Mf enriched in waters contacting mafic rocks

? not clearly defined

As will be discussed in later Sections, a number of the minor elements may have value for lithological discrimination, mineralization pathfinders or as indicators of the degree of weathering. However, the usefulness of these elements depends on regional groundwater effects, as detailed below.

Many elements have higher concentrations in acid groundwaters, such as occur in the Kalgoorlie region. These include Al, F, Li, Ge, Y and the REE, and U (Figures A1.20, A1.23, A1.36, A1.38, A1.45, A1.46 and A1.54). Although extensively redistributed in the regolith, because of the dominance of the pH control, they are not expected to be useful for Au exploration in the Kalgoorlie region.

6.2 Rare earth elements

The REE have particularly high concentrations in the Kalgoorlie region, with light REE concentrations (*e.g.*, La and Ce; Figures A1.45 and A1.46) greater than those for most of the base metals and only exceeded by the major elements, B, F and Sr. A compendium of recent published data on dissolved REE concentrations (Table 3) shows the average REE content of the Wollubar groundwaters to be about 5 times that of the highest recorded REE concentrations outside the Yilgarn Craton (Carmenellis metasediment, England), and the highest individual sample (Woll3; Appendix 1) is about 20 times greater.

Based on a recorded abstraction rate of 2.4×10^9 L/year for the Wollubar palaeochannel bore field (Commander *et al.*, 1992; used for mill operations at New Celebration and Jubilee) in 1990, it is calculated that approximately 4000 kg of total REE were abstracted from the study area (Table 4) over that year. The high REE concentrations are primarily related to hydrogeochemical rather than lithological effects, presumably due to the interaction of the solids with highly acid and saline groundwaters.

These acid groundwaters are particularly enriched in the light REE. For example, a Er vs. La plot (Figure 6) shows all Er/La values to be below the Chondrite ratio ($\text{Er/La} = 0.68$; Taylor and McLennan, 1985), and that many have ratios less than post-Archaeon shales (0.063; *ibid.*), despite the abundant greenstones in that catchment. It is postulated that this represents a preferential dissolution of the light REE, possibly due to heavy REE being predominantly incorporated into more resistant minerals than for light REE. In addition, the Er/La ratio distinguishes the groundwaters, from the western (0.023 ± 0.006), intermediate (0.030 ± 0.006) and eastern (0.052 ± 0.013) parts of the Wollubar palaeochannel, Steinway (0.15 ± 0.06) and Argo (0.09 ± 0.04). These differences presumably relate to the lithology and regolith at each site.

Table 3: Comparative REE concentrations from ground and surface waters (for brevity, not all REE are shown)

			Dissolved Concentration (µg/L)								
Sample Site		Ref	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb
Argo		1	118	227	100	18	5.4	21	15	8.5	5.8
Steinway		1	213	517	251	51	16	63	49	27	17
Wollubar		1	471	691	231	45	12	40	27	13	9.4
Golden Hope		1	1.0	1.3	0.7	0.3	0.1	0.3	0.2	0.2	0.2
Central groundwaters		1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Northern groundwaters		1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mulga Rock		1	1.3	3.8	2.3	1.0	0.5	1.0	0.6	0.5	0.5
Palo Duro basin,	Sawyer Granite	2	20	40	27	7.3	2.1	10			1.8
Texas - Deep	" Carbonate		0.9	1.4	0.6	0.1	0.03	0.1			0.03
Basin Brine	Friemel Granite		0.2	0.3	0.1	0.02	0.004	0.03			0.01
Carmmenellis,	Granite	3	2.3	4.6	2.9	0.7	0.10	0.7	0.5	0.2	0.2
England	Metasediment		95	8.3	69	12	2.4	12	6.3	2.4	1.2
Rivers	Amazon	4	0.05	0.1	0.08	0.02	0.005	0.03	0.02	0.01	0.009
	Connecticut		0.6	0.8	0.4	0.08	0.01	0.07	0.05	0.03	0.03
Estuarine	Amazon	4	0.2	0.5	0.2	0.05	0.01	0.05	0.04	0.02	0.01
waters	Connecticut		0.2	0.4	0.2	0.04	0.008	0.03	0.03	0.02	0.006
Coastal sea	Amazon		0.02	0.04	0.02	0.004	0.001	0.006	0.003	0.003	0.004
waters	Connecticut	4	0.04	0.06	0.04		0.001	0.010	0.006	0.004	0.004
Black Sea	Maximum level	5	0.01	0.03	0.01	0.002	0.001	0.003	0.003	0.003	0.002
Sea water	shallow	6	0.004	0.001	0.002	0.000	0.000	0.001	0.001	0.001	0.001
	deep		0.007	0.001	0.005	0.001	0.000	0.002	0.002	0.002	0.002
Buzzard Bay	pore water	7	0.2	0.6	0.2	0.05	0.01	0.05			
Val-les-Bains	Delicieuse	8		0.1	0.1	0.04	0.01	0.06	0.07	0.06	0.08

References:

1. This study - mean concentrations
2. Gosselin *et al.* (1992) - high REE samples
3. Smedley (1991) - high REE samples
4. Elderfield *et al.* (1990) - high REE samples
5. German *et al.* (1991) - highest REE sample
6. Piepgras and Jacobsen (1992) - mean concentrations
7. Sholkovitz *et al.* (1989) - highest REE sample
8. Michard *et al.* (1987) - highest REE sample

Table 4: Calculated mean concentrations and total quantities of REE abstracted from the Wollubar bore field in 1990

	Mean Conc. (mg/L)	Abstraction (kg /year)
La	0.41	998
Ce	0.69	1677
Pr	0.10	232
Nd	0.35	838
Sm	0.053	128
Eu	0.012	29
Gd	0.043	105
Tb	0.013	31
Dy	0.029	71
Ho	0.005	12
Er	0.014	33
Tm	0.002	4
Yb	0.009	23
Lu	0.001	4
Total REE	1.7	4190

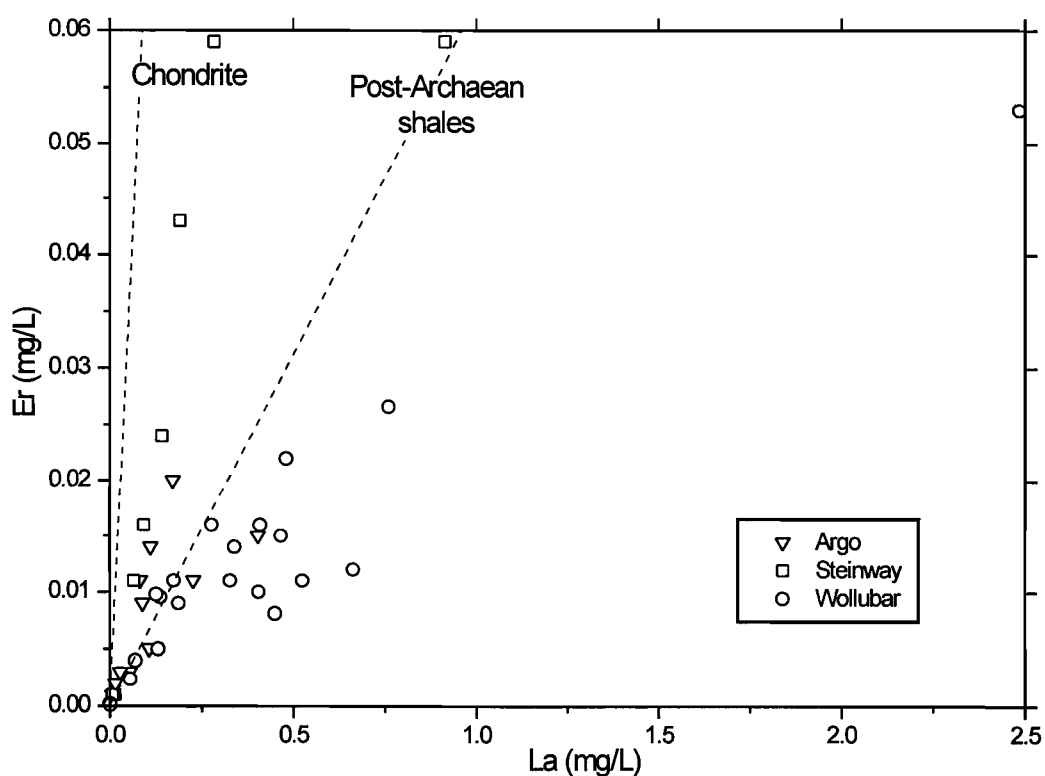


Figure 6: Er vs. La for Kalgoorlie groundwaters (dashed line represents the Chondrite Er/La ratio)

6.3 Base metals and gallium

Dissolved concentrations of the base metals (Mn, Co, Ni, Cu and Zn) and Ga are less closely correlated with acidity than the REE (Figures A1.29, A1.31 - A1.35). These elements do show scope for lithological discrimination (Section 8.2), though work to date has not clearly indicated a usefulness for direct exploration for Au using groundwater. Two elements which show a surprising (on the basis of their normal aqueous chemistry) lack of correlation with acidity are Cr and Sc (Figures A1.25 and A1.28). Scandium has a complex chemistry, with its major aqueous form varying from Sc^{3+} at pH 3, to varying hydrolysed forms (*e.g.*, ScOH^{2+}) nearer neutrality, with species such as ScCl_2^+ in saline waters (Cotton and Wilkinson, 1980), which may cause the observed behaviour. In addition, Sc may be a useful pathfinder for Au (Section 8.5). Dissolved Cr concentrations can be very high (Figure A1.28), with no pH relationship, and shows an absolute correlation with ultramafic rocks (Section 8.2). Moreover, these concentrations of Cr appear to be strongly over-saturated with respect to secondary Cr oxides above pH 6 (Figure A2.24). The reason for this calculated disequilibrium is not clear: it may be that the weathering reactions releasing Cr cause oxidation to CrO_4^{2-} , which has a much higher mobility than Cr^{3+} . A high oxidation state for Cr is also suggested by its highly anti-pathetic relationship with Fe (Figure 7), possibly due to the capacity of dissolved Fe to reduce CrO_4^{2-} to the less soluble Cr^{3+} ion.

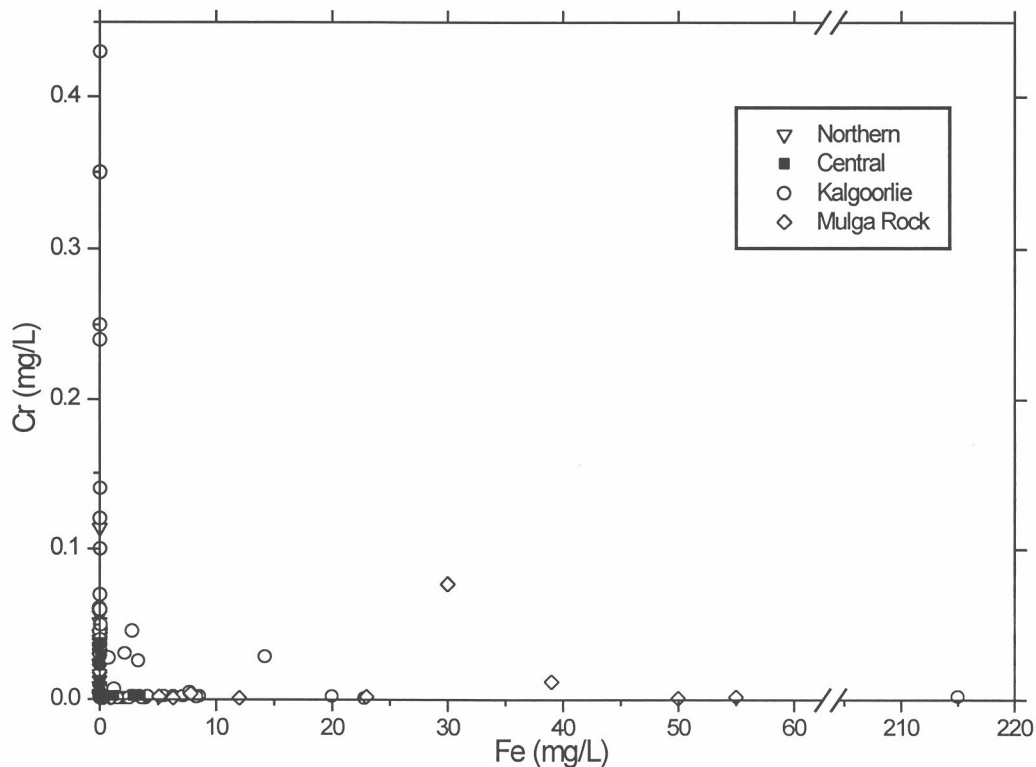


Figure 7: Dissolved Cr vs. Fe for Western Australian Groundwaters

6.4 Metalloids

A number of elements, including As, Sb, Mo, W, Bi and, possibly, Zr and Tl (Figures A1.37, A1.39, A1.40, A1.44, A1.47, A1.50 and A1.52) are very low in acid groundwaters, but have higher concentrations above pH 6.5, particularly for the Central groundwaters. These elements commonly occur as oxy-anions (*e.g.*, H_2AsO_4^-), which are better adsorbed by Fe oxides (or other) surfaces at low pH, due to protonation resulting in positive charge on surfaces when the pH is below the point of zero charge (PZC). This implies that the acid (particularly Kalgoorlie) groundwaters will be poor media

for the use of these elements as exploration pathfinders. Molybdenum differs from the other elements in this group in having significant, though lesser, concentrations at low pH - the reason for this difference is not known, but this observation is consistent with the potential of Mo as a pathfinder element in groundwater.

6.5 Iodine

The concentration and speciation of dissolved iodine may be important for the solubility of Au. Iodine may be present in a number of forms with contrasting oxidation states, including I^- (as free, weakly or strongly bound iodide), I_2 , IO^- and IO_3^- . The iodide ion may well be an important ligand for Au (Section 7.2), whereas the other, oxidized, forms could well be important in maintaining oxidizing conditions for Au dissolution. To date, iodine has been determined as “free iodide” (probably uncomplexed and weakly complexed forms of I^- ; Figure A1.21) and/or as total iodine (*i.e.* all forms; Figure A1.22). Though total iodine is 4 - 10 times more abundant than free iodide, the latter still has significant concentrations, indeed much greater than for sea water. The source of this iodine is not certain though a number of investigations (Andrews *et al.*, 1984; Chitayeva *et al.*, 1971; Fuge and Johnson, 1984, 1986; Fuge *et al.*, 1986, 1988; Xuejing *et al.*, 1981) have demonstrated that I may behave as a chalcophile element, with major enrichments associated with sulfide zones.

6.6 Northern groundwaters

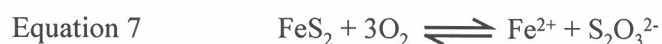
As implied in the previous Sections, the Northern groundwaters have low concentrations of most elements, with a few exceptions:

- (i) P (Figure A1.19) and V (Figure A1.27) concentrations are higher than for other groundwaters, probably due to the low concentration of metals causing precipitation of these elements, particularly Ca (which precipitates P as apatite; Figure A2.33), Fe (which precipitates P as strengite; Figure A2.34; and V as Fe vanadate) and Pb (which precipitates V as chervitite; Figure A2.20);
- (ii) Si concentrations match those at the other regions (Figure A1.24);
- (iii) Sc concentrations are only slightly lower on average than the other regions (Figure A1.25);
- (iv) Cr concentrations can be high in the Northern region (Figure A1.28), with a similar amount of enhancement in ultramafic groundwaters to elsewhere in the Yilgarn;
- (v) though dissolved concentrations of the oxy-anions are lower in the Northern region than in the Central area, several, namely As, Mo, Sb and W (Figures A1.37, A1.40, A1.44 and A1.47) still have significant concentrations in the Northern groundwaters;
- (vi) Rb concentrations are much higher than expected, on the basis of the sea water Rb/TDS (Figure A1.9) and/or Rb/K (Figure A1.15) ratios. This is consistent with the observed potential of Rb as a pathfinder element for Au in non-saline environments (Section 8.5).

7. GOLD HYDROGEOCHEMISTRY

7.1 Thiosulfate dissolution

During initial sulfide weathering (Section 0) in neutral to alkaline conditions, significant concentrations of the intermediate sulfur compounds thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}) are commonly produced (Granger and Warren, 1969; Goldhaber, 1983; Mann and Webster, 1990):



In such conditions, Au will dissolve as the thiosulfate complex $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$. Given the conditions required for thiosulfate generation, and its instability towards oxidation, particularly in acid

conditions, it is expected that Au thiosulfate will only be important for the groundwater mobility of Au at the weathering interface. A number of groundwaters sampled from rock or saprock within mineralized zone have anomalous Au (1 - 41 µg/L). However, this has only been observed in drill holes from within pits, indicating that the drill hole has to very closely intersect mineralization in order to give high dissolved Au concentrations. Indeed, it is possible that these high dissolved Au concentrations may be partially or wholly an artifact, due to destabilization of the rock by exposure to air after excavation of the pit, with release of unnaturally high concentrations of thiosulfate. Whatever the cause for the high dissolved Au concentrations in these conditions, sampling of groundwaters near to anomalous areas of this type, at Mt Gibson (Gray, 1991) and Lawlers (Gray, 1994), indicate little groundwater Au dispersion, suggesting that sampling deep groundwaters for Au is a poor exploration method.

7.2 Halide (iodide and chloride) dissolution

In shallow groundwaters, particularly in the Kalgoorlie region, the high acidity will destabilize thiosulfate. However, saline/acidic/oxidizing (Figure 2) groundwaters may be highly effective in dissolving Au as the chloride or iodide complex. The hatched area in Figure 2 is the zone for which up to 2 µg/L (ppb) Au will be dissolved as AuCl₂⁻ in a 1 M Cl solution (about twice sea water). This is approximately the mean salinity for Kalgoorlie groundwaters and the upper range for Central groundwaters. A significant proportion of the Kalgoorlie groundwaters are within the Eh range required. However, thermodynamic calculations suggest that AuCl₂⁻ may not be the most significant complex, even in these highly saline conditions. Based on free iodide and total iodine determinations of (Table 2; Section 6.5), available iodide (free plus loosely complexed iodide) could be reasonably expected to commonly be greater than 10⁻⁵ M (1.3 ppm). As Au binds very strongly to iodide, this concentration of available iodide will considerably extend the theoretical range for the dissolution of at least 2 µg/L Au (from 690 to 600 mV; Figure 2). If a lesser dissolved Au concentration of 0.2 µg/L, which more closely matches the anomalous groundwaters in the Central region, is used, the required Eh for Au dissolution is lowered further to about 550 mV, which includes many of the Kalgoorlie groundwaters.

The possibility of Au iodide dissolution is also important because sorption studies (Gray, 1990b, unpublished data) indicate Au iodide is absorbed much less by most regolith and soil materials, even in neutral conditions. This would imply a high mobility, including the possibility of Au diffusing upwards into the overlying soil, and therefore forming soil anomalies correlating with mineralization.

As expected, there is a weak correlation between dissolved Au concentrations and Eh (Figure 8). However, it is clear that virtually none of the Central groundwaters have Eh values high enough to explain the observed concentrations of dissolved Au. One possibility is that surface- or micro-processes generate transient highly oxidizing conditions that can dissolve Au. Once dissolved, the Au-halide complex is meta-stable, and may be only slowly removed from solution, except in Fe-rich solutions:



A number of acid groundwater sites (Butt *et al.*, 1993) show a strong antipathetic relationship between dissolved Au and Fe, supporting the hypothesis that dissolved Fe is important in precipitating Au from halide complexes (Equation 8). Such a mechanism will have major implications for the control of supergene depletion and enrichment zones, and for the interpretation of drilling data.

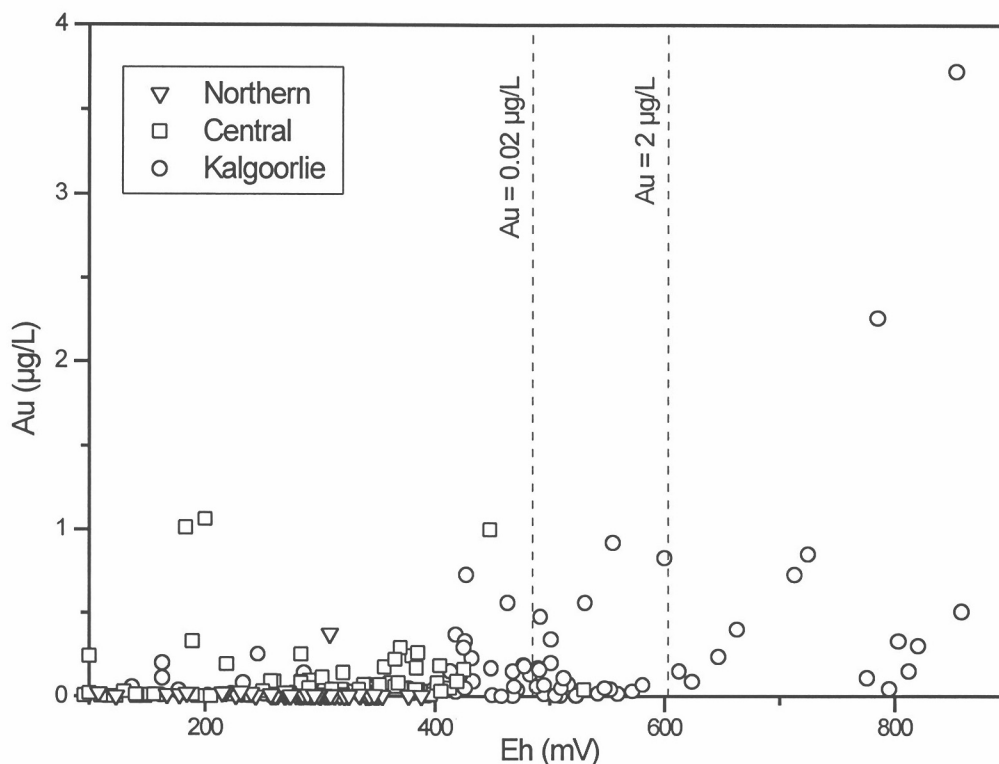


Figure 8: Dissolved Au vs. Eh for the Western Australian sites

7.3 Regional differences in Au hydrogeochemistry and implications for supergene mobilization

The importance of halides for the dissolution of Au is illustrated by the low dissolved Au concentrations in the Northern region (Figure 9), which have groundwaters with low Cl, I and Eh. Over 80% of the Northern groundwaters have dissolved Au concentrations $\leq 0.01 \mu\text{g/L}$, which is well into background for the other regions. The few Au groundwaters in the Northern region are from within pits and appear to represent localized thiosulfate dissolution (Section 7.1). The Kalgoorlie region has the highest mean dissolved Au content, consistent with the observed optimal conditions for dissolution (Section 7.2), with the Central region showing moderate levels of dissolved Au. This has major implications for the interpretation of dissolved Au data for exploration, as discussed further in Section 8.5.

It appears that present-day conditions at Lawlers and Baxter are not conducive to the supergene mobilization of Au. It is not known whether these present conditions are representative of groundwater chemistry in (or in part of) the Northern region for the arid period(s) during which supergene Au occurred to the south. Clearly, determination of the past groundwater conditions would be useful in terms of dating supergene haloes. Gold mobilization occurred during lateritization, so laterite (where present) is still an effective sample medium; drilling for supergene haloes would only be effective, if past conditions have been more conducive to Au halide dissolution.

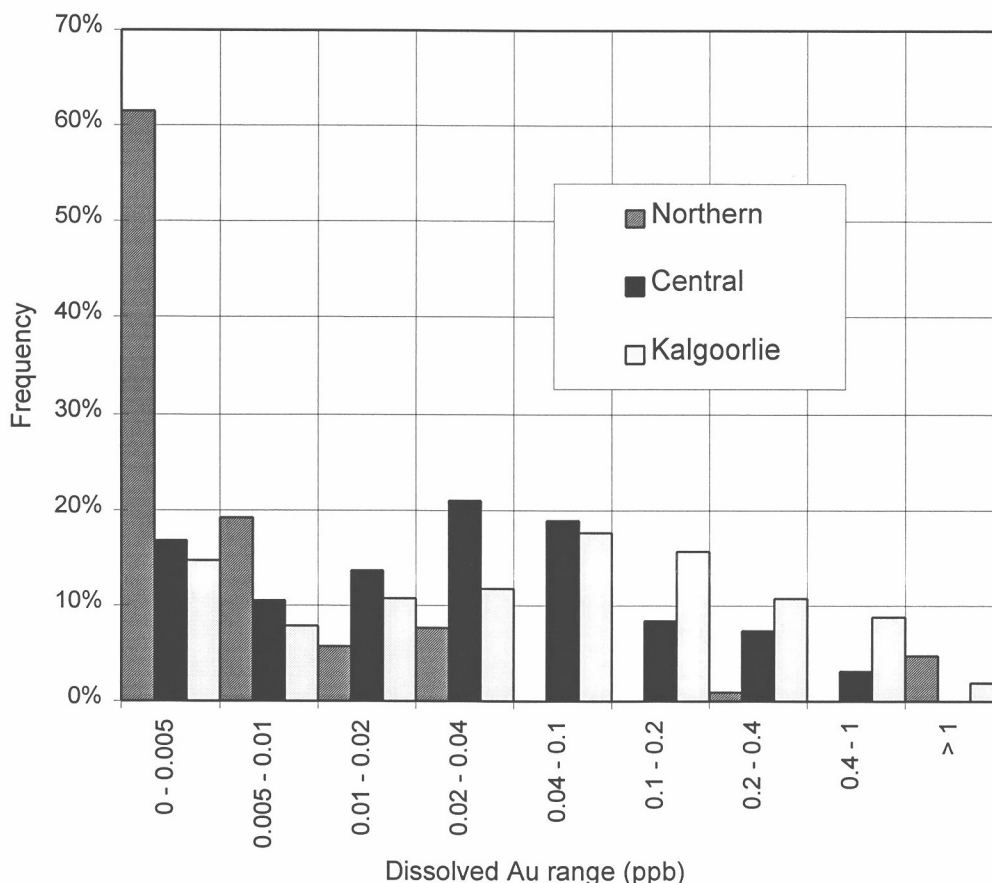


Figure 9: Distribution of dissolved Au concentrations for the Northern, Central and Kalgoorlie groundwater regions

In contrast, extensive supergene mobilization of Au is expected to have occurred and be occurring in the Central and Kalgoorlie regions. Oxidizing conditions in the upper parts of the groundwater will lead to extensive dissolution of Au, which will diffuse through the water mass. Where dissolved Au-halide contacts dissolved Fe, possibly derived from saprolite and saprock weathering, Au will be reduced (Equation 8), resulting in characteristic horizontal and sub-horizontal supergene anomalies. The lower dissolved Au in Central groundwaters, which is postulated to be due to the less acidic groundwater conditions, suggests this process may take longer for this area, though extensive redistribution would still be expected over the long period of surface weathering. In addition, the observation of Br depletion in some Central groundwaters suggests that past conditions may have been more oxidizing (Section 5) and Au solubility even higher.

As implied in these discussions, further prediction of the form and extent of supergene Au mobilization is dependent on enhanced understanding of both the processes of Au halide dissolution and precipitation, and on the ability to predict past groundwater conditions. The latter may never be completely feasible, though hydrogeochemical (*e.g.*, Br depletion) or regolith (*e.g.*, secondary alunite) parameters may give useful clues as to past conditions.

8. IMPLICATIONS FOR EXPLORATION

8.1 Possible applications

Hydrogeochemistry may be of value to exploration because:

1. geochemical anomalies may be broader in groundwater than in the regolith;
2. groundwater compositions are partly controlled by basement geology and, hence, may indicate lithologies not intersected or identified by drilling;
3. areas of high reactivity (*e.g.*, faults and shear zones) may have distinct hydrogeochemical signatures even where they are unremarkable in terms of elemental abundances, and where drilling makes petrographic study difficult;
4. hydrogeochemical studies may yield further information on the processes of weathering, which may enhance understanding of saprolite geochemistry.

Possible applications for hydrogeochemistry are discussed below.

8.2 Lithological discrimination

One example of the potential use of hydrogeochemistry in lithological discrimination is illustrated in Figure 10. By comparing the sample location with the known geology, groundwaters at Panglo (Gray, 1990a) have been characterized into those in contact with shales, with mafic and with ultramafic lithologies. These different groundwater groups are clearly delineated by plotting each water, using an ultramafic ($\text{Ni}+2\text{Cr}$) vs. a mafic ($\text{Mn}+13\text{Co}+9\text{Zn}+36\text{Cu}$) index. This discrimination is effective even for waters in contact with highly weathered rocks. Hydrogeochemistry may also indicate shear zones; two samples at the top right of the plot appear to be from shear zones which, at Panglo and elsewhere, are rich in dissolved base metals.

This procedure will presumably be most effective for a consistent sample medium (in terms of acidity and, possibly, salinity), and different sites may well have to be treated separately. The concentrations of base metals in acidic, shallow Kalgoorlie groundwaters will be significantly higher than those in Central, Northern or deeper Kalgoorlie groundwaters. However, dissolved Cr contents can be used to recognise ultramafic rocks across all regions. Groundwaters contacting ultramafic rocks contain consistently high (0.01 - 0.43 mg/L) dissolved Cr concentrations, whereas other waters have Cr concentrations below detection. Though further studies are required to fully understand this phenomenon (Section 6), the effect is highly robust and offers a straight-forward method for delineating ultramafic occurrences. There may well be further scope for characterization of other rocks in particular groundwater types - and hence offer useful methods for identifying extremely weathered rocks without the requirement for expensive deep drilling.

8.3 Influence of fault zones

Fault zones might well be expected to influence groundwaters characteristics. Weathering is generally deeper along faults and shears, which may have distinct chemistries and are commonly zones of enhanced water flow. At the Wollubar channel (Gray, 1993b), groundwater close to Boulder-Lefroy shear has a much higher Al concentration than expected at that particular pH (the high Al sample at pH 4.9 in Figure A1.23), reflected in this sample having the highest degree of oversaturation with respect to jurbanite (Figure A2.12). In addition, the groundwater has raised concentrations of Si, Fe and Sc, Y, REE, Pb and U. These high concentrations may well reflect the influence of highly active weathering in the shear zone on the chemistry of the groundwater in the palaeochannel. Similarly, at Panglo, strong base metal enrichment of groundwaters (Figure 10; Section 8.2) may reflect the proximity of a fault zone.

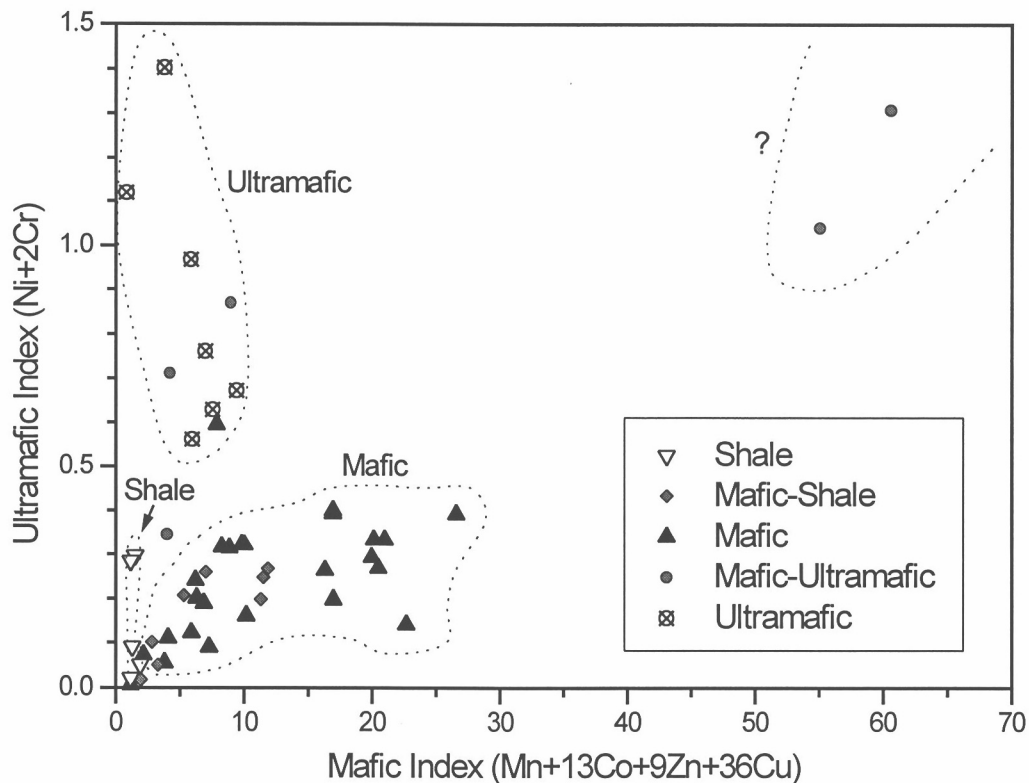


Figure 10: Mafic vs. ultramafic indices for groundwaters at Panglo.

8.4 Presence of sulfides

Groundwaters in contact with sulfide-rich rocks buffered by alkaline minerals (*e.g.*, carbonates) may be neutral to alkaline at depth, and acid as they become oxidizing closer to the water-table, particularly in the Kalgoorlie region. The deep, neutral waters close to sulfides are characterized by:

1. near neutral pH and relatively low Eh;
2. enrichments in Fe, SO₄ (possibly from sulfides), HCO₃, Mg and, to a lesser extent, Ca and Sr (possibly from carbonates). This element association probably reflects oxidation of sulfides at depth, with neutral pH conditions being maintained by carbonate buffering;
3. enrichment in several anionic chalcophile pathfinder elements, including As, Mo, Ag, Sb, I, Hg and Tl.

The acid/oxidized waters may well lose most of these signatures, because most of the anionic chalcophile elements are precipitated in acid conditions (with the possible exception of Mo; Section 6.4), Fe is precipitated, HCO₃ removed, and SO₄, Mg, Ca and Sr enrichments may be obscured in saline groundwaters. Thus, with the major exception of dissolved Au, few elements give useful Au exploration data in acid groundwaters.

8.5 Presence of Au mineralization

The clearest indication of Au mineralization in Kalgoorlie and Central groundwaters is given by dissolved Au. It is not clear whether other elements, such as As or Sb, specifically indicate Au mineralization or merely the presence of sulfides. Interpretation of dissolved Au concentrations is complicated by two mechanisms for transport of Au in groundwater (thiosulfate and halide complexing, Section 7), with a third mechanism (organic complexation) specific to soils. Where Au appears to be dissolving in thiosulfate form, as at Boags and the Hornet pit at Mt. Gibson, the

distribution of dissolved Au closely matches that of mineralization, but this effect is highly localized and is expected to be commonly missed.

In oxidizing environments, Au dissolves to form chloride or iodide complexes (Section 7.2) and where this mechanism is expected to be active, high concentrations of dissolved Au are observed. However, Au concentration is strongly affected by factors not directly related to mineralization (Eh and dissolved Fe; Section 7.2), and the distribution of dissolved Au only approximately matches that of primary mineralization. However, this technique would still provide useful extra exploration information. A few other elements, such as As, Sb, Mo, I and various base metals may also have value as pathfinders, though they commonly have reduced concentrations in acid conditions (Section 6) and analyses for these elements in saline groundwaters may be difficult, expensive or of poor sensitivity. For the Kalgoorlie region, a limited suite of parameters, namely salinity, pH, Eh, dissolved Au, Fe, Cr, and possibly other base metals, could be analysed cheaply (using standard probes, sorption onto carbon for Au, and ICP-AES and/or colorimetric analyses for Fe and Cr) but extending this to the other elements of interest will add considerably to cost, with little added exploration benefit. A threshold dissolved Au concentration of approximately 0.05 $\mu\text{g/L}$ would appear to locate most mineralized areas. For the Central areas, a slightly lower dissolved Au threshold (0.02 $\mu\text{g/L}$) appears appropriate (Figure 11), and a number of chalcophile elements (*e.g.*, As, Sb, Mo, W, Tl, Bi) may also give valuable exploration data. However, further work is required to study the relative degrees of groundwater dispersion of these elements.

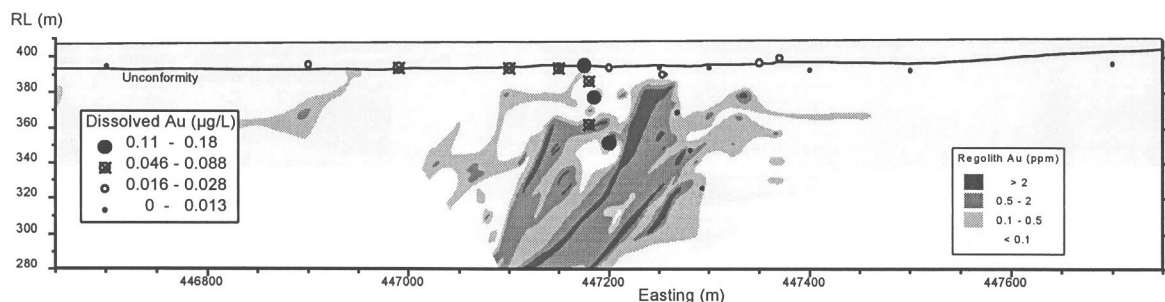


Figure 11: Dissolved Au distribution at Golden Delicious, superimposed on regolith Au contours (from Bristow *et al.*, 1996).

In the Northern region, dissolved Au contents are much lower, though higher values may still correlate with mineralization. However, even though Au and indicator elements will occur at low concentrations, the low salinity means that multi-element ICP-MS analyses are both cheap and highly sensitive. At Baxter (Gray, 1995), a number of indicator elements either correlated closely with the position of buried mineralization (Rb, Sc, Mo, W) or were useful for lithological discrimination (Cr, Ni, As). In addition, the low variation in salinity, Eh and pH with depth indicates that sample depth is less critical than at other sites.

Groundwaters appear to have a limited ability to “see through” barren transported overburden, as opposed to its success when sampling groundwater even from supposedly depleted *in situ* material (*e.g.*, Panglo; Gray, 1990a). It appears to be most useful in the highly active Kalgoorlie groundwaters, with those sampled from the Wollubar palaeochannel appearing to show significant influences from underlying rocks (Gray, 1993b), and poor for the least active groundwaters in the Northern region (*e.g.*, Lawlers; Gray, 1994). However, the degree of interference from the overburden will depend on the element used, with chemically conservative species, such as SO_4 , appearing to give good signals even in overburden (*e.g.*, Figure 5), and more active elements, such as

Mo or Au giving poor signals in groundwaters from barren overburden. It is recommended that, if possible, groundwaters be sampled below the transported overburden for optimum results.

Use of groundwater for exploration in Kalgoorlie and Central regions is best restricted to shallow samples, with depth being less critical in the Northern region. Waters should be contacting or within a few metres of *in situ* material. Particularly in the Kalgoorlie region, it may well be more cost-effective to restrict analyses of the saline waters to a select group of parameters, which should at least include salinity, pH, Eh, Au, Fe and Cr. A more expanded analytical suite, including As, Sb, Mo, W, Bi and Tl, may well be useful, though at significant cost, for Central groundwaters. In comparison, for the Northern groundwaters multi-element analyses will be much cheaper and have been shown to be effective.

ACKNOWLEDGEMENTS

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APPENDICES

Appendix 1: Element/Ion Concentration Plots

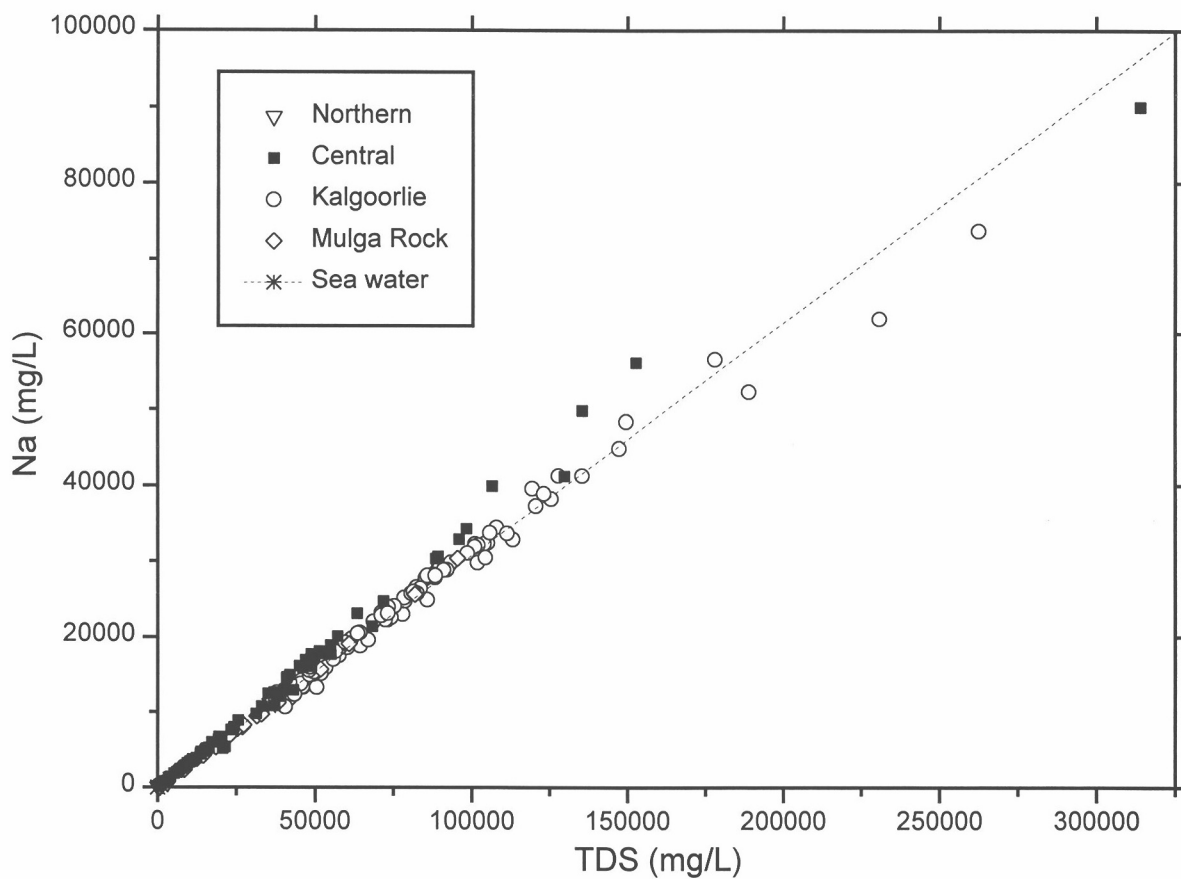


Figure A1.1: Na vs. TDS for Western Australian groundwaters.

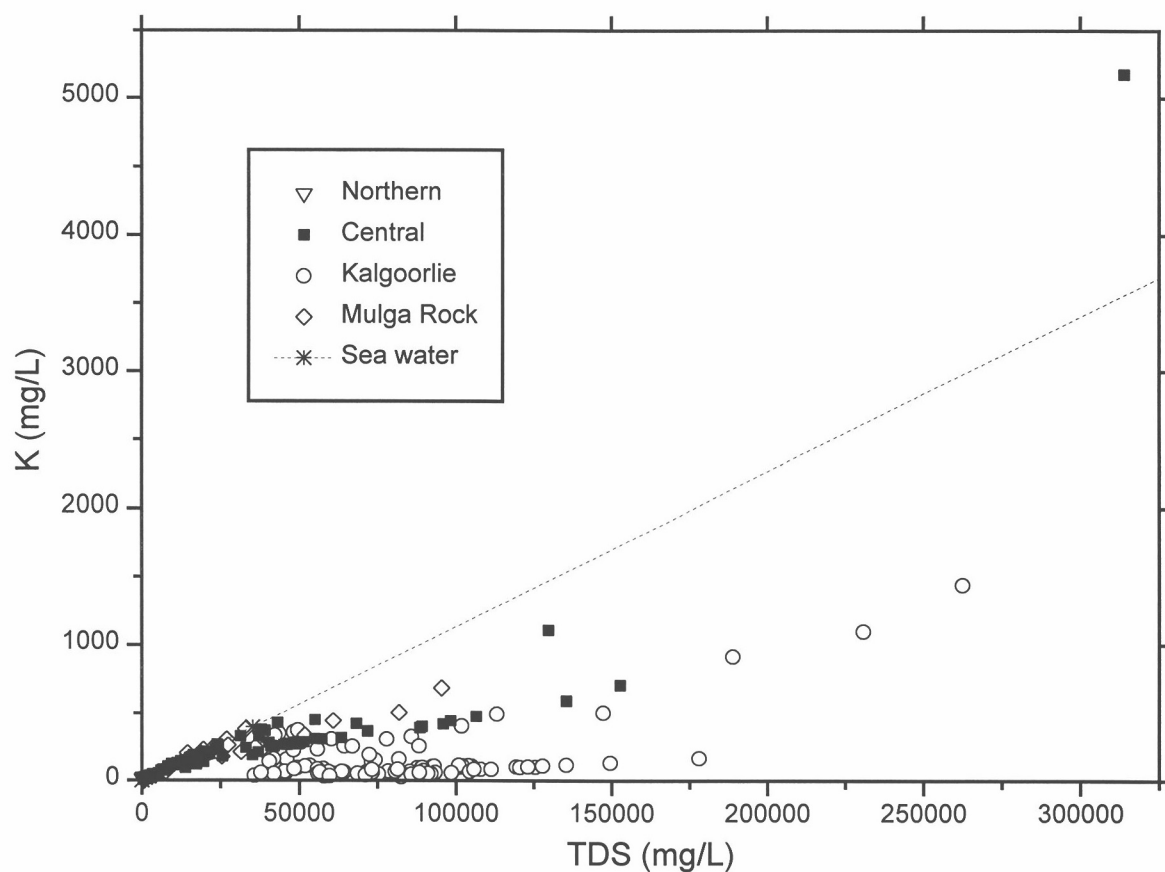


Figure A1.2: K vs. TDS for Western Australian groundwaters.

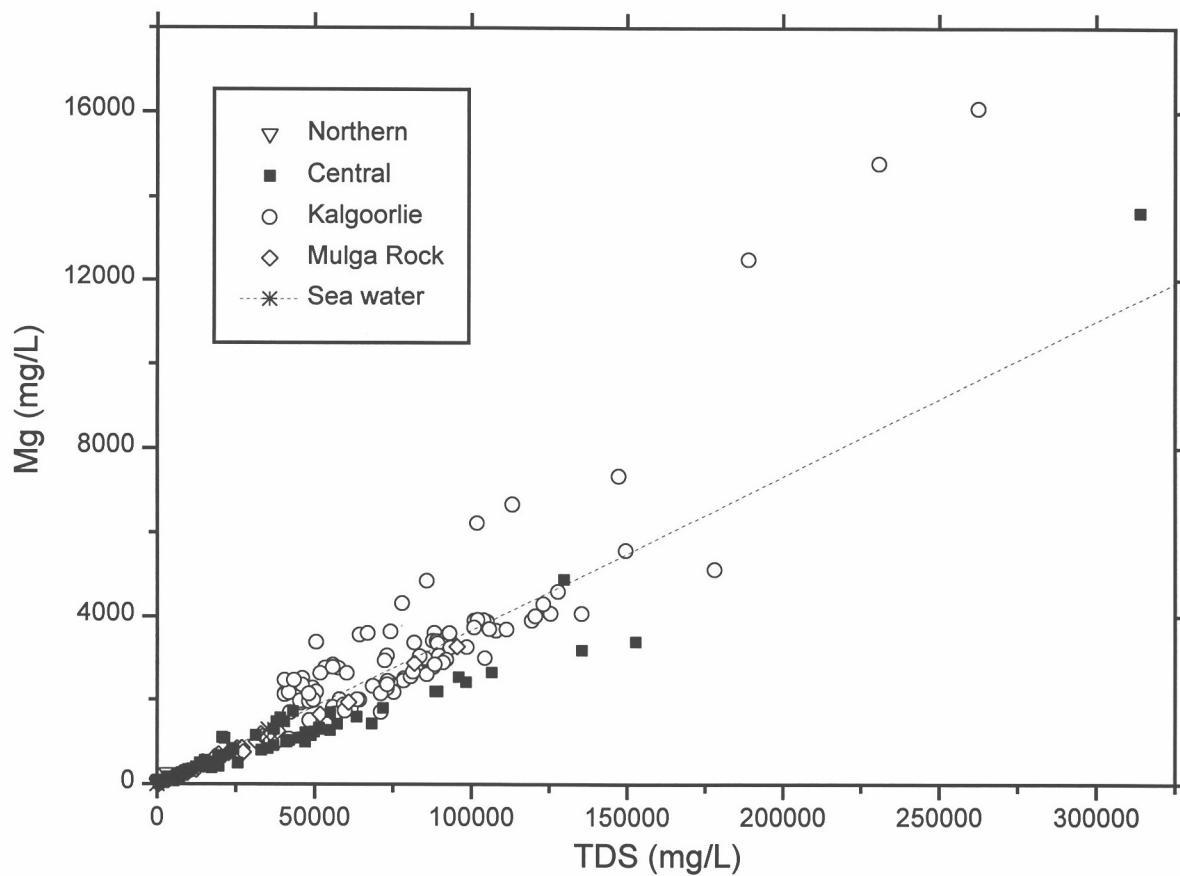


Figure A1.3: Mg vs. TDS for Western Australian groundwaters.

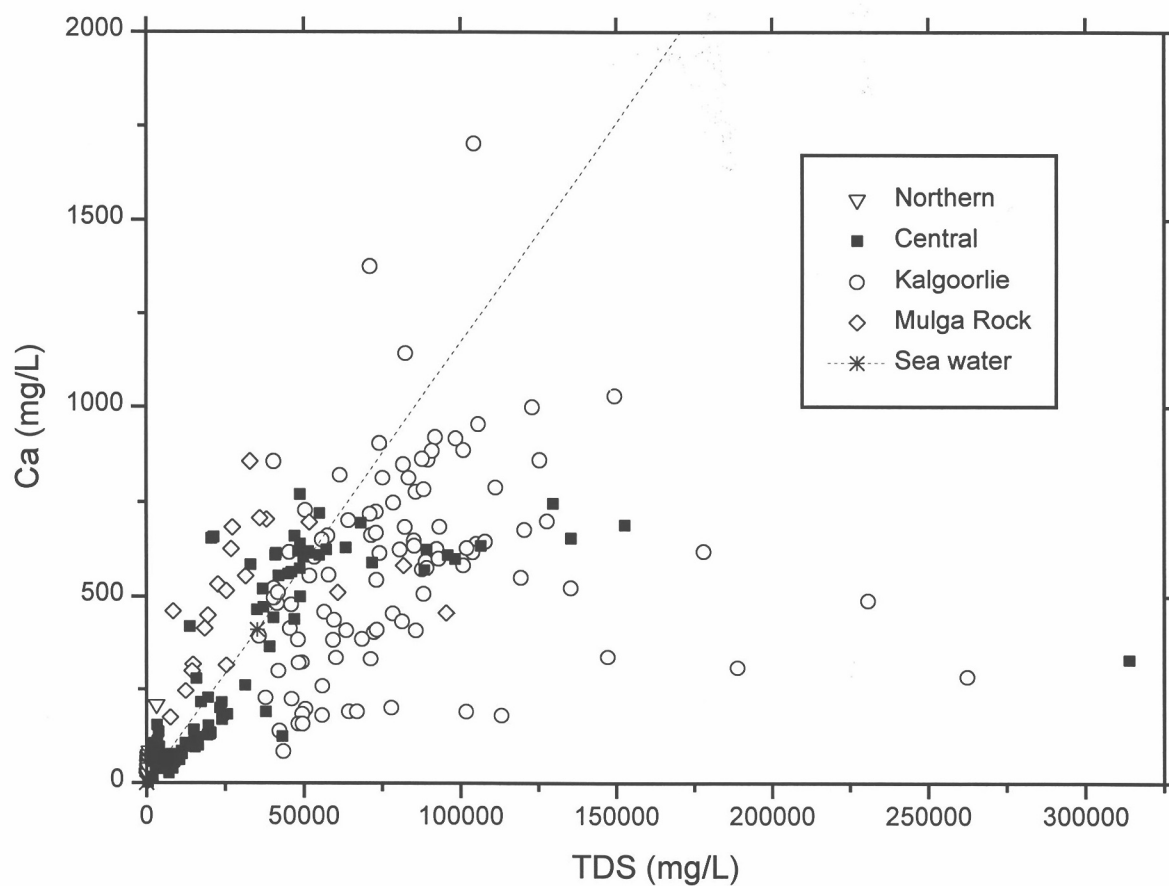


Figure A1.4: Ca vs. TDS for Western Australian groundwaters.

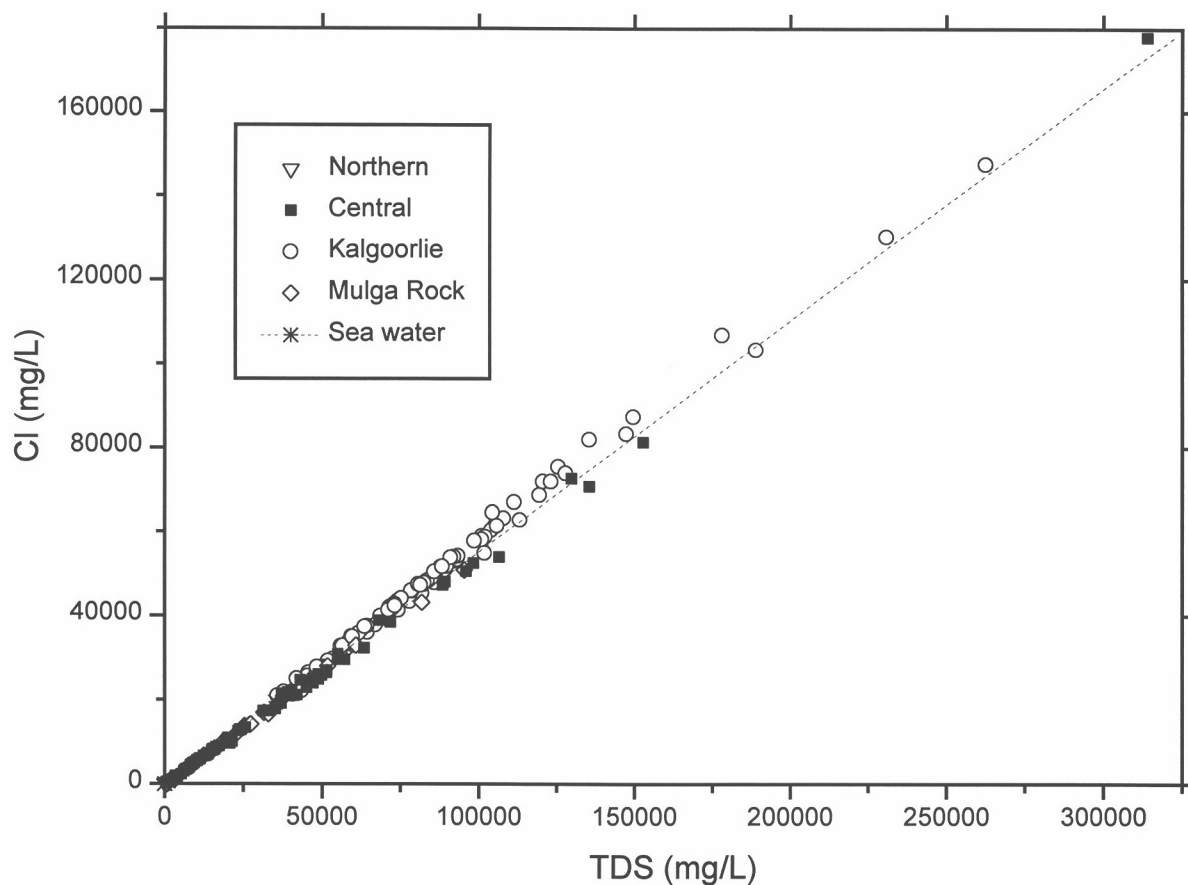


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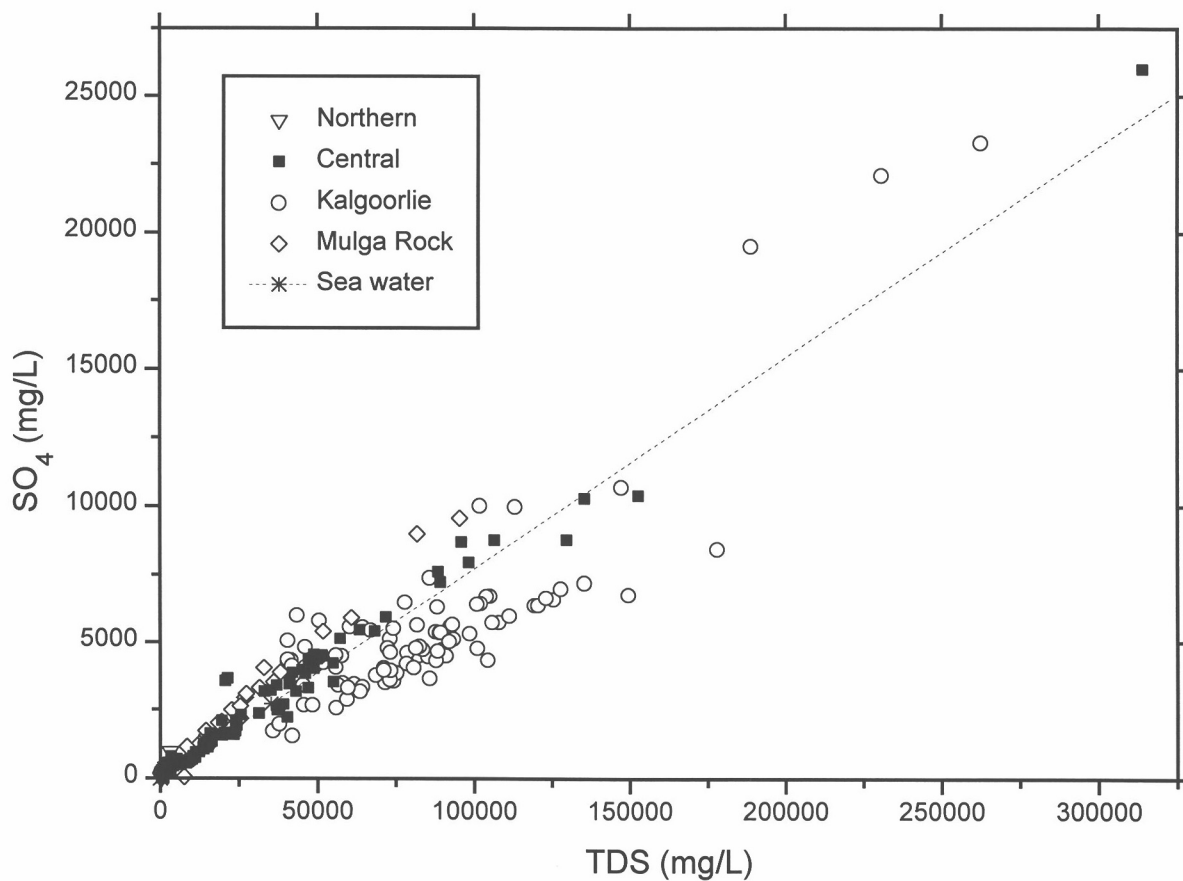


Figure A1.6 SO_4 vs. TDS for Western Australian groundwaters.

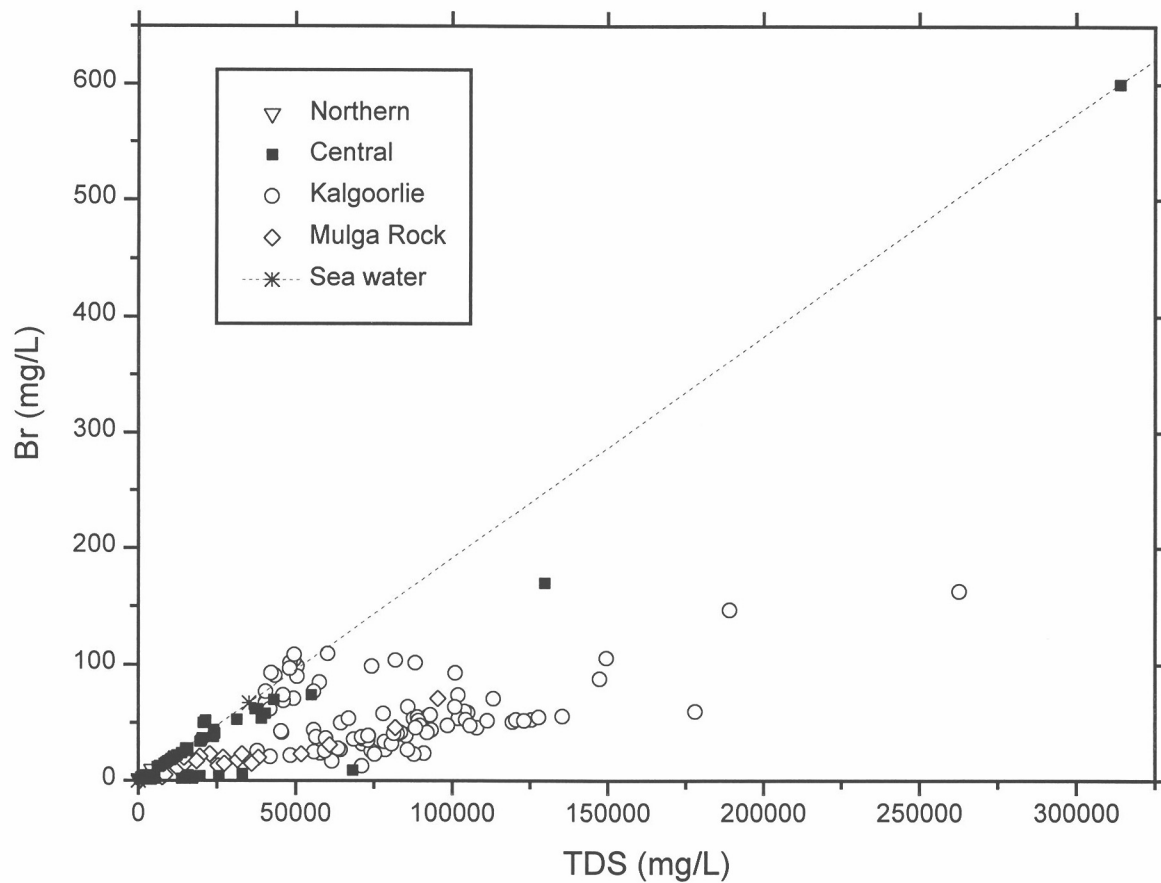


Figure A1.7: Br vs. TDS for Western Australian groundwaters.

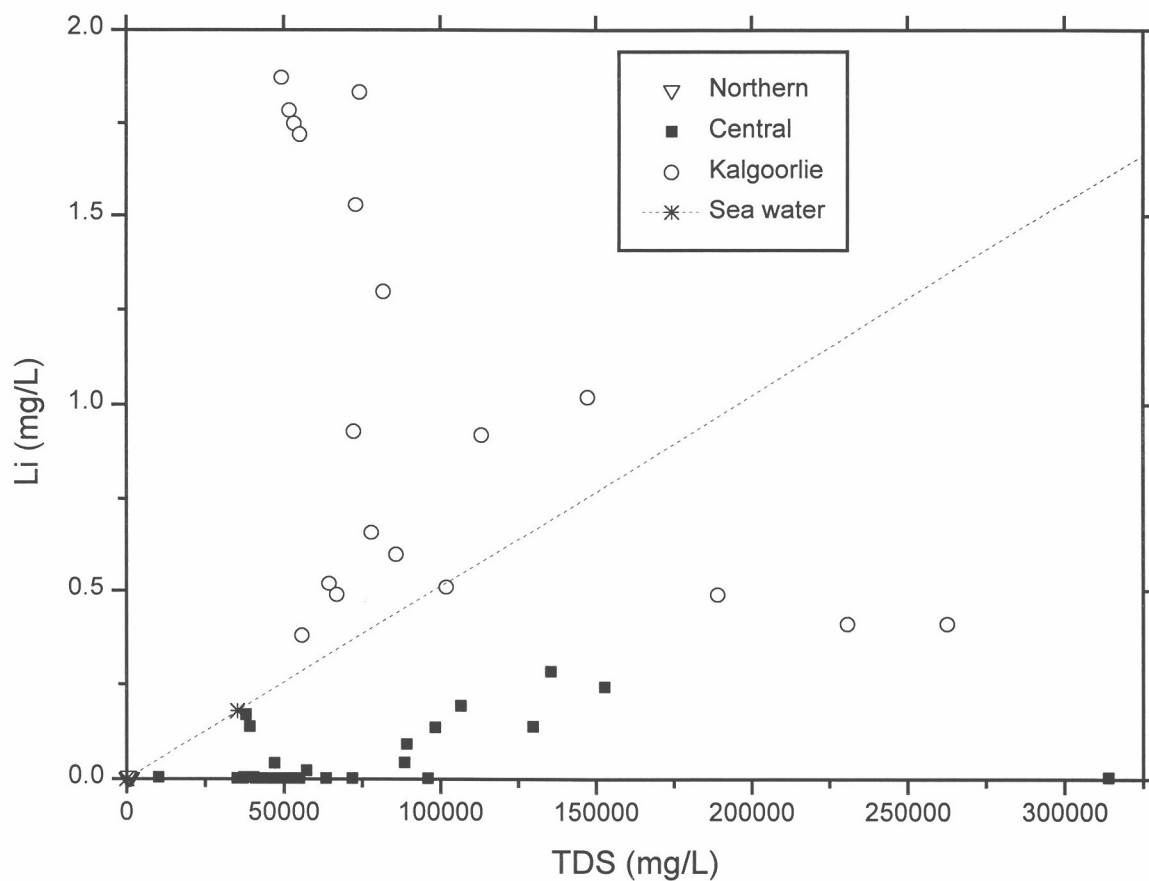


Figure A1.8: Li vs. TDS for Western Australian groundwaters.

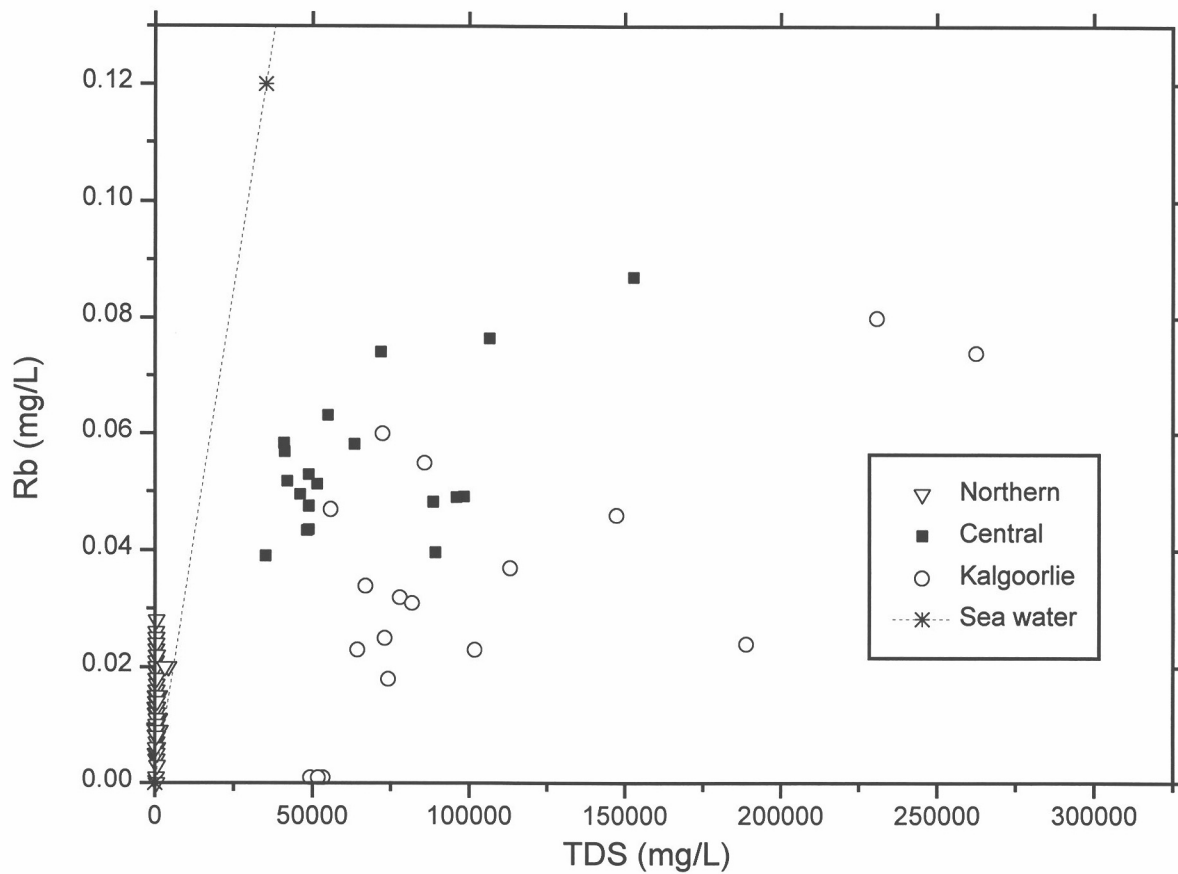


Figure A1.9: Rb vs. TDS for Western Australian groundwaters.

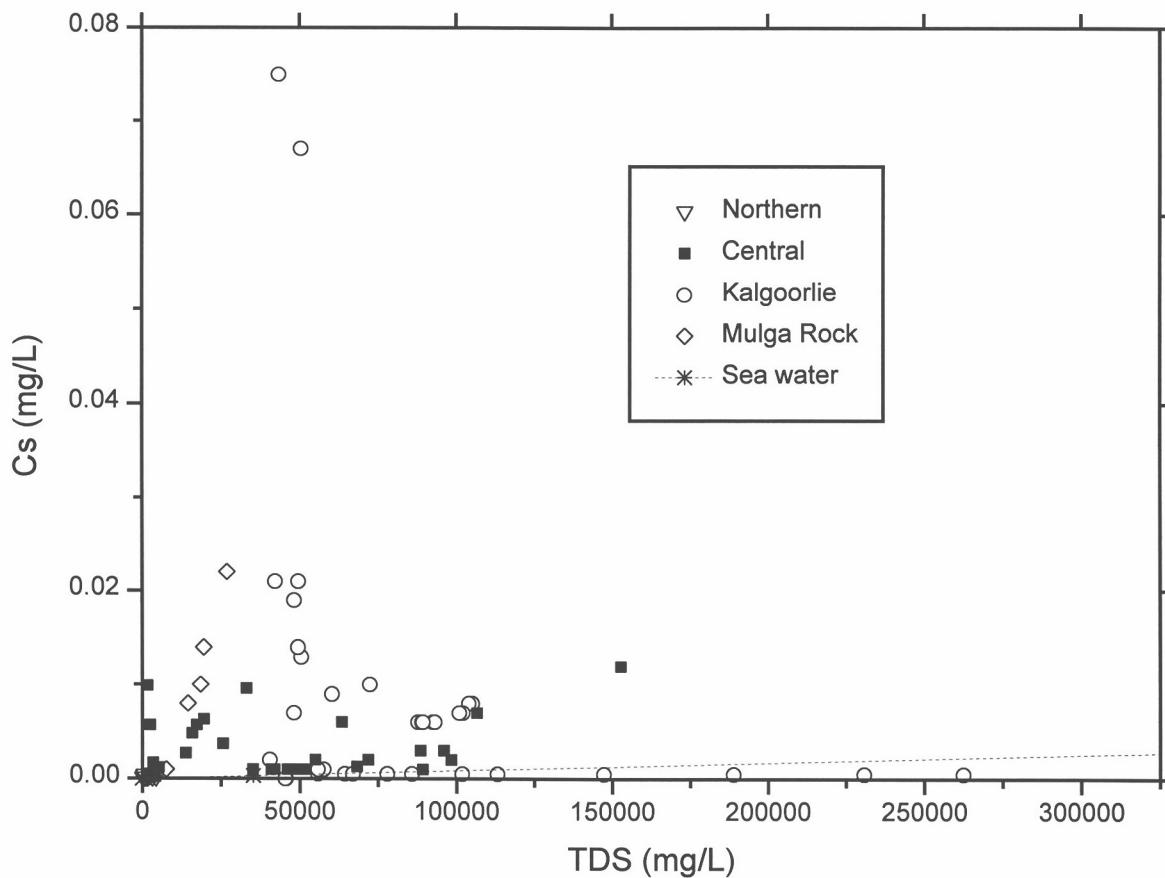


Figure A1.10: Cs vs. TDS for Western Australian groundwaters.

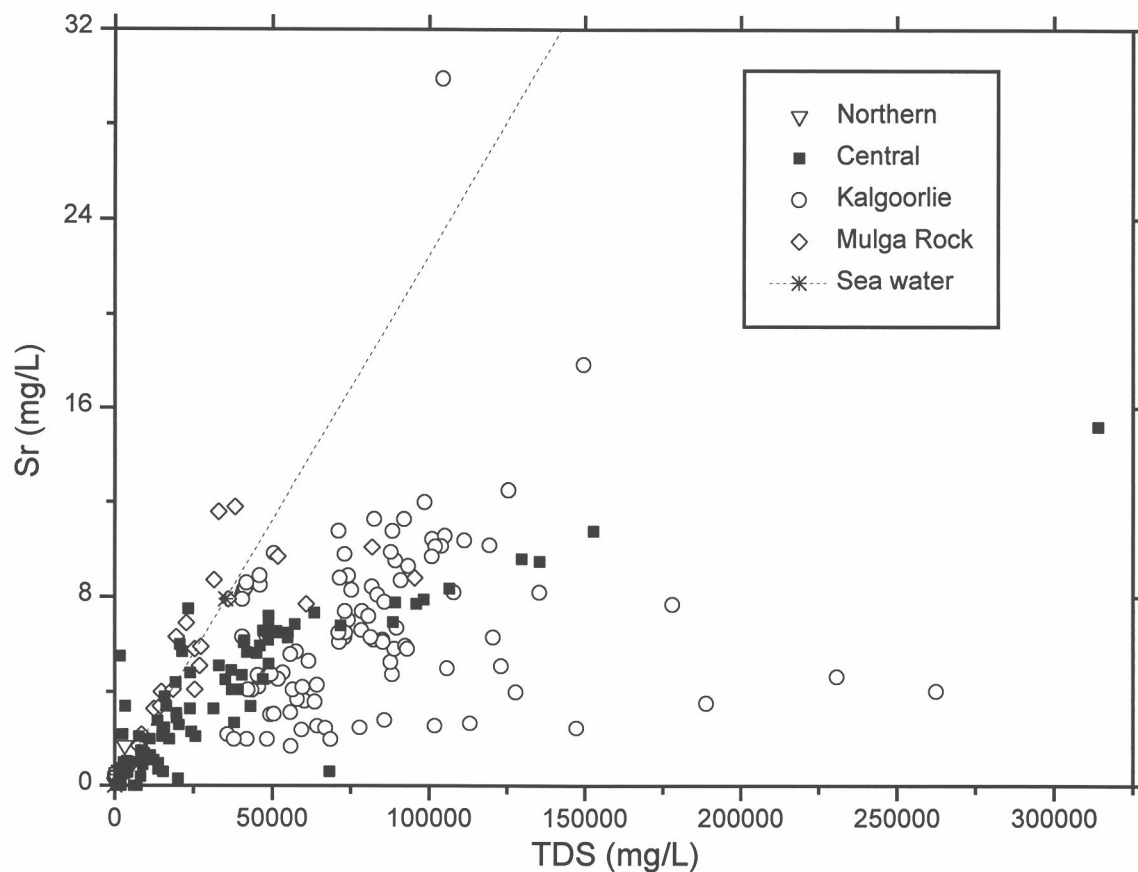


Figure A1.11: Sr vs. TDS for Western Australian groundwaters.

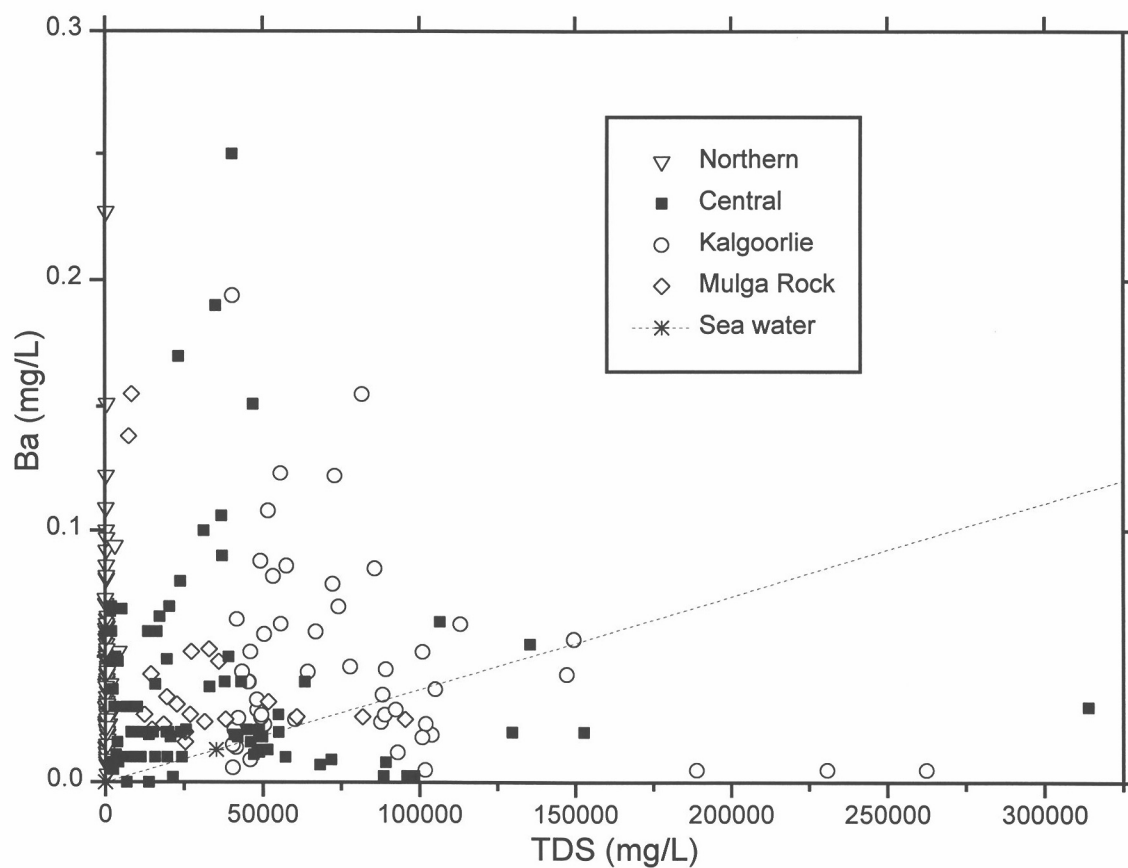


Figure A1.12: Ba vs. TDS for Western Australian groundwaters.

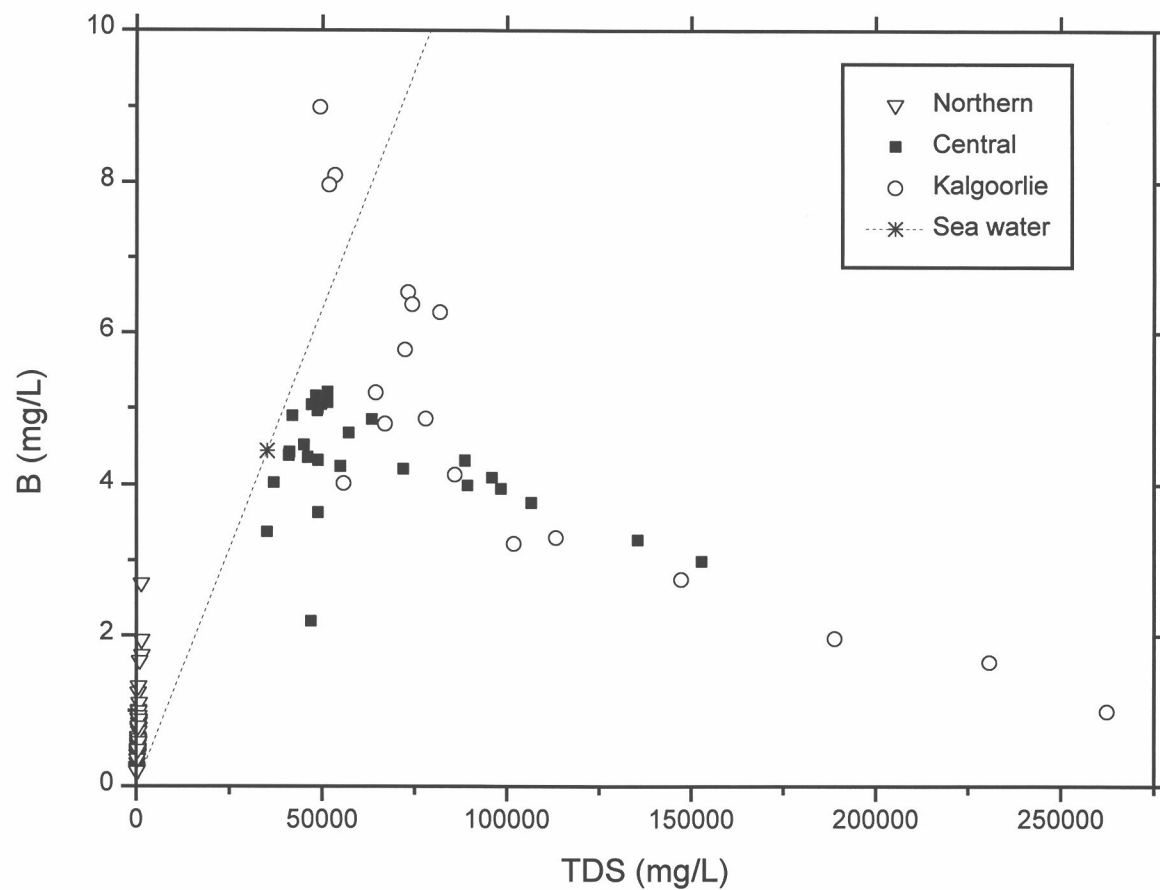


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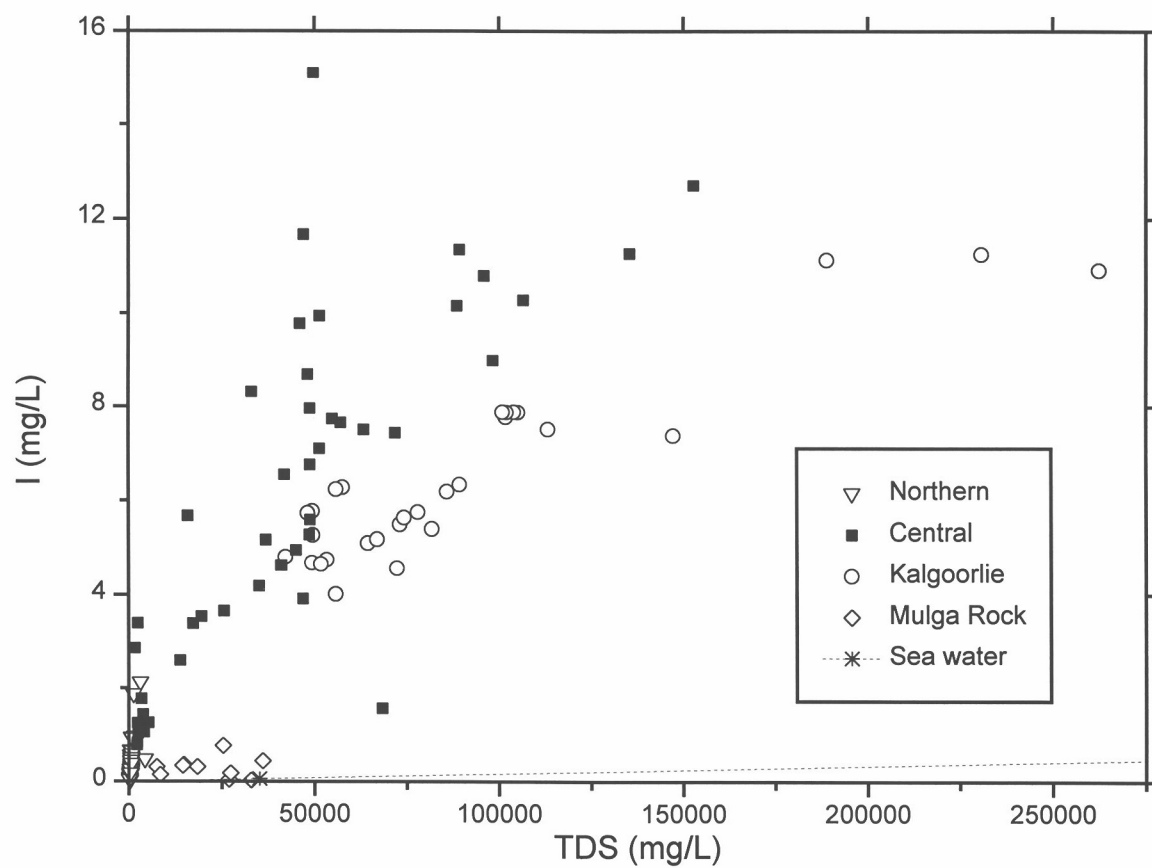


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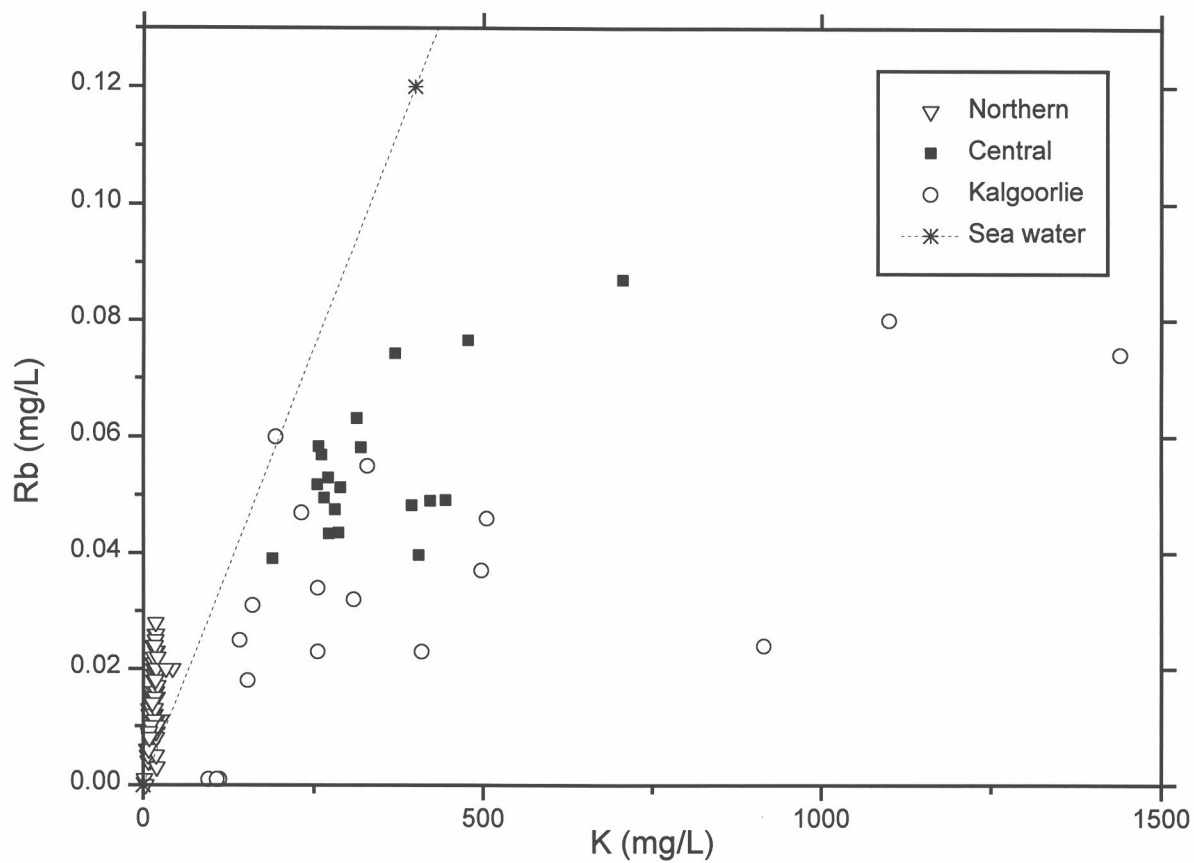


Figure A1.15: Rb vs. K for Western Australian groundwaters.

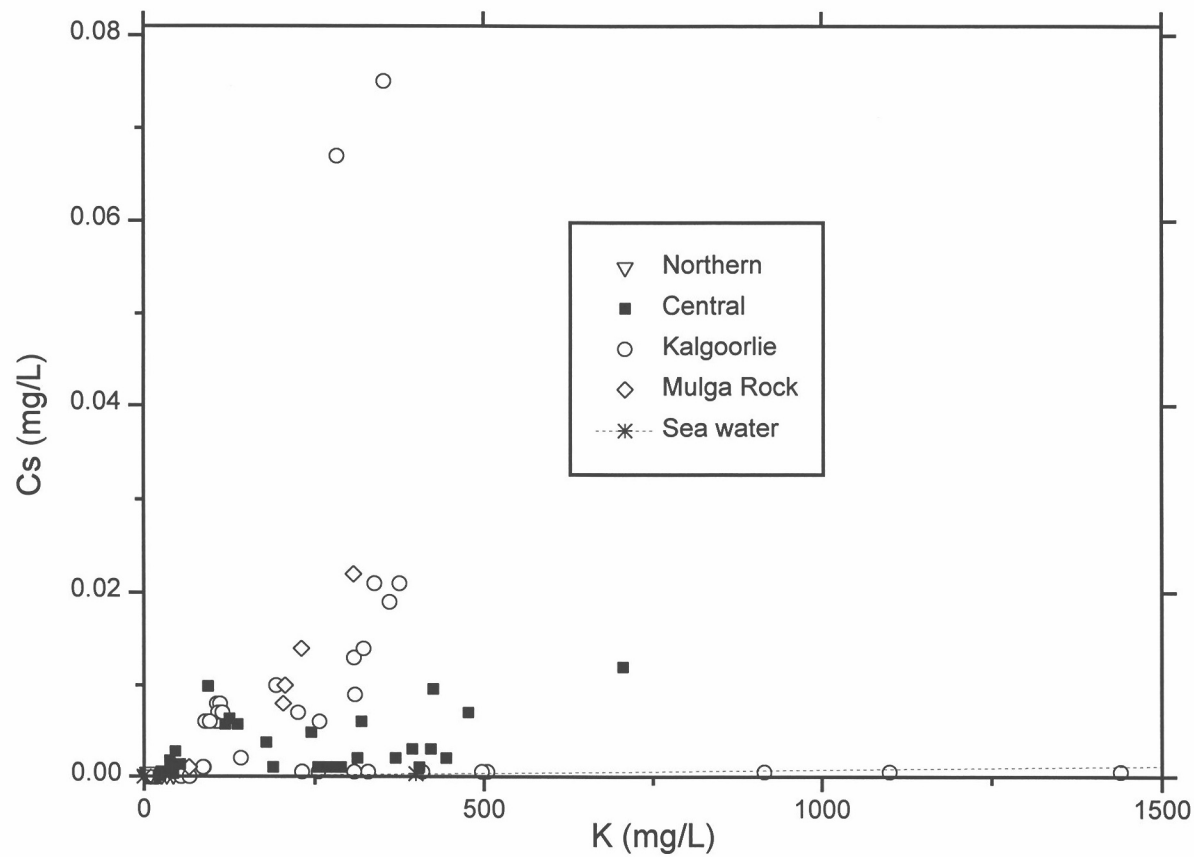


Figure A1.16: Cs vs. K for Western Australian groundwaters.

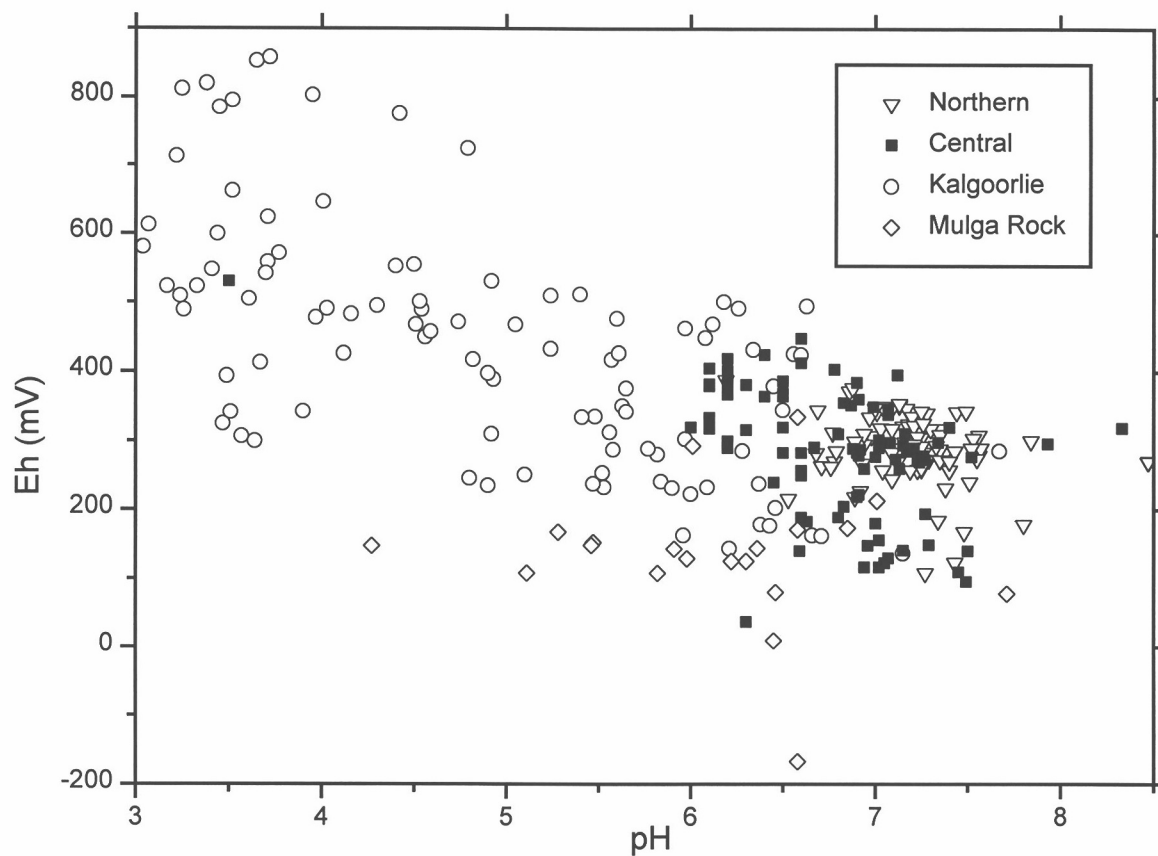


Figure A1.17: Eh vs. pH for Western Australian groundwaters.

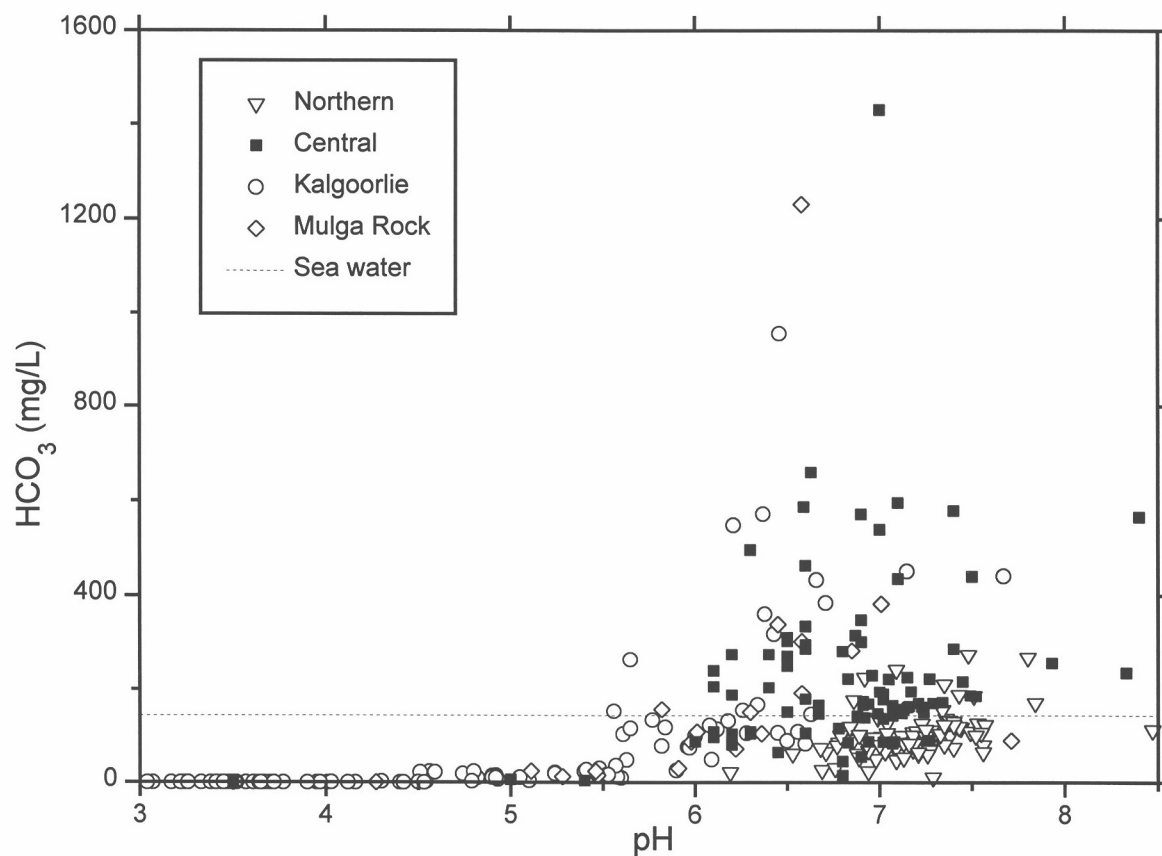


Figure A1.18: HCO_3^- vs. pH for Western Australian groundwaters.

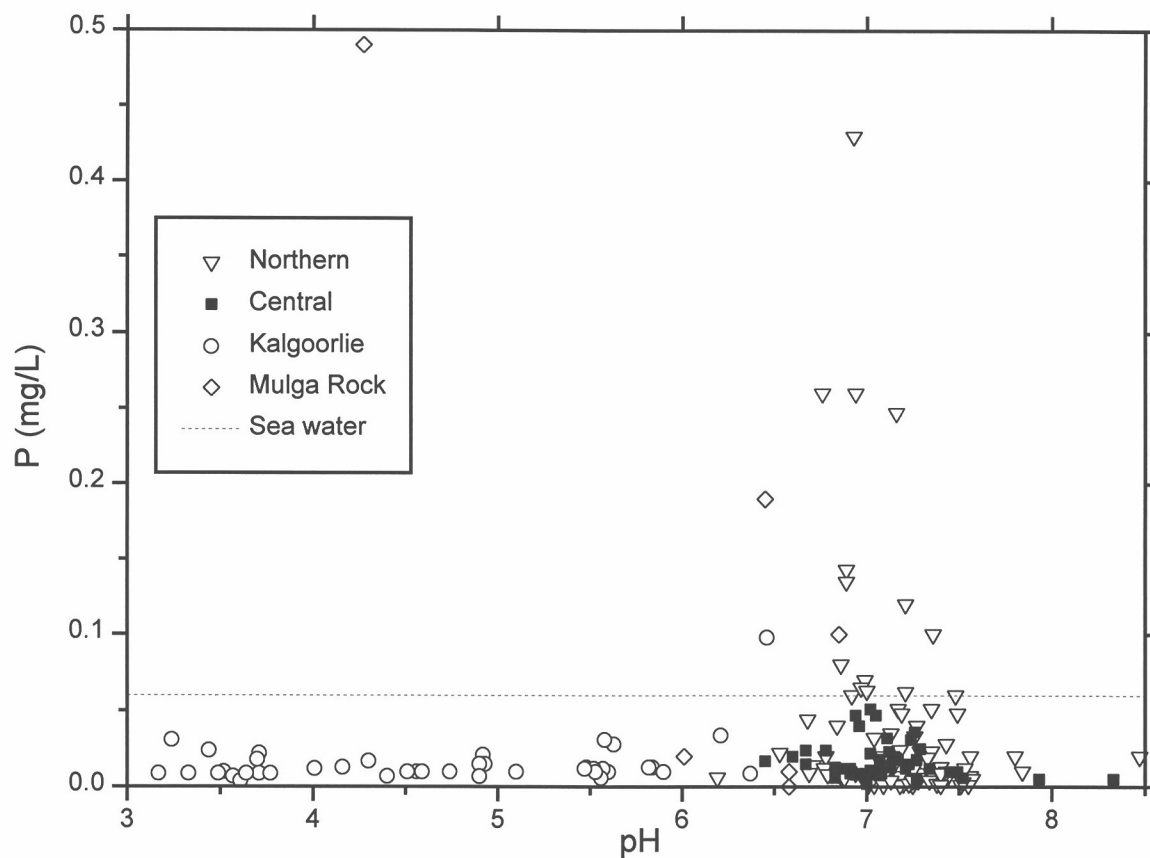


Figure A1.19: P vs. pH for Western Australian groundwaters.

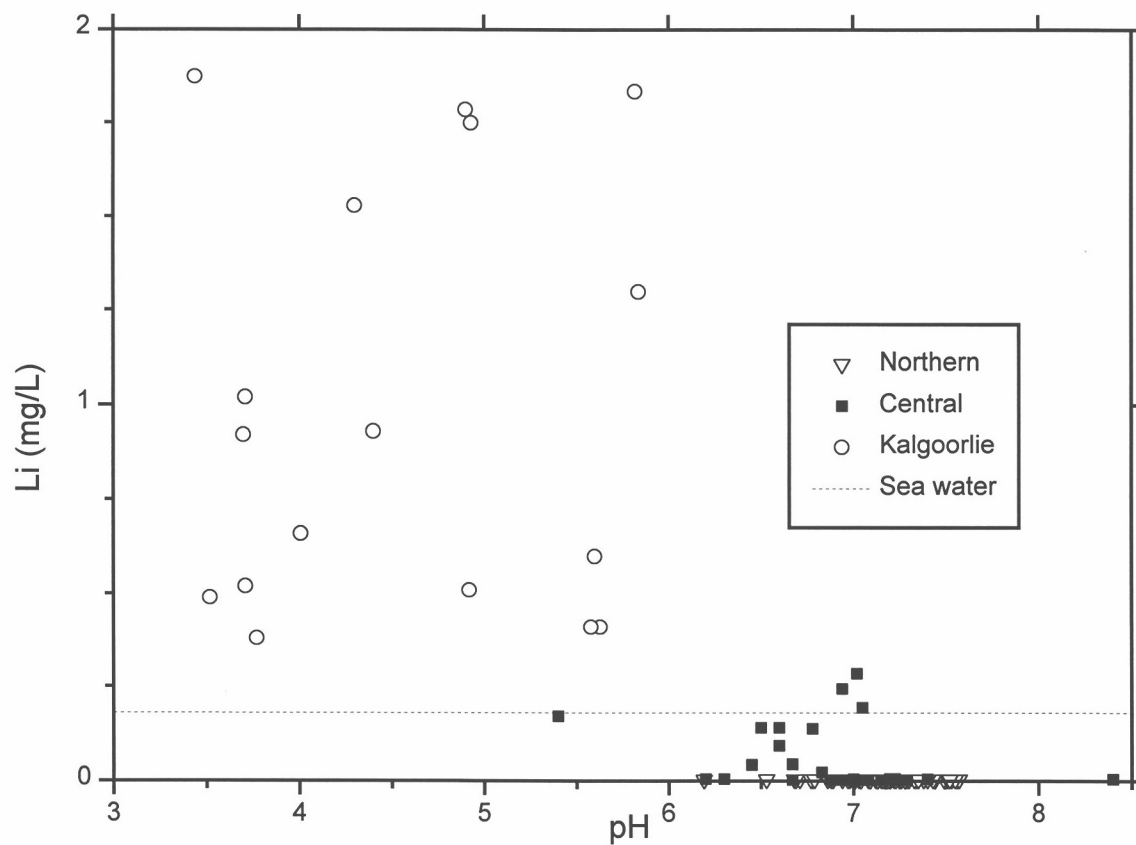


Figure A1.20: Li vs. pH for Western Australian groundwaters.

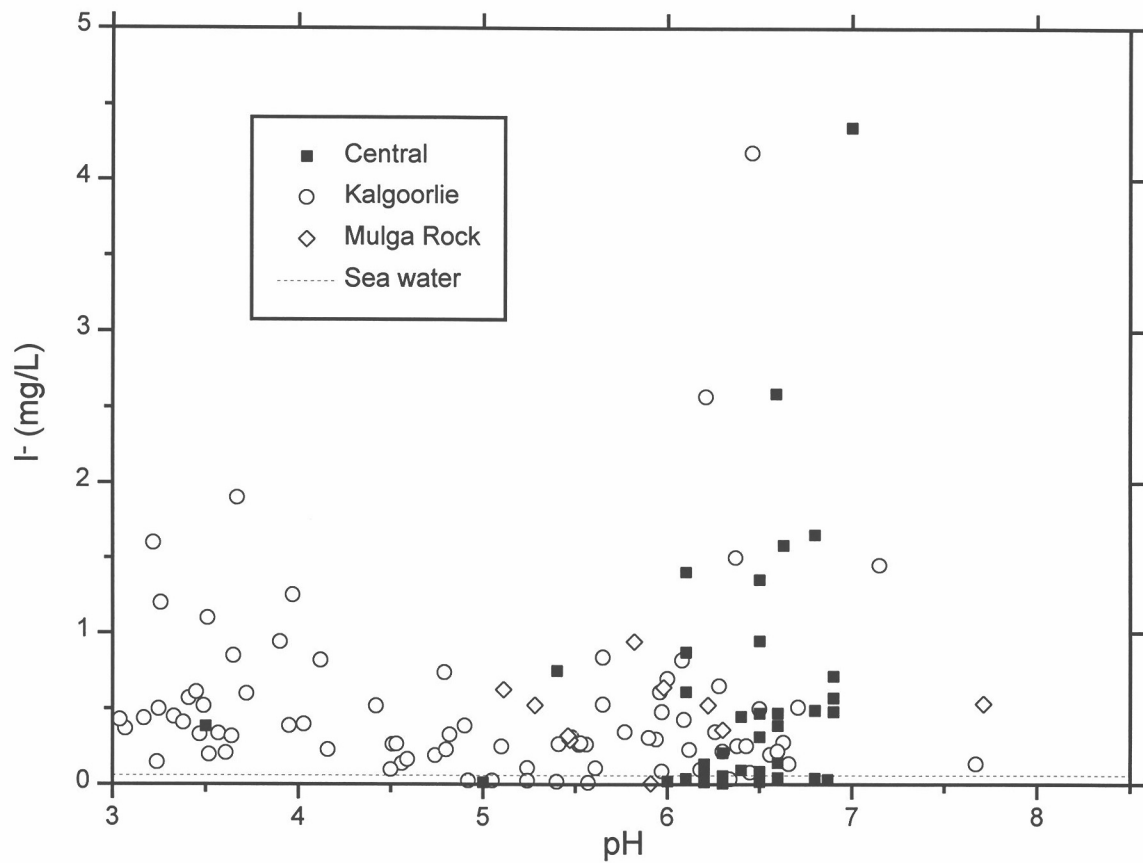


Figure A1.21: Free Iodide vs. pH for Western Australian groundwaters.

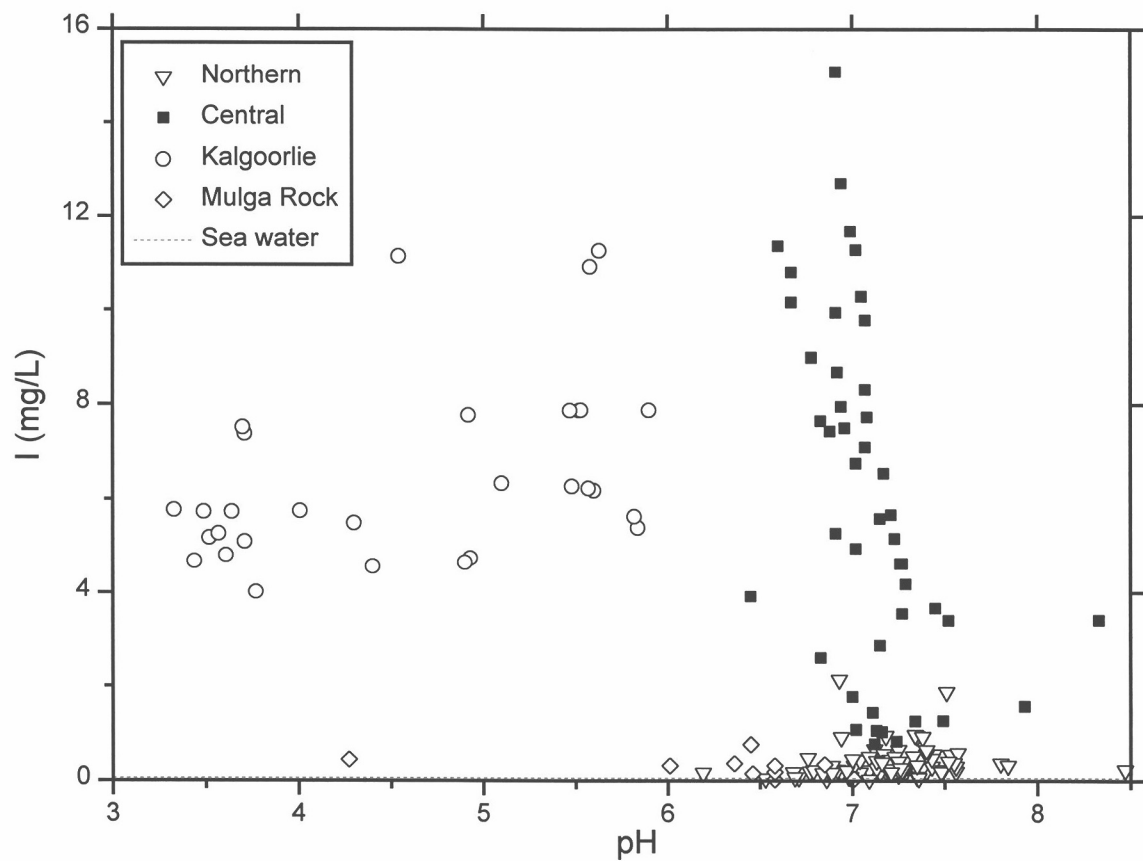


Figure A1.22 Total Iodine vs. pH for Western Australian groundwaters.

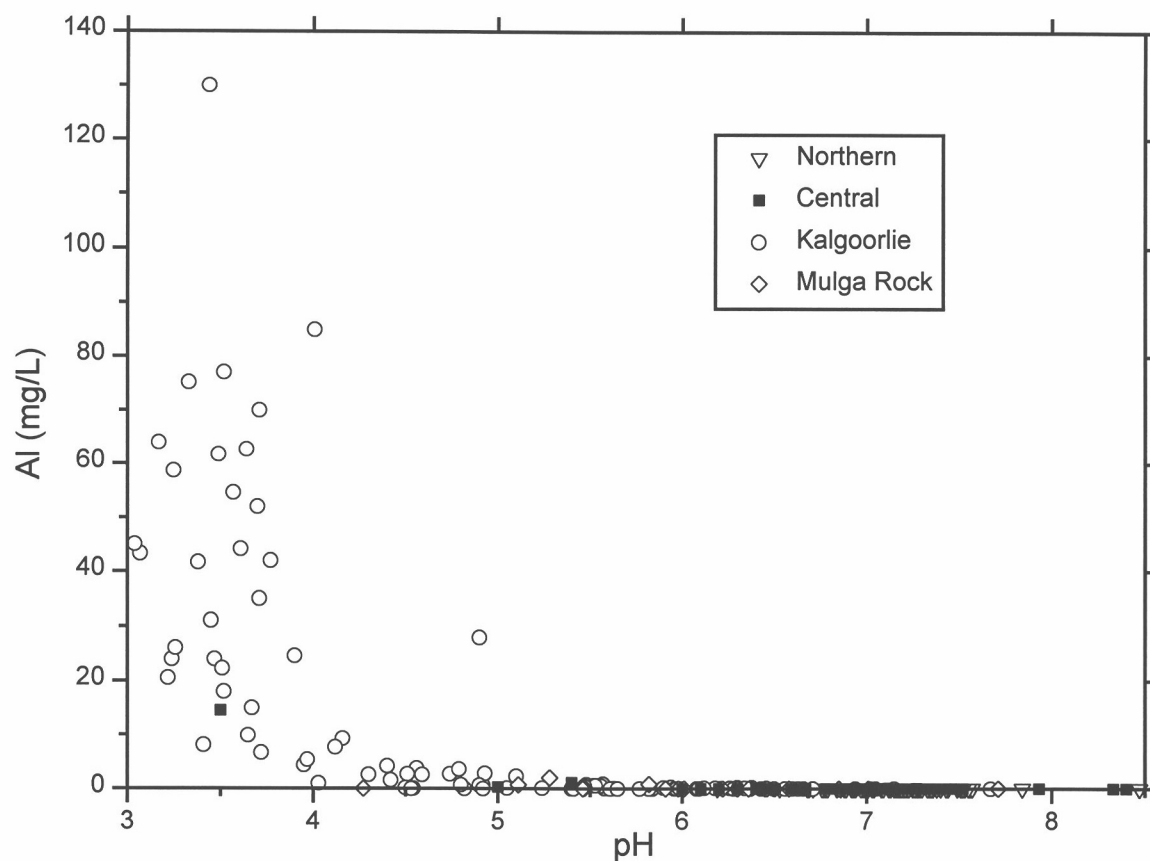


Figure A1.23: Al vs. pH for Western Australian groundwaters.

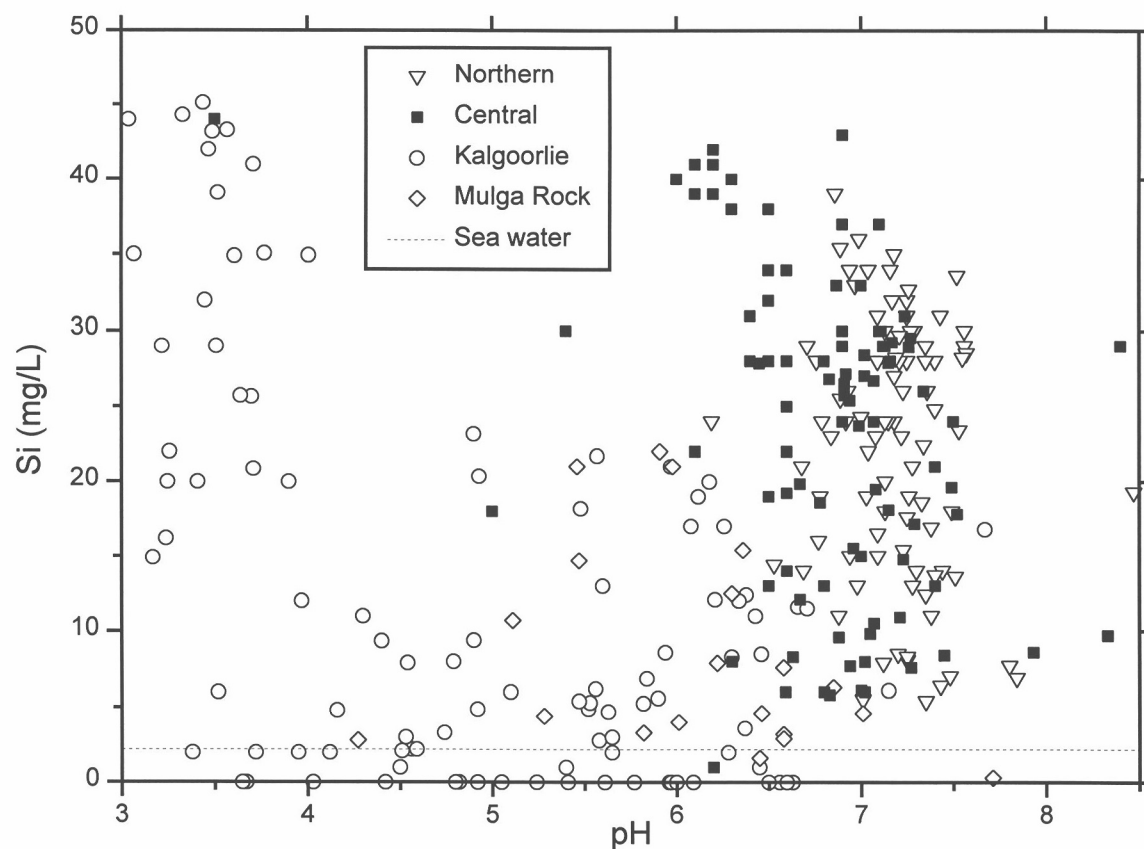


Figure A1.24: Si vs. pH for Western Australian groundwaters.

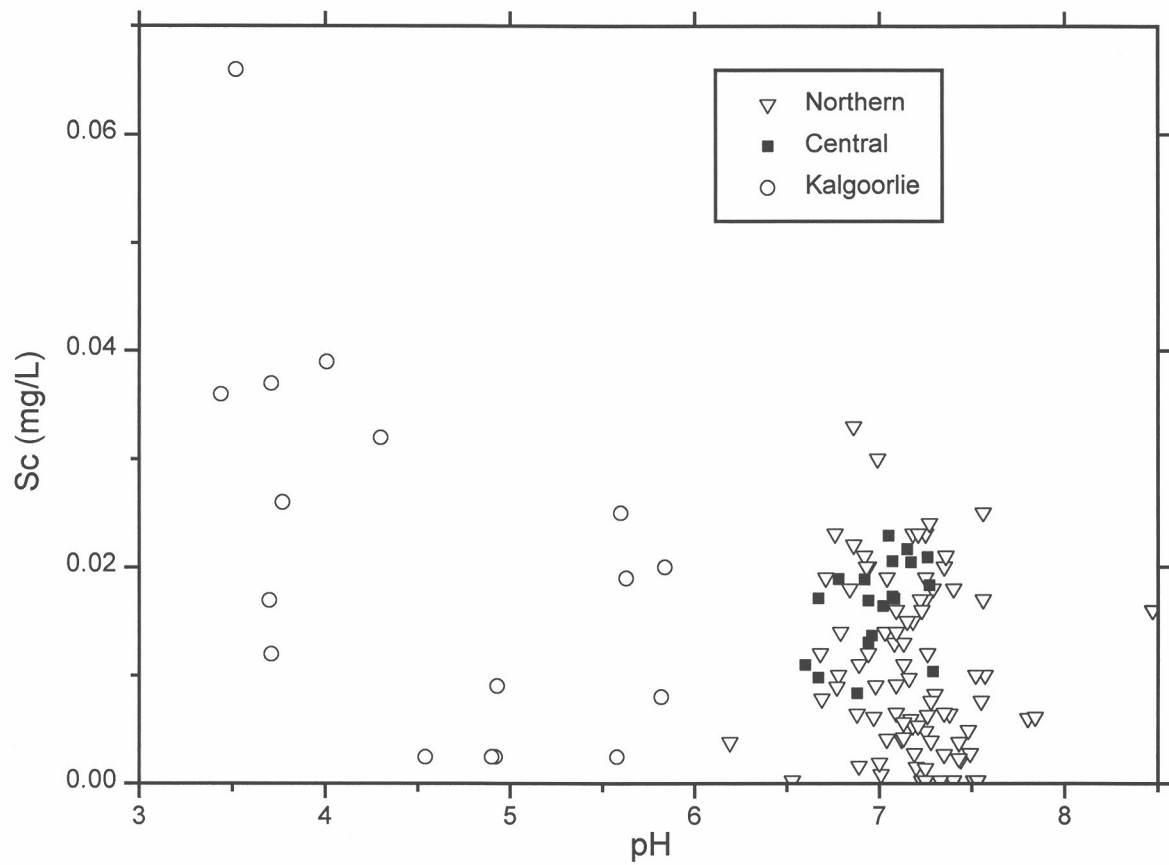


Figure A1.25: Sc vs. pH for Western Australian groundwaters.

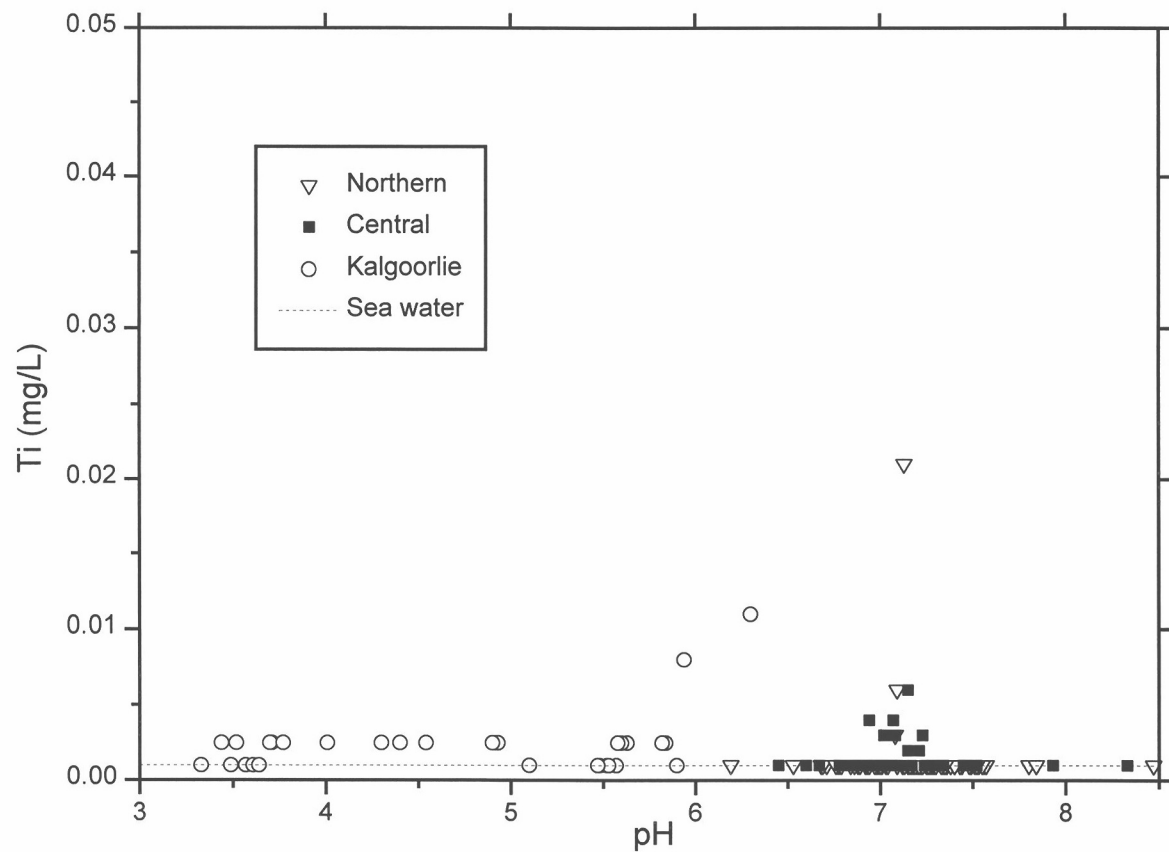


Figure A1.26: Ti vs. pH for Western Australian groundwaters.

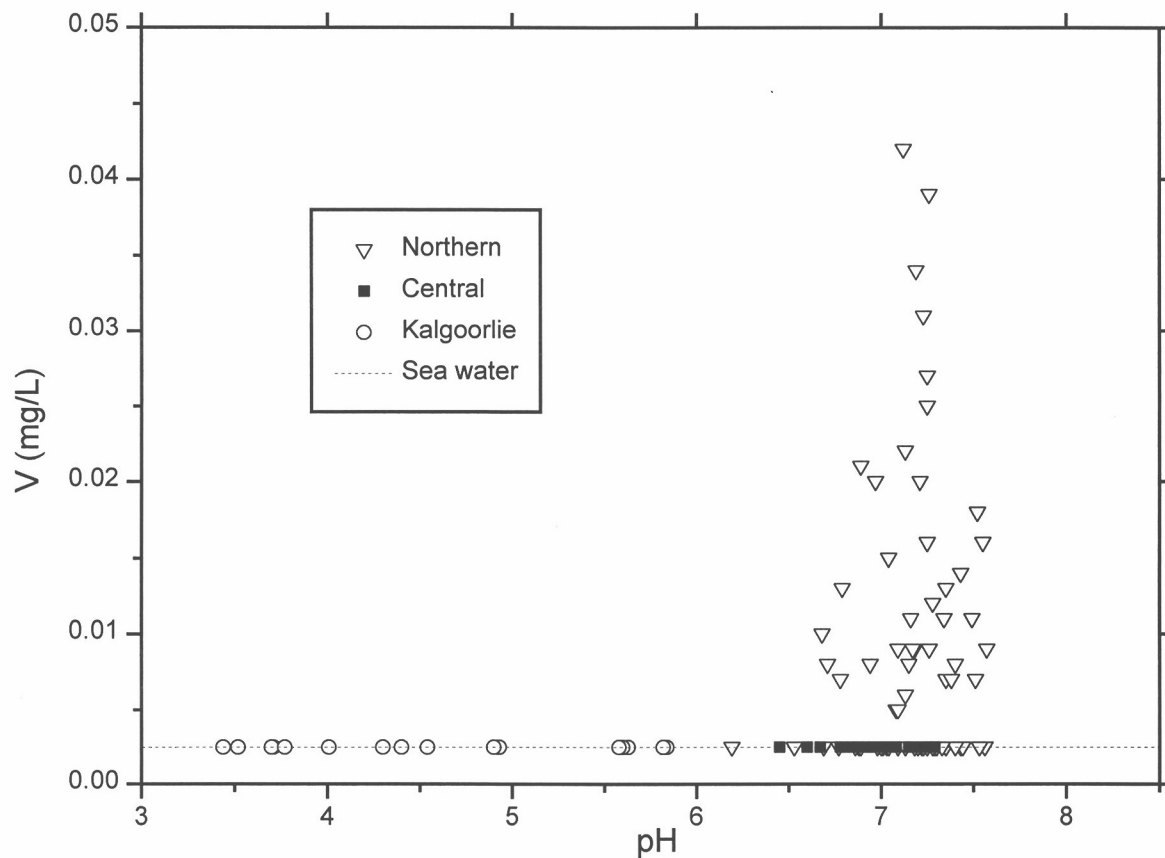


Figure A1.27: V vs. pH for Western Australian groundwaters.

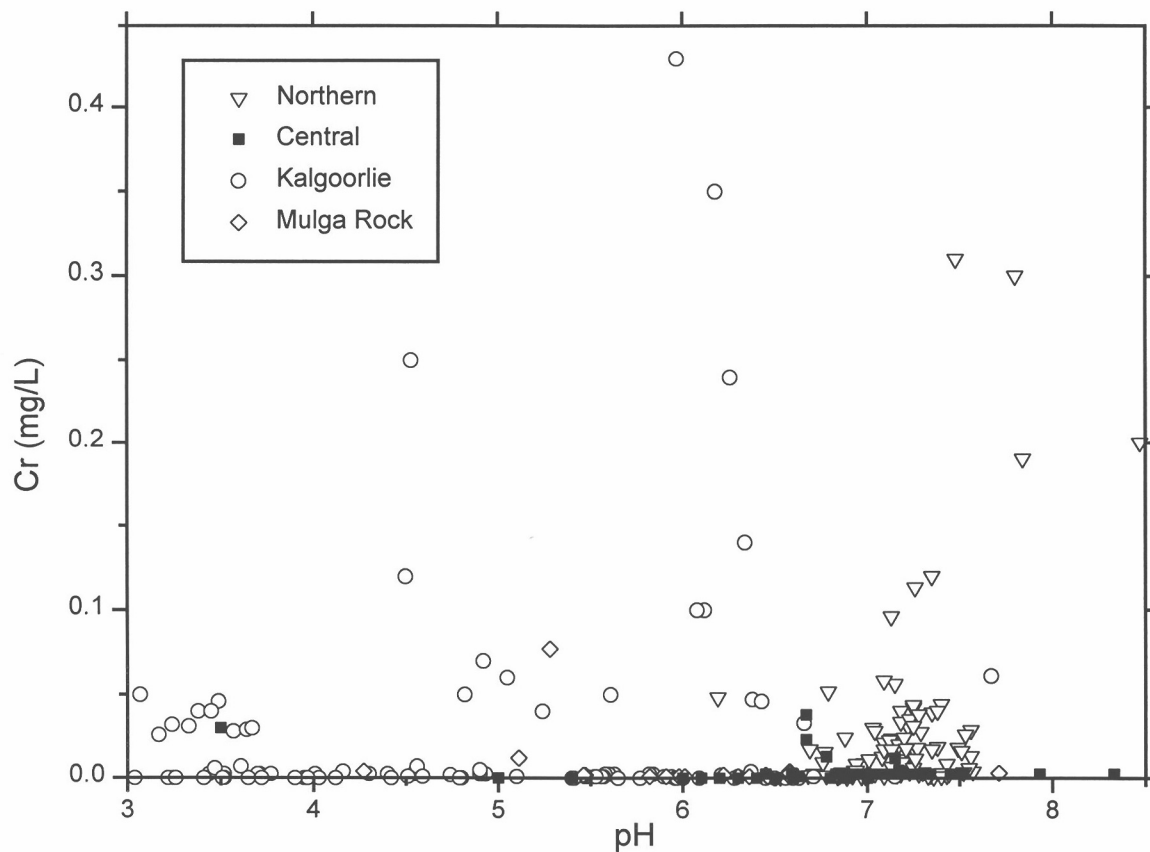


Figure A1.28: Cr vs. pH for Western Australian groundwaters.

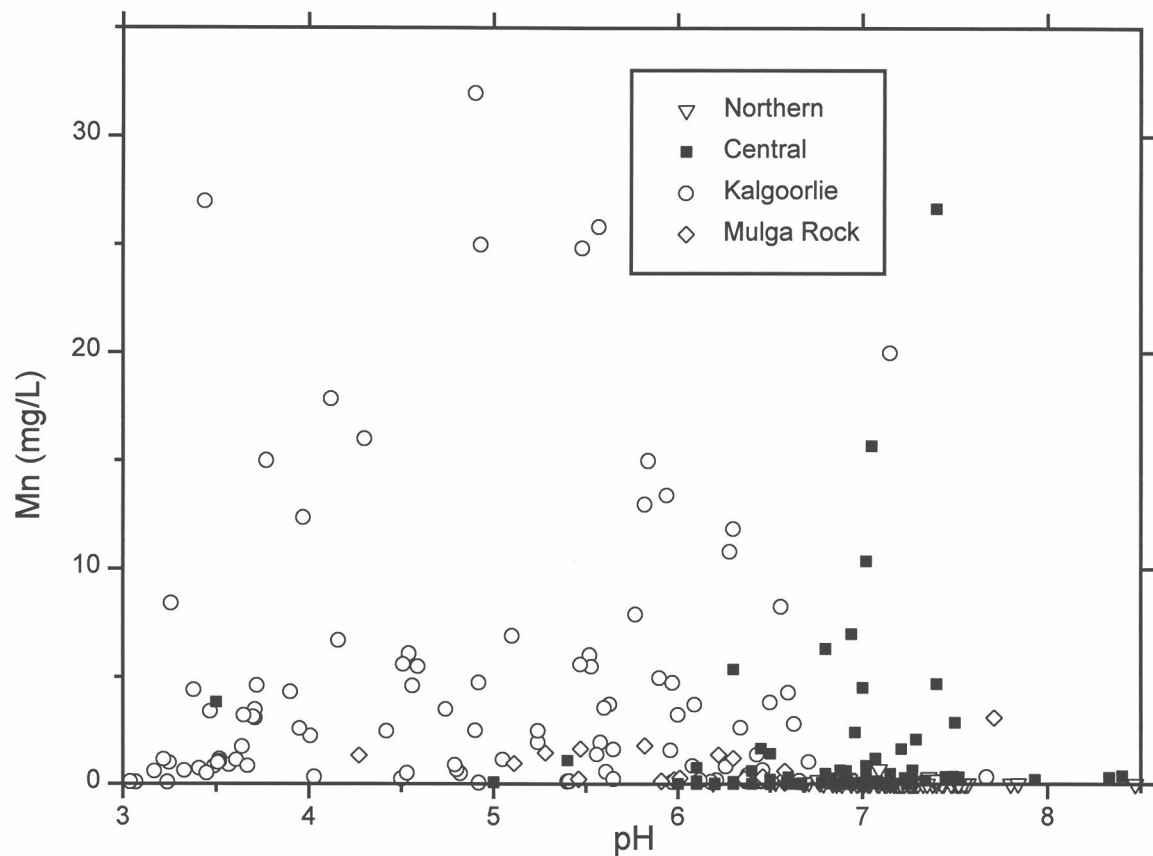


Figure A1.29: Mn vs. pH for Western Australian groundwaters.

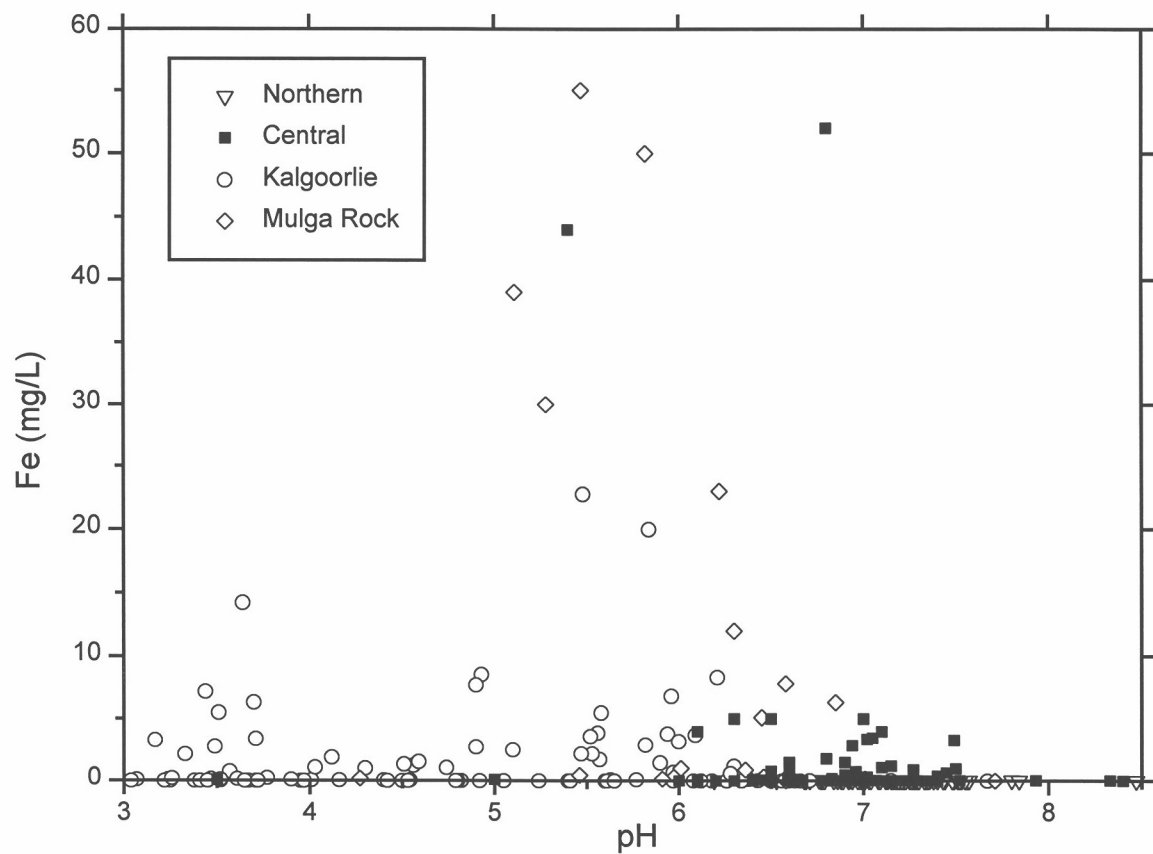


Figure A1.30: Fe vs. pH for Western Australian groundwaters.

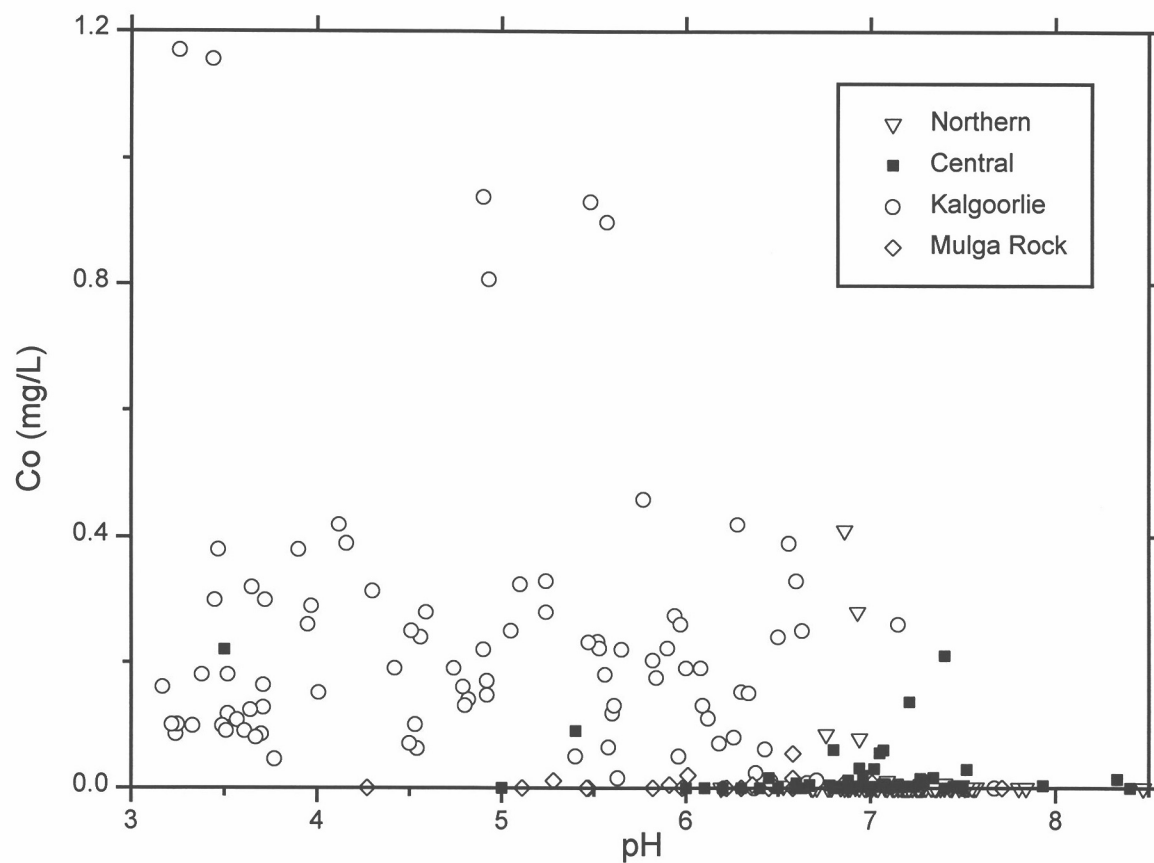


Figure A1.31: Co vs. pH for Western Australian groundwaters.

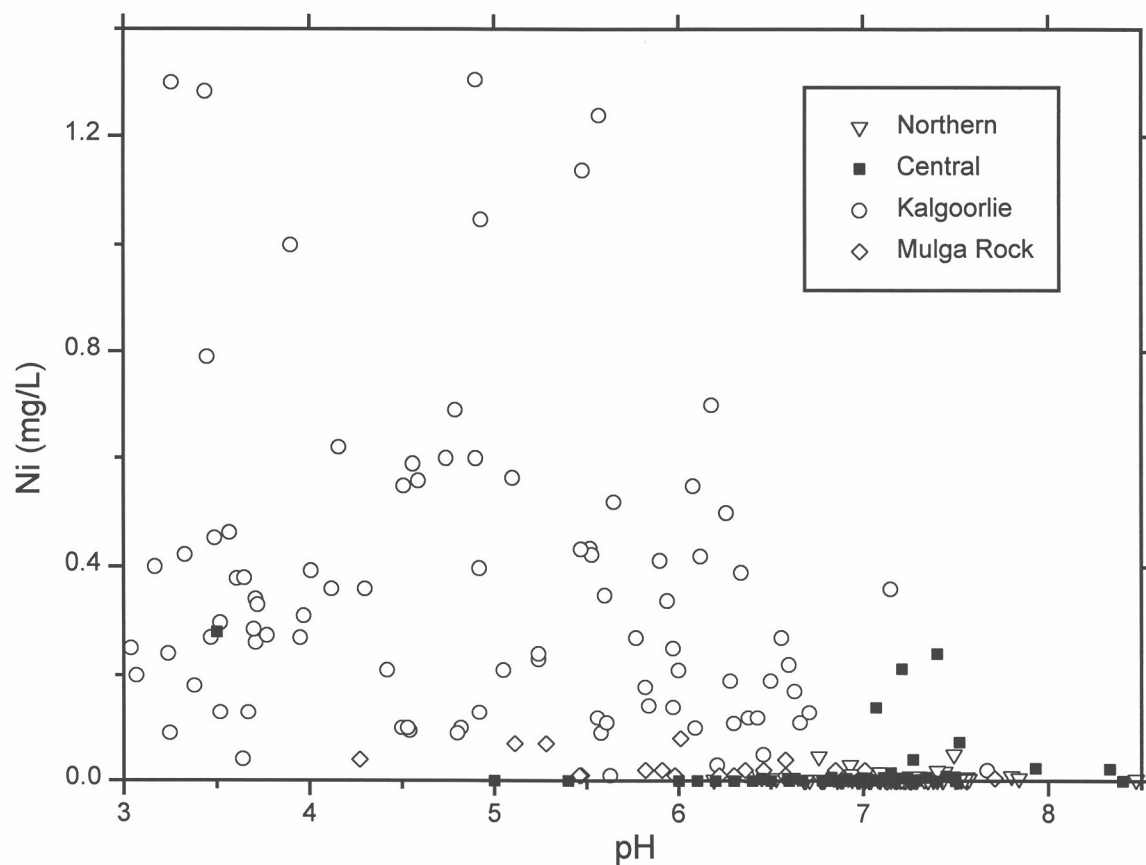


Figure A1.32: Ni vs. pH for Western Australian groundwaters.

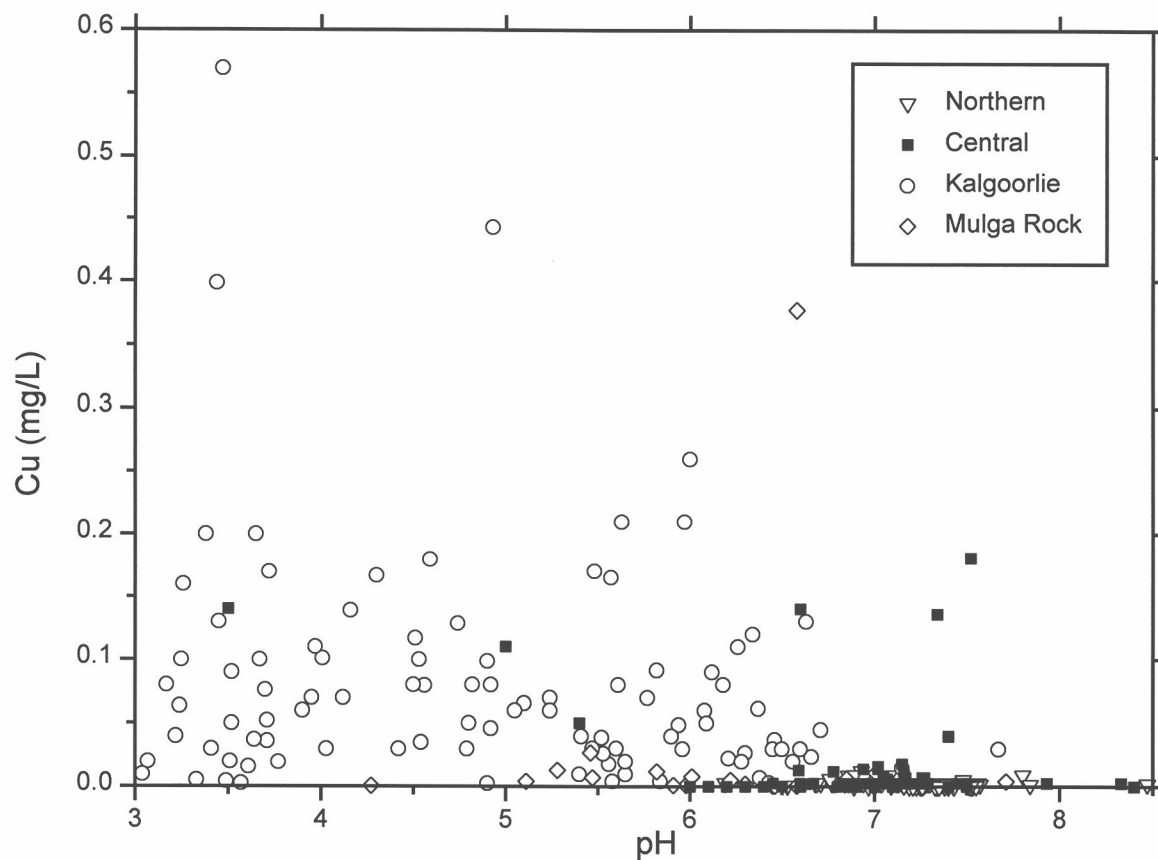


Figure A1.33: Cu vs. pH for Western Australian groundwaters.

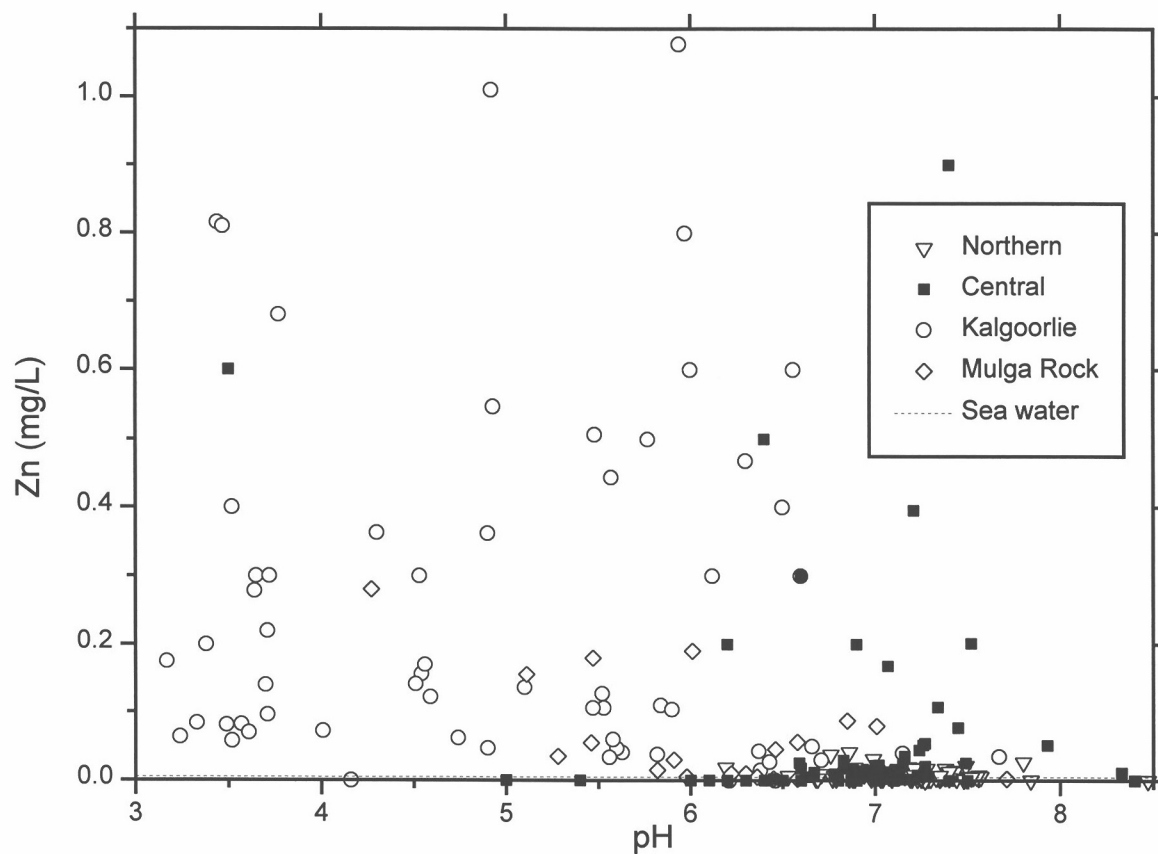


Figure A1.34: Zn vs. pH for Western Australian groundwaters.

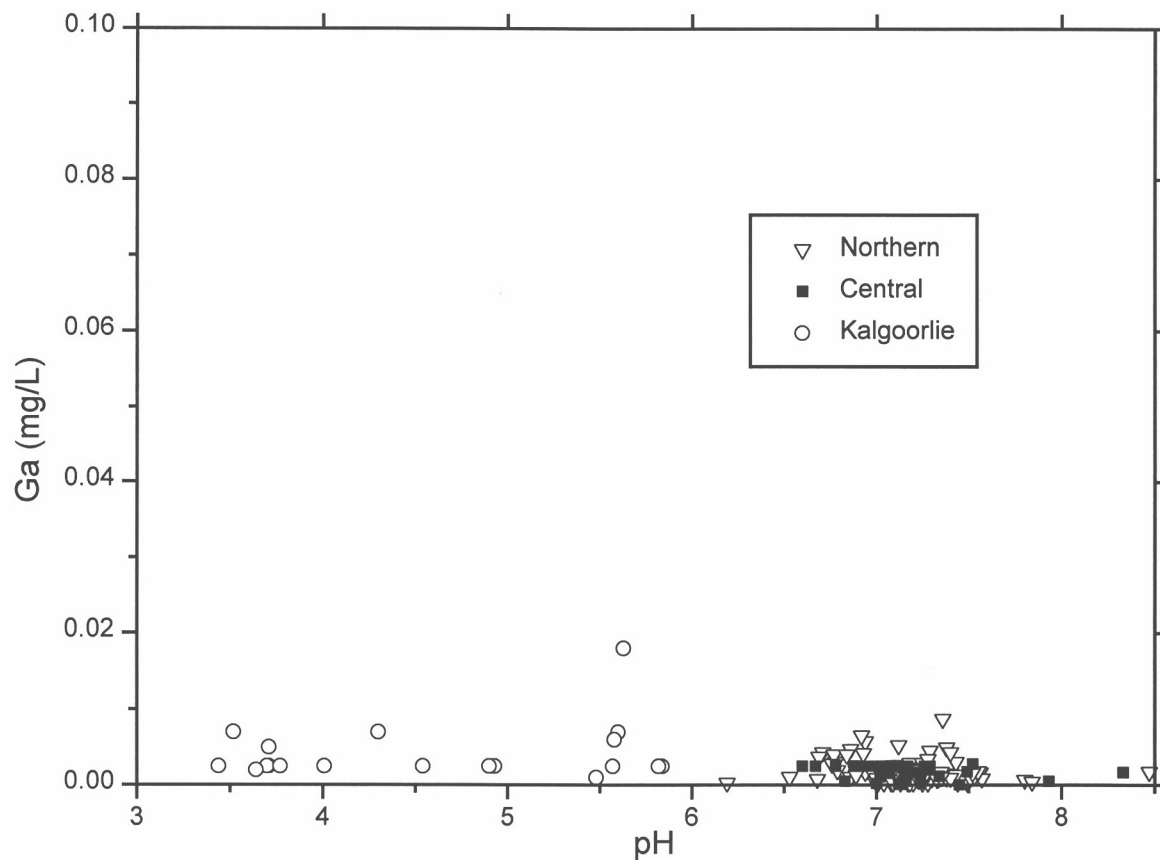


Figure A1.35: Ga vs. pH for Western Australian groundwaters.

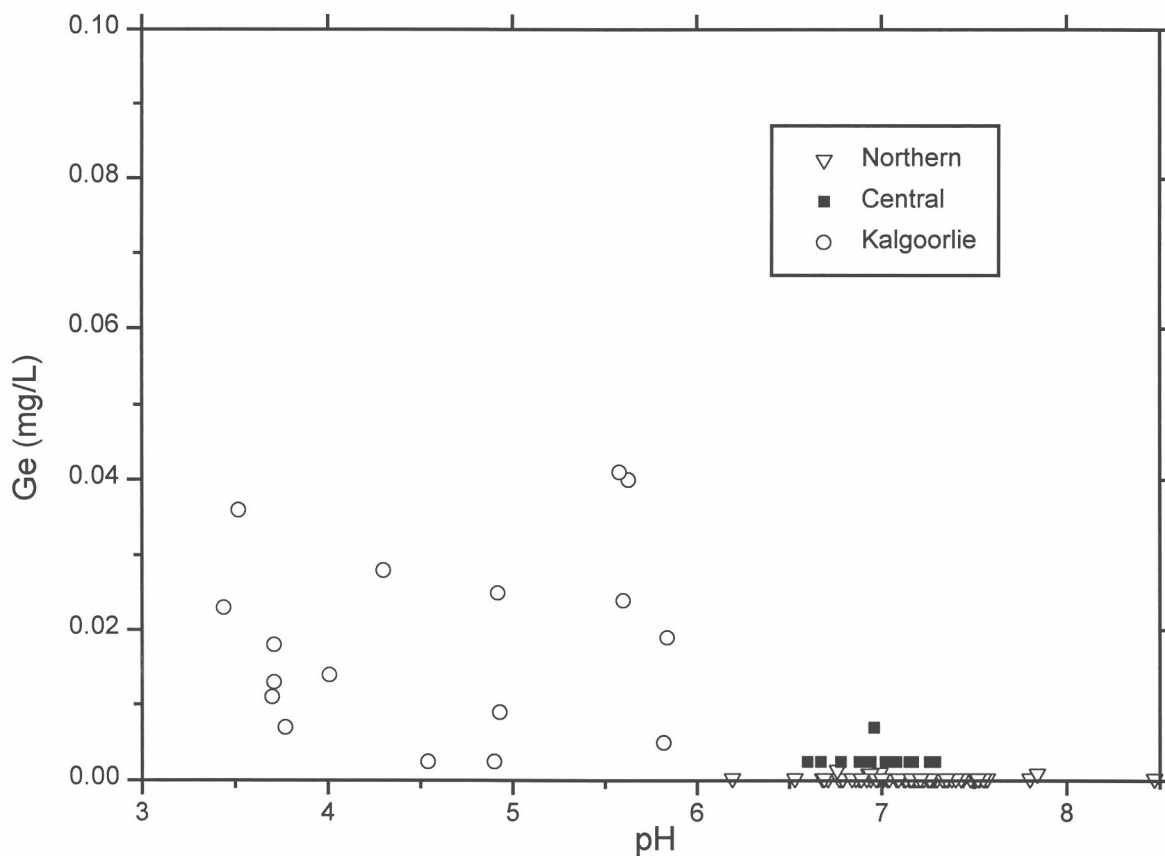


Figure A1.36: Ge vs. pH for Western Australian groundwaters.

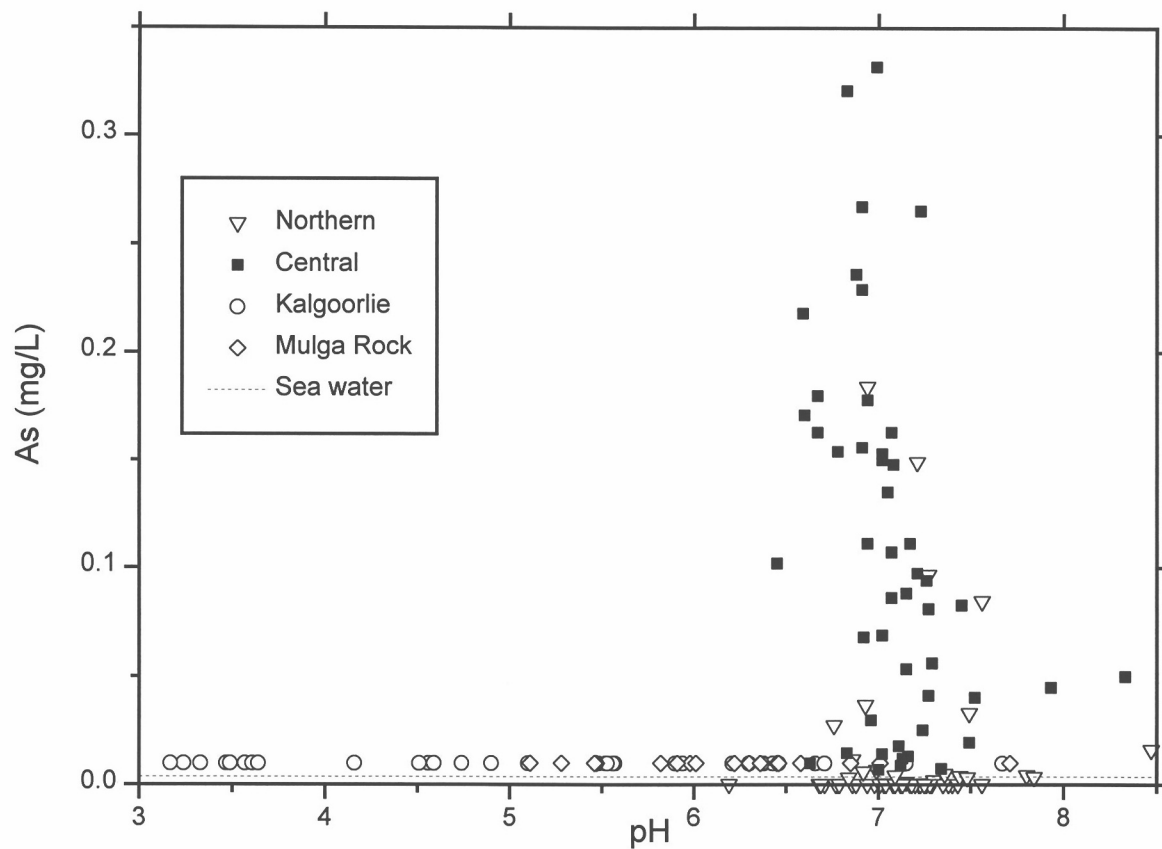


Figure A1.37: As vs. pH for Western Australian groundwaters.

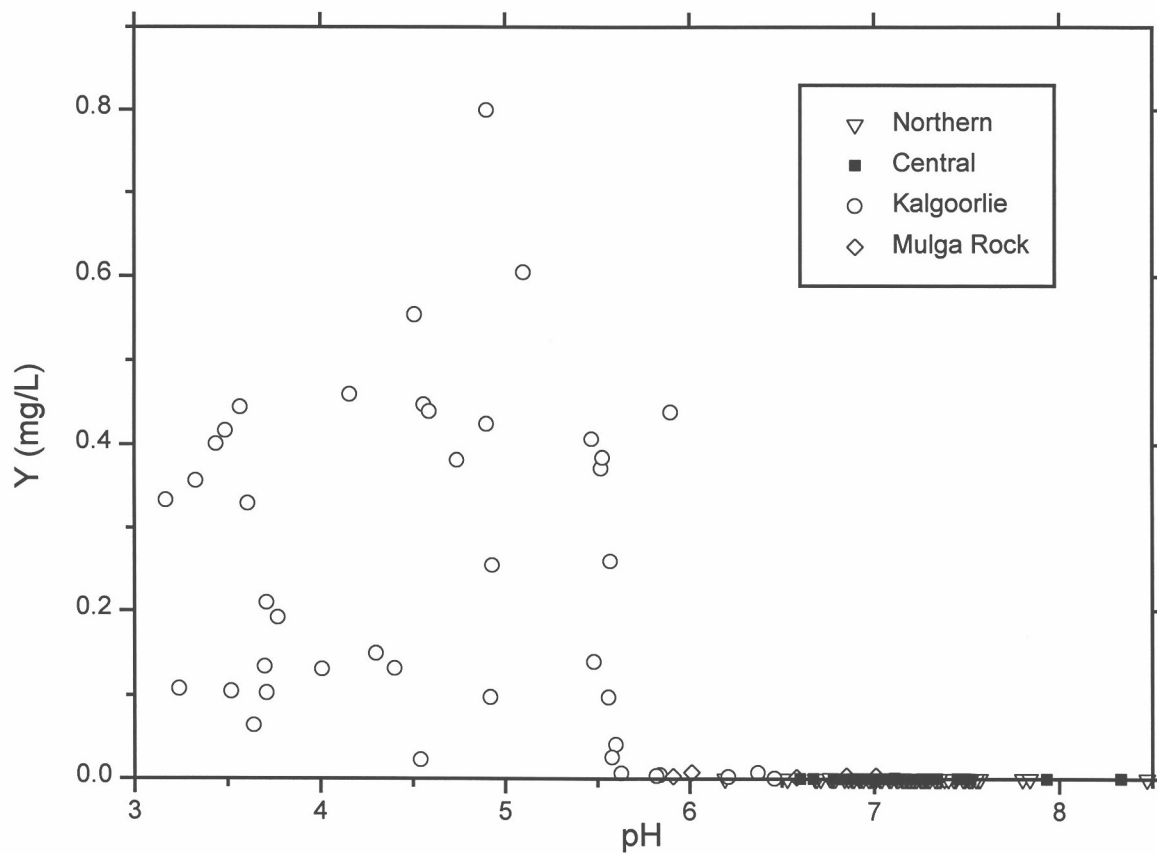


Figure A1.38: Y vs. pH for Western Australian groundwaters.

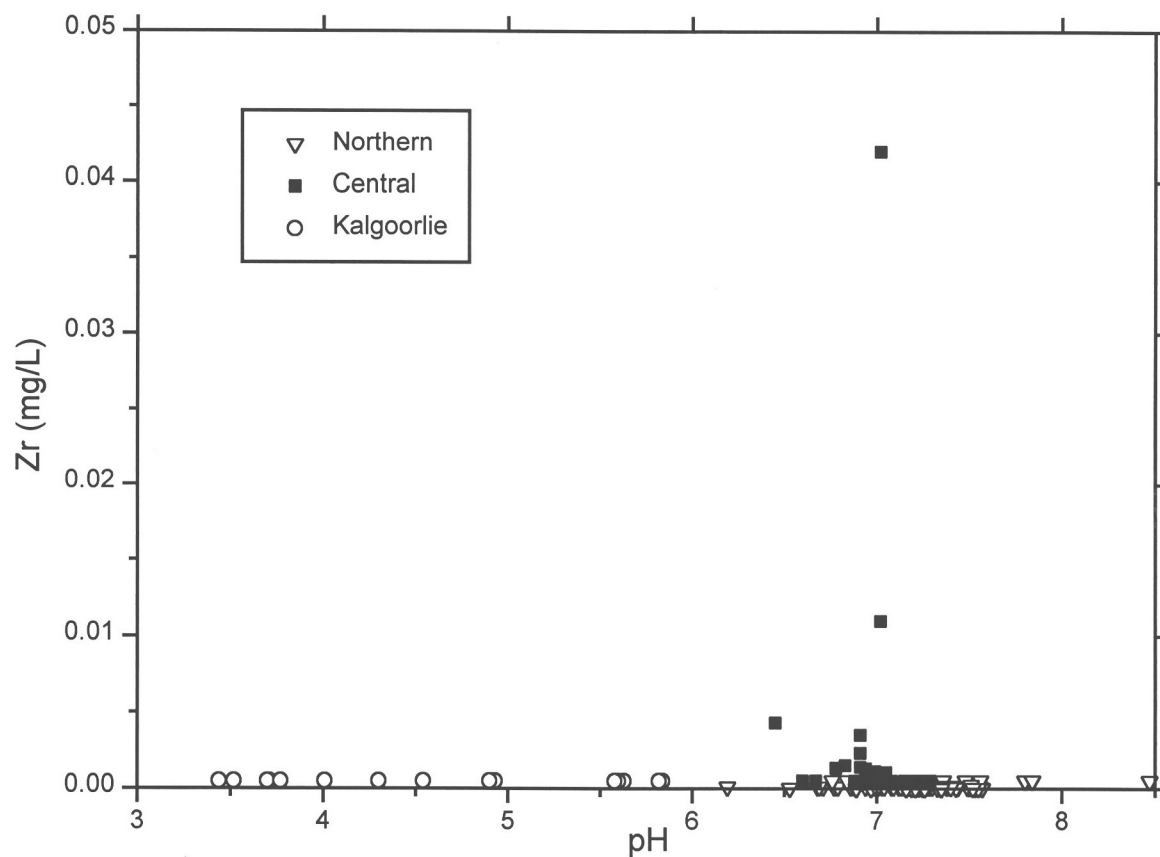


Figure A1.39: Zr vs. pH for Western Australian groundwaters.

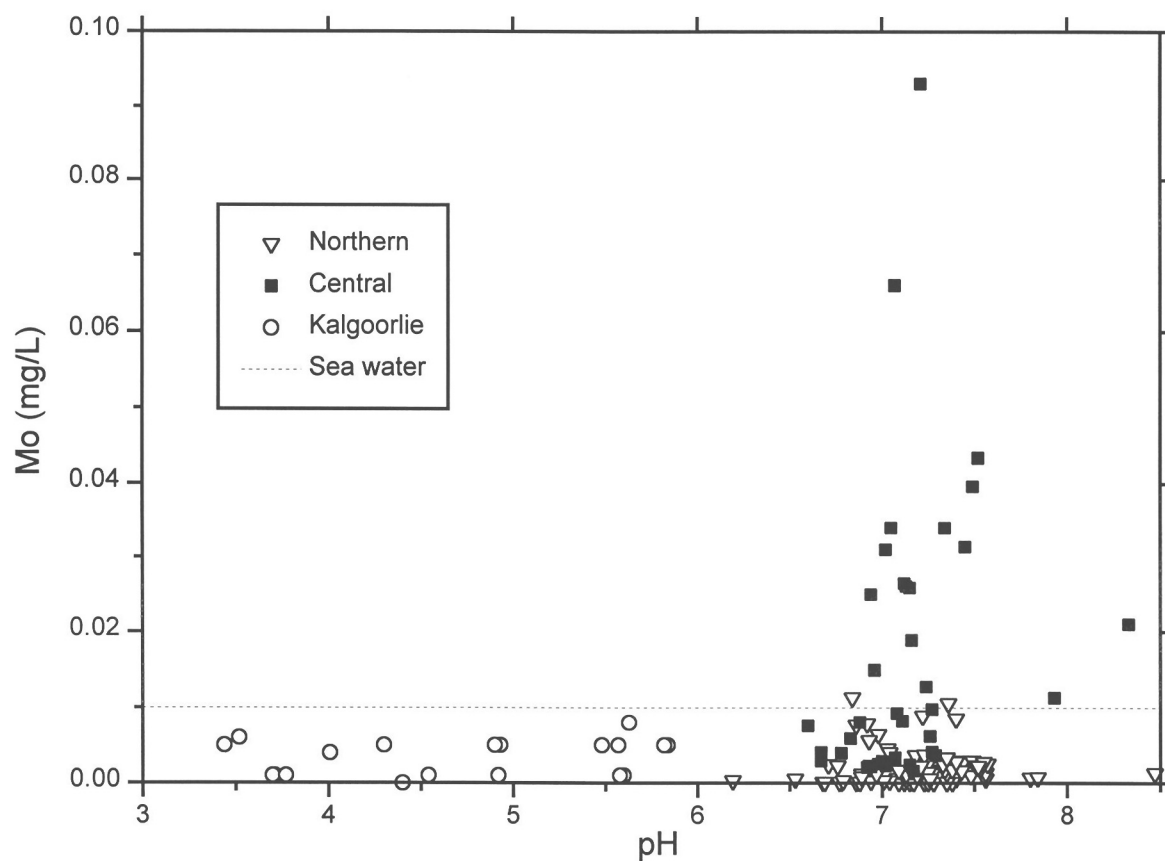


Figure A1.40: Mo vs. pH for Western Australian groundwaters.

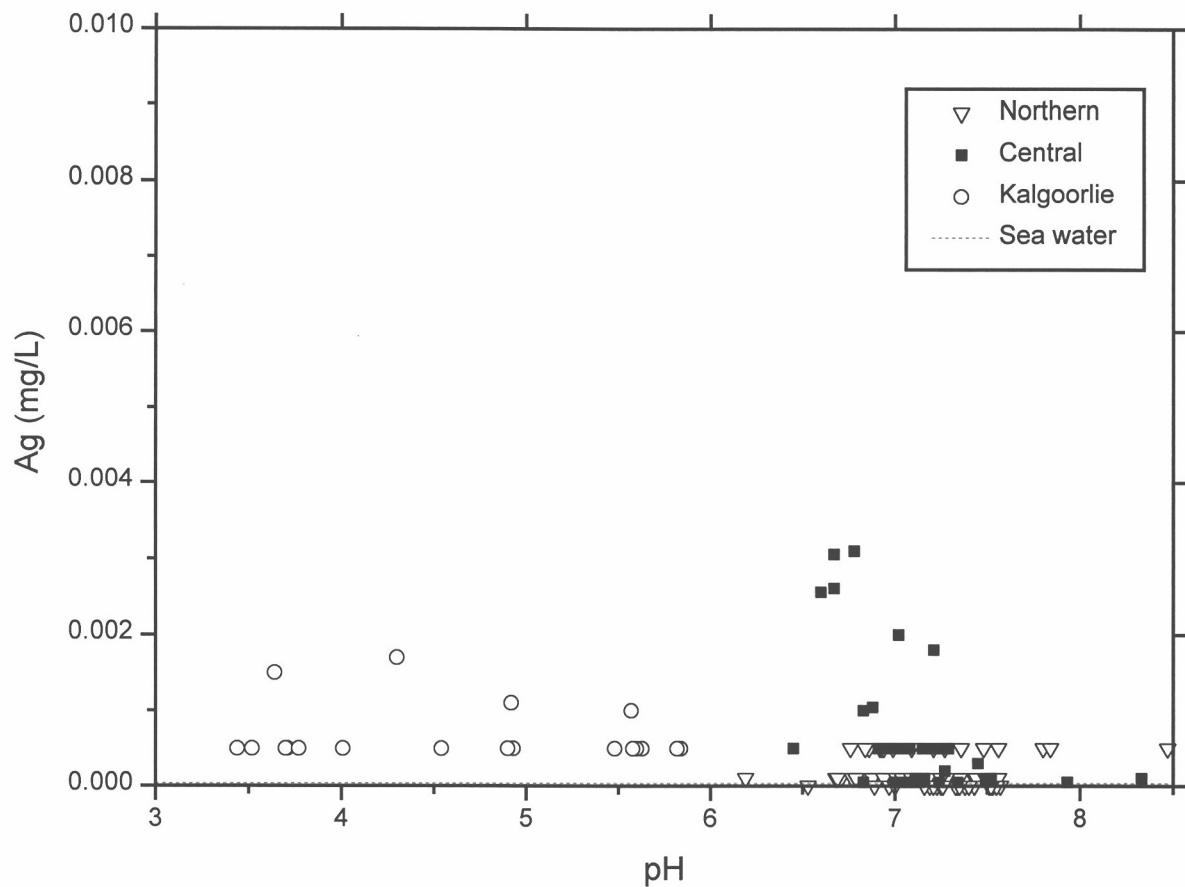


Figure A1.41: Ag vs. pH for Western Australian groundwaters.

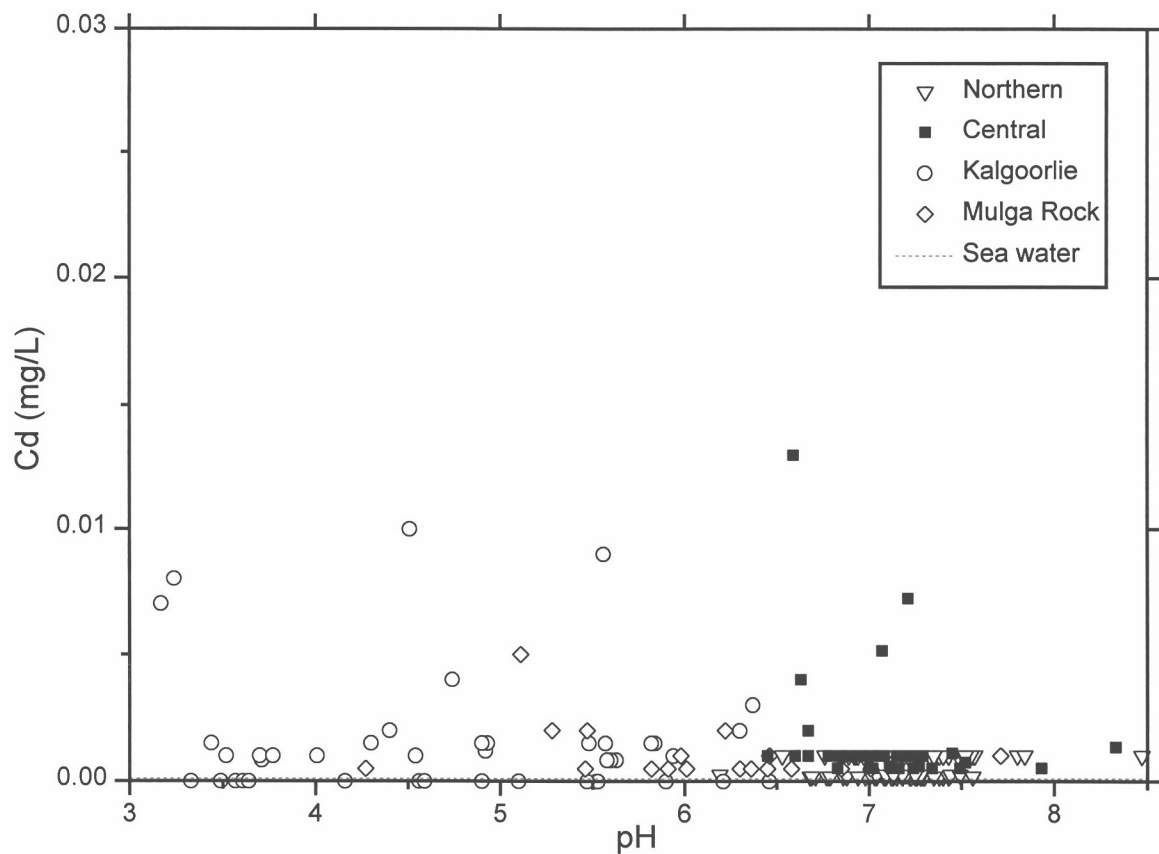


Figure A1.42: Cd vs. pH for Western Australian groundwaters.

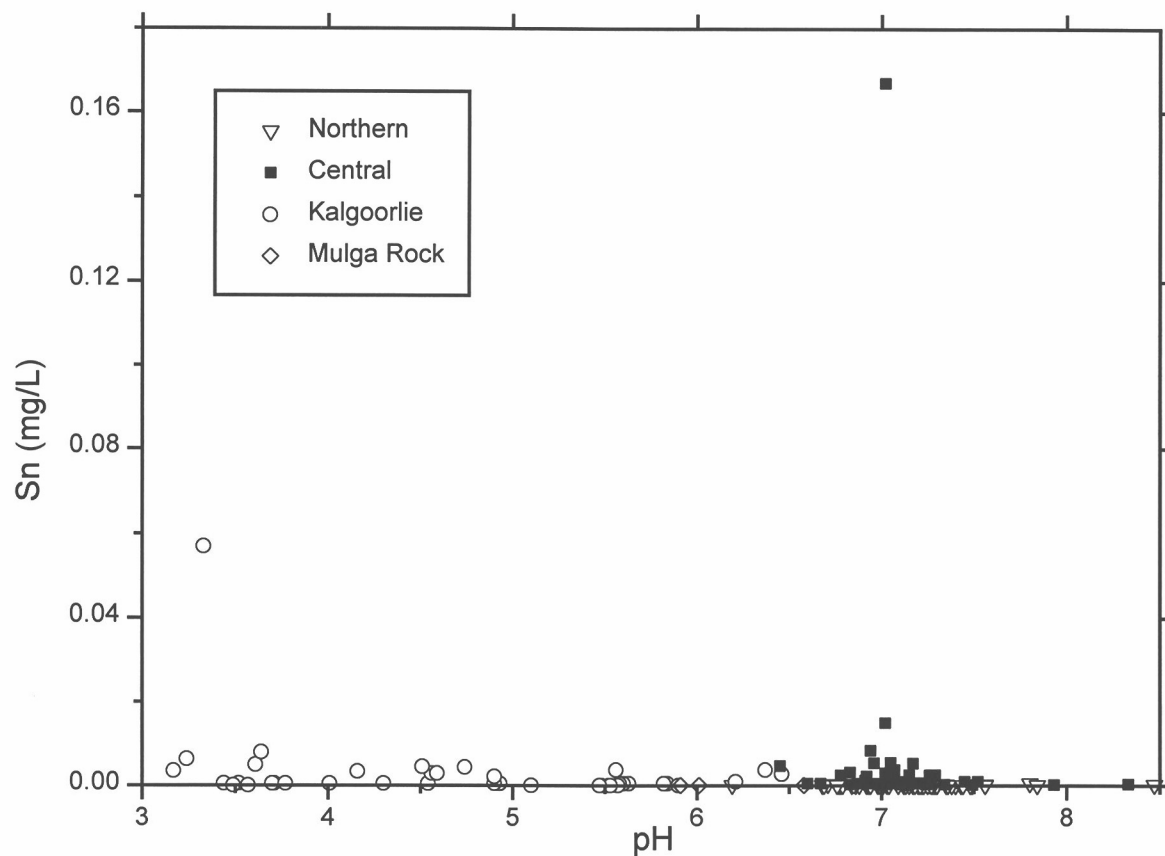


Figure A1.43: Sn vs. pH for Western Australian groundwaters.

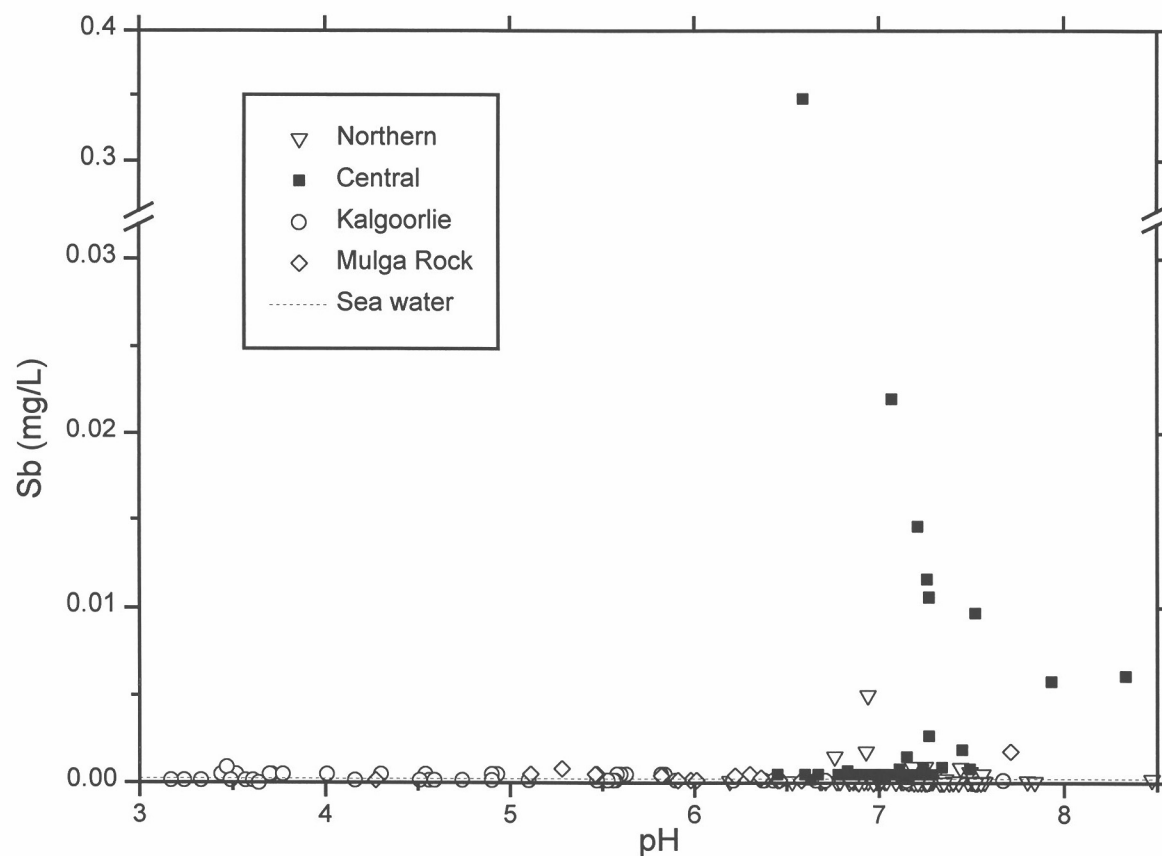


Figure A1.44: Sb vs. pH for Western Australian groundwaters.

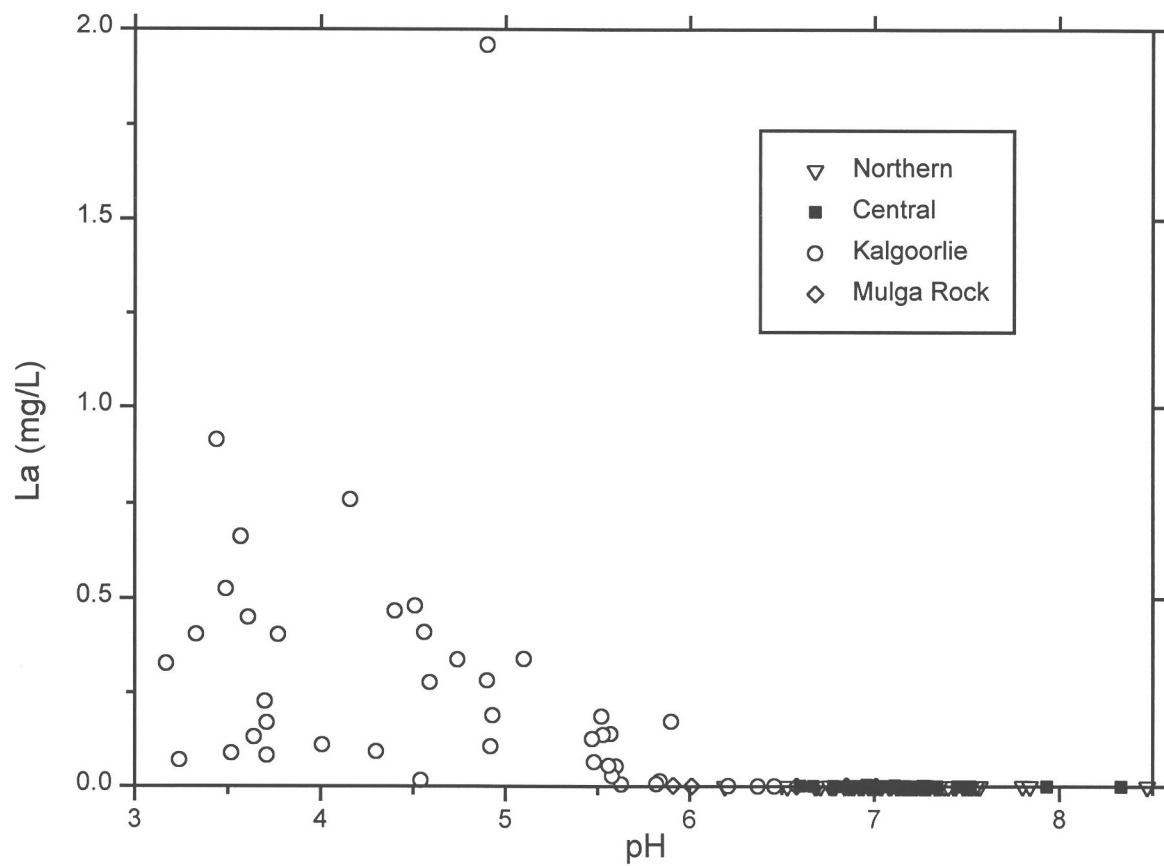


Figure A1.45: La vs. pH for Western Australian groundwaters.

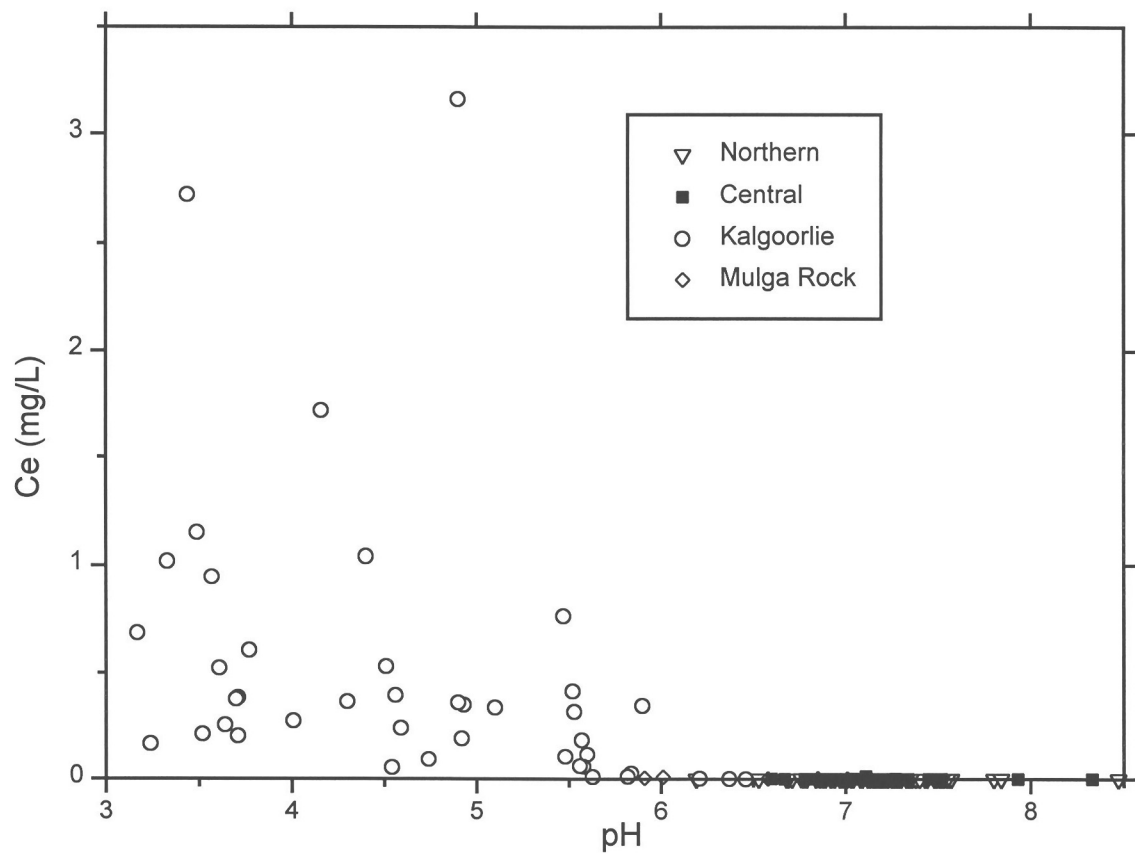


Figure A1.46: Ce vs. pH for Western Australian groundwaters.

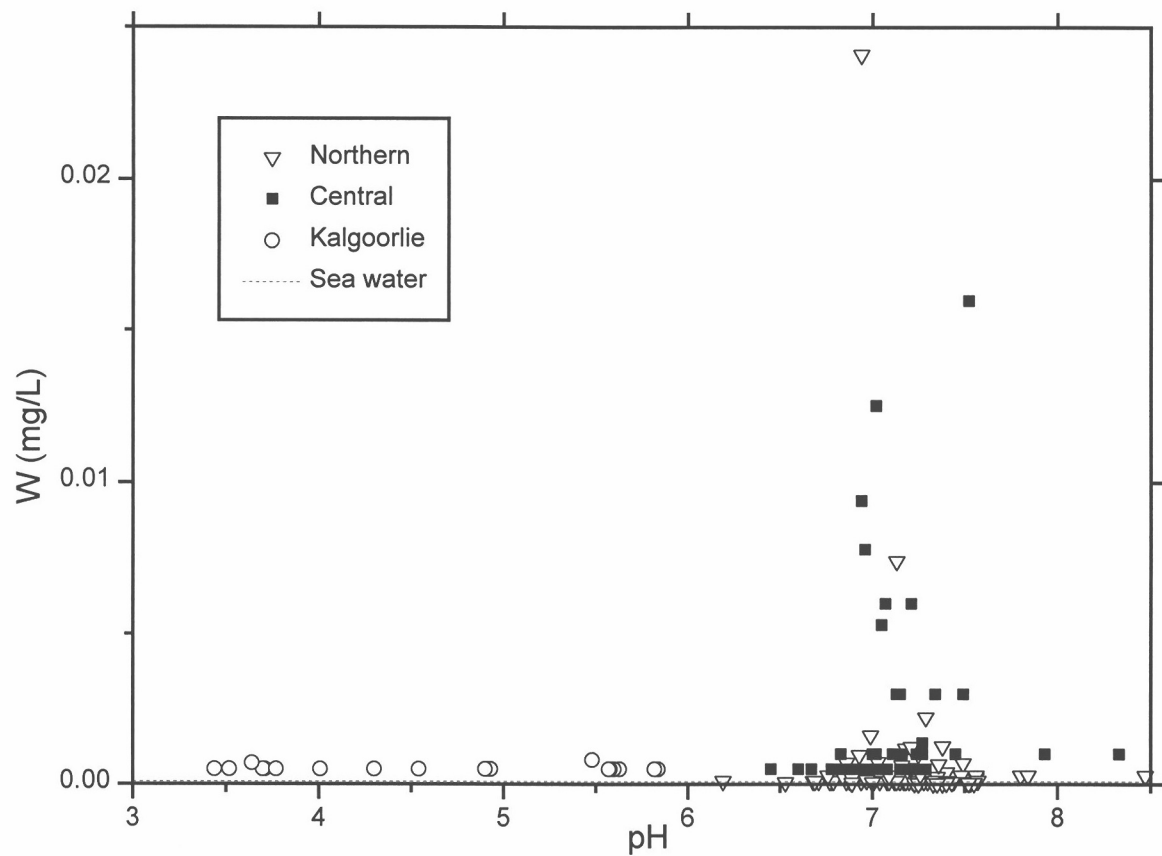


Figure A1.47: W vs. pH for Western Australian groundwaters.

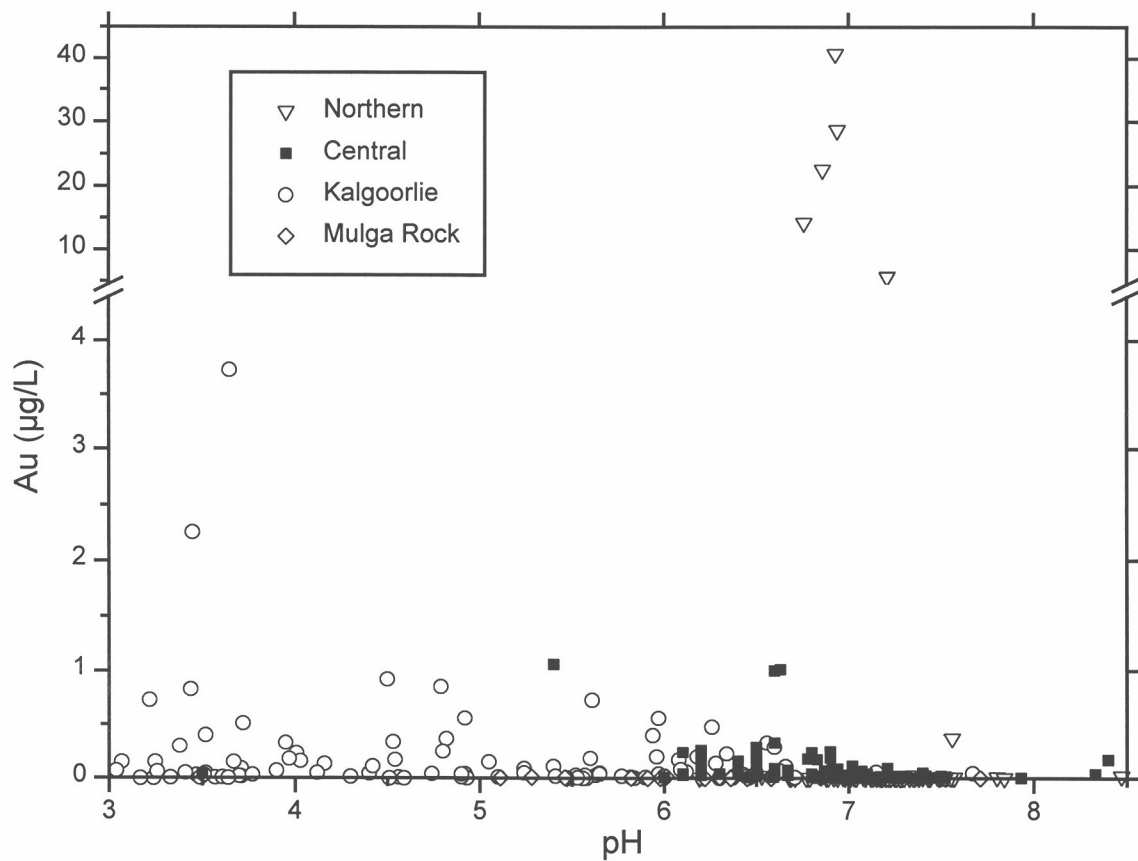


Figure A1.48: Au vs. pH for Western Australian groundwaters.

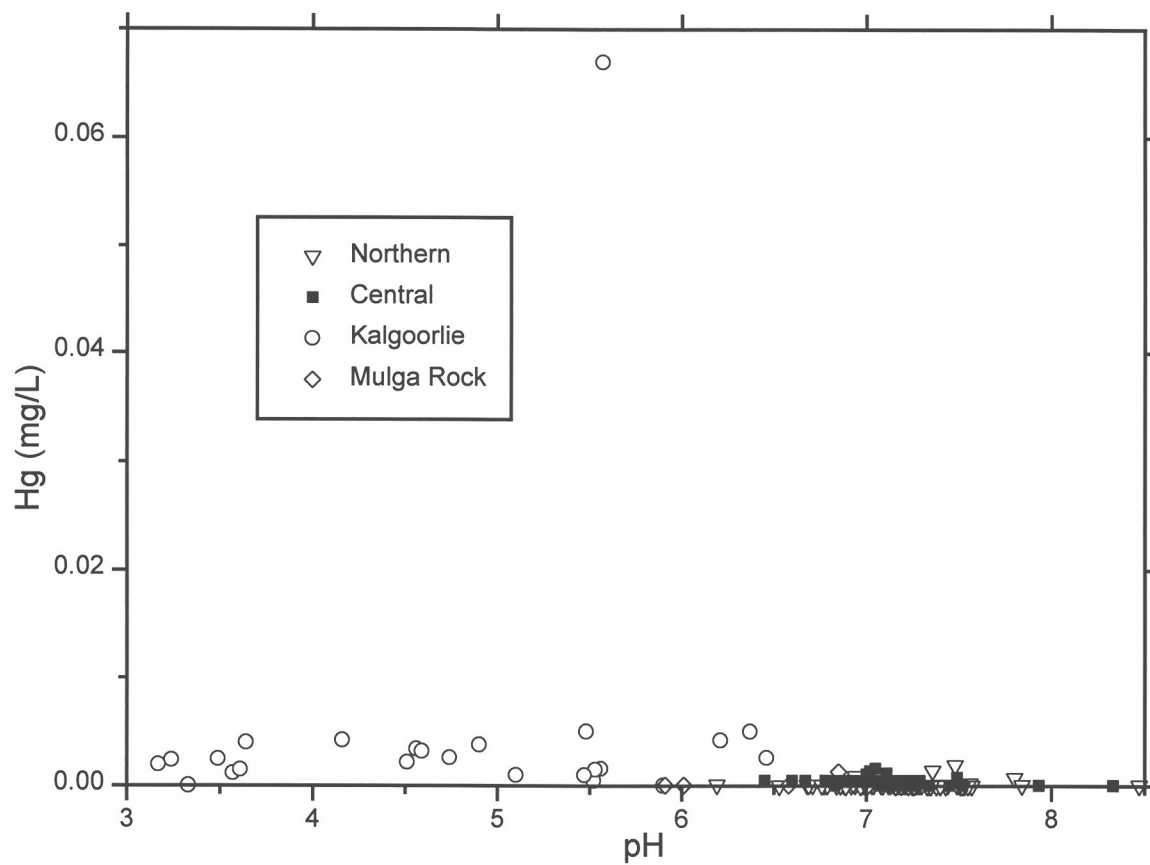


Figure A1.49: Hg vs. pH for Western Australian groundwaters.

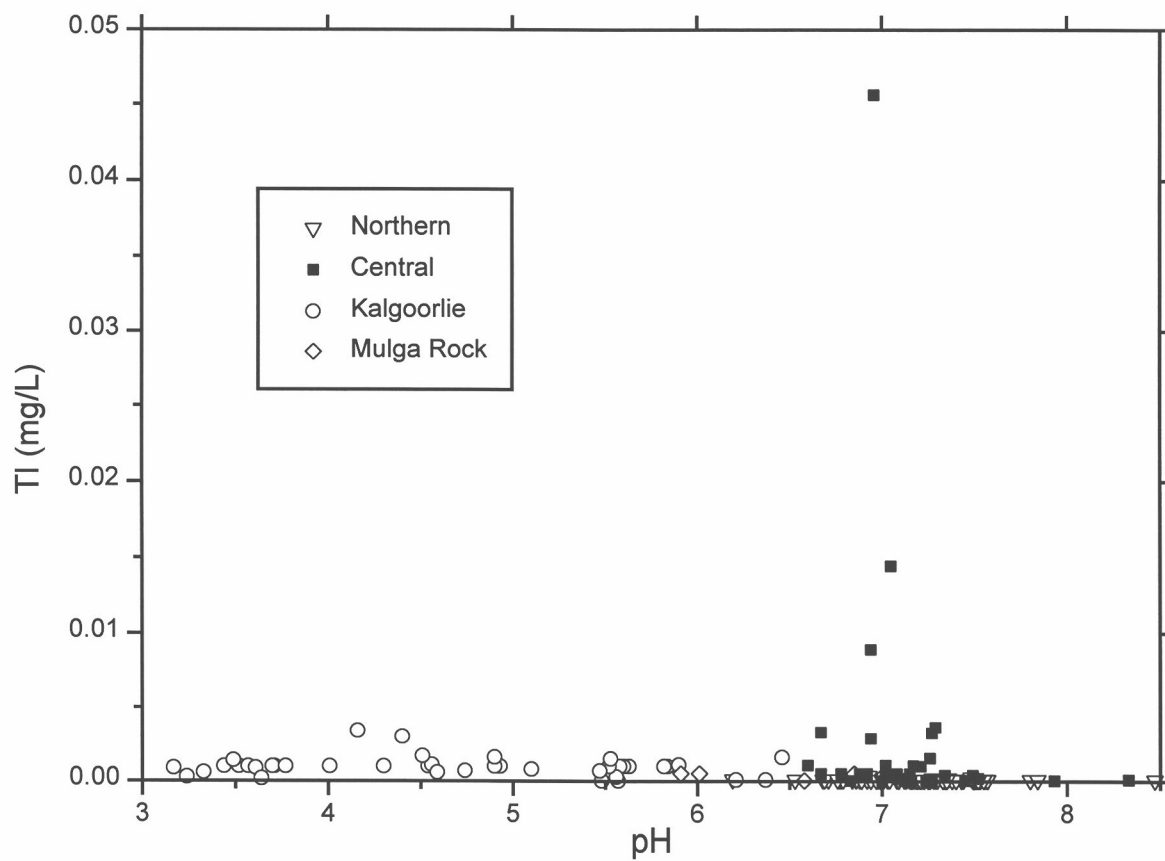


Figure A1.50: Tl vs. pH for Western Australian groundwaters.

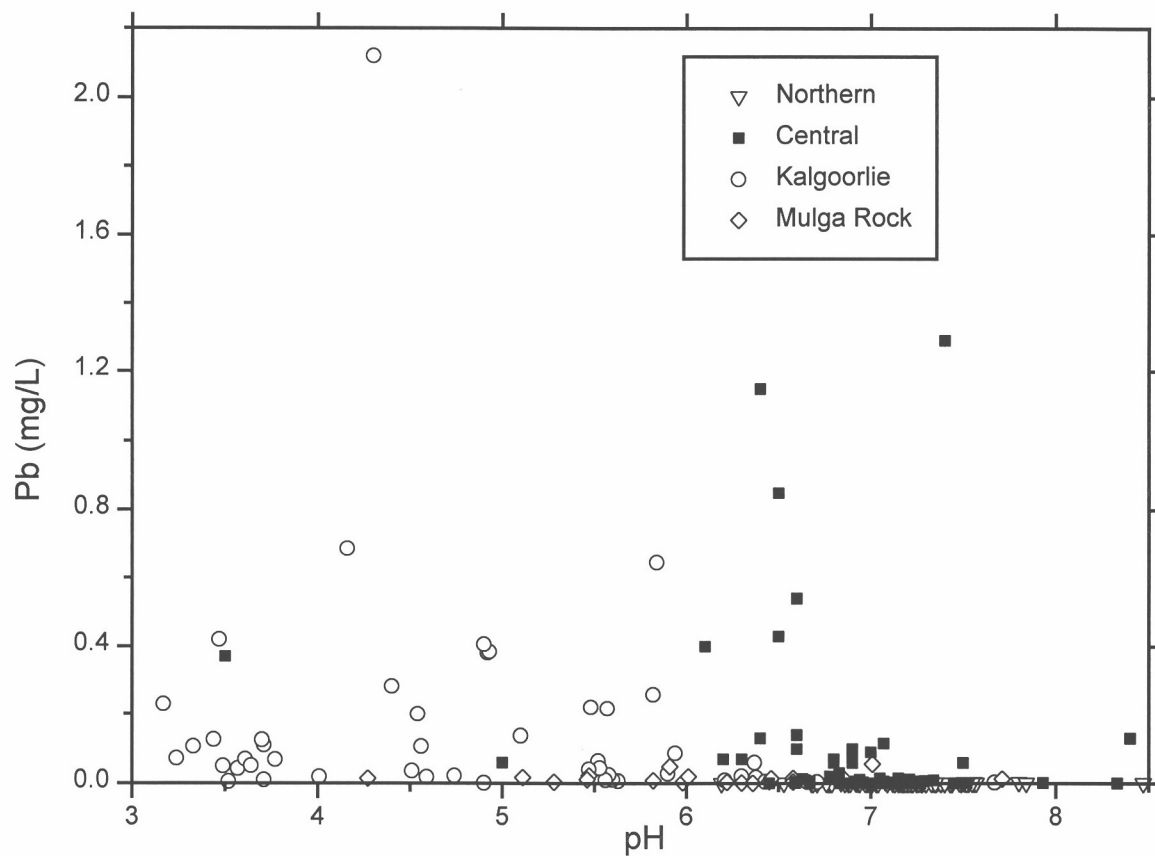


Figure A1.51: Pb vs. pH for Western Australian groundwaters.

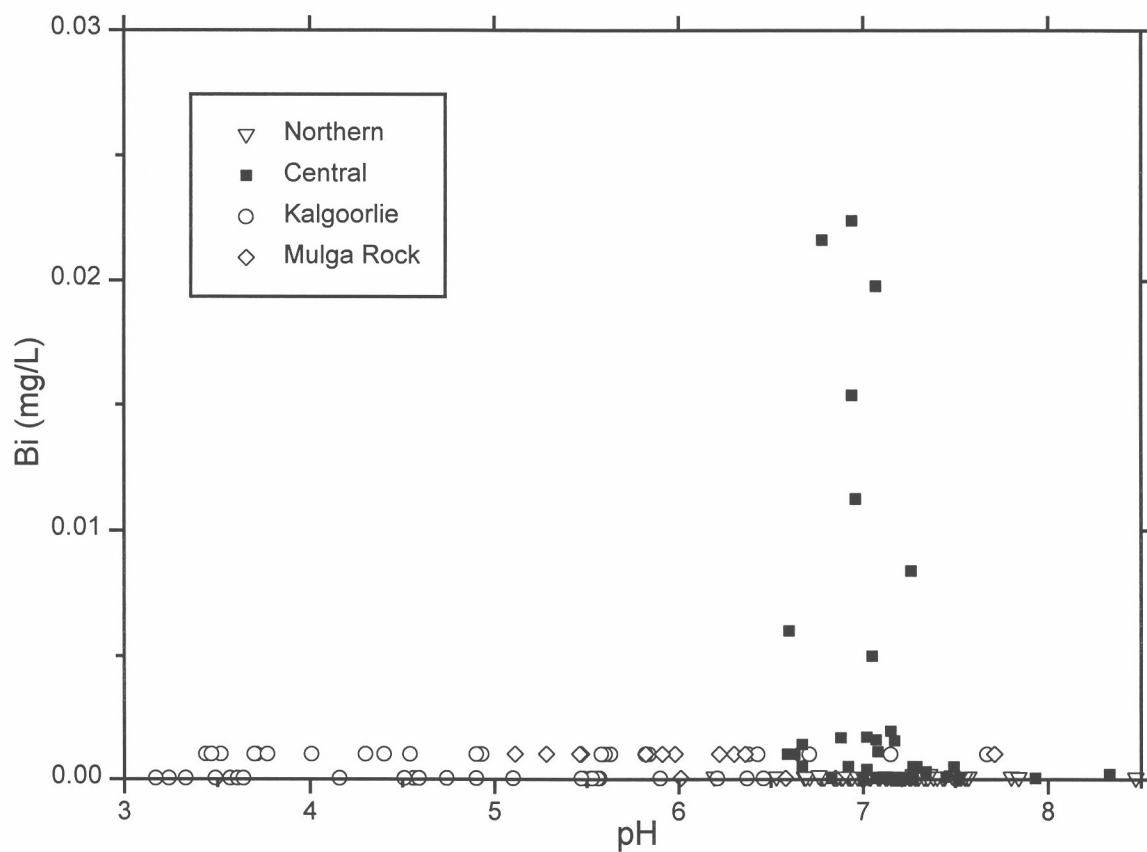


Figure A1.52: Bi vs. pH for Western Australian groundwaters.

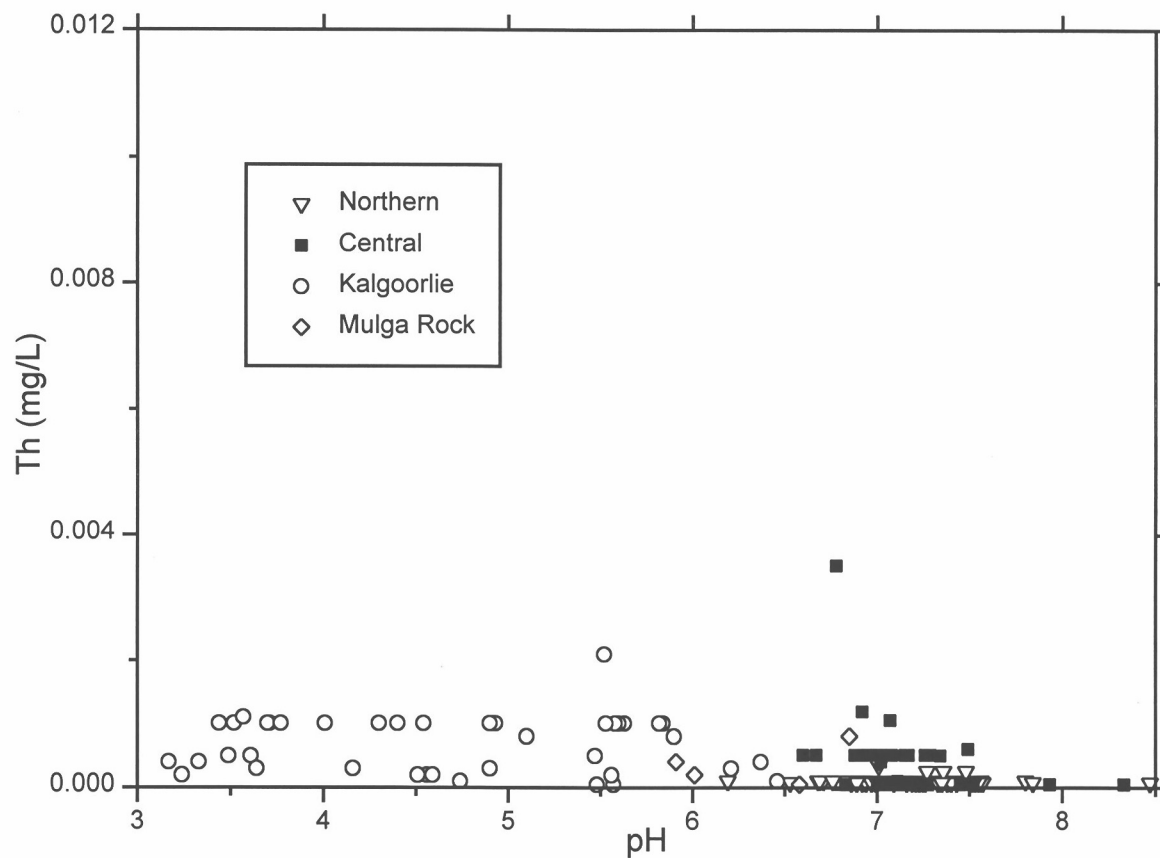


Figure A1.53: Th vs. pH for Western Australian groundwaters.

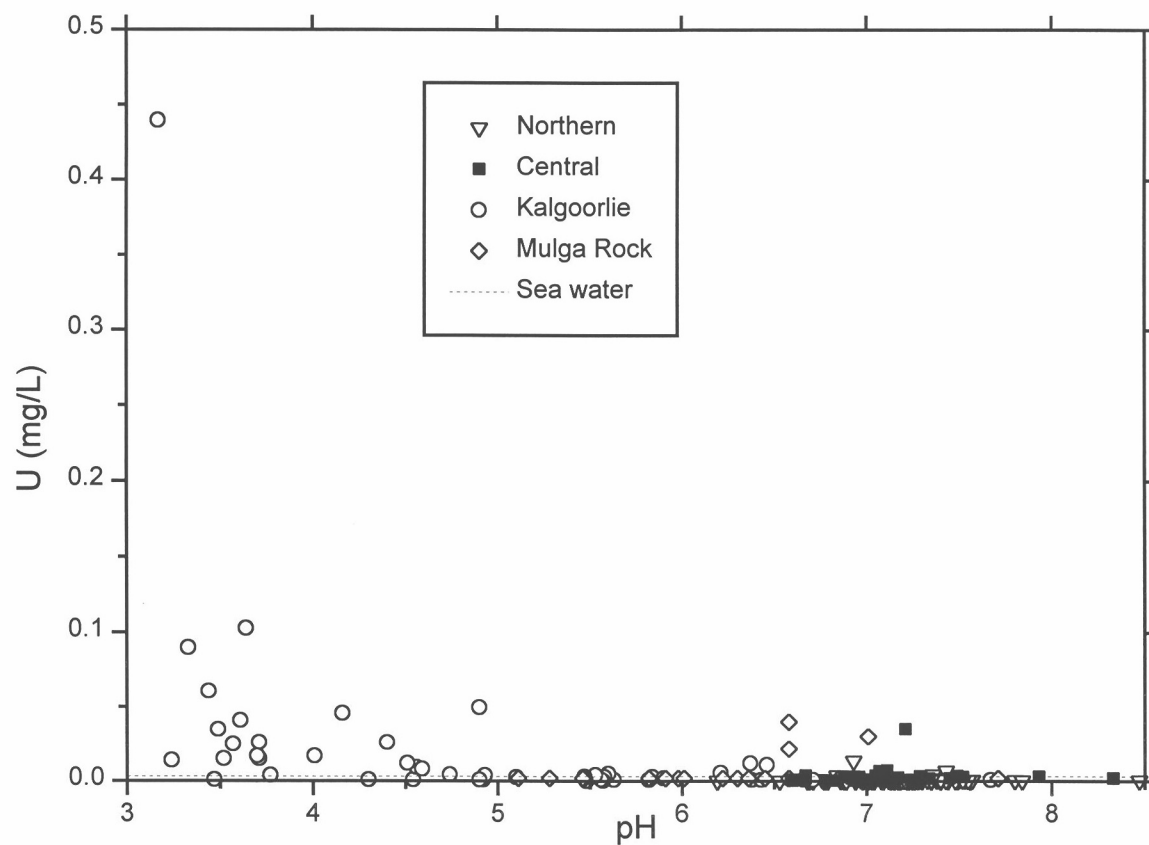


Figure A1.54: U vs. pH for Western Australian groundwaters.

Appendix 2: Speciation Analysis Output

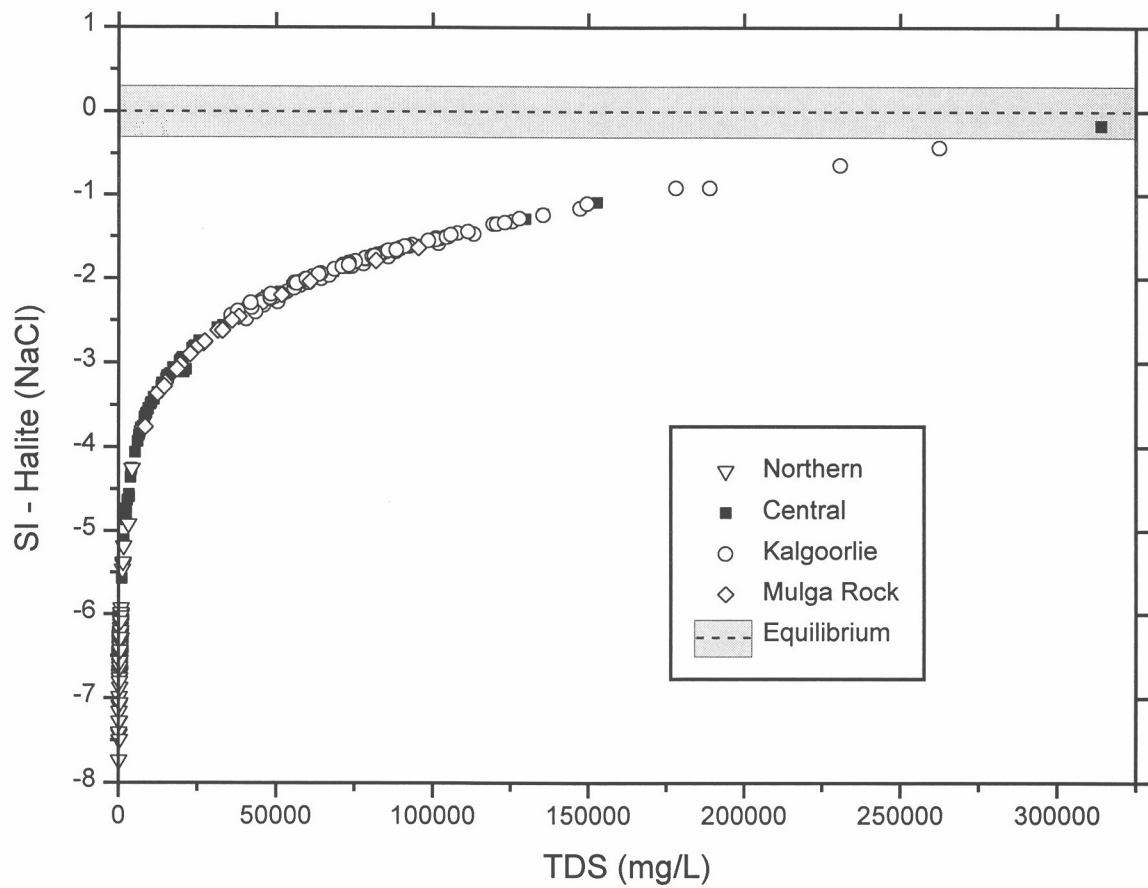


Figure A2.1: SI for halite vs. TDS for Western Australian groundwaters.

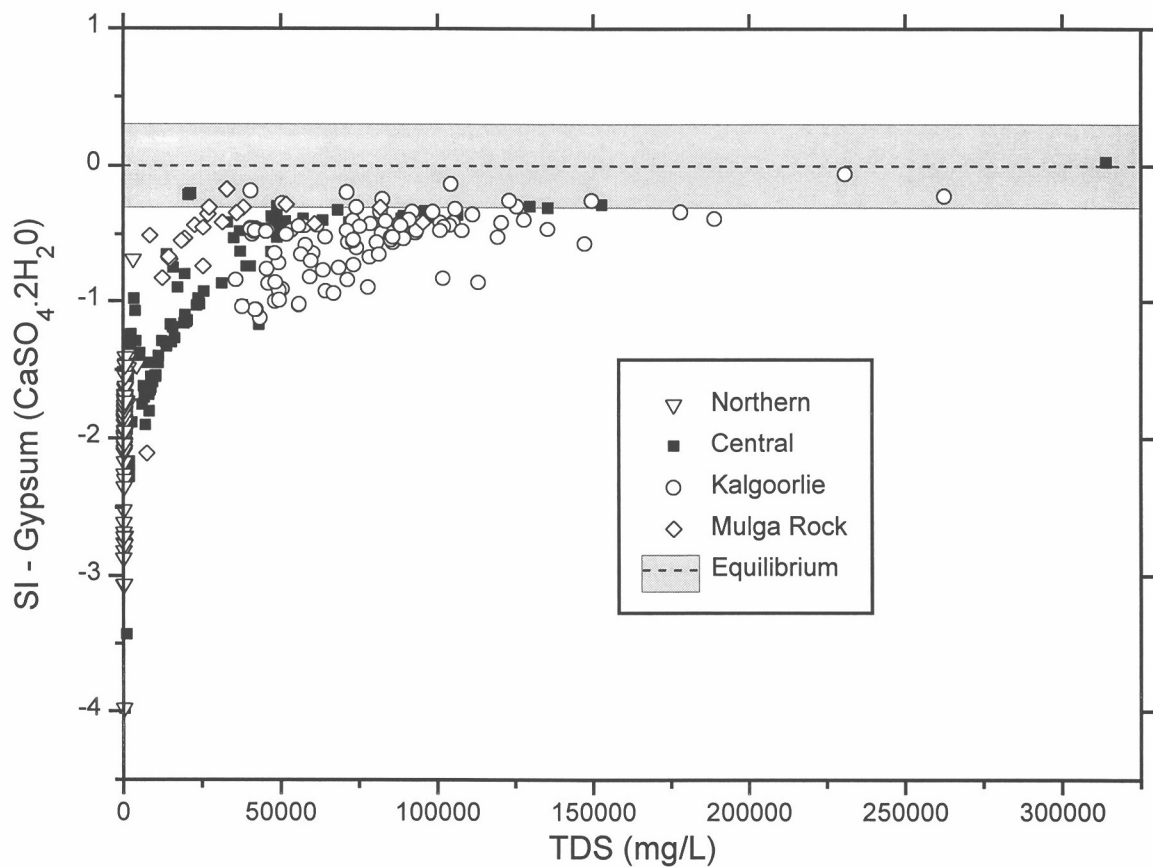


Figure A2.2: SI for gypsum vs. TDS for Western Australian groundwaters.

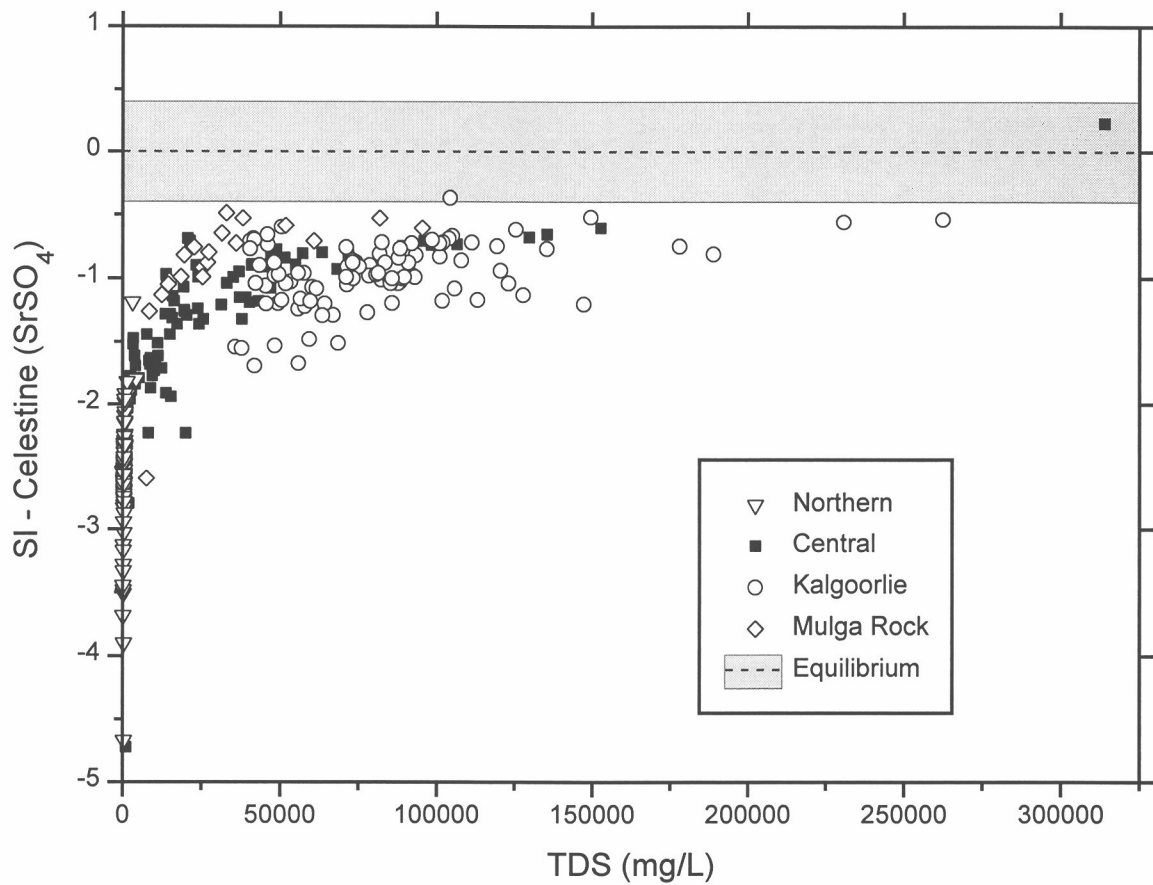


Figure A2.3: SI for celestine vs. TDS for Western Australian groundwaters.

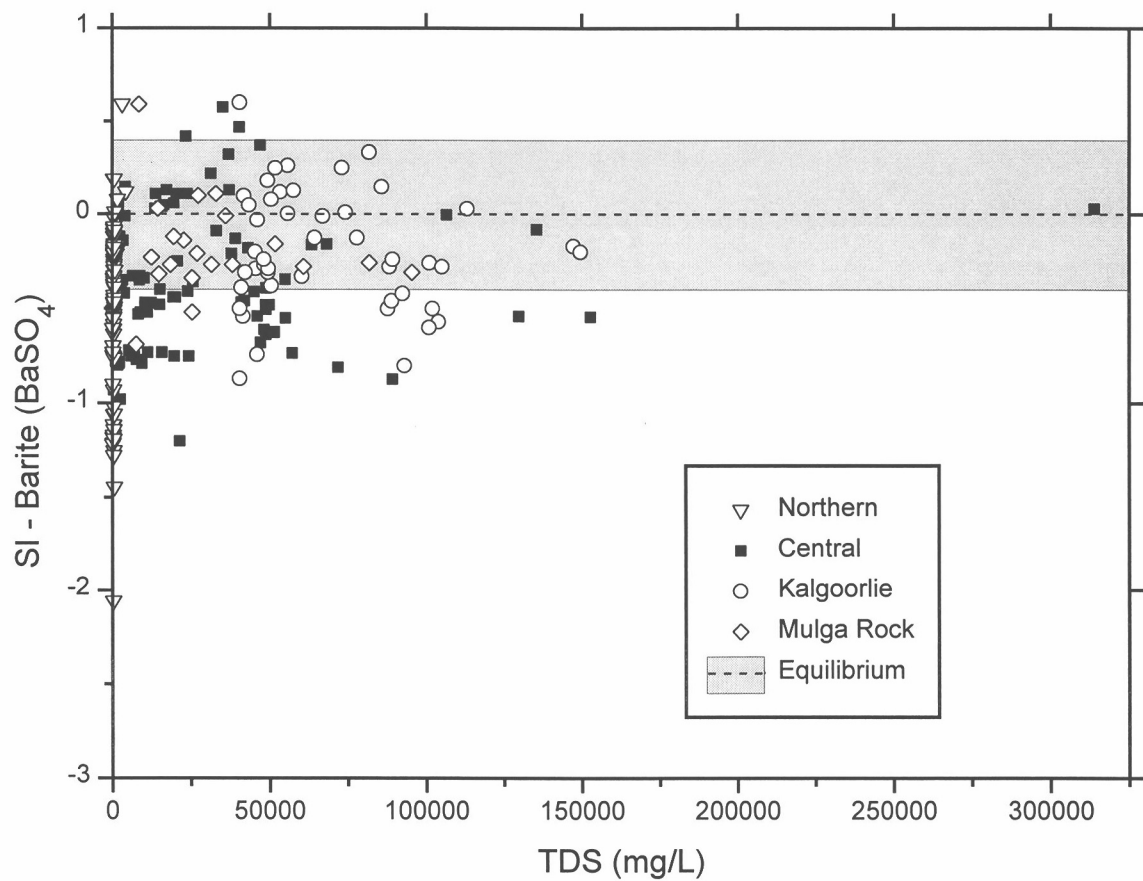


Figure A2.4: SI for barite vs. TDS for Western Australian groundwaters.

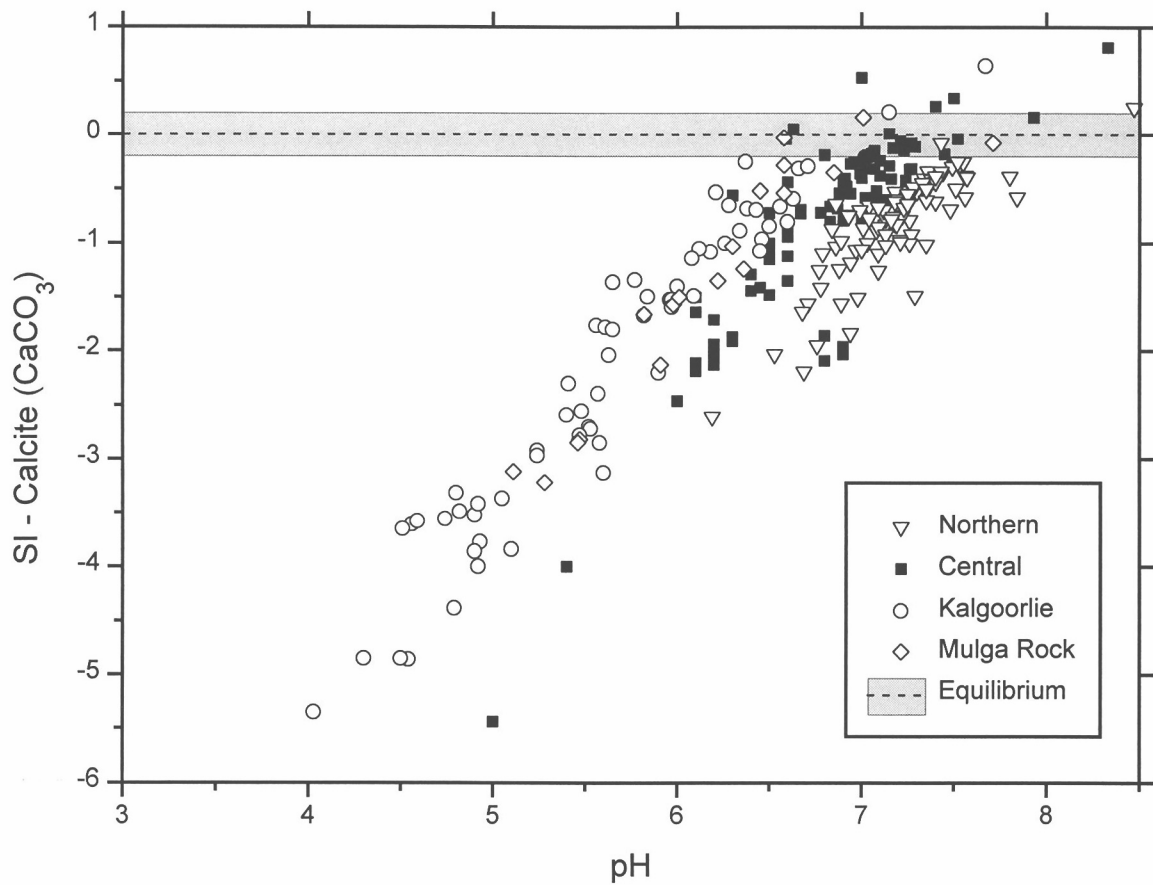


Figure A2.5: SI for calcite vs. pH for Western Australian groundwaters.

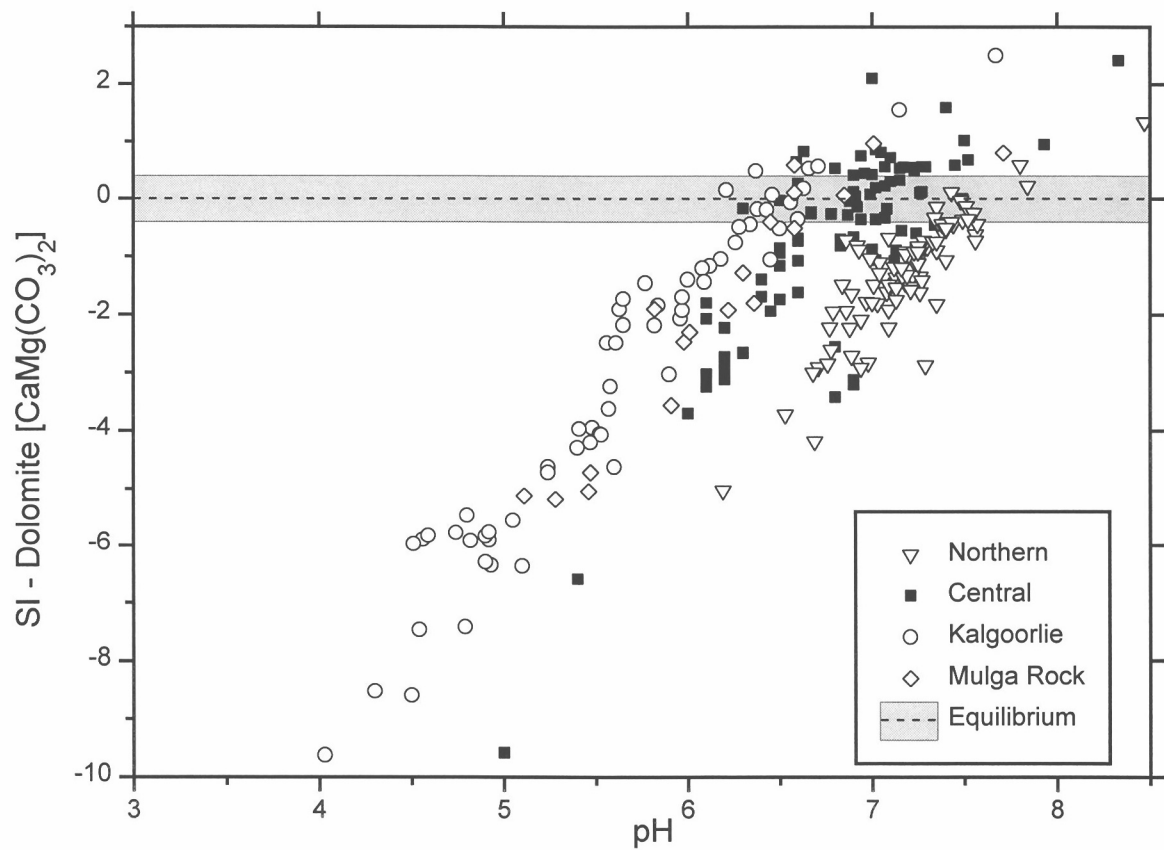


Figure A2.6: SI for dolomite vs. pH for Western Australian groundwaters.

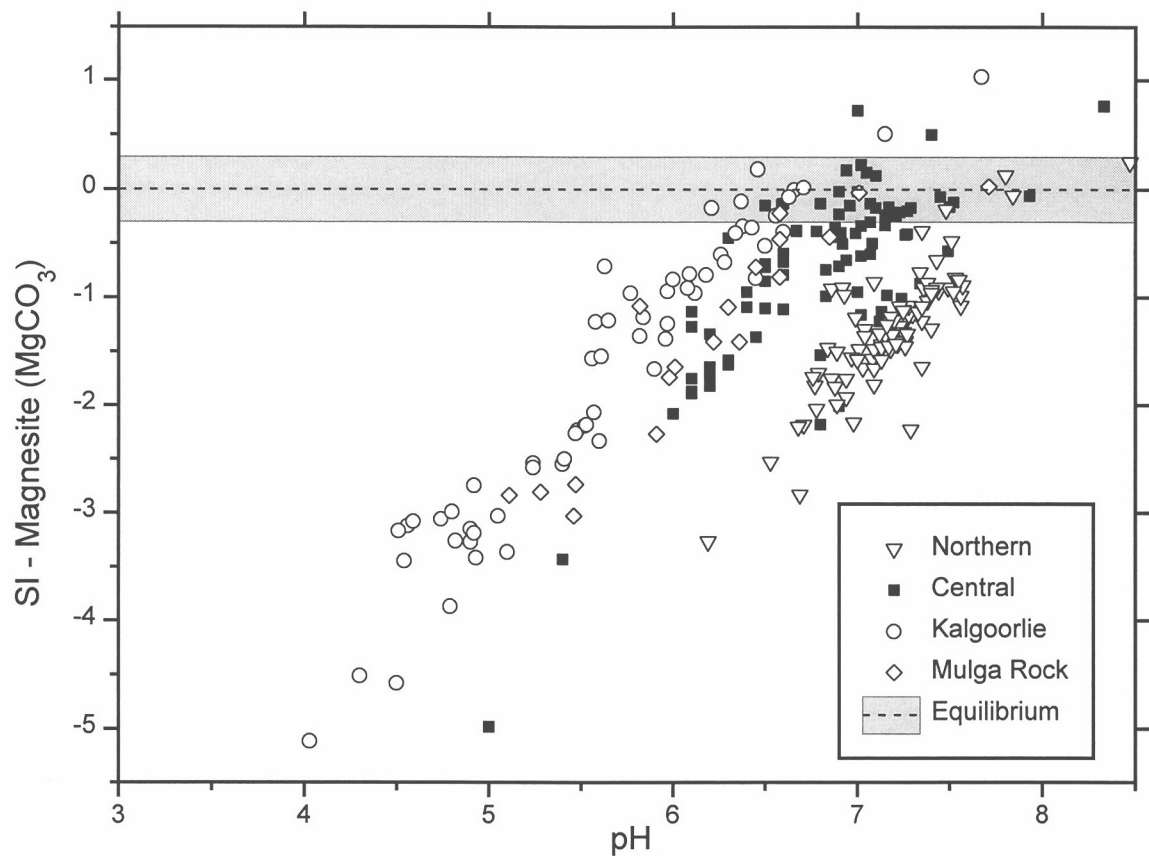


Figure A2.7 SI for magnesite vs. pH for Western Australian groundwaters.

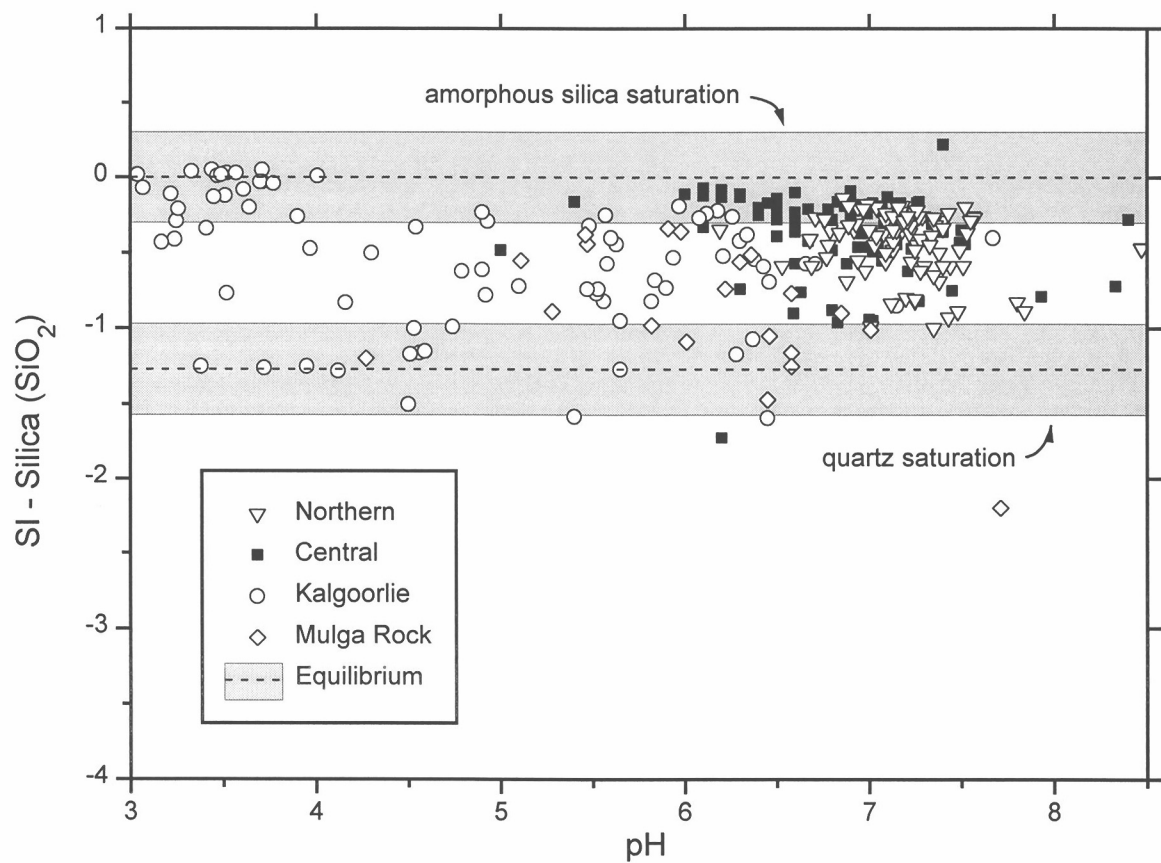


Figure A2.8: SI for silica vs. pH for Western Australian groundwaters.

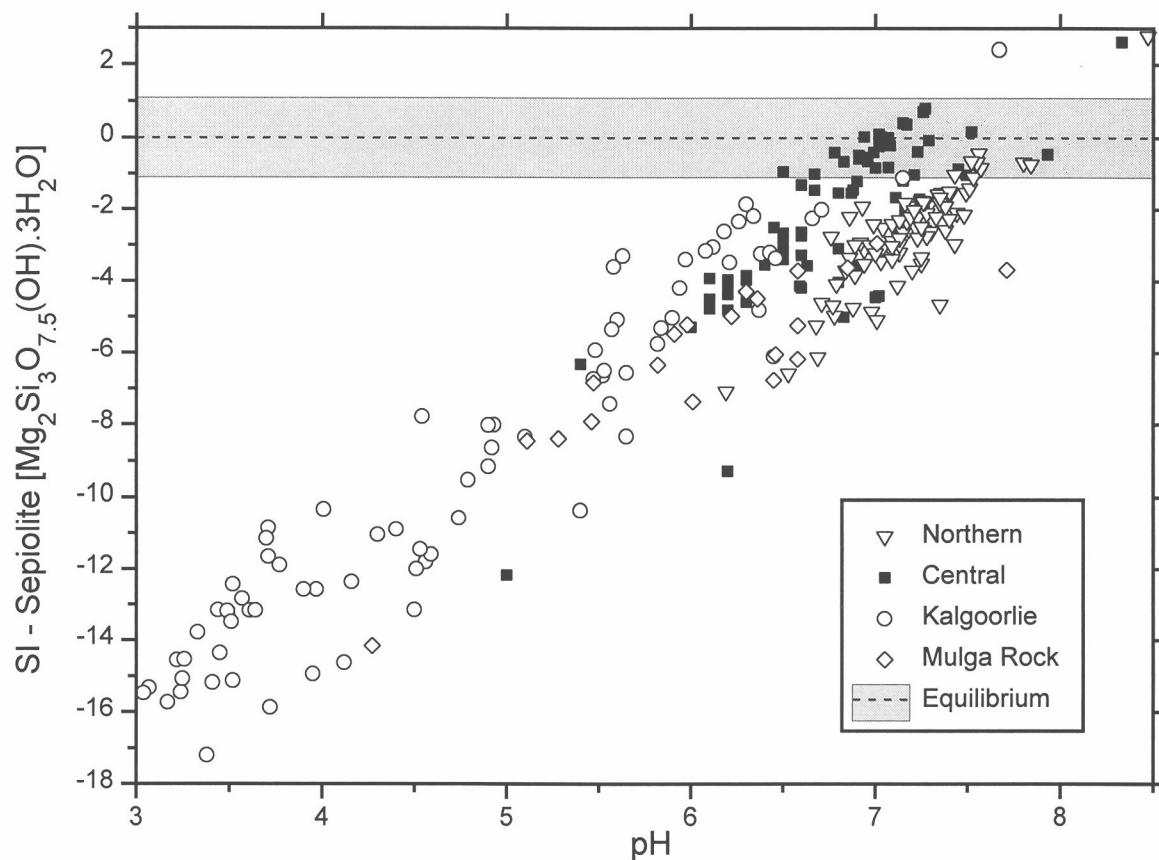


Figure A2.9: SI for sepiolite vs. pH for Western Australian groundwaters.

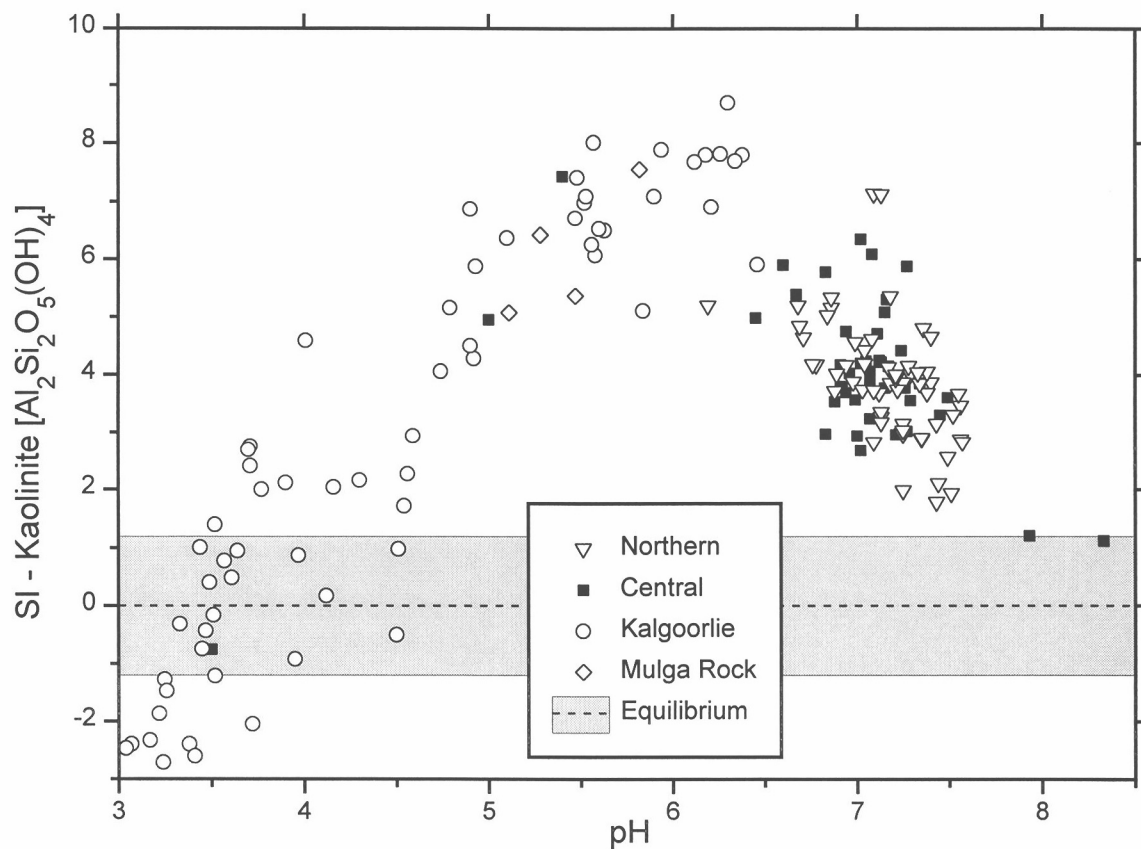


Figure A2.10: SI for kaolinite vs. pH for Western Australian groundwaters.

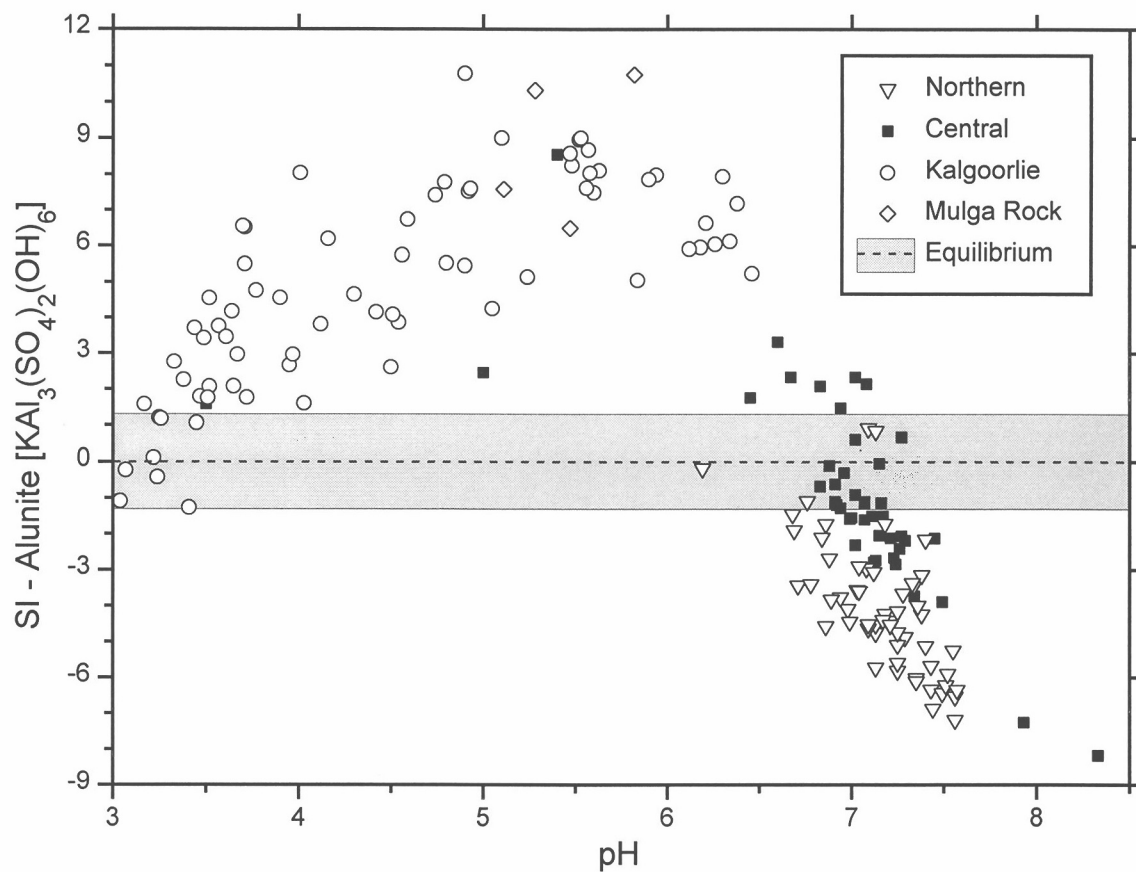


Figure A2.11: SI for alunite vs. pH for Western Australian groundwaters.

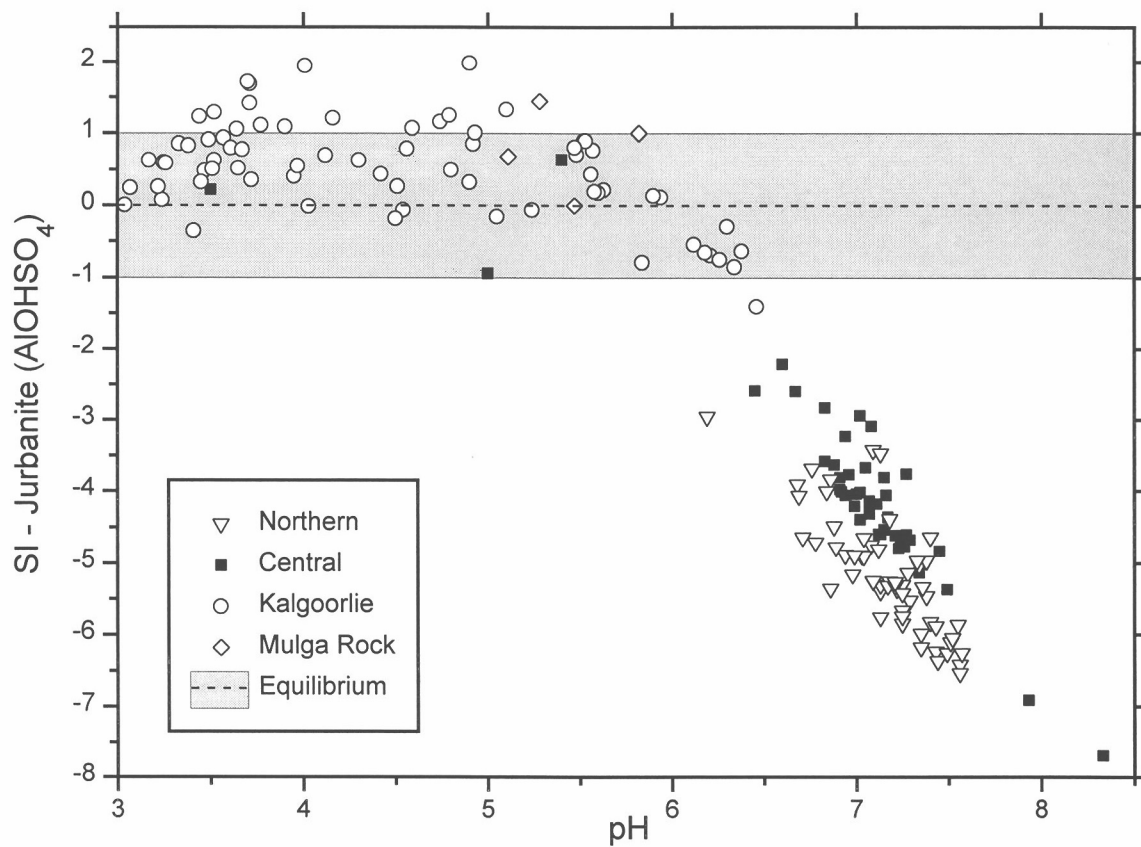


Figure A2.12: SI for jurbanite vs. pH for Western Australian groundwaters.

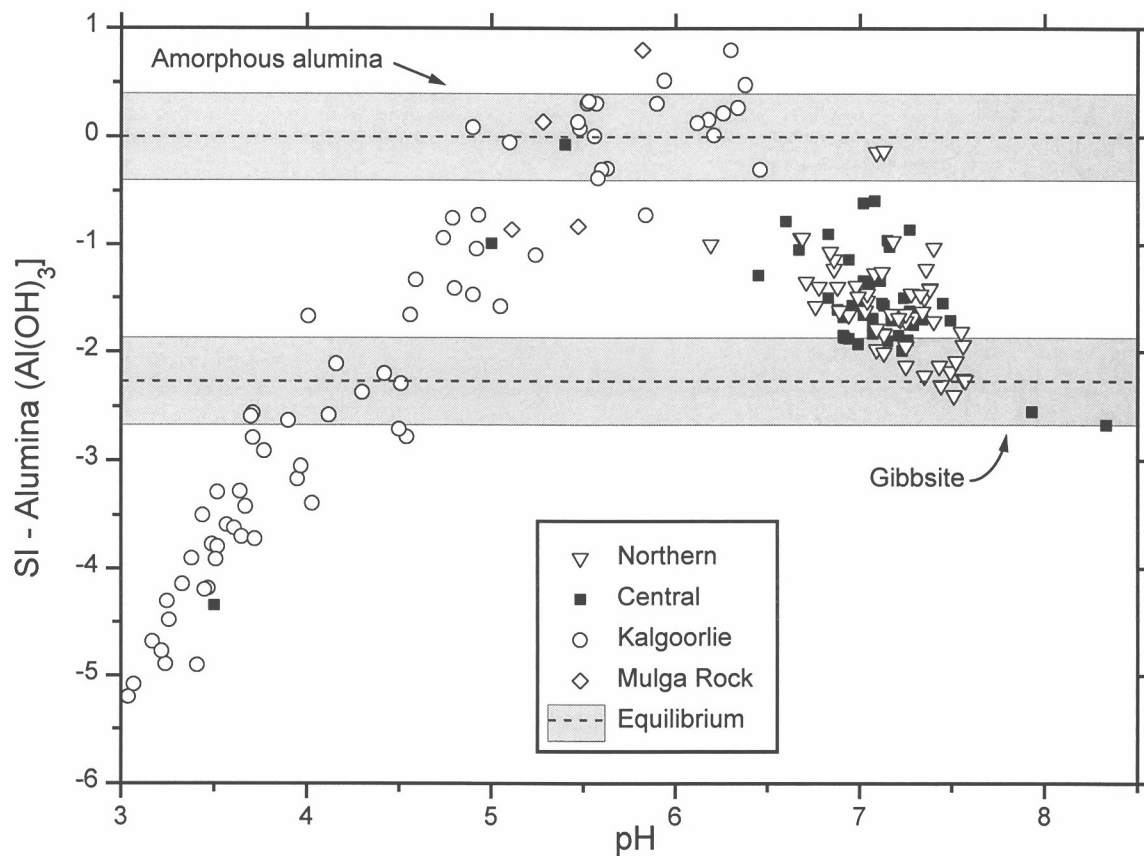


Figure A2.13: SI for alumina vs. pH for Western Australian groundwaters.

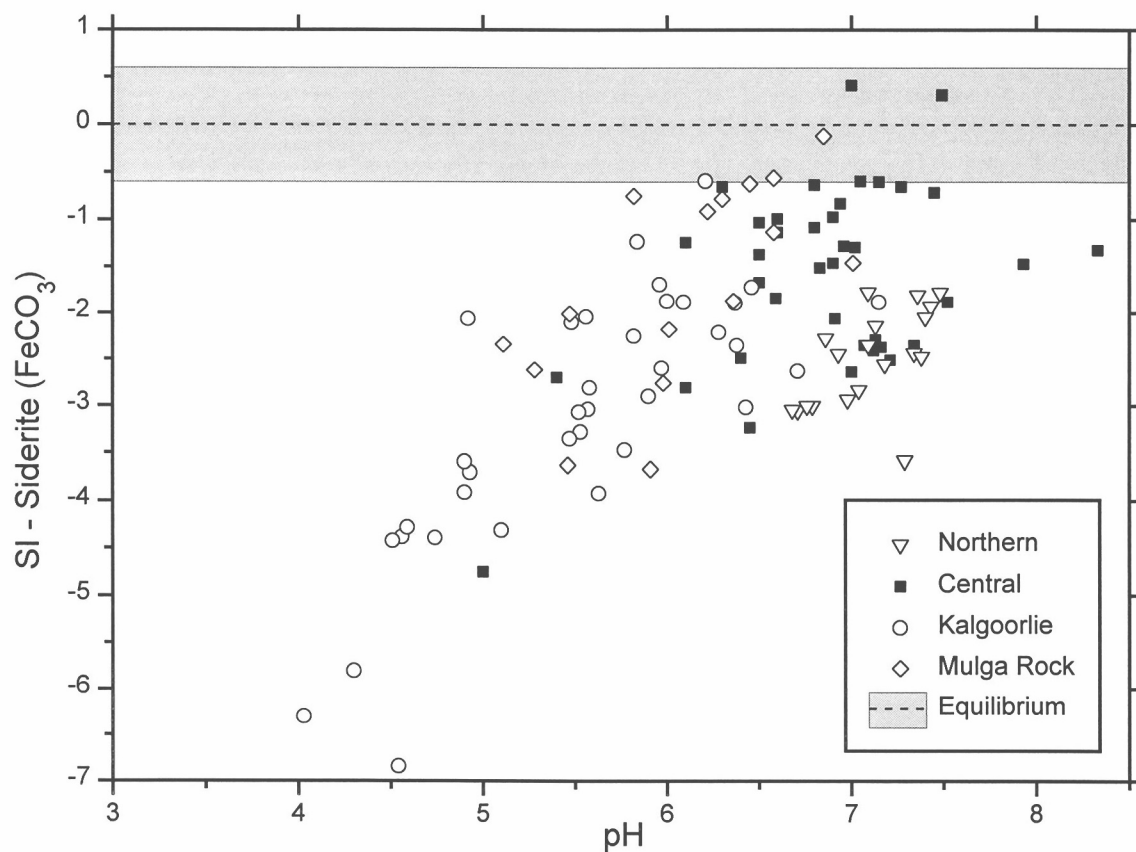


Figure A2.14: SI for siderite vs. pH for Western Australian groundwaters.

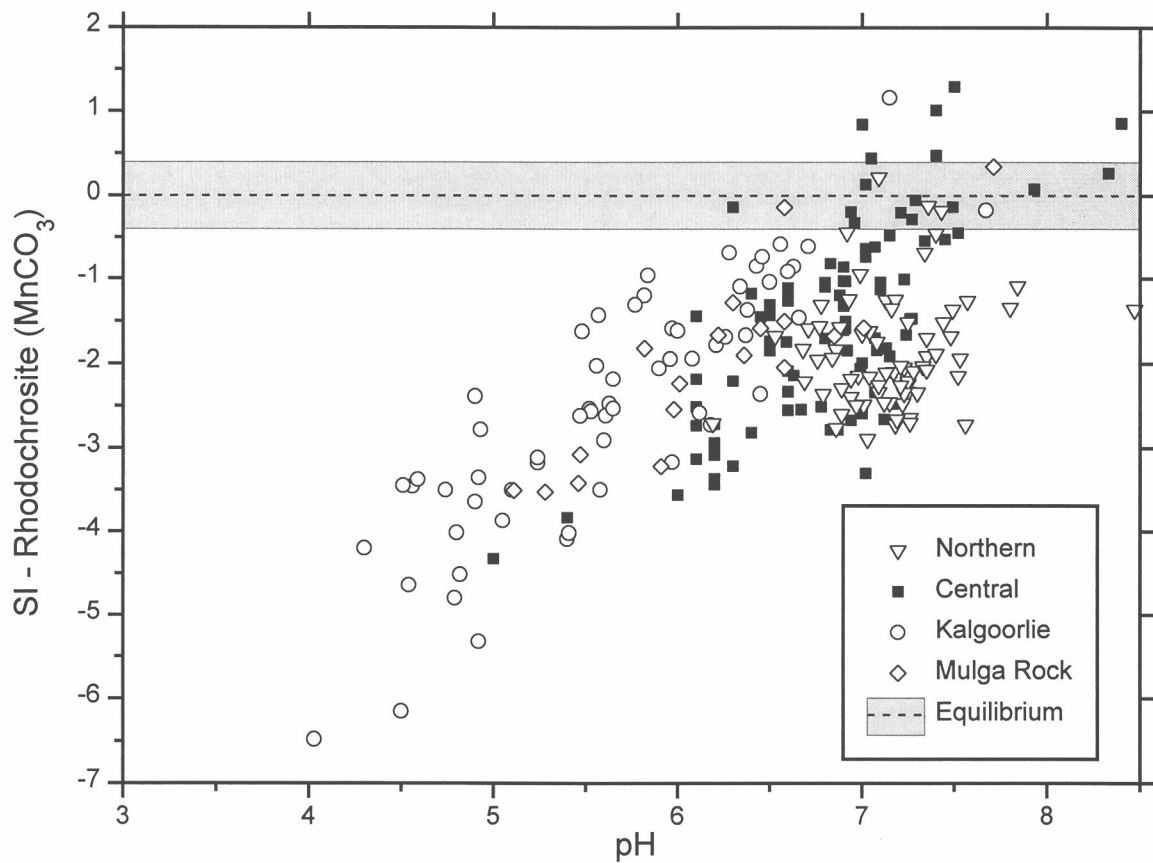


Figure A2.15: SI for rhodochrosite vs. pH for Western Australian groundwaters.

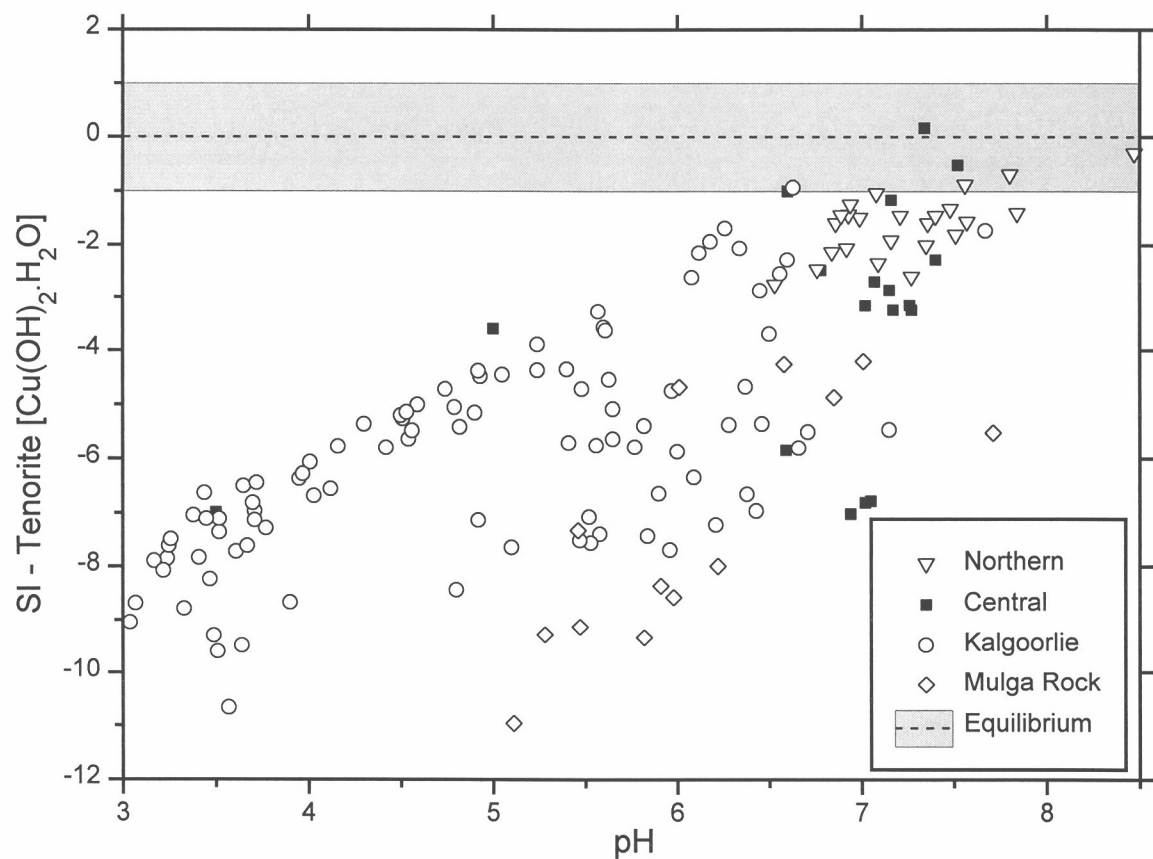


Figure A2.16: SI for tenorite vs. pH for Western Australian groundwaters.

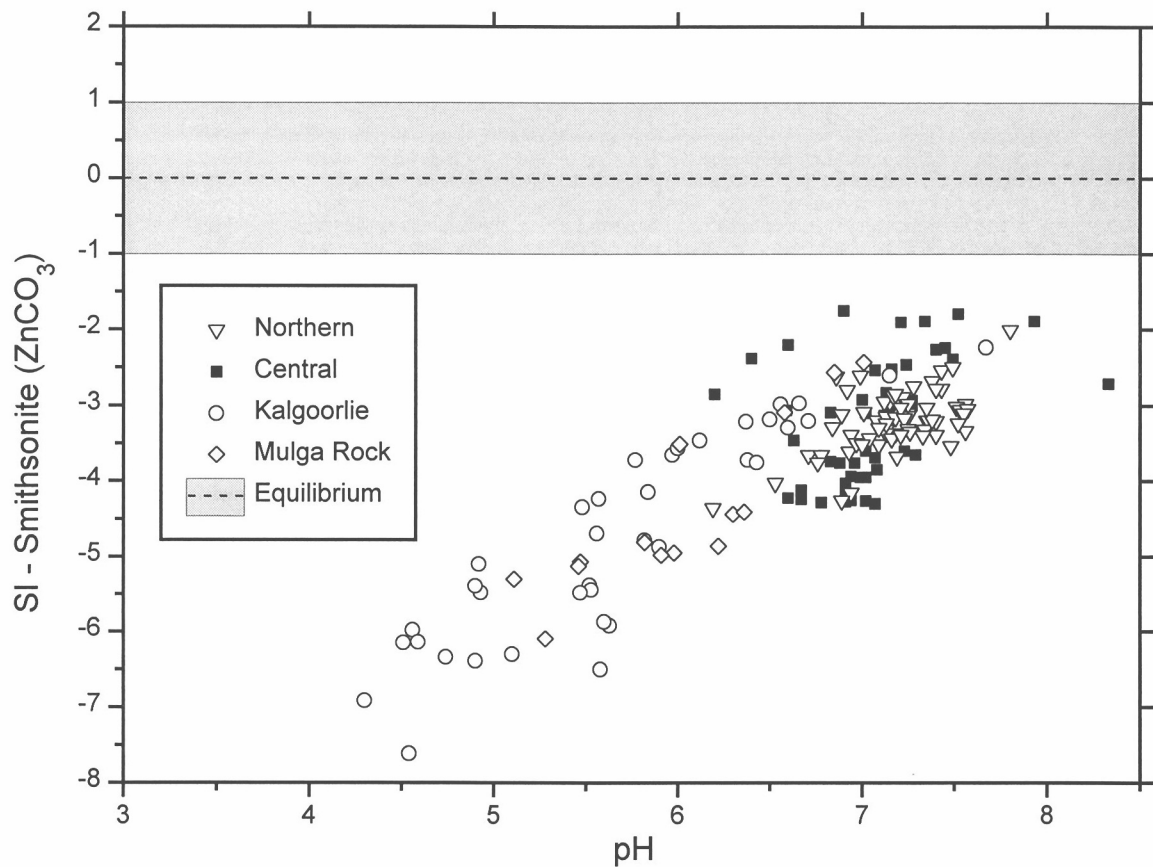


Figure A2.17: SI for smithsonite vs. pH for Western Australian groundwaters.

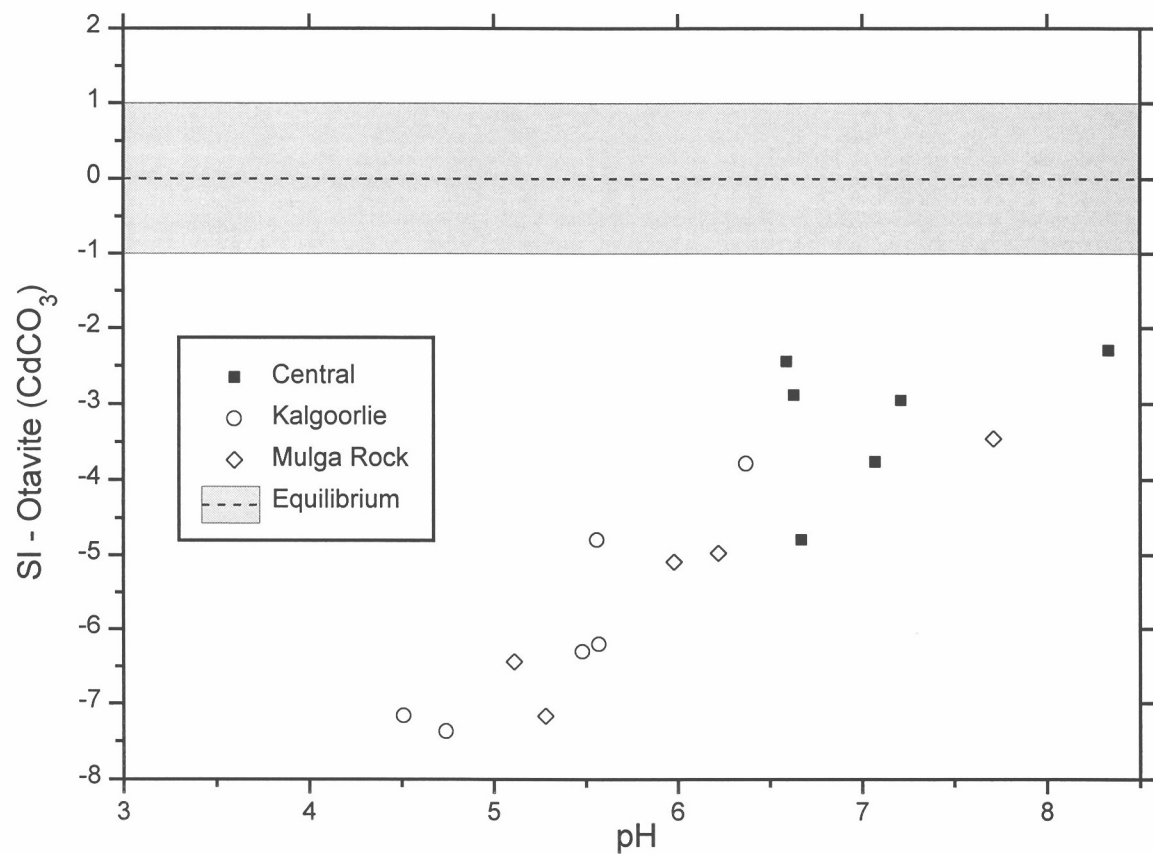


Figure A2.18: SI for otavite vs. pH for Western Australian groundwaters.

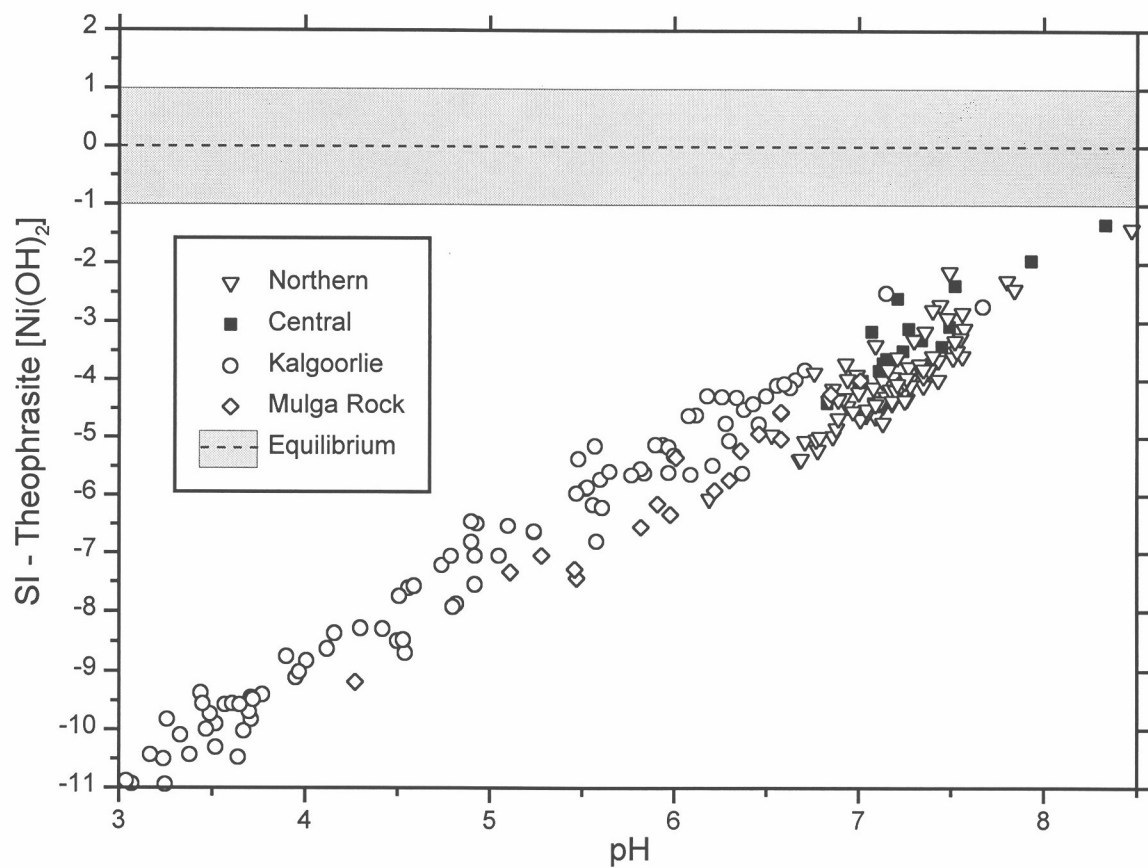


Figure A2.19: SI for theophrasite vs. pH for Western Australian groundwaters.

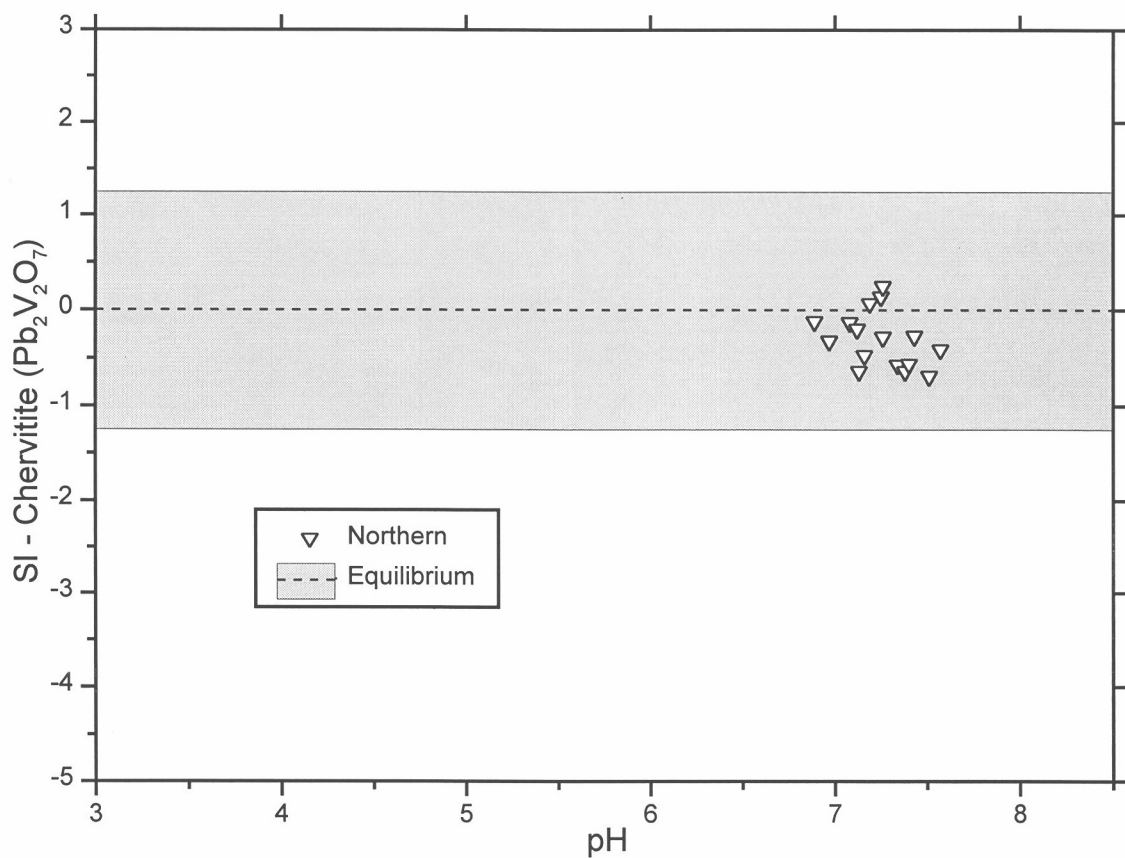


Figure A2.20: SI for chervitite vs. pH for Western Australian groundwaters.

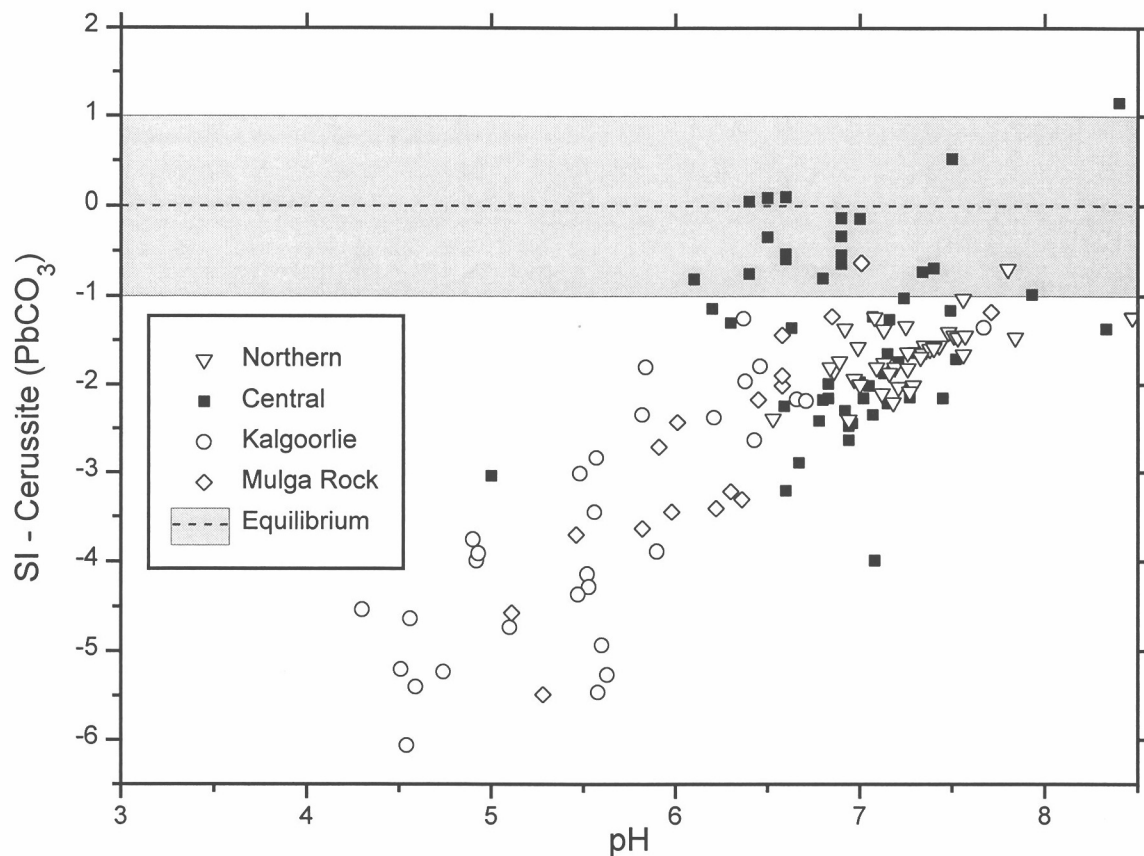


Figure A2.21: SI for cerussite vs. pH for Western Australian groundwaters.

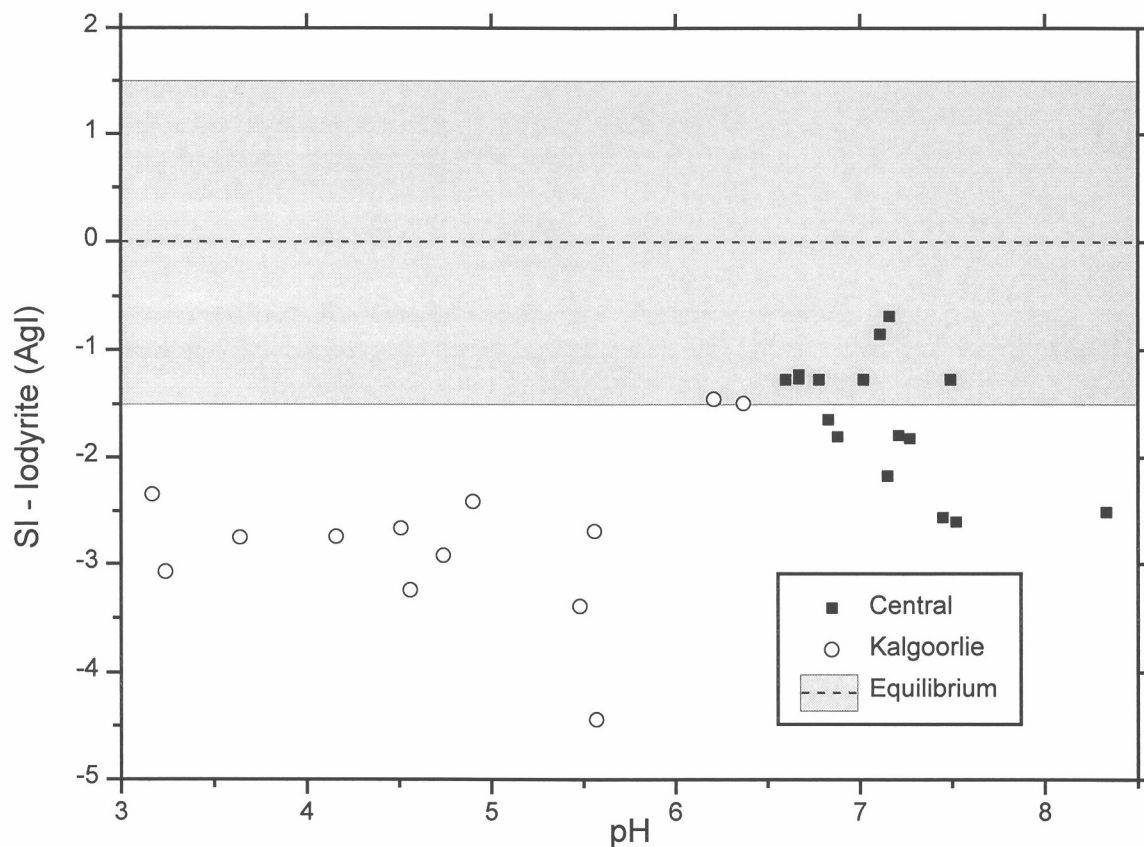


Figure A2.22: SI for iodyrite vs. pH for Western Australian groundwaters.

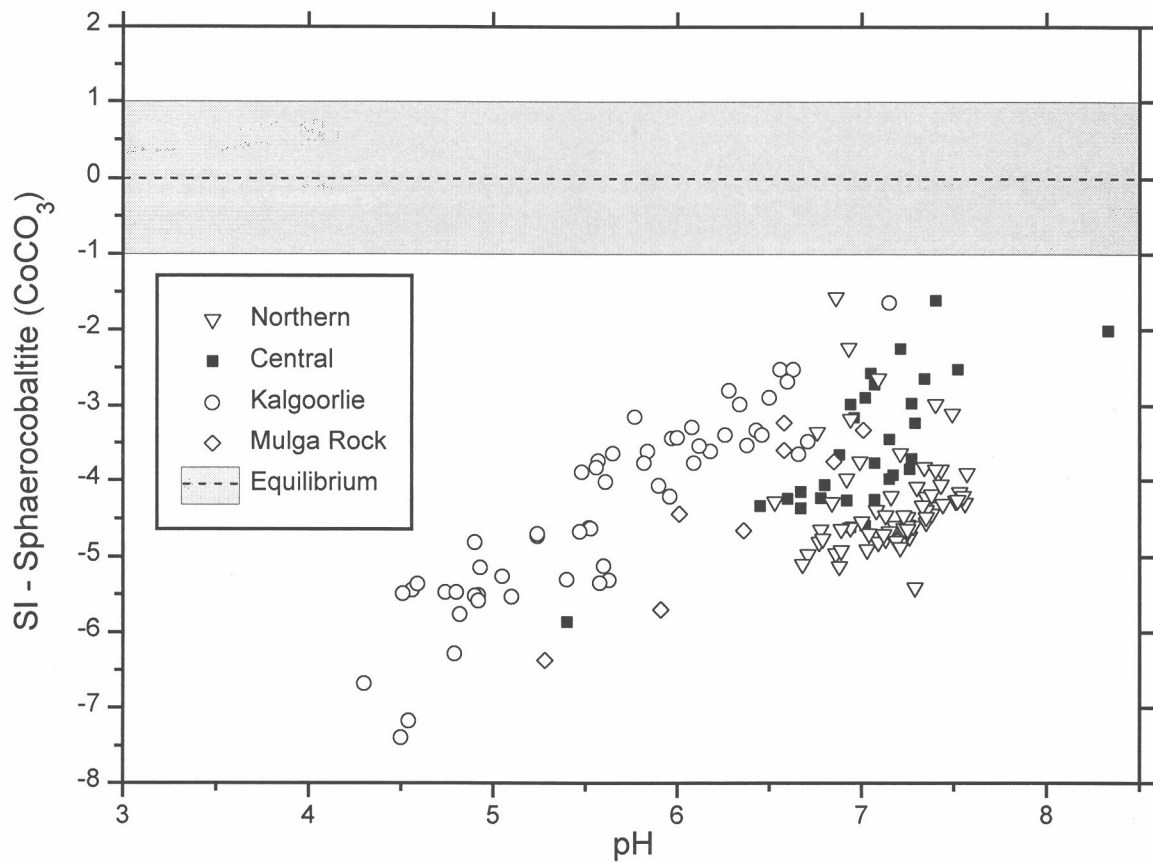


Figure A2.23: SI for sphaerocobaltite vs. pH for Western Australian groundwaters.

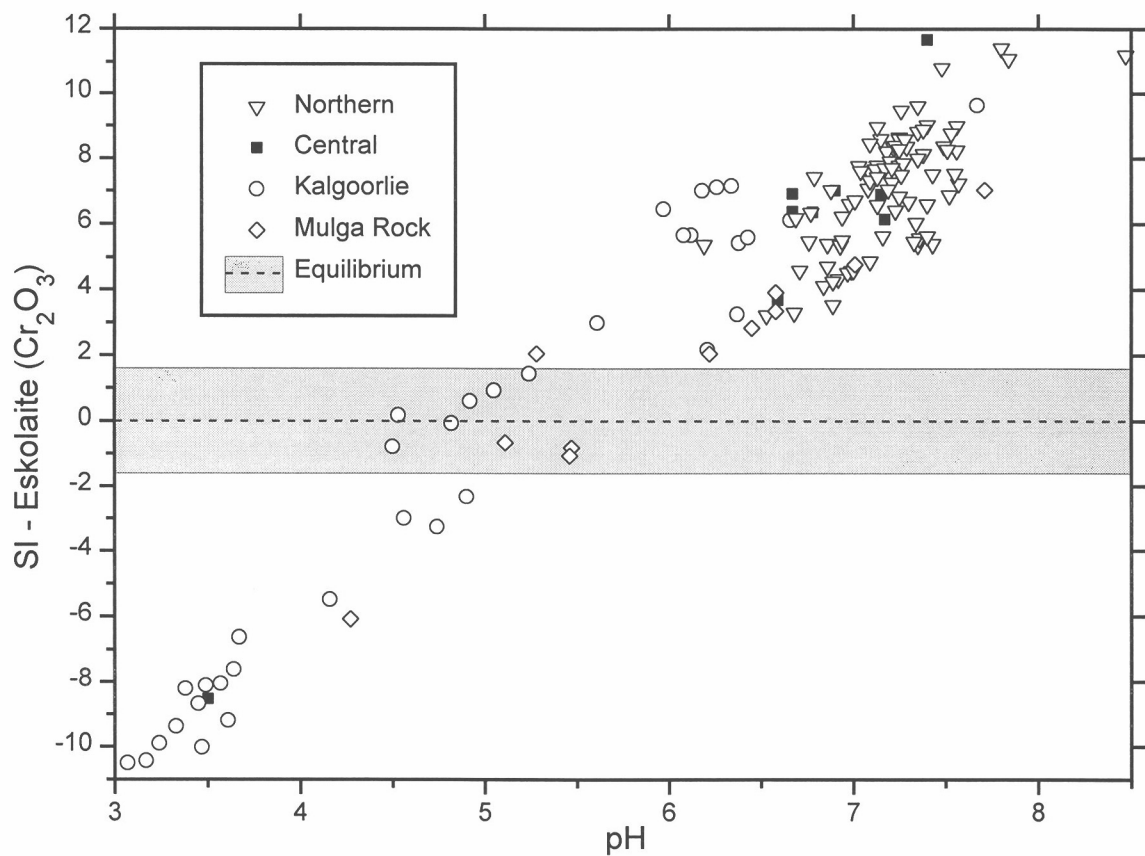


Figure A2.24: SI for eskolaite vs. pH for Western Australian groundwaters.

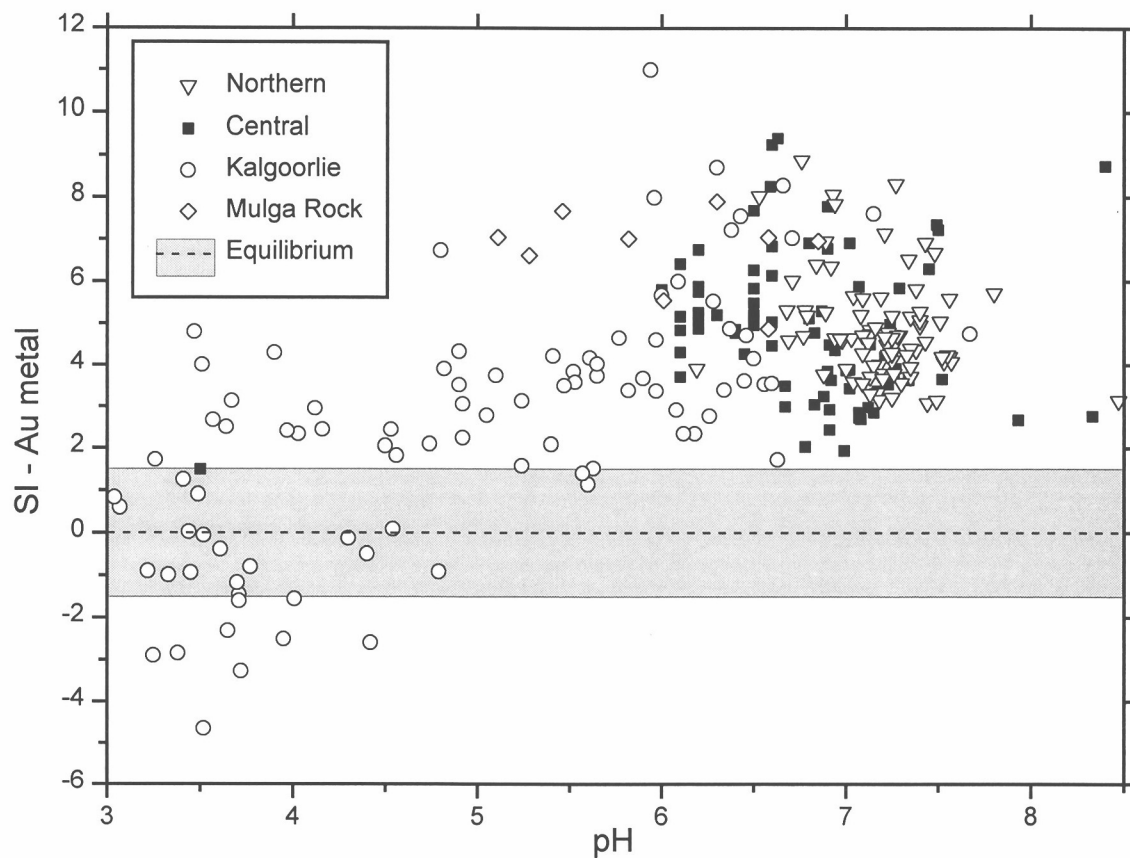


Figure A2.25: SI for Au metal vs. pH for Western Australian groundwaters.

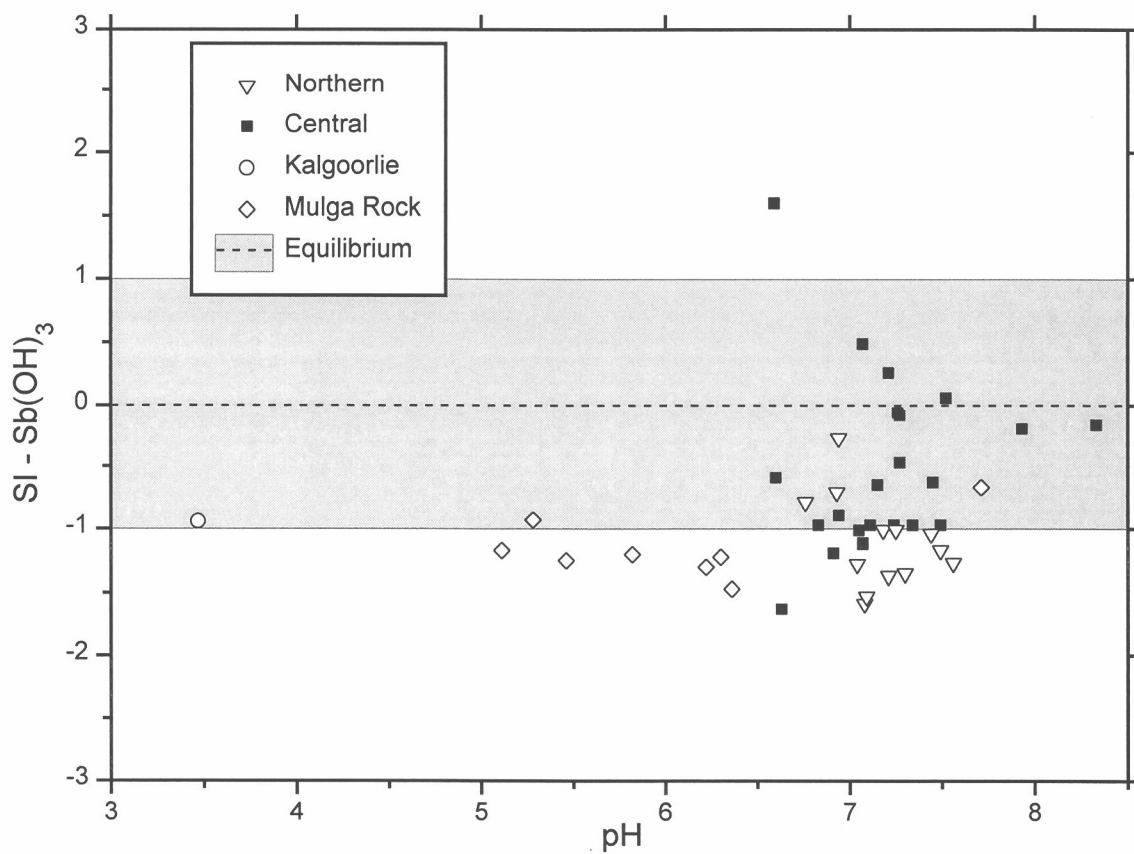


Figure A2.26: SI for Sb(OH)_3 vs. pH for Western Australian groundwaters.

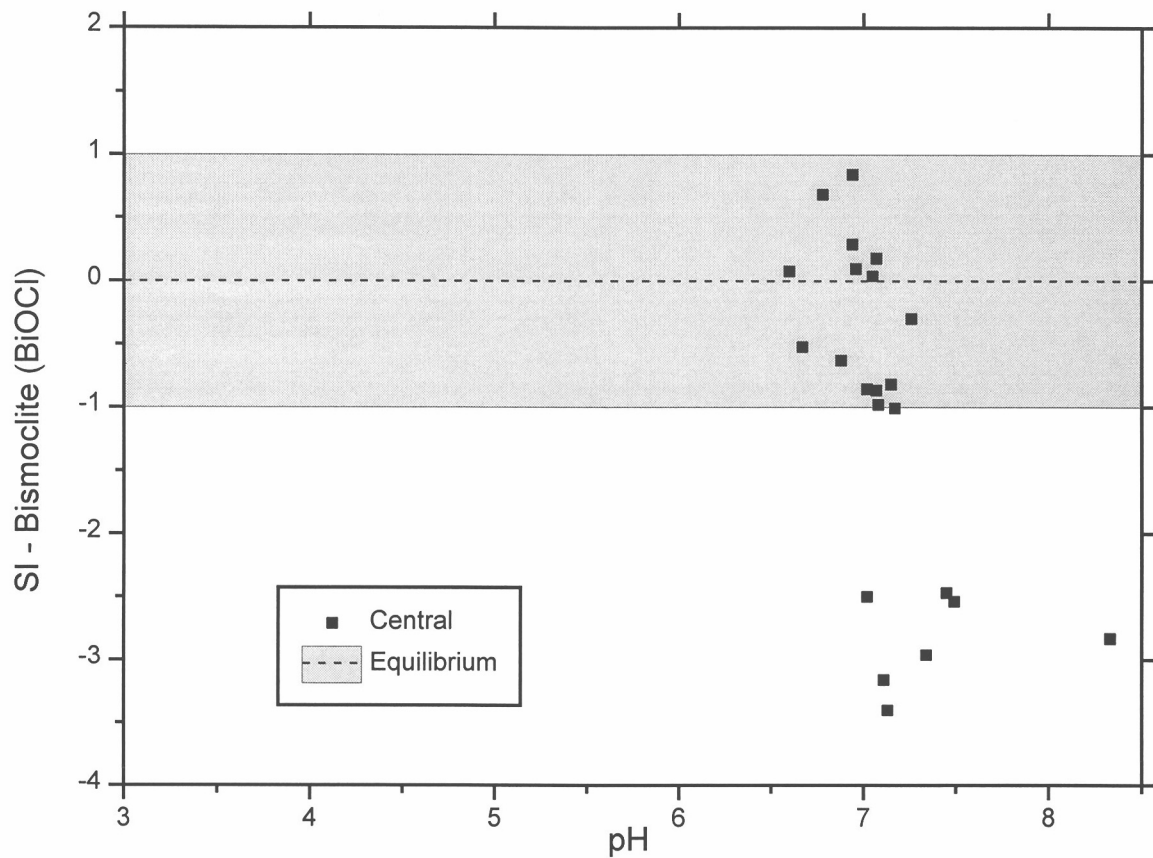


Figure A2.27: SI for bismoclite vs. pH for Western Australian groundwaters.

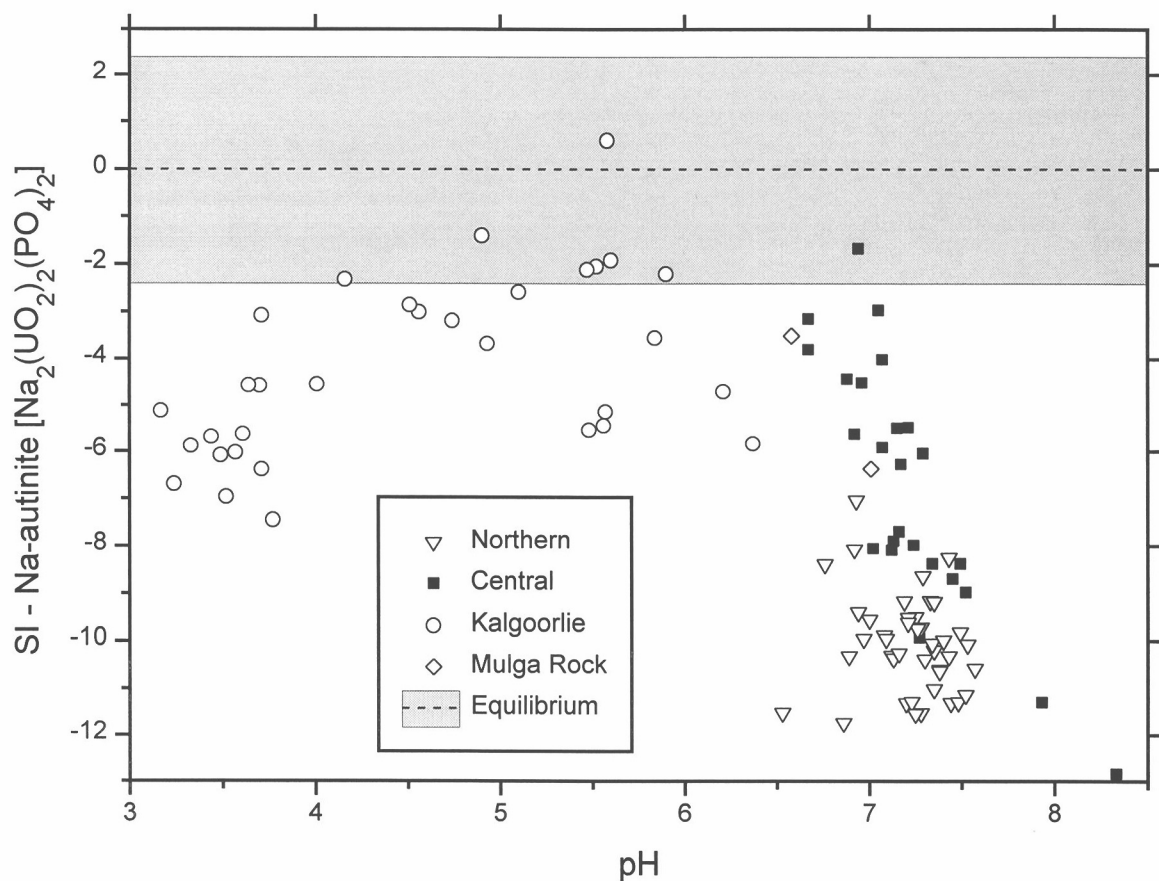


Figure A2.28: SI for Na-autinite vs. pH for Western Australian groundwaters.

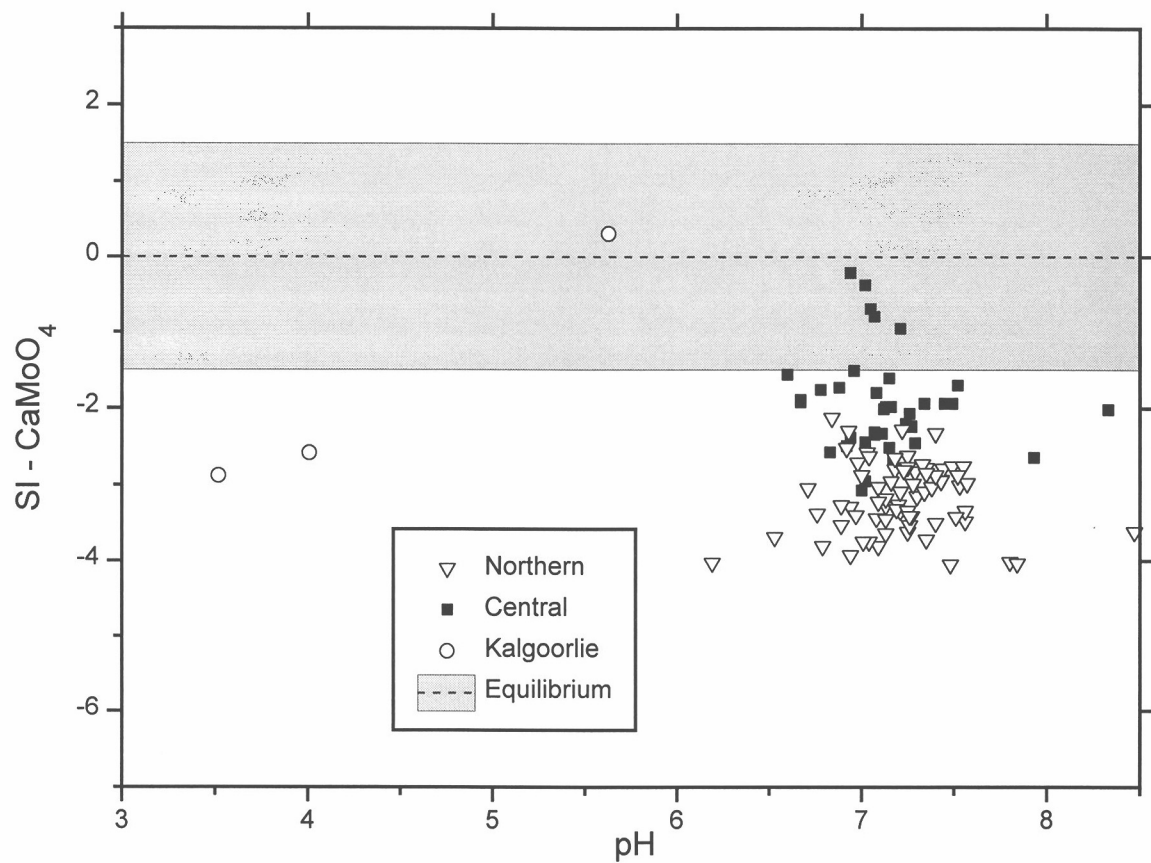


Figure A2.29: SI for CaMoO_4 vs. pH for Western Australian groundwaters.

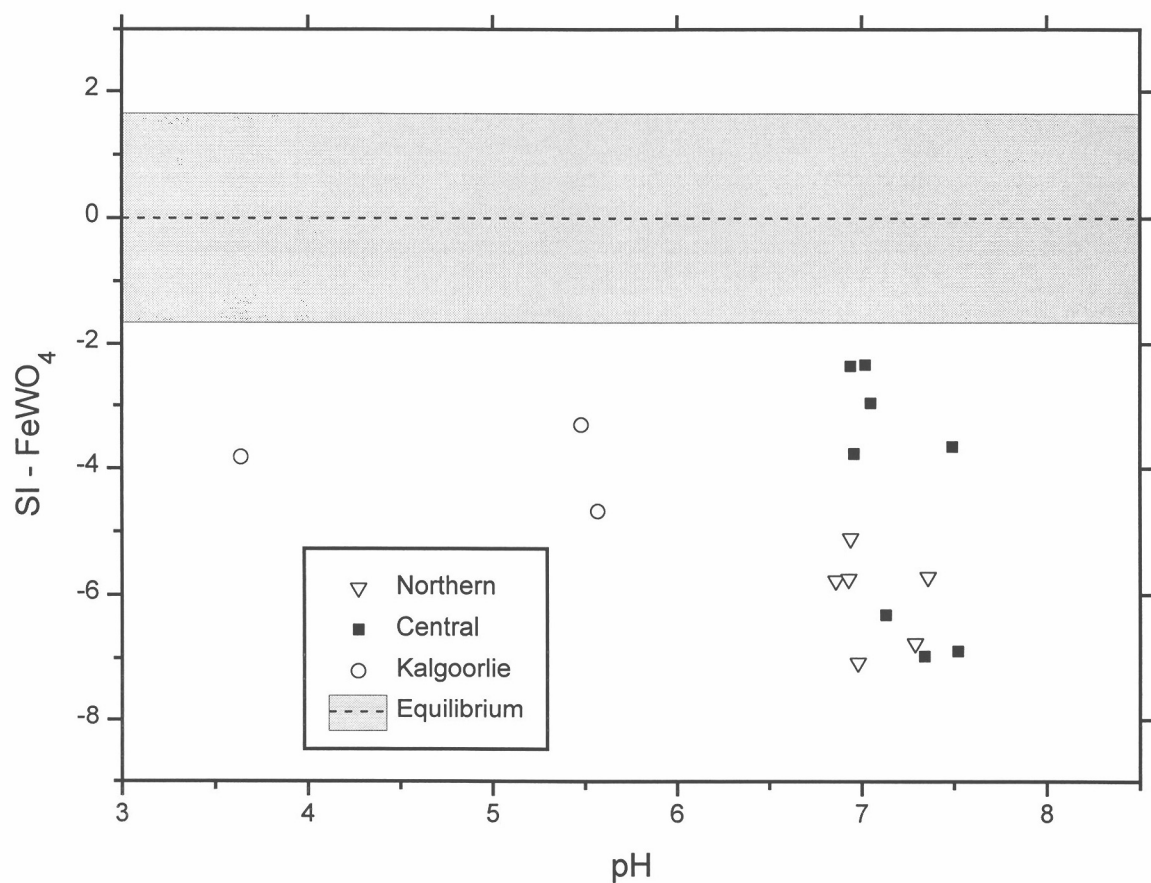


Figure A2.30: SI for FeWO_4 vs. pH for Western Australian groundwaters.

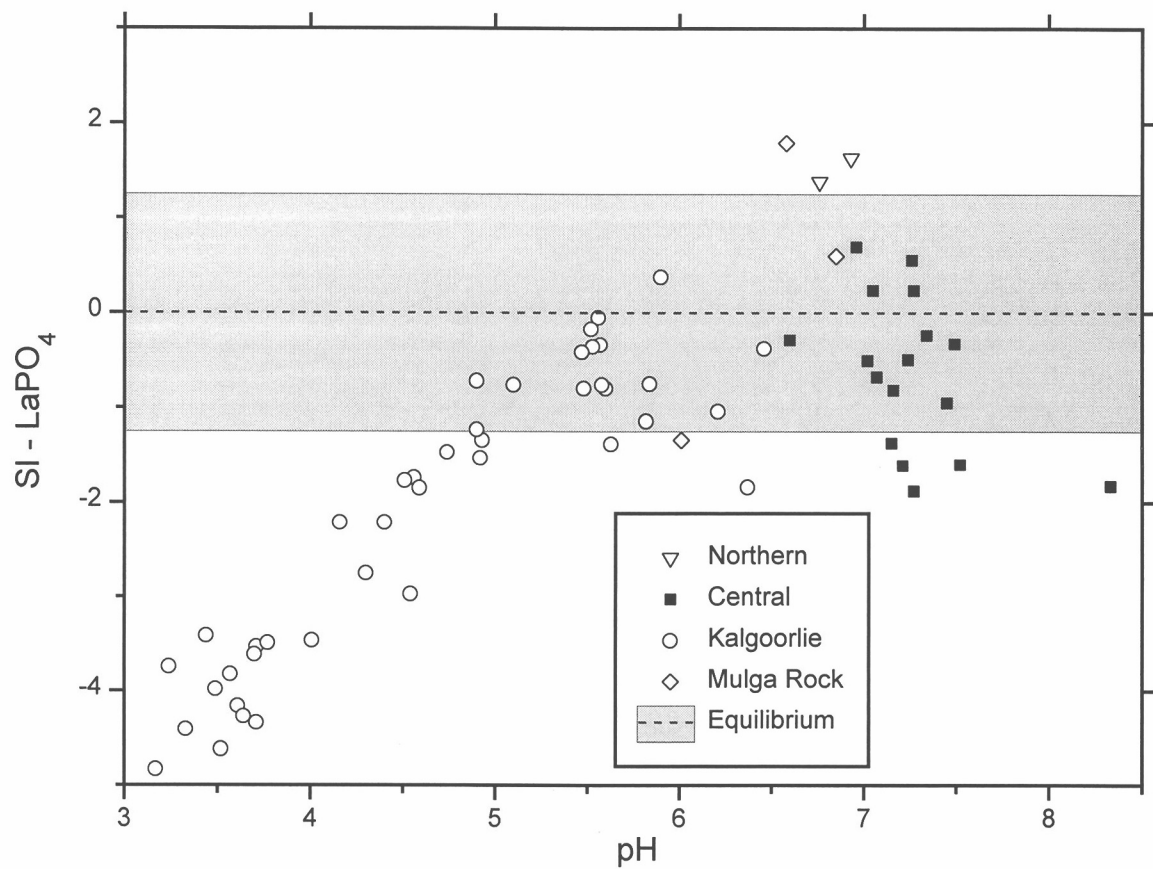


Figure A2.31: SI for LaPO_4 vs. pH for Western Australian groundwaters.

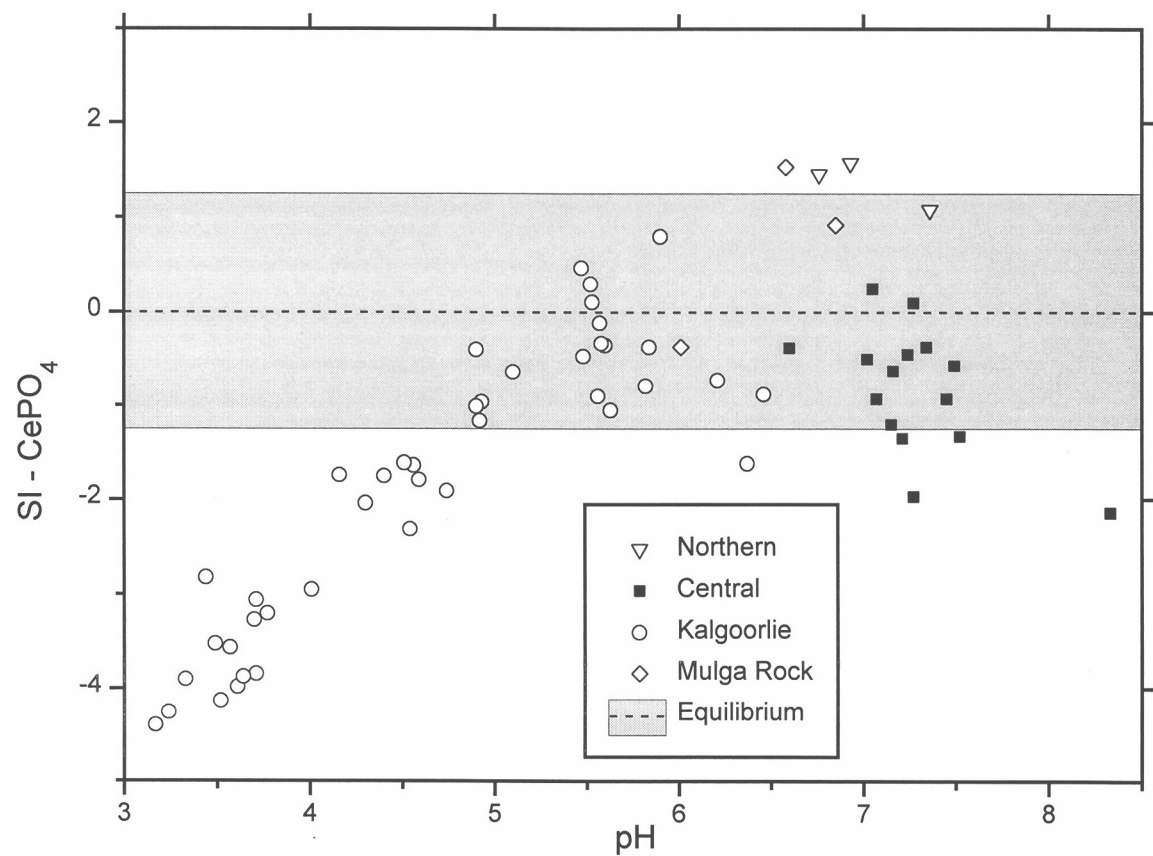


Figure A2.32: SI for CePO_4 vs. pH for Western Australian groundwaters.

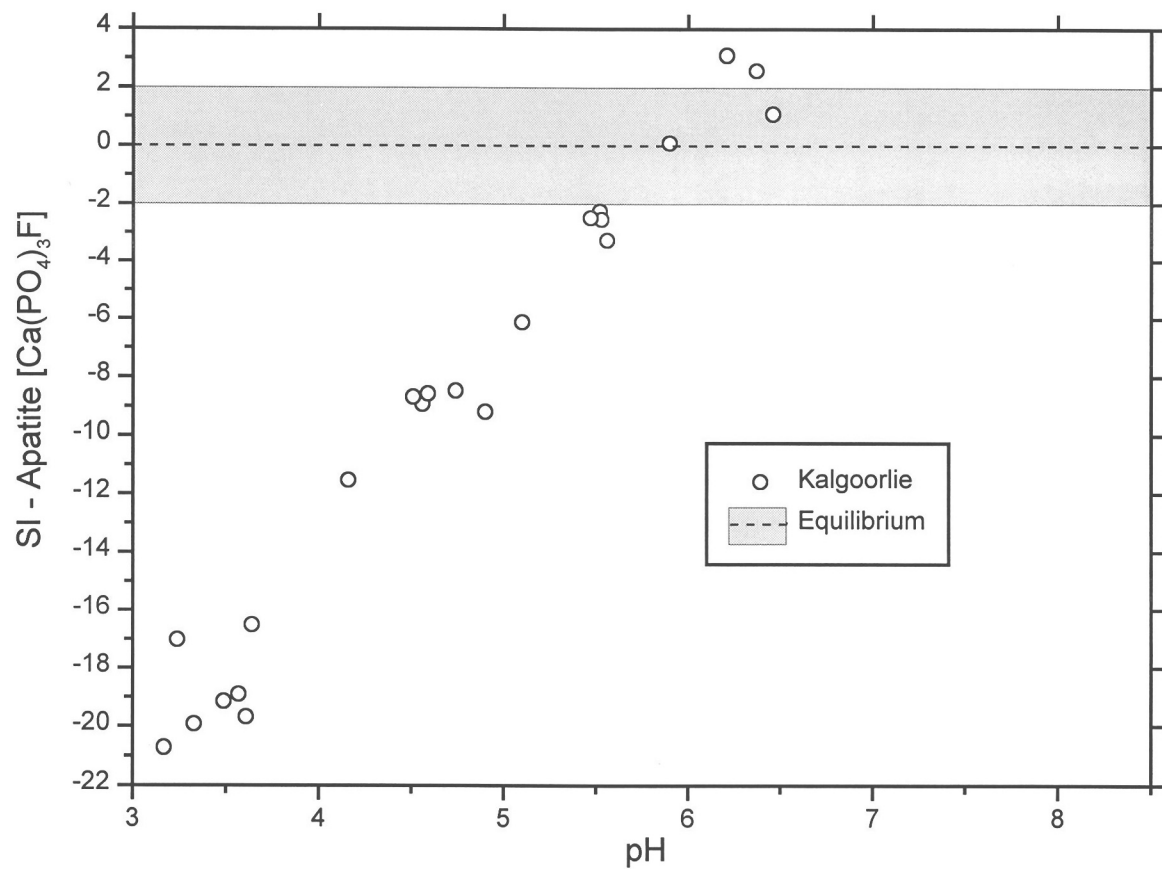


Figure A2.33: SI for apatite vs. pH for Western Australian groundwaters.

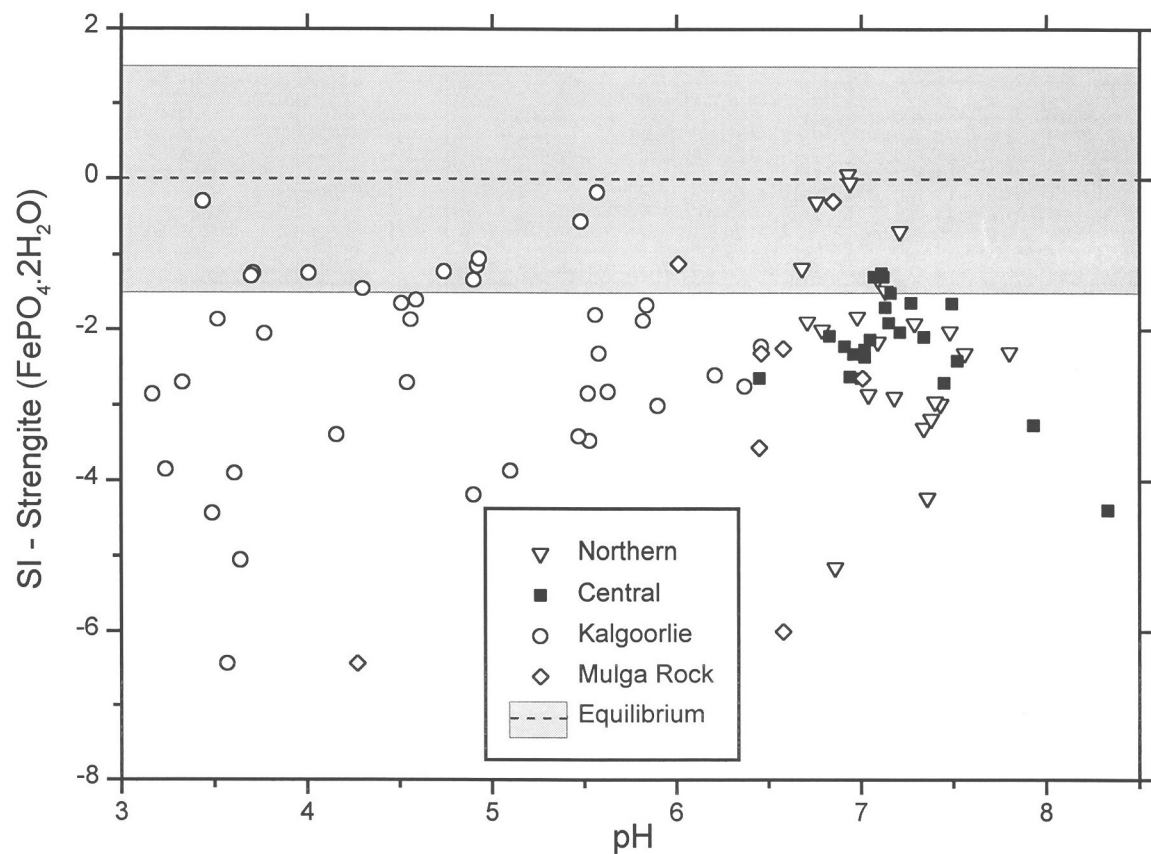


Figure A2.34: SI for strengite vs. pH for Western Australian groundwaters.