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TEILTA REGOLITH PROJECT: GROUNDWATER GEOCHEMISTRY

Patrice de Caritat and Dirk Kirste

CRC LEME OPEN FILE REPORT 158

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ABSTRACT

The groundwaters from the Teilta 1:100,000 mapsheet area were sampled and analysed with the aim of studying the processes that affect their composition, in a bid to further develop hydrogeochemistry as a tool for mineral exploration in areas of regolith cover. Those groundwaters are quite distinct in hydrogeochemical character from most of the other groundwaters studied in the Curnamona Province. They are Na-HCO_3 rich, warm and may be quite reducing. They are particularly depleted in SO_4, which tends to have an average to high $\delta^{34}S$ composition. We interpret this to be a reflection of the incursion of Great Artesian Basin groundwaters at the northern end of the regional study area. These waters have undergone bacterial sulfate reduction (BSR). The combined effect of BSR is to make the waters look 'less interesting' from a mineral exploration perspective (lower excess S, and higher S isotopic ratio). The lesson for mineral exploration is that less stringent selection criteria (lower Relative S excess, higher S isotopic composition of dissolved SO_4 cutoffs) should be applied to groundwaters that have been affected by BSR, when trying to identify those that indicate interaction by sulfide mineralisation under cover. Even despite this, a few groundwater compositions suggest proximity to mineralisation, using the indicators developed in Caritat et al. (in press).

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INTRODUCTION

The present study area is in the Broken Hill region of western NSW (Figure 1). Broken Hill is host to a single known supergiant Pb-Zn-Ag orebody (~300 Mt) and within the region there are numerous smaller Pb-Zn-Ag, Cu-Au, Sn, W and U deposits (Stevens and Burton, 1998). These occur mainly in the Paleo- to Neoproterozoic basement rock sequences, which outcrop in the Barrier, Olary and Flinders Ranges. Mineral exploration in areas of exposed bedrock has continued for over 100 years, yet additional significant mineral discoveries have been limited. The focus of exploration is turning towards the sediment-covered margins of the Broken Hill Domain.

Exploration in these sediment-dominated areas is made more difficult by the inability to see through this sediment blanket. Methodologies that aid in this, such as sequential/selective digestion of regolith materials, biogeochemistry and hydrogeochemistry, are being developed and tested within CRC LEME to help delineate how mineralisation can be recognised in the subsurface. One of the most promising techniques involves the use of groundwater chemistry to identify prospective areas. If a groundwater has interacted with mineralisation at depth, there may be changes in the major, minor, trace element and/or isotope composition resulting in a chemical signature of that mineralisation. If the geochemical signature is preserved, the groundwater may then be transported and if the flow path is intersected by a bore from which groundwater can be sampled, then there is potential for this medium to be very useful in mineral exploration. A hydrogeochemical exploration survey based on previously existing sampling points (bores, wells, springs, seepages) or a relatively cheap sparse network of exploration drill holes is likely to be useful on a regional scale at first, as groundwater anomaly footprints are likely to be larger than those of regolith/soil. Once a sub-area has been identified by hydrogeochemistry as having a high potential to host a blind ore deposit, more detailed (and expensive) exploration tools, such as dense drilling, can be focused on this much smaller area, thus enabling potentially substantial cost savings. Recent work on hydrogeochemical applications to mineral exploration include studies by Leybourne et al. (1998), Gray (2001) and Carey et al. (2003) among others. This study is a preliminary report of the findings of a hydrogeochemical study of Teilta 1:100,000 mapsheet.

The Teilta 1:100,000 scale mapsheet (map number 7136) was suggested by the New South Wales Department of Mineral Resources (NSW DMR) as a specific area worthy of a detailed, integrated regolith study by CRC LEME. As a result, a 'Teilta regolith project' with various components (regolith-landform mapping, regolith geochemistry, plant geochemistry and groundwater geochemistry) was designed. Initial fieldwork started in February 2002 followed by sample analyses and data interpretations. This report, which aims to document and interpret the major processes that affect groundwater chemistry in the Teilta area, is part of a series covering this project (e.g., Ruperto, 2004).

The climate of the Teilta area is predominantly dry with hot summers and mild winters. The mean annual minimum and maximum temperatures are 15 and 24 °C, respectively, and the mean annual rainfall is about 220-230 mm, with rainfall events being erratic both in intensity and location (Bureau of Meteorology, 2004). The landscape is dominated by dunefields, sandplains and alluvial plains with minor ranges, tablelands and hills (southeastern corner of the map); the three main soil and vegetation classes over the mapsheet are reported by Lawrie and Stanley (1980) to be:

- 'Gumpopla': Parallel dunes of deep red clayey sand with sparse mulga, areas of unpalatable shrubs, abundant forbs and grasses. Narrow scalded alluvial flats, sandy red earths and texture-contrast soils with calcareous subsoils or earthy pans exposed in scalds. Abundant chenopods, perennial grasses and forbs, canegrass and bluebush in small brown and grey cracking clay pans.
- 'Allandy': Extensively scalded alluvial flats; loamy surfaced brown texture-contrast soils and brown clays, both with strong surface crusts, sparse mulga and scattered unpalatable shrubs with forbs and grasses. Dunes of deep yellowish-red clayey sand with slightly denser mulga.
- 'Katalpa': Gently undulating plain, relief to 10 m; stony surfaces with red desert loams and sparse vegetation, bands of stone-free red clays in gilgai depressions with abundant saltbush. Less stony areas of loose, highly gypsic, yellowish-brown calcareous loams and clay loams with sparser saltbush. Drainage tracts of deep loamy alluvium, bluebush and saltbush and fringing river red gums.

The Teilta mapsheet (Figure 1) contains the ‘Tindara’ area, which Stevens and Burton (1998) reported was identified by BHP Minerals geologists (Cameron, 1992, 1993) north of 31 °S in the Broken Hill Domain of the Curnamona mineral province. The area has very little bedrock outcrop, which occurs mainly in the southeastern corner of the mapsheet. Based on aeromagnetics and 11 BHP drillholes, Cameron (1992, 1993) interpreted it to contain a very large area of both Willyama and Adelaidean rocks under a few tens to about 200 m of cover. Stevens and Burton (1998) gave a basement interpretation diagram for the NSW Broken Hill Domain from 30 °S to 32.5 °S. It shows a narrow, northwest-trending extension Willyama Supergroup rocks crossing the Teilta mapsheet, flanked by Adelaidean and Paleozoic rocks. Despite the weakly magnetic character of most of the area interpreted as Willyama Supergroup, Stevens and Burton (1998) suggested exploration should not be stopped at this early stage of understanding and data gathering. The project reported here and in accompanying CRC LEME reports (e.g., Ruperto, 2004) is a contribution to this endeavour from the regolith perspective.

GEOLOGICAL SETTING

The Curnamona Province consists of a sequence of Broken Hill equivalent rocks and Adelaidean rocks (Fig. 1). The former include complexly deformed high-grade metamorphic rocks of the Early Proterozoic Willyama Supergroup; the latter are more gently folded, mostly lower greenschist-grade Late Proterozoic sediments with minor volcanic rocks. This basement is variably covered by Paleozoic, Mesozoic and Cenozoic sediments. Detailed accounts of the geology of the Broken Hill Domain (see Fig. 1) have been reported in a number of studies (e.g., Stevens, 1980, 1986; Willis et al., 1983; Page and Laing, 1992; Stevens and Corbett, 1993) and are briefly summarised below.

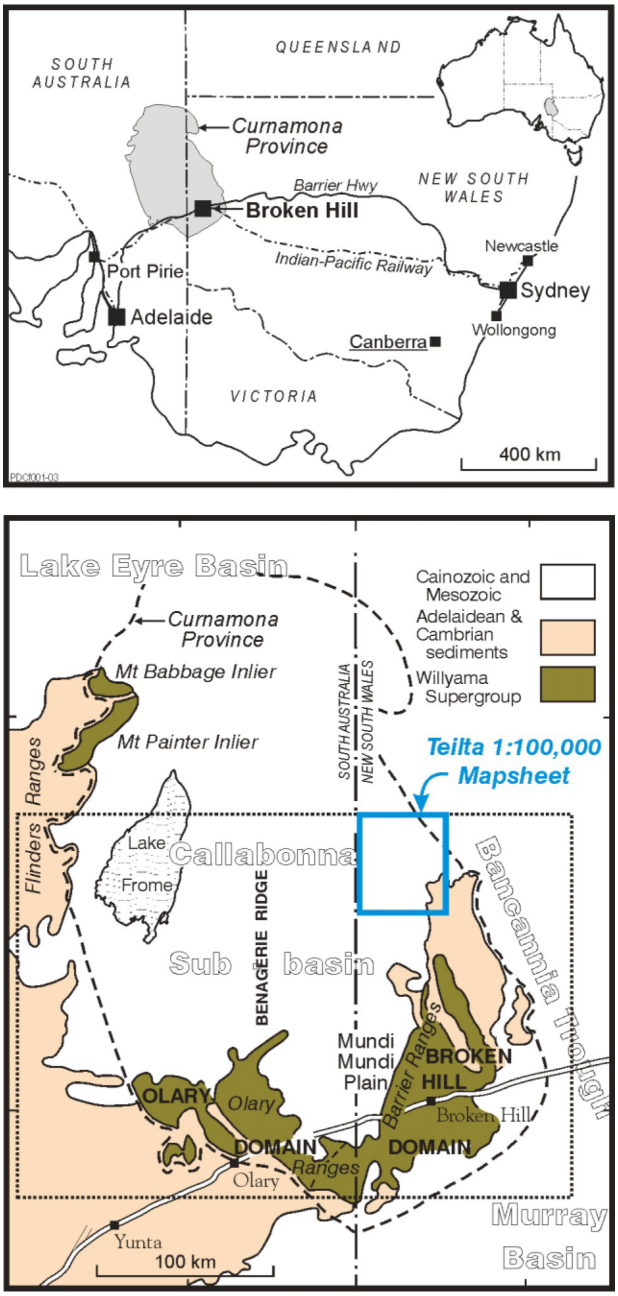

Figure 1. Location of the Broken Hill region and Curnamona Province in western New South Wales and eastern South Australia (top). The lower figure shows main geological and cultural features, the regional hydrogeochemistry study area (stippled rectangle, Caritat et al, in press) and the Teilta 1:100,000 mapsheet area (thick blue square).

The Willyama Supergroup comprises aluminous metasedimentary gneisses, plus locally abundant albite-rich rocks, basic gneisses (amphibolites), lesser quartzo-feldspathic gneisses and substantial bodies of deformed pegmatite and leucocratic quartzo-feldspathic rocks. The Willyama Supergroup can be found within the Broken Hill Domain, where it includes the Thackaringa and Broken Hill Groups, the Olary

Domain, and the Redan Geophysical Zone (southeast of Broken Hill), which both contain abundant albite and calc-albitite (Stevens and Corbett, 1993).

The Adelaidean sequence unconformably overlies the Willyama Supergroup and can be correlated with the more extensive occurrence of Adelaidean rocks in South Australia (Cooper et al., 1978; Preiss, 2000). It consists of a sequence of quartzite, quartzite conglomerate, limestone, siltstone, sandstone, shale, dolomite and diamictite (Willis et al., 1983; Stevens et al., 1988; Stevens and Corbett, 1993).

The Mesozoic Eromanga Basin, which is part of the Great Artesian Basin (GAB), is an extensive epicratonic sedimentary basin that occupies a large extent of central Australia (Krieg et al., 1995) to the north of the exposed Broken Hill and Olary Domains. Its southern boundary over the Curnamona Province extends as far south as the southern edge of Lake Frome and, further to the east, crosses roughly diagonally from southwest to northeast across the Teilta study area (Vine, 1976; Wecker, 1989).

The thick fluvio-lacustrine sedimentary succession of the Cenozoic Lake Eyre Basin, which extends across a vast area of central Australia, directly overlies downthrown Proterozoic rocks west of the Broken Hill Domain in the southern Curnamona Province, whereas further north it covers Eromanga Basin sediments. This basin is interpreted to have formed by tectonic subsidence in northeastern South Australia during the Late Paleocene (Callen et al., 1995). The Lake Eyre Basin comprises a number of sub-basins, including the Callabonna Sub-basin that covers most of the study area. Quaternary sediments and soils commonly cover Tertiary units. Deposition in the Lake Eyre Basin occurred in three phases (Callen et al., 1995):

(1) In the first phase, sandstone, carbonaceous clastics and conglomerate of the Eyre Formation were deposited during the latest Paleocene to Middle Eocene.

(2) The second phase includes deposition of grey, green and white clay, fine-grained sand and carbonate, with minor conglomerate of the Namba Formation during the Oligocene to Pliocene. It is informally divided into a lower member characterized by smectite and cyclic deposition, and an upper member with illite and kaolinite. The

Namba Formation was deposited in low-energy lacustrine environments (Callen, 1990).

(3) The third phase was characterized by the deposition of red and yellow-brown sand and sandy clay, and the development of gypsum and carbonate paleosols during the Pliocene to Quaternary.

The regional regolith and landscape features of the Broken Hill region are now being extensively studied. Recent studies include those of Hill et al. (2000), Hill (2000), Gibson (2000), Caritat et al. (2000a, 2000b, 2001, in press) and Tonui et al. (2003). Depth to fresh bedrock in the region varies from minimal in bedrock-dominated terrains up to approximately 200 m under basin cover (Caritat et al., 2000a; Tonui and Caritat, 2003). The dominant regolith materials in the region include saprolite, sediments, soils, ferricretes, silcretes, siliceous and/or ferruginous lags and carbonate accumulations (e.g., Hill, 2000; Hill et al., 2000). Areas of deepest weathering occur in areas of high preservation potential, including down-tilted fault block margins, under duricrust or lag-strewn surfaces, and in localised areas isolated from regional erosion or base-level lowering (Hill, 2000).

SAMPLING AND METHODS

During February 2002, 29 groundwater samples and one surface water sample were collected from within the Teilta 1:100,000 mapsheet area, and around its immediate periphery (Fig. 2, Table 1). Other samples form the regional study area, which extends some 300 km east-west and 200 km north-south were collected at other times (Caritat et al., 2001, in press; Kirste et al., 2003) and are shown here to give a regional context to the Teilta groundwater chemistry.

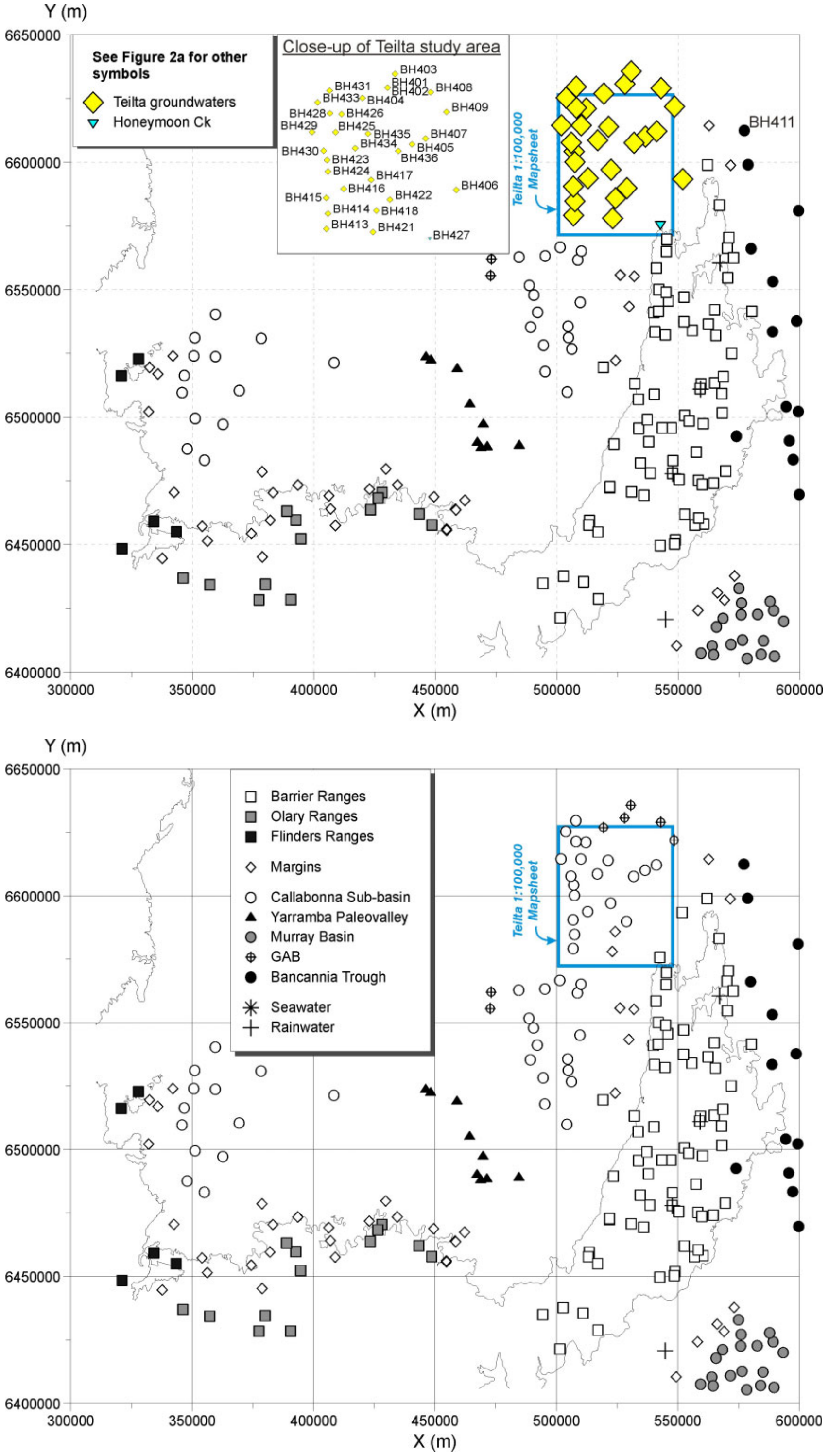

Figure 2. Location of the groundwater samples collected for the regional hydrogeochemical study, with samples classified according to field-determined groups (a, top). The bottom figure (b) highlights the samples from the Teilta 1:100,000 mapsheet and immediate surroundings considered for this report. Inset shows sample identification used in text. Coordinates: meters UTM Zone 54 WGS84; Outline: 200 m elevation contour.

Figure 2. Location of the groundwater samples collected for the regional hydrogeochemical study, with samples classified according to field-determined groups (a, top). The bottom figure (b) highlights the samples from the Teilta 1:100,000 mapsheet and immediate surroundings considered for this report. Inset shows sample identification used in text. Coordinates: meters UTM Zone 54 WGS84; Outline: 200 m elevation contour.

SampleID	Site	Station	Northing	Easting	Alt (m)
BH401	New Flow Bore/Lake Ellis Bore	Pine Ridge	6630716	528091	94
BH402	New Flow Bore/Lake Ellis Bore	Pine Ridge	6630716	528091	94
BH403	Old Flow Bore	Pine Ridge	6635676	530654	93
BH404	Talga Bore	Pine Ridge	6626915	519383	81
BH405	Well Bore	Pine Ridge	6610037	536508	107
BH406	Tunyarto Bore	Westwood Downs	6593372	551839	153
BH407	House Bore	Pine Ridge	6612136	541159	109
BH408	Sulphur Lake Bore	Pine Ridge	6629036	542932	92
BH409	No. 1 Bore	Pine Ridge	6621842	548467	108
BH413	Mt Bull Bore	Avenel	6579143	506905	83
BH414	Two Mile Bore	Avenel	6584733	507468	86
BH415	Middle Bore	Avenel	6590497	506856	87
BH416	North Bore	Avenel	6593752	512885	101
BH417	Minogues Bore	Teilta	6597071	522359	101
BH418	Lassiters Bore	Teilta	6585864	524198	117
BH421	House Bore	Teilta	6578025	523017	120
BH422	BHP Bore	Joulnie	6589852	528870	117
BH423	House Bore	Pine View	6604232	507133	81
BH424	South Bore	Pine View	6600080	507451	93
BH425	Middle Bore	Pine View	6614439	510094	87
BH426	Cattle Bore	Pine View	6621061	512169	79
BH427	Puddle in Honeymoon Creek	Mt Westwood	6575748	542640	172
BH428	Stantons Bore	Pine View	6621363	508110	83
BH429	Redferns Bore	Pine View	6614485	501948	79
BH430	New Bore	Pine View	6607679	505980	84
BH431	Mollies Bore	Pine View	6629613	508018	79
BH433	Starvation Bore	Pine View	6625316	503865	75
BH434	Strip Bore	Pine View	6608590	516849	93
BH435	Albs Bore	Pine View	6613912	521323	84
BH436	Tindara Bore	Pine View	6607605	531808	118

Table 1. Details of the water samples collected for the Teilta regolith project. Coordinates (meters UTM Zone 54 WGS84) and altitude (m above sea level) from GPS readings.

Groundwater was sampled from most existing boreholes and wells that were accessible and useable. These included mostly pastoral boreholes and, more rarely, exploration boreholes. Water was retrieved using *in-situ* equipment (windmills, submersible electric pumps, etc.) or a submersible Bennett™ pump powered by an air compressor and mounted on a 4-wheel-drive trayback vehicle. All samples were collected after sufficient pumping of the bores to ensure that water representative of the groundwater in the aquifer was being considered. This was determined by monitoring temperature (T), electrical conductivity (EC), pH, redox potential (Eh), and dissolved oxygen (DO) until stable readings were obtained over at least 3 or 4 consecutive readings (15-20 minutes). At that point, a groundwater sample was taken for field and lab analysis. Those field parameters (T, EC, pH, Eh and DO) were measured in the field using a set of Orion™ electrodes and meters.

Field determination of total alkalinity was performed by titration of a water aliquot of 10 or 25 mL by 0.01 M HCl to the methyl orange end-point. Generally oxidizing conditions and therefore expected low organic acid contents suggest total alkalinity is equivalent to bicarbonate alkalinity (Hem, 1992). Finally, concentrations of Fe^{2+} and S^{2-} were determined in the field by spectrophotometry using a Hach® DREL/2000 Direct Reading Spectrophotometer and following Hach® methods #8146 (1,10 phenanthroline method) for Fe^{2+}, #8131 (methylene blue method) for S^{2-}). This was done immediately after sampling (within 5-10 minutes) to ensure the best possible measurement of these unstable parameters.

Distilled water used in the field and laboratory was 18 MΩ-cm Milli-Q® water. The nitric acid used was 69% BDH nitric acid distilled in a nitric acid still, free of any ICP-MS detectable contaminant. Filters used were 90 mm diameter Pall Gelman Supor®-450 hydrophilic polyethersulfone membranes with a nominal 0.45 µm pore size. Sample handling was carried out with talcum-free non-sterile latex gloves. All sampling bottles were new and rinsed three times with the water to be sampled (filtered or not, as appropriate for each aliquot) prior to collection of the actual sample. Chemicals were added using glass or disposable polyethylene pipettes. Upon return to the laboratory, the samples were routinely subjected to a comprehensive analytical protocol, including the determination of:

- Laboratory pH and EC by standard methods,
- Br^-, Cl^-, NO_3^-, SO_4^{2-} by Ion Chromatography (IC),
- Al, B, Ba, Ca, Cu, Fe, K, Li, Mg, Mn, Na, S, Si, Sr, Zn by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES),
- F^-, I^- by Ion Specific Electrode (ISE),
- Ag, Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Cu, Dy, Er, Eu, Ga, Gd, Gd, Ge, Hf, Ho, La, Li, Lu, Mn, Mo, Mo, Nb, Nd, Ni, Pb, Pb, Pr, Rb, Sb, Sb, Sc, Sm, Sm, Sn, Sn, Sr, Ta, Tb, Th, U, W, Y, Yb, Zr by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS),

- Au on activated C sachets by Instrumental Neutron Activation Analysis (INAA), and
- Stable and radiogenic isotopes ^{13}C, ^{2}H, ^{18}O, ^{34}S and $^{18}O(SO_4^{2-})$, ^{36}Cl, $^{87}Sr/^{86}Sr$ and $^{208}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ by standard methods.

Further details on sampling and preparation methods are given elsewhere (Caritat et al., 2001, in press; Kirste et al., 2003).

QA/QC

15 rinse blanks (at least one at the beginning and one at the end of each fieldtrip) were taken in the field to monitor possible cross-contamination between samples during fieldwork (e.g., during filtering) and transport. 15 travel blanks (at least one at the beginning and one at the end of each fieldtrip) were taken in the field to monitor the quality of the distilled water used and possible contamination from transport. 28 field and lab duplicate samples (circa one every tenth borehole) were used to estimate field reproducibility and analysis precision. Internal and external international standards (SLRS-4 Riverine water from the National Research Council, Canada) and spiked samples were used to estimate analysis recovery and accuracy.

In terms of charge balance, the majority of the water analyses fall between –5 and +5%, and only a few analyses have charge balances between 5 and 10%, on both the negative and positive sides.

RESULTS AND DISCUSSION

Figure 2 shows the location of the samples under consideration, these occur in the northern part of our regional study area. The Teilta samples are identified as yellow diamonds (groundwater) or blue upside-down triangle (surface water, BH427) for easy recognition (Fig. 2b), but their landscape/hydrogeomorphic position is ‘Callabonna Sub-basin’ for the most part, ‘Great Artesian Basin’ (GAB) or ‘Margins’ (Fig. 2a).

The Piper and Ludwig-Langelier diagrams (Fig. 3) show that most of the Teilta groundwaters are clearly different from the bulk of the regional groundwaters. This is indicated by the anionic composition of these waters, which is dramatically depleted in SO_4. The Teilta waters also tend to have more HCO_3 (higher alkalinity) than most other waters in the region. The Teilta groundwaters tend to be more Na-rich (K being a considerably less abundant cation) but their Ca/Mg ratio is very similar to that of the regional waters. This Na-HCO_3 composition is typical of groundwaters from the GAB (e.g., Herczeg et al., 1991), and indicates that in this northern part of the regional study area we detect significant influence of GAB aquifers, either through tapping those directly, or leakage (and mixing) into shallower aquifers.

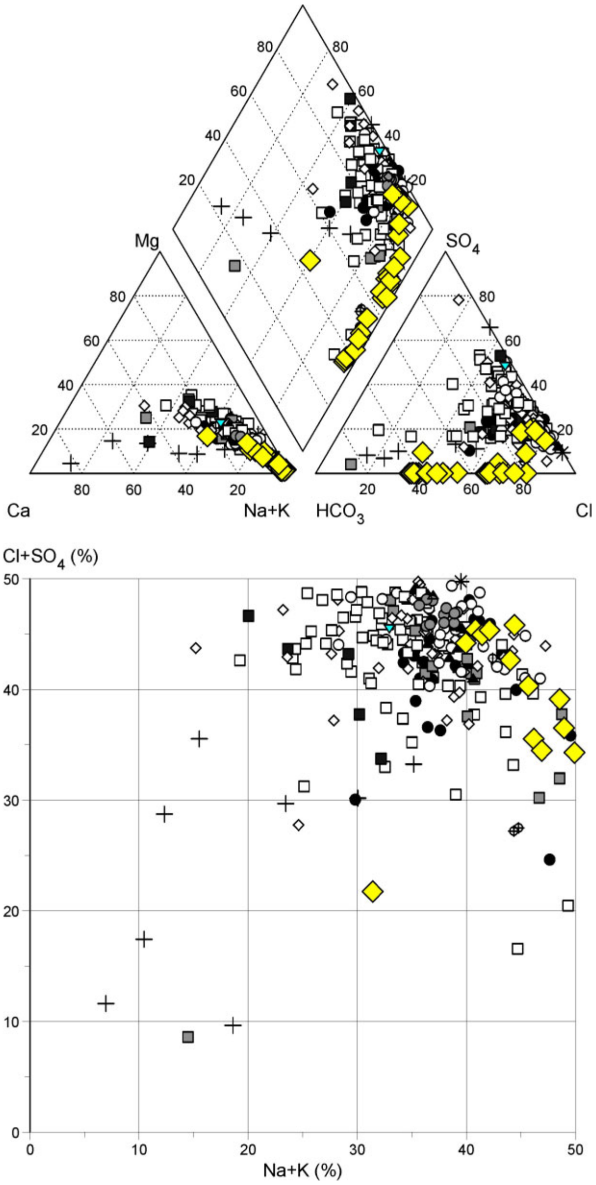

Figure 3. Piper and Ludwig-Langelier diagrams showing the relative major cation and anion composition (in meq/L) of the groundwaters from the regional hydrogeochemical study and the Teilta project. See Figure 2 for symbol legend.

Figure 4 shows that the Teilta groundwaters have pH values typical for the region (ca 6.9 to 7.9) but tend to be unusually warm (23 to 45 °C). They are relatively fresh (mostly between 2000 and 7000 mg/L TDS), yet they clearly include many waters with anomalously high HCO_3^- concentrations, up to 1800 mg/L .They are also among the most reduced in the region, as shown by the low pe (a calculated redox indicator) and dissolved oxygen (DO) values, and by the presence of significant concentrations of reduced S (up to 30 mg/L S^{2-}) and Fe (up to 3 mg/L Fe^{2+}). There is, however, no covariance between S^{2-} and Fe^{2+}.

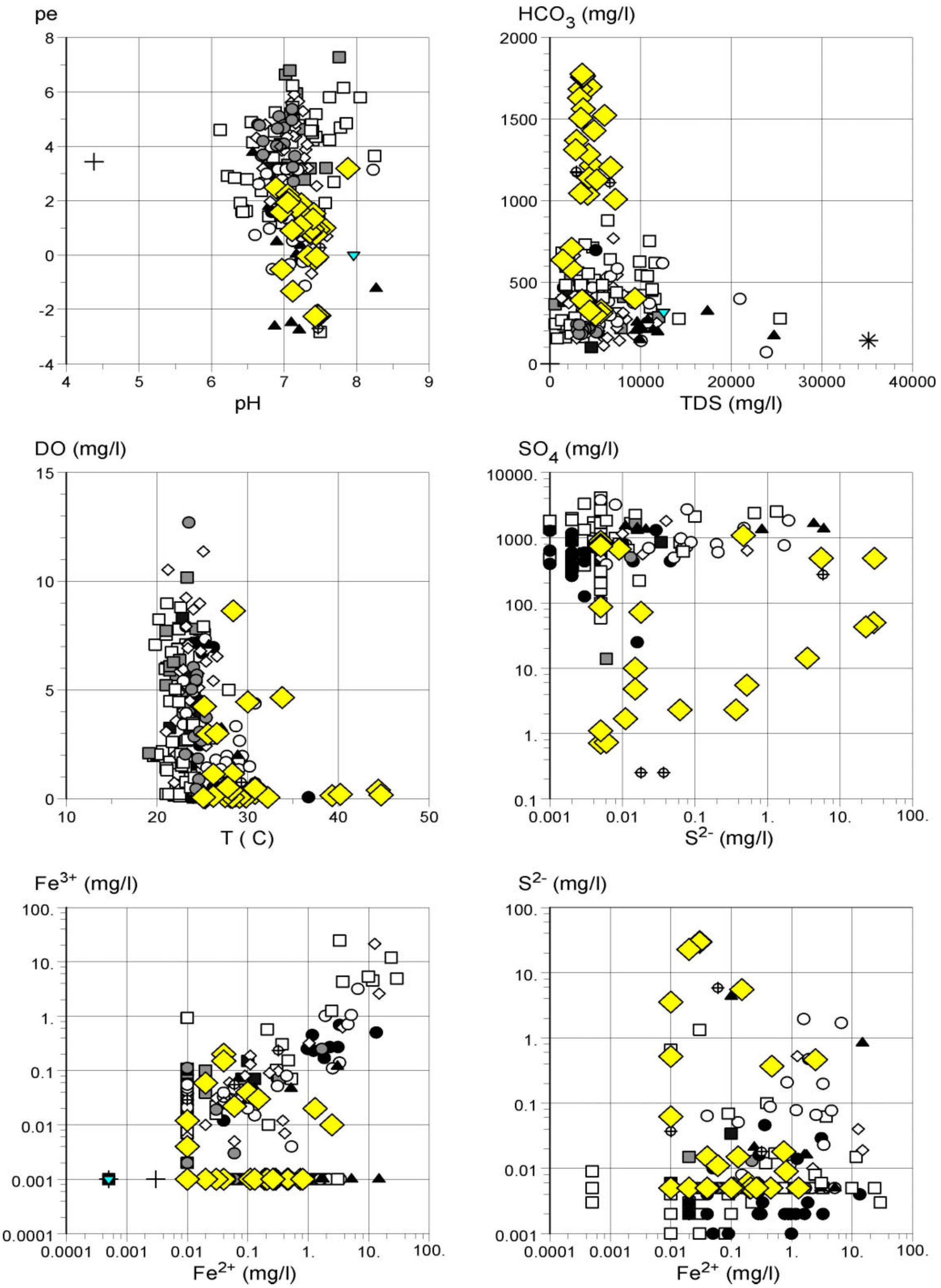

Figure 4. Scatterplots showing the relationships between pe, pH, alkalinity (HCO3), total dissolved solids (TDS), temperature (T), dissolved oxygen (DO), and SO4, S2-, Fe3+ and Fe2+ concentrations in the groundwaters from the regional hydrogeochemical study and the Teilta project. See Figure 2 for symbol legend.

The dominant process to have affected the Teilta waters is evaporation (Fig. 5), which increases the Na, Cl and Br concentrations along the rainwater to seawater line (the rainwater compositions are from our regional study, see Fig. 2, and from Blackburn and McLeod, 1983; the seawater compositions are from Drever, 1997). In addition to evaporative concentration, all waters show an addition of Na relative to Cl, which may be due to mineral-water interaction (plagioclase dissolution, i.e., weathering) since removal of Cl is unlikely at these low ionic strengths (strong undersaturation relative to halite). Based on the Na-Cl relationships, the surface water from the puddle in Honeymoon Creek (BH427), is the second most evaporated water from the Teilta area (after BH422, the BHP exploration bore on Joulnie station), and also shows Na addition relative to typical rainwater Na/Cl ratios.

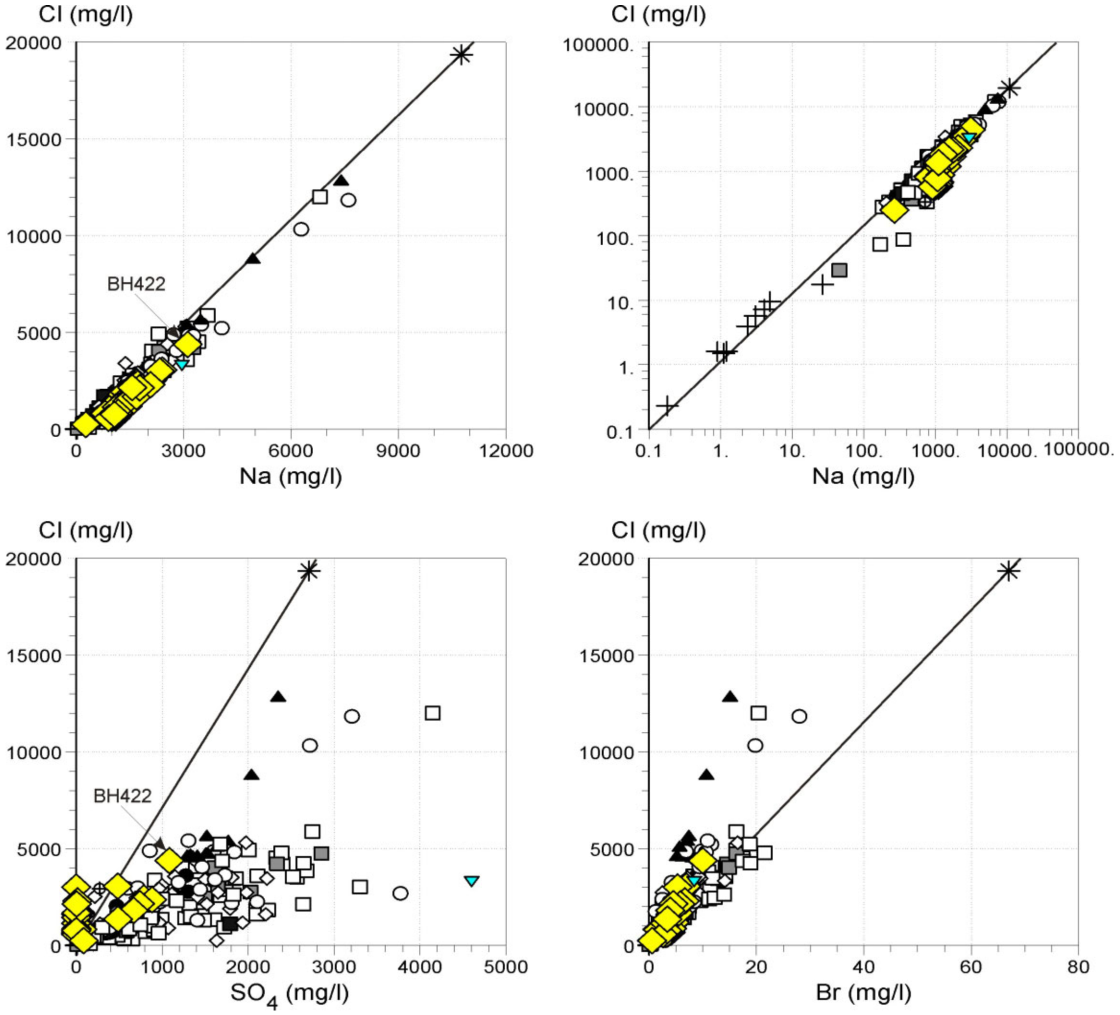

Figure 5. Scatterplots showing the relationships between Cl, Na, SO4 and Br concentrations in the groundwaters from the regional hydrogeochemical study and the Teilta project. Solid lines indicate trends of rainwater evaporation (or seawater dilution). See Figure 2 for symbol legend.

Compared to the regional groundwaters, the Teilta samples tend to contain less SO_4 (Fig. 5). However, a few groundwaters from Teilta (including BH422) and, especially, the surface water sample have more SO_4 than would be predicted from the Cl concentration based on seawater the ratio, i.e., they have an excess SO_4 (for a full development of this concept see Caritat et al., in press). On the Cl vs Br plot, the Teilta groundwaters form two groups: one has low Cl and Br concentrations and Cl/Br ratios similar to seawater; the other has somewhat higher concentrations of these conservative anions but also higher Cl/Br ratios, suggesting an addition of Cl (removal of Br being unlikely). The surface water sample falls into the latter category.

The ion ratio diagrams of Figure 6 are useful in differentiating between evaporation (or dilution), on the one hand, and addition (or removal) of ions through other processes, on the other hand. This is because evaporation and dilution conserve ionic ratios at the concentration range typical of this region (i.e., below seawater salinities). Thus, we can detect that the Teilta groundwaters have experienced a removal of SO_4 decoupled from any changes to the Na or Cl concentrations. The increase in the Cl/SO_4 ratio (i.e., decrease in SO_4 relative to Cl) is also mostly unrelated to a systematic change in Cl/Ca ratio, indicating that gypsum precipitation is not the process that drives SO_4 removal. This, in addition to the presence of reduced sulphur in the groundwater samples and the low temperatures, indicates that bacterial sulfate reduction (BSR) is the process responsible for the removal of dissolved SO_4 from many of the Teilta groundwaters.

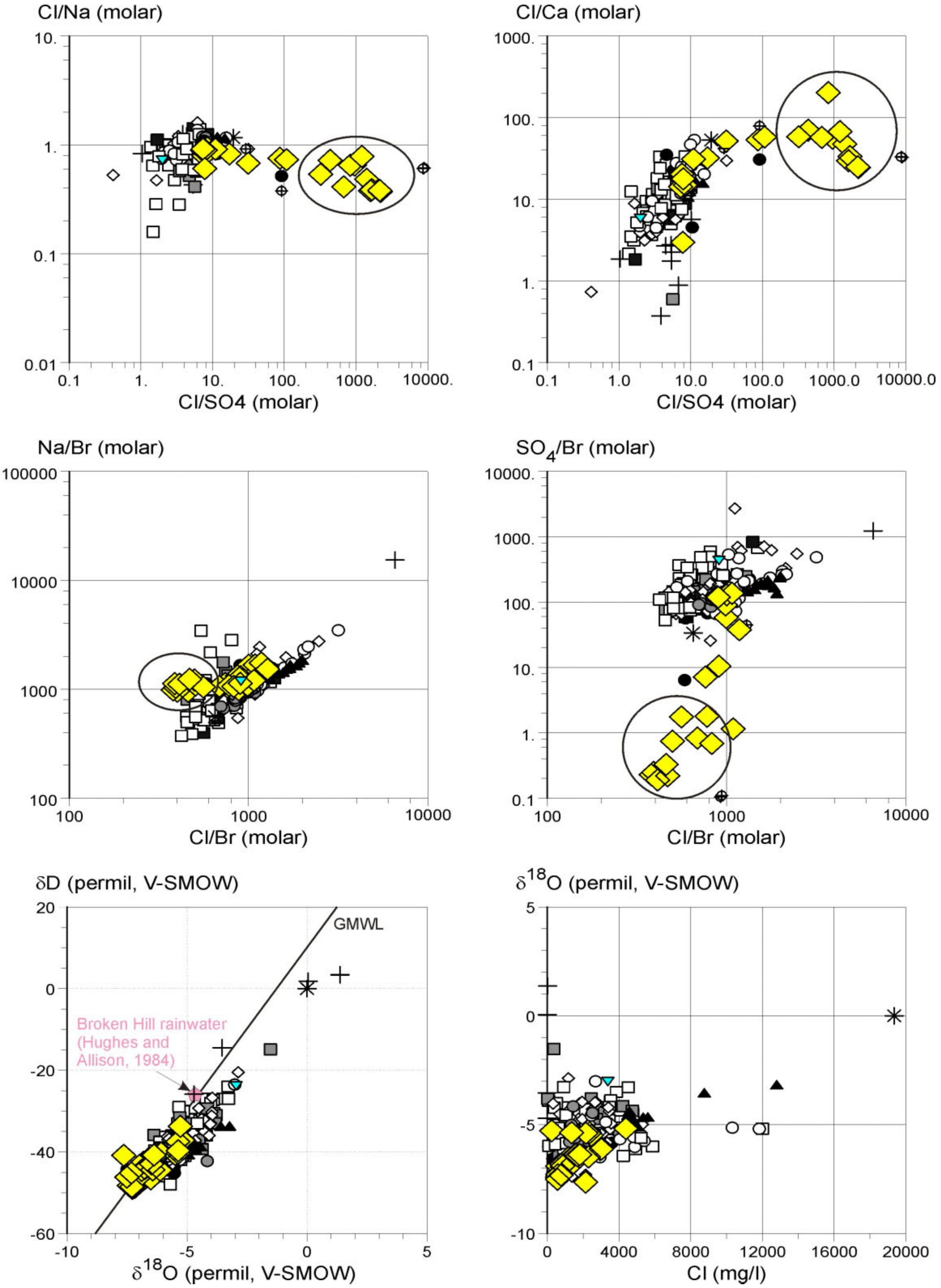

Figure 6. Scatterplots showing the relationships between Cl/Na, Cl/SO4, Cl/Ca, Na/Br, Cl/Br and SO4/Br ratios, δD, δ18O and Cl concentrations in the groundwaters from the regional hydrogeochemical study and the Teilta project. The circled samples in the top four diagrams are from the northern part of the Teilta study area (GAB influenced). GWML = global meteoric water line (Craig, 1961). See Figure 2 for symbol legend.

The group of Teilta groundwaters with low Cl/Br molar ratios (<~600) mentioned earlier also has Na/Br ratios at the lower end of the range exhibited by all the Teilta groundwaters and very low SO_4/Br ratios (circled samples in Fig. 6). These waters, which come from the northernmost part of the Teilta study area, tend to be relatively fresh (TDS approximately 4000 mg/L) and have high HCO_3^- concentrations (1200 to 1800 mg/L) and high Cl/SO_4 ratios. This northern group clearly has a distinct GAB geochemical fingerprint, whereas the southern group is more typical of waters from the Callabonna Sub-basin and/or Barrier Ranges. This has implications for using hydrogeochemistry for mineral exploration in the area (see below).

Oxygen and deuterium (D) isotopes of the Teilta groundwaters are amongst the most depleted of the region (δD = -30 to -50 permil and $\delta^{18}O$ = -8 to -5 permil, V-SMOW; see Fig. 6), and more depleted than average Broken Hill precipitation (δD = -25.9 and $\delta^{18}O$ = -4.71 permil, V-SMOW; Hughes and Allison, 1984). Although it is a simplification of complex processes (Hartley, 1981), it is possible that these isotopically depleted values reflect precipitation and recharge under different climatic and geographic conditions. Conditions that commonly yield isotopically depleted precipitation include higher latitudes and lower temperatures.

Evaporation and evapotranspiration can be distinguished using a $\delta^{18}O$ vs Cl plot (Fig. 6), since evaporation will result in an increase of both parameters in groundwater, whilst evapotranspiration only increases Cl (roots are not selective toward $H_2{}^{18}O$ or $H_2{}^{16}O$ molecules) (Barnes and Turner, 1998). The diagram shows that evaporation affects most Teilta groundwaters (diagonal trend), while evapotranspiration dominates in a few cases (horizontal trend).

The diagrams on Figure 7 relate to S concentrations and S isotopes. The Teilta groundwaters are distinct from the other groundwaters in the region for having low SO_4 concentrations. In fact, the SO_4 concentrations can be as low as that of local precipitation. The diagram of SO_4/Cl vs SO_4 supports the interpretation that GAB groundwaters have undergone BSR, rather than having low SO_4 content for any other reason (e.g., dissolution of halite in rainwater). A similar pattern exists using Br (an even more conservative anion in this system) instead of Cl (not shown). The generalised compositional evolution is thus:

1) rainwater undergoes evaporation resulting in SO_4 concentrations going from levels <10 mg/L to 100-10,000 mg/L, whilst the SO_4/Cl ratio remains largely constant;
2) many groundwaters from the region experience SO_4 addition, increasing both SO_4 concentrations and SO_4/Cl ratios (Caritat et al., in press);
3) the Teilta-GAB groundwaters, conversely, undergo BSR, which reduces their SO_4 concentrations and SO_4/Cl ratios simultaneously, reverting to SO_4 concentrations typical of rainwater but with much higher Cl/SO_4 ratios.

The few non-Teilta groundwaters that follow the same trends are also from the northern part of the regional study area (e.g., BH411), and are similarly interpreted to reflect the influence of the GAB.

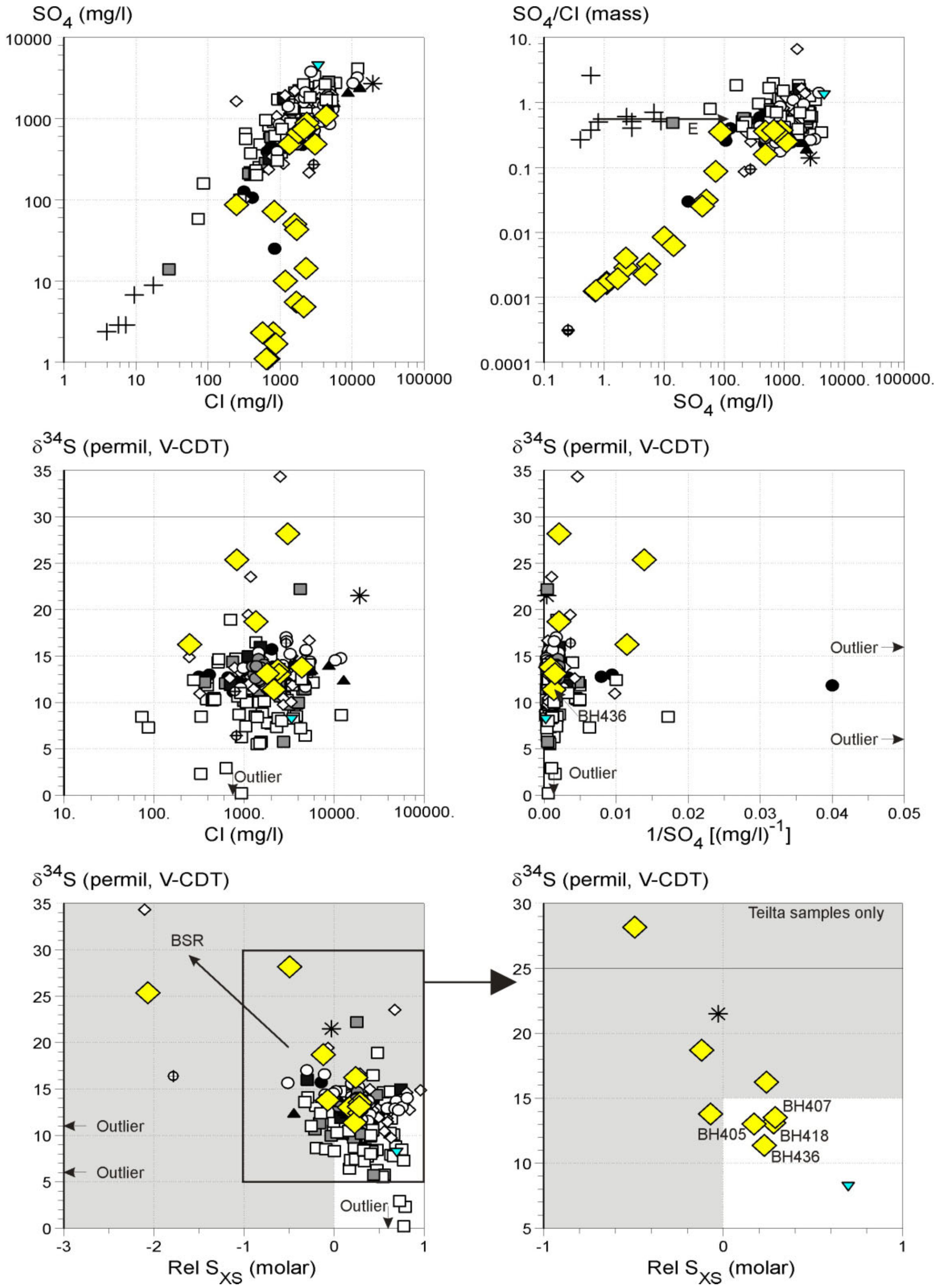

Figure 7. Scatterplots showing the relationships between SO4, Cl, SO4/Cl, □34S, 1/SO4 and Relative S excess (Rel SXS; see text) concentrations in the groundwaters from the regional hydrogeochemical study and the Teilta project. The unshaded areas in the bottom two figures represent waters that suggest addition of isotopically light S, for instance from Broken Hill type base metal sulfide mineralisation. E = evaporation of rainwater; BSR = bacterial sulfate reduction. See Figure 2 for symbol legend.

Only 10 Teilta waters (including surface water BH427) were analysed for S isotopes because the extremely low SO_4 concentrations of the others precluded separation of enough $BaSO_4$ precipitate. Most of the Teilta groundwaters have $\delta^{34}S$ signatures compatible with variable mixtures of (more or less evaporated) rainwater and seawater (both sulfate and dimethyl sulfide) having undergone BSR. BSR decreases the concentration and increases the proportion of ^{34}S in dissolved SO_4 because it is a microbially mediated process, which favours reduction of isotopically lighter S, thus preferentially reducing $^{32}SO_4$ to $H_2{}^{32}S$ over $^{34}SO_4$ to $H_2{}^{34}S$ (Strebel et al., 1990; Machel et al., 1995).

Caritat et al. (in press) determined the range of rainwater $\delta^{34}S$ in the region to be ~ +12.5 to +15 permil. Isotopic signatures above this range are more difficult to reconcile with the addition of light S (see below), but values below this range, especially where they coincide with positive values of relative S excess (see Caritat et al., in press), are strong indicators of interaction with sulfide minerals, which have an average $\delta^{34}S$ value of 0 permil for Broken Hill type sulfide mineralisation (Bierlein et al., 1996). Based on this, five Teilta waters have both a positive relative S excess value and $\delta^{34}S$ <+15 permil (Fig. 7): BH427 (Honeymoon Creek puddle), BH436 (Tindara bore), BH405 (Well bore), BH418 (Lassiters bore) and BH407 (Pine Ridge House bore), in order of increasing $\delta^{34}S$ values. These are of immediate interest in that they suggest interaction with mineralisation under the surface. However, because BSR will tend to decrease the relative S excess and increase the $\delta^{34}S$ of dissolved SO_4, it is possible that more groundwaters could be of interest in this context. For instance a groundwater that has experienced BSR may have a $\delta^{34}S$ value at +19 permil. If it subsequently inherits a small amount of S from sulfide oxidation (at, say, 0 permil), depending on relative proportions, the resulting $\delta^{34}S$ value of the groundwater may be +17 permil, for instance. Such a water should not be dismissed as only indicating a rainwater signature with a seawater S component. Thus, the selection criteria used for waters having undergone BSR (or mixed with BSR-affected waters) should be less stringent that for the other groundwaters.

The Sr concentrations of the Teilta groundwaters (Fig. 8) are comparatively low in relation to the regional dataset. The Sr-Cl systematics are consistent with dilution of seawater or, alternatively, rainwater evaporation (increasing element concentrations) followed by calcite precipitation, which incorporates some Sr (decreasing the Sr/Cl ratio and Sr concentration).

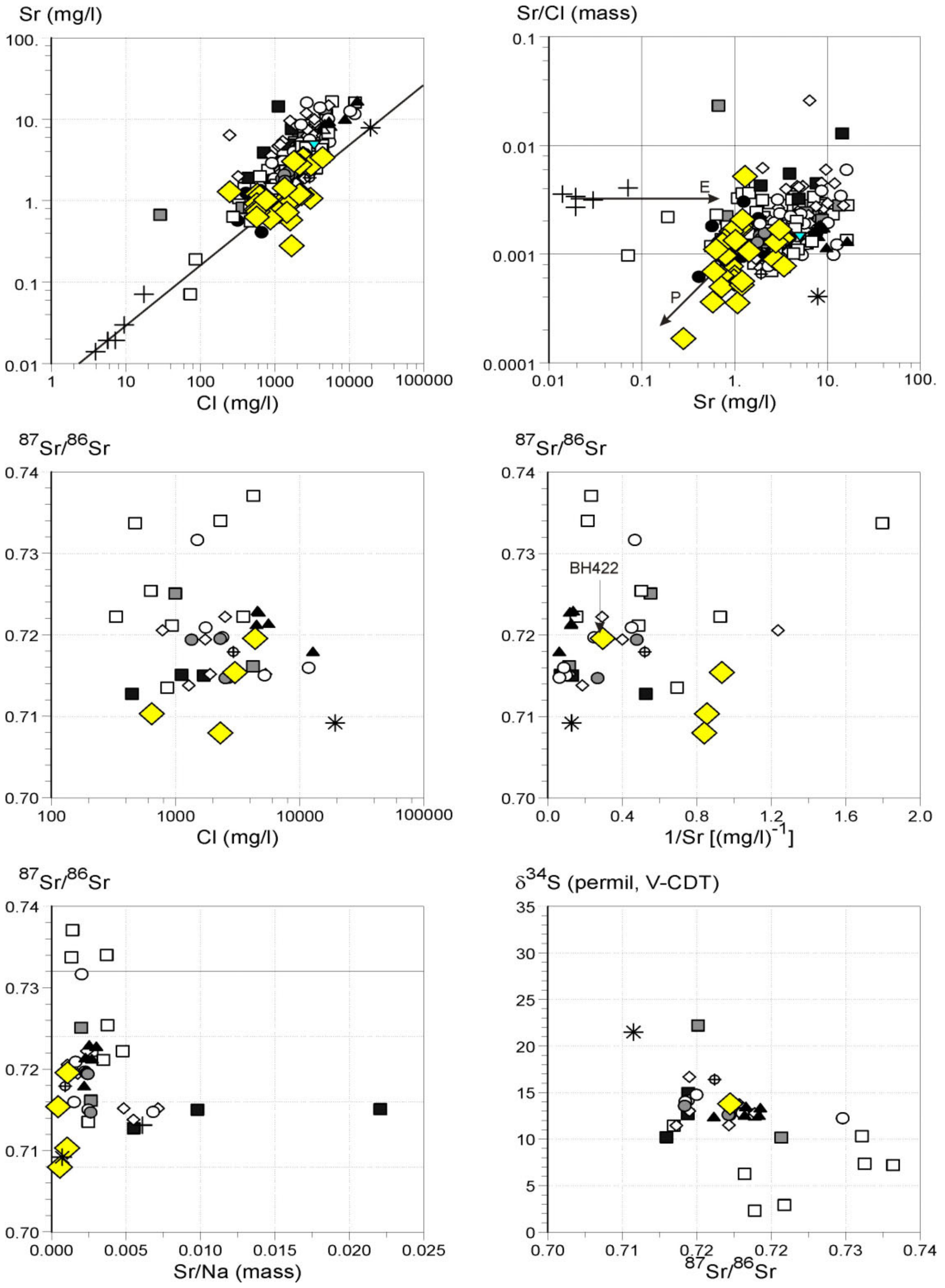

Figure 8. Scatterplots showing the relationships between Sr, Cl, Sr/Cl, 87Sr/86Sr, 1/Sr, Sr/Na and□34S in the groundwaters from the regional hydrogeochemical study and the Teilta project. Solid line indicates trend of rainwater evaporation (or seawater dilution). E = evaporation of rainwater; P = precipitation of calcite/calcrete incorporating Sr. See Figure 2 for symbol legend.

We determined the Sr isotopic composition of four Teilta groundwaters (Fig. 8). The resulting $^{87}Sr/^{86}Sr$ values tend to be at the lower end of the regional dataset, with the highest value being 0.71958 for BH422 (BHP bore). This value is intermediate between typical Adelaidean and Willyama end-members (see Caritat et al., in press), whilst the other three samples have $^{87}Sr/^{86}Sr$ ratios too low to reflect a typical Willyama-type Sr isotopic signature in groundwater ($^{87}Sr/^{86}Sr > 0.73$). The $^{87}Sr/^{86}Sr$ vs Sr/Na diagram suggests that the Teilta groundwaters reflect silicate hydrolysis (low Sr/Na ratios) more than calcite dissolution (high Sr/Na ratios) (Harrington and Herczeg, 2003). This, combined with the low $^{87}Sr/^{86}Sr$ values of the three samples is compatible with Adelaidean rocks/minerals having interacted with these three Teilta groundwaters. The fourth water (BH422) suggests hydrolysis of silicates of a Sr-isotopic type intermediate between Adelaidean and Willyama end-members.

Only one Teilta groundwater, BH422, was analysed for both S and Sr isotopes, and on the $\delta^{34}S$ vs $^{87}Sr/^{86}Sr$ diagram it falls close to middle of the observed ranges. Considering that the BSR may have increased the $\delta^{34}S$, this water still is consistent with positive mineralisation indicators. Caritat et al. (in press) also considered the use of Pb isotopes in groundwater to constrain mineralisation styles, but no Pb isotopes were determined on Teilta groundwaters so this can not be achieved here.

IMPLICATIONS FOR MINERAL EXPLORATION

The groundwaters from the Teilta area show the influence of groundwaters typical of the GAB, the concealed southern extent of which coincides with the study area. The GAB groundwaters have been affected by bacterial sulfate reduction (BSR), which decreases the sulfate concentration in the groundwaters. This process also results in a heavier S isotopic composition of the remaining sulfate dissolved in groundwater. The combined effect of BSR is thus to make the waters look ‘less interesting’ from a mineral exploration perspective (lower excess S, and higher S isotopic ratio). The lesson for mineral exploration is that less stringent selection criteria (lower Relative S excess, higher S-isotopic composition of dissolved SO_4) should be applied to groundwaters that have been affected by BSR, when trying to identify those that indicate interaction by sulfide mineralisation under cover.

CONCLUSIONS

The groundwaters from the Teilta area are quite distinct in hydrogeochemical character from most of the other groundwaters studied in the Curnamona Province. They are Na-HCO_3 rich, warm and may be quite reducing. They are particularly depleted in SO_4, which tends to have average to high $\delta^{34}S$ signatures. We interpret this to be a reflection of the incursion of GAB groundwaters at the northern end of the regional study area. These waters have undergone bacterial sulfate reduction (BSR). A few groundwaters suggest proximity to mineralisation, using the indicators developed in Caritat et al. (in press); these are BH427, BH422, BH436 and BH418. Of these, perhaps the most surprising is BH427, which is a surface water sample from a permanent 'puddle' in Honeymoon Creek. It is possible that this 'puddle' or spring is the surface expression of a fracture system draining mineralisation at depth. The contained water retains a hydrogeochemical signature of this interaction despite undergoing strong evaporation.

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