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Chlorine stable isotope studies of old groundwater, southwestern Great Artesian Basin, Australia

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Abstract

Stable Cl isotope ratios ($^{37}Cl/^{35}Cl$) were measured in groundwater samples from the southwestern flow system of the Great Artesian Basin, Australia to gain a better understanding of the Cl^- sources and transport mechanisms. $\delta^{37}Cl$ values range from 0‰ to −2.5‰ (SMOC), and are inversely correlated with Cl^- concentration along the inferred flow direction. The Cl isotopic compositions, in conjunction with other geochemical parameters, suggest that Cl^- in groundwaters is not derived from salt dissolution. Mixing of the recharge water with saline groundwater cannot explain the relationship between $\delta^{37}Cl$ and Cl^- concentration measured. Marine aerosols deposited via rainfall and subsequent evapotranspiration appear to be responsible for the Cl^- concentrations observed in wells that are close to the recharge area, and in groundwaters sampled along the southern transect. $\delta^{37}Cl$ values measured in the leachate of the Bulldog shale suggest that the aquitard is the subsurface source of Cl^- for the majority of groundwater samples studied. Diffusion is likely the mechanism through which Cl^- is transported from the pore water of the Bulldog shale to the aquifer. However, a more detailed study of the aquitard rocks is required to verify this hypothesis.

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1. Introduction

The Great Artesian Basin (GAB) covers approximately one-fifth of the Australian continent. It underlies arid and semi-arid regions, and is the most important source of water in these regions. Several recent publications have focused on the southwestern flow systems of the GAB, using various isotope techniques such as ^{36}Cl, ^{81}Kr and ^{4}He. Love et al. (2000) used ^{36}Cl measurements to estimate groundwater residence time along two different flow paths. Water chemistry, H and O stable isotopes, and advection/diffusion modeling were also considered to assess the relative importance of the various processes affecting Cl^- and ^{36}Cl distribution. It was suggested that the Cl^- concentrations in groundwater were derived mainly from evapotranspiration as well as from aquitard addition, whereas processes

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such as halite dissolution and mixing between groundwaters were found to be insignificant. ^{36}Cl ages ranging from 200 to 600 ka were calculated for the confined aquifers in the southwestern GAB. Collon et al. (2000) used ^{81}Kr to determine groundwater ages between 225 and 400 ka for water from four wells in the same area. Lehmann et al. (2003) compared the isotopic parameters ^{81}Kr, ^{36}Cl, ^{4}He and δ^{37}Cl measured in these wells to further discern the contribution of different sources to the Cl$^-$ concentrations. Based on ^{3}He/^{4}He ratios and δ^{37}Cl values measured, they concluded that Cl$^-$ was transported from the pore waters of the confining shale.

Interpretation of ^{36}Cl data in terms of water residence times requires an understanding of the origin of Cl$^-$. The groundwater age can be calculated based on measured, initial, and secular equilibrium of the ^{36}Cl/Cl ratio when no sources or sinks for Cl$^-$ exist in the system (Bentley et al., 1986). However, ^{36}Cl may have been added to the groundwater system through processes such as subsurface production, diffusion from porewaters, or mixing. These processes must be evaluated to determine their contributions to the measured ^{36}Cl. Stable Cl isotope ratios (^{37}Cl/^{35}Cl) have been widely used to investigate local sources of Cl$^-$, mixing of fluids, and interaction between rock and fluids in basinal environments (e.g. Kaufmann et al., 1992; Eggenkamp and Coleman, 1998; Eastoe et al., 2001). Coupled with other geochemical parameters, the stable Cl$^-$ isotope ratio has proven to be a useful tool for identifying solute sources and for distinguishing solute transport mechanisms (e.g. Eggenkamp et al., 1994; Eastoe et al., 1999; Hendry et al., 2000; Godon et al., 2004).

Naturally-occurring fractionation of stable Cl isotopes can result from partitioning of these isotopes between minerals and aqueous solution. The heavier isotope (^{37}Cl) is generally preferred by the structures of minerals due to the stronger bonding of Cl$^-$ in solid phases relative to aqueous solution (Magenheim et al., 1995). Schauble et al. (2003) calculated the equilibrium Cl isotope fractionation using vibrational spectra and force-field modeling, and estimated that silicates were approximately 2–3‰ enriched compared to the coexisting brines. Eggenkamp et al. (1995) determined a fractionation factor of 1.00026 between halite and the saturated solution using laboratory experiments. Precipitation and dissolution of evaporite minerals have been identified as the dominant process for Cl isotope fractionation observed in both the Palo Duro and Gulf Coast Basins (Eastoe et al., 1999, 2001).

Chlorine isotope fractionation measured in field-scale studies is more often attributed to physical processes such as diffusion, ion-filtration, and mixing between two different sources (Stewart and Spivack, 2004). Diffusion occurs in response to concentration gradients, and results in separation of ^{35}Cl and ^{37}Cl because ^{35}Cl is more mobile than ^{37}Cl. As a result, the solution becomes more depleted in ^{37}Cl away from the concentrated source. Desaulniers et al. (1986) reported a decrease in Cl$^-$ concentration and δ^{37}Cl in pore waters of glacial deposits with increasing distance from the underlying bedrock. They were the first to attribute the depletion in ^{37}Cl to the upward diffusion of Cl$^-$ through low permeable sediments. Ion filtration, on the other hand, results in an enrichment in ^{37}Cl downgradient. This process occurs when a saline solution is forced through a charged clay membrane. Due to its higher mobility, ^{35}Cl$^-$ is more readily repelled by the negative charges on clay minerals (Phillips and Bentley, 1987). Godon et al. (2004) attributed negative δ^{37}Cl values observed in pore fluids of mud volcanoes to ion filtration processes induced by compaction of the sediments. Chlorine isotopic composition can also be used, in conjunction with Cl$^-$ concentration, to determine if mixing is the mechanism responsible for Cl isotopic change in a groundwater system. For example, based on the correlation between δ^{37}Cl and Cl concentration, Hendry et al. (2000) were able to delineate mixing process between five different end-members in a clay-rich aquitard system.

The objective of this study was to characterize the origin and possible mechanism of Cl$^-$ accumulation in the groundwaters from the SW flow systems of the GAB using stable Cl isotopes. The Cl isotopic composition, chemical composition, and stable H and O isotopes were determined in groundwaters sampled from 24 wells. To understand the potential correlation between Cl$^-$ measured in groundwater and that present in both the aquifer and aquitard, leaching experiments on selected rock core samples were conducted to extract the Cl$^-$ in pore water. The Cl isotopic composition of the leachates was measured. In this study, the different processes examined by Love et al. (2000) were again evaluated using stable Cl isotope ratios. To better understand the ^{36}Cl dating results, attempts were made to estimate the quantity of Cl$^-$ derived from recharge input compared to Cl$^-$ from subsurface addition.

2. Study area

The study area is located within the southwestern flow system of the Great Artesian Basin, near Lake Eyre. Centered in Macumba, this area extends approximately 150 km from west to east and 250 km from north to south (Fig. 1). The dominant groundwater flow direction in the study area is from the NW and western margins toward the SE.

Love et al. (2000) measured ^{36}Cl, chemical and isotopic compositions of the groundwaters from a northern transect (10 wells) and a southern transect (11 wells). Compared to their study area, the present work covers the major part of the northern transect, with eight wells sampled between Marys Well and Duckhole (Fig. 1). Three unconfined wells close to the recharge area were not examined in this study. Although the wells along the southern transect studied by Love et al. (2000) were not sampled, two additional wells (Raspberry and Freeling) located very close to this transect were examined. These wells are regarded as being from the southern transect. Upgradient of these two transects the aquifer either outcrops or is unconfined. Besides these two transects, there are two major differences in sample locations between the current study and Love et al. (2000). The study area is extended further north (Macumba area), with groundwater from 10 wells from Mt. Dare to Macumba included in the current study. Four samples from other locations near the two transects (Plantation, Ockenden, Milne Springs and Six Mile) were also examined.

The main aquifer system comprises the Jurassic-aged Algebuckina Sandstone and the Cretaceous-aged Cadna-owie Formation (J-K aquifer) (Wopfner et al., 1970; Habermehl, 1980). The Algebuckina Sandstone rests on highly weathered and kaolinised basement rocks, and comprises a lower kaolinitic sandstone unit and an upper, well-sorted clean sandstone (Parkin, 1969). The Cadna-owie Formation disconformably overlies the Algebuckina Sandstone and consists primarily of feldspathic sandstone, and micaceous and carbonaceous siltstone, representing the sedimentary record of Early Cretaceous marine transgression (Wopfner et al., 1970). The thickness of the aquifer is fairly

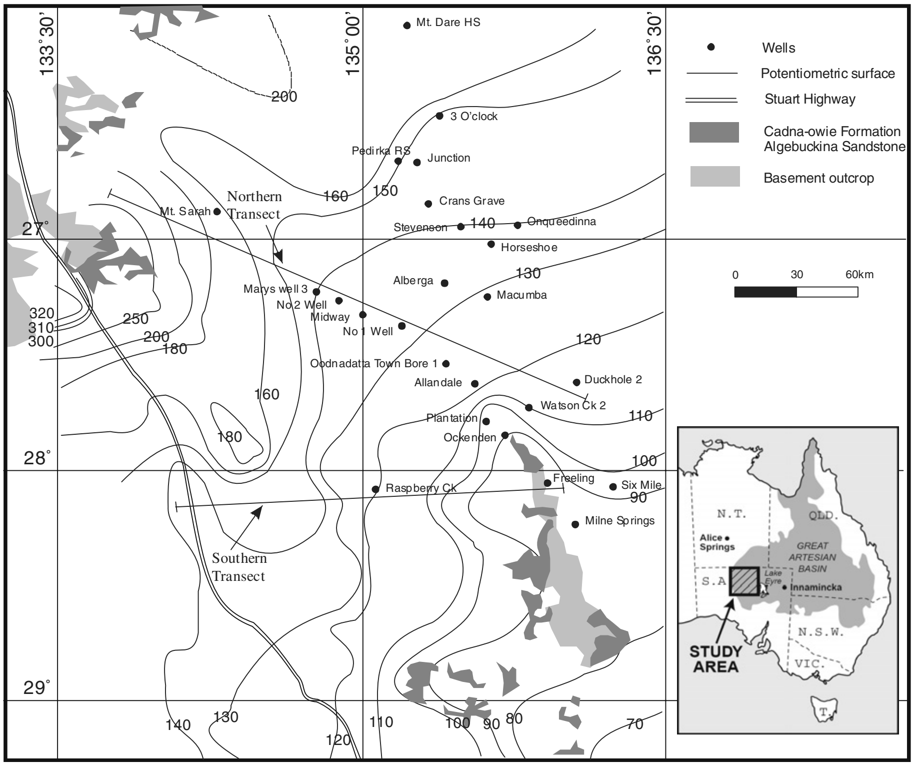

Fig. 1. Location map of the study area, SW Great Artesian Basin, Australia, showing potentiometric contours (meters above sea level) and sampling wells. Both northern and southern transects studied by Love et al. (2000) are marked.

uniform in the study area, with a maximum thickness of 200 m.

The Cadna-owie Formation is conformably overlain by the Bulldog Shale. The basal parts of the Bulldog Shale consist of a thinly interbedded silt and shale sequence, grading up into dark grey shale (Parkin, 1969). The thickness of the Bulldog shale varies, and is generally less for the southern transect, varying from less than 100 to 200 m. Along the northern transect, the thickness varies from approximately 110 m in Marys Well to 250 m in Duckhole, and reaches a maximum of 500 m in Oodnadatta. The Bulldog Shale is comformably overlain by a glauconitic sand of the Oodnadatta Formation. The remaining part of the Oodnadatta Formation consists largely of silty shale and some lenticular limestones. Together with the Oodnadatta Formation, the Bulldog Shale forms a regional aquitard. Overlying the regional aquitard is a shallow unconfined aquifer consisting of fine-grained sand and silcrete.

3. Methods

3.1. Field sampling and measurements

Groundwater samples were collected from flowing or pumping bores during three field trips between January 1998 and November 1999. At least three borehole casing volumes of groundwater were extracted before a water sample was taken. Each groundwater sample was divided into two portions. One portion was retained for stable O, H and Cl isotope analyses, and the other portion was filtered through 0.45 μm filter paper for chemical analysis. Samples for cation analysis were acidified to a pH value of less than 2.

Parameters such as pH, electrical conductance, and alkalinity of the groundwater samples were measured at the field sampling sites, and temperature of selected samples was also recorded. The results of the field measurements are summarized in Table 1.

Table 1
Chemical composition of groundwater samples from southwestern Great Artesian Basin, Australia

Sample name	pH	TDS (mg/L)	Temperature (°C)	Concentration (mg/L)							
				Ca	Mg	Na	K	Cl	HCO_3	SO_4	Br
Macumba area											
Mt. Dare HS	7.4	1133		45	16	310	11	403	159	177	0.72
3 O'clock	7.2	987	45	54	27	230	16	352	128	171	0.79
Pedirka RS	7.8	1261		62	35	300	21	463	183	195	1.11
Junction	7.1	1425	46	72	34	320	22	468	281	222	1.06
Crans Grave	7.4	1861	48	74	22	510	23	631	262	330	1.79
Stevenson	7.3	1994	49	64	15	580	18	681	268	360	2.41
Onqueedinna	7.4	2516	45	83	11	780	18	996	226	390	3.05
Alberga	7.5	2000	49	72	19	560	21	648	281	390	2.42
Horseshoe	7.7	2498	39	81	13	760	18	949	250	419	3.18
Macumba	7.8	2906	36	54	4	970	9	1260	238	360	3.44
Northern transect											
Marys Well	7.4	2024		108	35	482	35	682	278	388	3.04
No. 2 Well	7.3	1919		76	30	504	30	647	269	345	2.82
Midway	7.5	1903		68	28	508	27	625	268	362	2.58
No. 1 Well	7.6	1953		66	27	533	25	675	283	324	2.14
Oodnadatta TB1	7.0	1906	45	65	29	528	21	690	270	292	1.93
Allandale	7.4	3573	44	130	20	1100	14	1670	238	390	2.79
Watson Ck2	7.4	2668	38	54	5	870	10	1090	267	367	2.70
Duckhole 2	7.5	2577	36	53	4	840	9	1060	268	337	2.60
Southern transect											
Raspberry Ck	6.8	3208	30	213	104	685	41	1190	269	700	4.10
Freeling	7.8	2453		33	5	801	8	975	254	362	2.25
Other locations											
Plantation	7.6	2408		66	26	711	21	880	257	431	2.44
Ockenden	7.7	2631		93	16	769	16	945	240	535	3.24
Six Mile	7.5	1533		84	55	373	28	670	94	209	1.40
Milne Springs	7.8	2439		50	11	760	14	972	263	356	2.32

3.2. Rock leaching experiments

To determine the Cl isotope ratio of the Cl^- that was present in pore solutions of the rocks, leaching experiments were conducted on rock core samples. The core samples were taken at different depths from four boreholes in the Macumba area, including Junction (145–430 m), Mt. Sarah (250–295 m), Onqueedina (520 m), and Duckhole (150–240 m). Most of the rock samples were dark gray shale, retrieved from the Bulldog formation. Two samples were from the J-K aquifer, consisting primarily of sand with a small portion of clay.

The rock samples were broken into pieces and placed into 250 mL high-density polyethylene bottles, into which 100 mL of doubly-deionized water was added. After 24 h of shaking, the rock samples were disaggregated in water. The slurry was centrifuged and a portion of supernatant was taken for the Cl isotope analysis. The remaining samples were allowed to stand at room temperature for an additional 9 months and occasionally shaken by hand. The mixtures of selected samples were then centrifuged to extract the remaining supernatant for Cl isotope analysis, to determine if any change in Cl isotope composition occurred after further disaggregation of the sedimentary rocks.

3.3. Chemical and isotopic analyses

Major ions including Ca, Mg, Na, K and S were analyzed using inductively coupled plasma spectrophotometry (ICP), and Br was analyzed using ion chromatography (IC). The Cl concentration was determined using colorimetric methods. The reported alkalinity values which were measured using potentiometric titration in the laboratory are similar to the field measurements using the standard Hatch kit. The analytical uncertainty for these techniques was less than ±3%. The total dissolved solid (TDS) was calculated by summing all dissolved constituents, with HCO_3 converted to equivalent CO_3 (Drever, 1997).

The method used for Cl isotope analysis was modified after Long et al. (1993). Chloride in groundwater samples and rock leachates was precipitated as AgCl, which was reacted with methyl iodide to produce methyl chloride. The Cl isotope ratio was determined using a VG Sira-9 isotope ratio mass spectrometer. The measured Cl isotope ratios are expressed in the delta notation, defined as parts per thousand or per mil (‰) $\delta^{37}Cl = (R_{sample}/R_{SMOC} - 1) \times 1000$, where R_{sample} is the $^{37}Cl/^{35}Cl$ ratio of the sample and R_{SMOC} is that of standard mean ocean chloride (SMOC). The precision for Cl isotope analysis is ±0.1‰ based on 1σ standard deviation of measurements on the standard. The H isotopic ratio was determined using an euro vector elemental analyzer (EA) coupled with a Micromass IsoPrime continuous-flow isotope ratio mass spectrometer (CF-IRMS). The O isotopic composition was determined using a CO_2 equilibration method. The analytical precision for δ^2H is ±1.0‰ and for $\delta^{18}O$ is ±0.2‰.

4. Results

4.1. Water chemistry

The chemical compositions of the groundwater samples are recorded in Table 1, together with the other geochemical parameters measured in the field. The groundwater samples were neutral to slightly alkaline, with pH values varying from 6.8 to 7.8. Measured groundwater temperatures were between 30 and 49 °C. The chemical composition of the groundwater samples are Na–Cl dominated, typical of groundwater compositions in the southwestern flow systems (Herczeg et al., 1991). The salinity of the groundwaters ranged between 1000 and 3600 mg/L, and was positively correlated with the Cl^- concentration ($r^2 = 0.93$). An overall increase in salinity was observed along flow directions, especially in the Macumba area. For the northern transect, salinities of the groundwaters sampled upgradient were relatively constant, and increased towards the end of the transect.

The concentrations of Na, Ca, HCO_3, SO_4, Br, and Br/Cl are plotted versus Cl in Fig. 2. A linear correlation between Na and Cl was observed throughout the entire concentration range (Fig. 2a). Most of the groundwater samples had a Na/Cl ratio greater than 1. A group of samples (Mt. Dare, 3 O'clock, Pedirka and Junction) from the Macumba area with low salinities had a Na/Cl ratio close to unity. A Na/Cl ratio of 1 was also measured in Allandale groundwater, which had the highest salinity. Raspberry and Six Mile had Na/Cl ratios of 0.89 and 0.86, respectively, close to the ratio measured in seawater.

The correlations between Ca, HCO_3, SO_4 and Cl are poor for the groundwaters. The Ca concentrations ranged mostly between 0.8 and 2.7 mM, with the exception of Raspberry, which had a Ca concentration of 5.3 mM (Fig. 2b). Allandale also had a

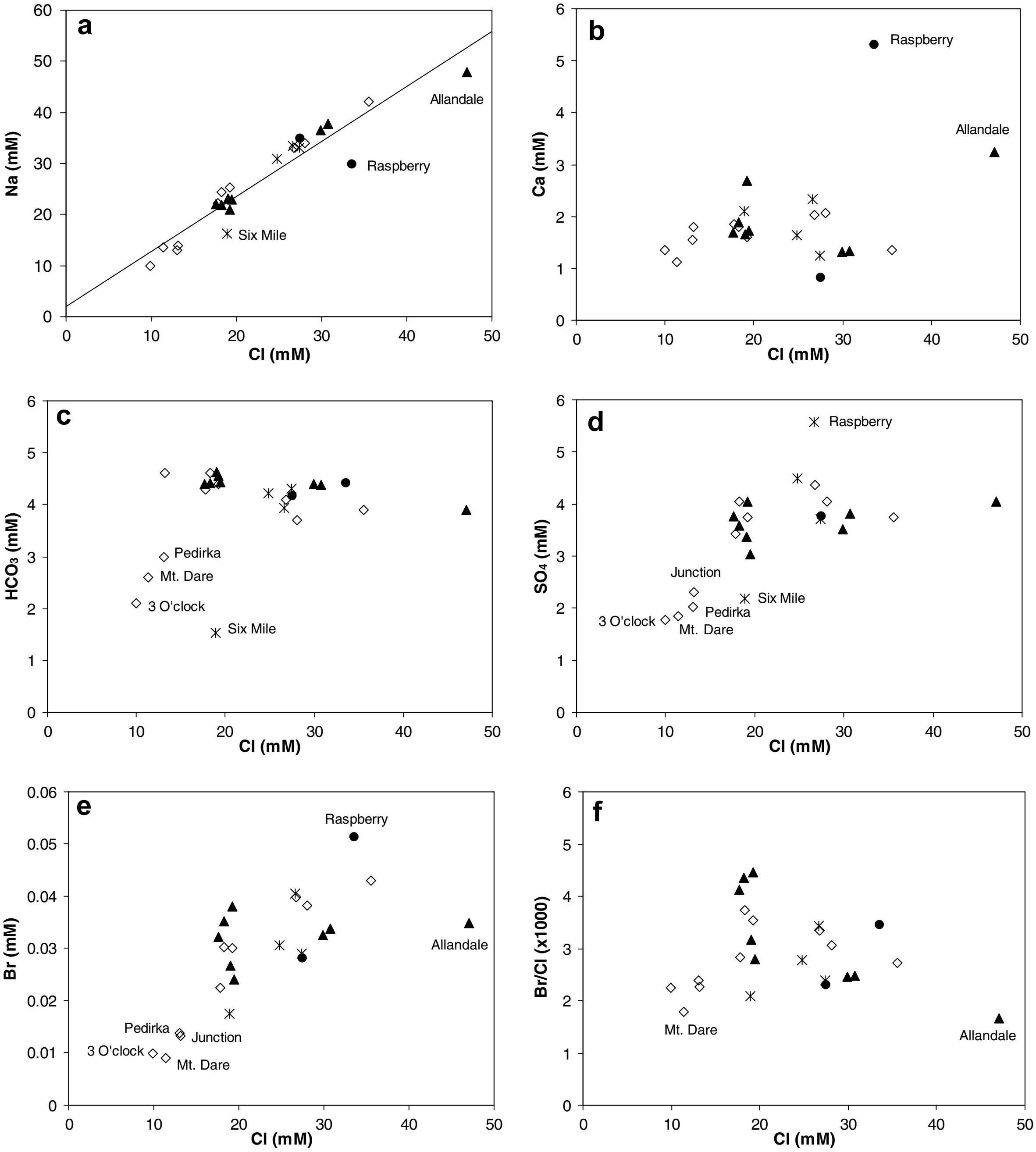

Fig. 2. Relationships between Cl^- and other major species measured in groundwater samples from southwestern GAB: (a) Na vs. Cl (the slope of the regression line throughout all the data points is 1.08); (b) Ca vs. Cl; (c) HCO_3 vs. Cl; (d) SO_4 vs. Cl; (e) Br vs. Cl; and (f) Br/Cl mass (1000×) vs. Cl.

higher Ca concentration relative to the rest of the samples. The HCO_3 concentration falls in the range between 3.7 and 4.7 mM for most of the samples, except for three Macumba samples (3 O'clock, Mt. Dare, and Pedirka) (Fig. 2c). The lowest HCO_3 concentration was measured in the Six Mile groundwater. Similar behavior was observed for SO_4, which ranged from 3.0 to 5.6 mM for most of the samples (Fig. 2d). Low SO_4 concentrations were also measured in four Macumba samples and in the sample from Six Mile. Similar to Ca, the highest SO_4 was observed in Raspberry. An overall increase in the Br concentration as a function of Cl was observed (Fig. 2e). Similar to SO_4, the lowest Br concentrations were found in four Macumba samples with low salinities, and the highest Br concentration was measured in Raspberry. The Br/Cl mass ratio had a narrow range between 0.0017 and 0.0045, with the lowest value being observed in Allandale (Fig. 2f).

4.2. Hydrogen and oxygen isotopes of groundwater

The H and O isotope compositions of the groundwater samples ranged from −56.7‰ to −39.8‰ and from −7.7‰ to −1.9‰, respectively (Table 2). In Fig. 3, the δ^{2}H values are plotted against δ^{18}O, along with the local meteoric water line (LMWL). The measured data all lie to the right of the local meteoric water line, indicating evaporation of rainfall during recharge. Most of the groundwater samples fall within a narrow range of δ^{18}O values between −6.4‰ and −5.7‰. The δ^{2}H value varies between −51‰ and −46‰. Three samples including Mt. Dare, 3 O'clock and Pedirka are outside of the range observed for both δ^{18}O and δ^{2}H. Given that residence times of up to 600 ka were reported for the groundwaters from this area (Love et al., 2000), it is not possible to determine the isotopic compositions of the recharge water based on the current local meteoric water line because this line varies as a function of climatic conditions.

Table 2
Chlorine, H and O stable isotopic compositions of groundwaters from southwestern Great Artesian Basin, Australia

Sample location	δ^{2}H (‰ VSMOW)	δ^{18}O (‰ VSMOW)	δ^{37}Cl (‰ SMOC)
Macumba area			
Mt. Dare HS	−56.7	−7.73	−0.07
3 O'clock	−53.5	−6.99	0.01
Pedirka RS	−39.8	−1.93	−0.38
Junction	−50.2	−6.27	−0.32
Crans Grave	−49.1	−6.32	−0.47
Stevenson	−47.5	−5.89	−0.63
Onqueedinna	−46.0	−6.13	−1.15
Alberga	−48.0	−6.30	−0.45
Horseshoe	−50.0	−5.68	−0.97
Macumba	−43.4	−6.03	−2.51
Northern transect			
Marys Well	−49.2	−5.84	−0.09
No. 2 Well	−47.9	−6.43	−0.09
Midway	−46.5	−6.34	−0.08
No. 1 Well	−48.7	−6.19	−0.25
Oodnadatta TB1[a]	−48.5	−6.33	−0.26
Allandale	−46.6	−5.90	−0.54
Watson Ck2[a]	−45.3	−5.89	−1.56
Duckhole 2[a]	−46.0	−5.85	−1.35
Southern transect			
Raspberry Ck[a]	−45.4	−5.66	−0.10
Freeling	−48.1	−6.07	−0.07
Others			
Plantation	−47.8	−5.82	−0.66
Ockenden	−46.1	−5.82	−0.65
Six Mile	−51.1	−6.32	−0.42
Milne Springs	−51.3	−6.14	−0.63

[a] The Cl isotopic composition has been published by Lehmann et al. (2003).

In Fig. 4, the δ^{18}O values of the groundwaters are plotted against the Cl^{-} concentrations. Samples that contain more than 500 mg/L Cl^{-} have an average δ^{18}O value of −6.0‰, with a standard deviation of 0.24. Large variations in δ^{18}O are seen in the samples with Cl^{-} concentrations below 500 mg/L, suggesting that these samples are from near the recharge area. As the groundwater flows downgradient, it appears that δ^{18}O values are averaged as a result of mixing of the different recharge waters.

4.3. Chlorine isotope ratios of groundwater

The δ^{37}Cl values measured for the groundwaters ranged from −2.5‰ to 0.0‰ (Table 2). In the Macumba area, the Cl isotope ratios decreased along the flow direction toward Macumba. The two wells farthest from Macumba (Mt. Dare and 3 O'clock) had δ^{37}Cl values that are close to SMOC, but decreased to −2.5‰ at Macumba. Similarly, the δ^{37}Cl values decreased along the flow direction of the northern transect. The first three samples on the transect (Marys Well, No. 2 Well, and Midway) also had δ^{37}Cl values similar to SMOC, and decreased to −1.6‰ in Watson. Two samples close to the southern transect (Raspberry and Freeling) had a δ^{37}Cl value of −0.1‰, within the analytical uncertainty of SMOC. Four samples located near the two transects (Plantation, Ockenden, Six Mile, and Milne Springs) had negative δ^{37}Cl values between −0.7‰ and −0.4‰.

The chlorine isotope compositions measured in all 24 groundwater samples are plotted against Cl^{-} concentrations in Fig. 5. A negative correlation between δ^{37}Cl and Cl is observed ($r^{2} = 0.9$). This correlation can be described by a second order polynomial equation. At lower Cl^{-} concentrations, δ^{37}Cl values are close to zero, but decrease gradually with increasing Cl^{-} concentration. A marked reduction in δ^{37}Cl values was observed at higher Cl^{-} concentrations. Allandale, Raspberry, and Freeling were not included in generating the correlation curve. Of this group, Raspberry and Freeling

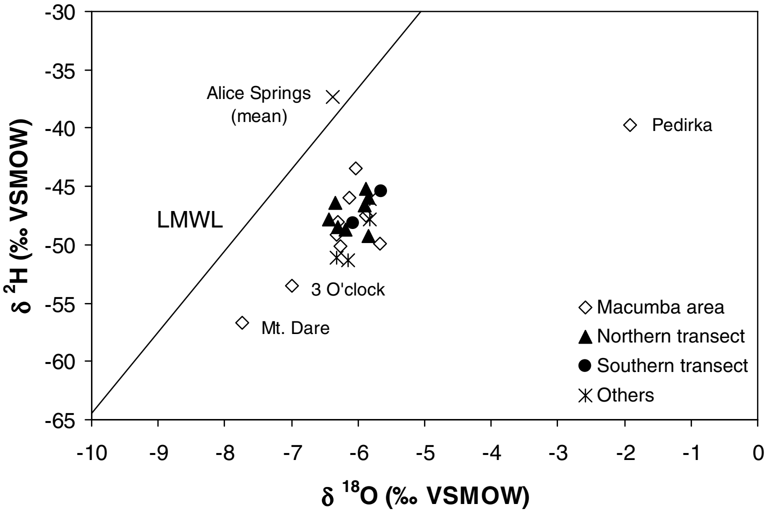

Fig. 3. Relationship between $\delta^{18}O$ and $\delta^{2}H$ of groundwater samples from southwest GAB. LMWL: local meteoric water line from Love et al. (2000), defined by $\delta^{2}H = 6.95\delta^{18}O + 5.06$. The precipitation weighed annual mean at Alice Springs is −37.3‰ and −6.38‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively (Love et al., 2000).

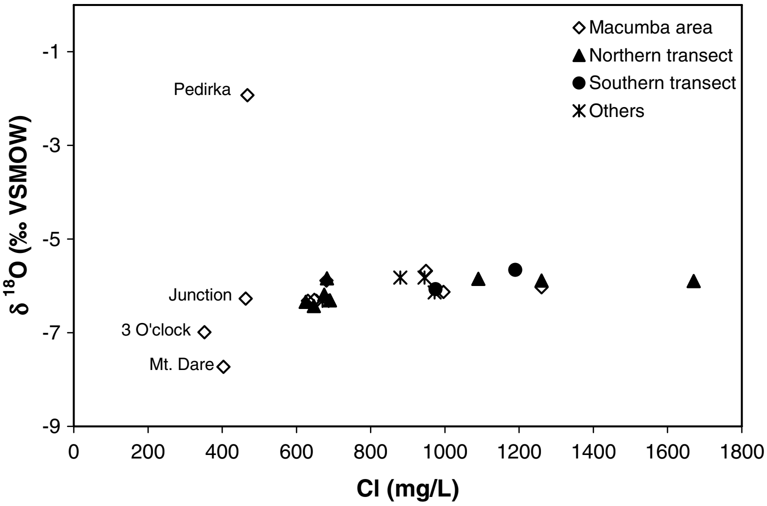

Fig. 4. Relationship between $\delta^{18}O$ composition and Cl^{-} concentration for groundwater samples from southwestern GAB.

are located close to the southern transect. The chemistry of Allandale is quite different from the rest of the samples from the northern transect, with exceptionally high Na and Cl concentrations.

4.4. Chlorine isotope ratios of rocks

Chlorine isotope compositions were measured in leachates of rock samples from four different locations, and the results are recorded in Table 3. The Cl isotope ratios measured in the leachates after 9 months were similar to the 24-h leachates. Any differences observed between the short-term and long-term results are within the analytical uncertainties. These results indicate that effective leaching can be achieved within 24 h, and that the measured Cl isotope values are representative of the leachable portion of Cl^{-} in the rocks.

Leachates of two Bulldog shale samples from Junction had $\delta^{37}Cl$ values of 0.0‰ and −0.9‰. A value of 0.2‰ was measured for the leachate of the aquifer material from the same borehole. Three Bulldog shale samples from Duckhole were leached for Cl isotope analysis. These samples were taken from the depths between 150 and 220 m, and had negative $\delta^{37}Cl$ values ranging from −2.0‰ to

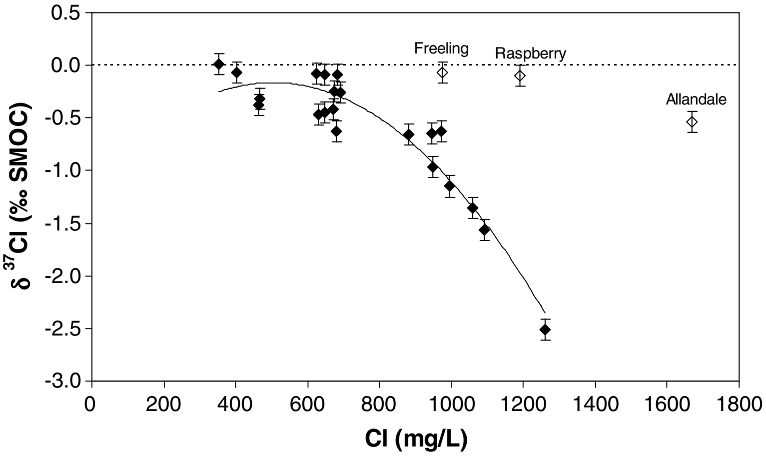

Fig. 5. δ^{37}Cl vs. Cl^- concentration for groundwater samples from southwest GAB. Solid line represents the regression line (2nd order polynomial) with the exclusion of Allandale, Raspberry, and Freeling.

Table 3
Chlorine stable isotopic composition of rock leachates from selected drill core samples from southwestern Great Artesian Basin, Australia

Sample name	Depth (m)	δ^{37}Cl (‰ SMOC)		Rock type
		1st Leaching	2nd Leaching	
Junction	147–175	−0.03	−0.20	Gray shale
	279–317	−0.90	−0.63	Dark gray shale
	420–427	0.21		Sand, pebble, clay (aquifer)
Onqueedina	516–519	−1.95		Dark gray shale
Duckhole 2	150–159	−1.95		Dark gray shale
	189–198	−1.79	−1.58	Gray shale
	210–216	−1.10		clay with sand particles
	231–243	−1.77		Sand and clay (aquifer)
Mt. Sarah	251–256	−1.17		Dark gray shale
	291–294	−0.25		Dark gray shale

−1.1‰. A δ^{37}Cl value of −1.8‰ was measured in the leachate of the aquifer sample also taken from Duckhole. Bulldog shale samples from Mt. Sarah had δ^{37}Cl values from −1.2‰ to −0.3‰. Mt. Sarah is located NW of the study area, near the northern transect. A highly negative value of −2.0‰ was measured in an Onqueedina shale sample retrieved from a depth of over 500 m.

5. Discussion

5.1. Source of chloride and chlorine isotopic compositions

Potential sources for the Cl^- observed in the groundwater samples include solutes in recharge water and subsurface addition. Chloride could be enriched in the recharge waters through processes such as evaporation/evapotranspiration, with marine aerosol as the major source of Cl^-. Recharge water could also gain Cl^- from dissolution of evaporites where these minerals are present. In general, an increase in the Cl^- concentration is observed along the flow directions. This concentration increase could be due to mixing of recharge water with saline groundwater, or due to the addition of Cl^- from a subsurface source including either the J-K aquifer or the overlying Bulldog shale.

The Cl isotopic composition, especially the relationship between δ^{37}Cl and the Cl^- concentration, can aid in determining the sources of Cl^- and mechanisms responsible for fractionation of Cl isotopes (Kaufmann et al., 1988). In this study, the measured relationship between δ^{37}Cl and the Cl^- concentration are compared with the calculated models for different processes to assess Cl^- sources and transport processes, and to determine their predominance at different locations. Additional geochemical parameters, such as Br/Cl ratio and the relationship between O isotopic composition of water and Cl^- concentration, are also used. The discussion is focused primarily on the stable Cl isotope results, and follows the framework presented by Love et al. (2000).

5.1.1. *Dissolution of evaporites*

Calf and Habermehl (1984) suggested that the water chemistry of the southwest GAB might be derived from the outcropping evaporitic and gypsiferous rocks near the western marginal recharge area. Of the evaporites, halite is the most common Cl-bearing mineral identified. Dissolution of halite is therefore evaluated to determine its potential contribution to the recharge water. Measurements on the stable Cl isotope ratios of halite are examined to determine if this parameter can be used to differentiate halite dissolution from other processes.

Previous studies on Cl isotopic compositions of naturally-occurring halite reveal a wide range in $\delta^{37}Cl$ values. Eggenkamp et al. (1995) measured a $\delta^{37}Cl$ range between −0.6‰ and 0.2‰ for halite from Permian salt formations of northern Europe. More extensive measurements were performed by Eastoe et al. (1999), who reported that the $\delta^{37}Cl$ values for halite samples from the Palo Duro Basin in the southern USA varied between −0.1‰ and 0.4‰. Eastoe et al. (2001) also studied Jurassic salt in the Gulf Coast Basin of the USA and $\delta^{37}Cl$ ranges of −0.5–0.3‰ (bedded) and 0.0–0.5‰ (diapiric) were determined. These studies show that both positive and negative $\delta^{37}Cl$ values are possible for halite derived from the evaporation of seawater. The $\delta^{37}Cl$ range measured for halite formation under evaporitic conditions was further evaluated by laboratory studies. Eggenkamp et al. (1995) applied a Rayleigh fractionation model to predict the evolution of $\delta^{37}Cl$ in salt precipitates during the evaporation of seawater. Using experimentally-determined fractionation factors between salt minerals (NaCl, KCl, and $MgCl_2 \cdot 6H_2O$) and brines, a range of 0.3‰ to −0.6‰ was calculated for halite precipitated from seawater with a $\delta^{37}Cl$ value of 0.0‰. In a laboratory study, Eastoe et al. (1999) evaporated seawater to measure $\delta^{37}Cl$ in the precipitated halite. The measured change in $\delta^{37}Cl$ (0.2‰ to −0.5‰) was in a good agreement with the range predicted by Eggenkamp et al. (1995).

Given that $\delta^{37}Cl$ values from halite dissolution are between −0.6‰ and 0.3‰, only five samples out of the 24 groundwaters examined in this study had $\delta^{37}Cl$ values which clearly lie beyond the range of halite dissolution. For the remainder of the groundwater samples studied, geochemical parameters other than Cl isotope ratio are required to understand the possible effect of halite dissolution on the groundwater compositions. The Br/Cl ratio is often used to identify processes related to precipitation and dissolution of halite. Ullman (1995) reported a Br/Cl mass ratio of less than 0.0001 for halite from Lake Frome, South Australia. The Br/Cl ratio measured in the current study varied from 0.0017 to 0.0045, very close to the range between 0.0021 and 0.0047 reported by Love et al. (2000). Two exceptions are groundwaters from Allandale and Mt. Dare, which had Br/Cl ratios of 0.0017 and 0.0018, respectively. The Br/Cl ratios determined in the current study are much higher than the value reported for halite by Ullman (1995), ruling out its potential contribution to the recharge water. This is consistent with the previous study which documented that evaporite deposits have not been identified in the study area (Love et al., 2000).

5.1.2. *Marine aerosol input and evapotranspiration*

Marine aerosol input has been considered to dominate the hydrogeochemistry of continental groundwater in Australia (Turner and Frape, 1995). Chloride concentrations of up to 120 g/L measured in hypersaline groundwaters from the paleochannel aquifers in Western Australia were attributed to the slow accumulation and deposition of atmospheric marine aerosols. In the study area, the main source of Cl^- in the recharge waters is likely from marine aerosol in rainfall. Although the regional rainwater Cl^- concentration was estimated to be 0.625 mg/L (Keywood, 1995), much higher concentrations could result from processes such as evaporation/evapotranspiration.

A $\delta^{37}Cl$ range between −0.9‰ and +2.5‰ has been reported for marine aerosol samples collected in Bermuda and in the central equatorial Pacific (Volpe and Spivack, 1994; Volpe et al., 1998). Volpe and Spivack (1994) observed a correlation between $\delta^{37}Cl$ and Cl^- deficit measured in aerosol particles. Based on the agreement between the measured and the laboratory-derived correlations, the authors argued that the enrichment in ^{37}Cl resulted from the volatilization of HCl from acidified aerosols. The presence of anthropogenic SO_2 and NO_x in the atmosphere was believed to be the cause of acidification. For marine aerosols derived from areas where there is no anthropogenic input, a δ^{37}Cl value close to SMOC is expected. Turner and Frape (1995) measured Cl isotopic compositions for low-salinity recharge waters in Western Australia, and reported a δ^{37}Cl range between $-0.4‰$ and $+0.4‰$. Marine aerosols were thought to be the main source of the Cl^-.

During evaporation/evapotranspiration, Cl isotope fractionation would only occur in acidic waters or when a Cl^--bearing salt mineral precipitates (Volpe and Spivack, 1994; Eggenkamp and Schuiling, 1995; Eggenkamp et al., 1995). The groundwater samples investigated in this study had pH values close to neutral or slightly alkaline. Although the chemistry of the groundwaters may have been modified after recharge, it is unlikely that the recharge water was highly acidic. The salinity measured in the groundwater ranged between 1000 and 3900 mg/L, ruling out the possibility of salt precipitation during evapotranspiration. Therefore, it is reasonable to assume that marine aerosol input and subsequent evapotranspiration would generate δ^{37}Cl values close to SMOC.

The Cl isotope ratios measured in this study showed an overall depletion in ^{37}Cl for all groundwater samples. Considering the analytical uncertainty for Cl isotope measurements of $\pm 0.1‰$, seven samples had δ^{37}Cl values similar to SMOC. These samples are from three different locations. Two of the samples (Mt. Dare and 3 O'clock) are from the northern margin of the Macumba area. In the northern transect, three samples including Marys Well, No. 2, and Midway had δ^{37}Cl values close to zero. Near the southern transect, samples from both Raspberry and Freeling also had Cl isotopic compositions similar to SMOC.

Both Mt. Dare and 3 O'clock had salinities of approximately 1000 mg/L, which were among the lowest values for the groundwater samples studied. These groundwaters were likely from near the recharge area as indicated by their low salinities and highly variable δ^{18}O values (see Fig. 4). The first three wells upgradient of the northern transect were very similar in chemical compositions, with a δ^{37}Cl value close to zero. The near zero δ^{37}Cl value may imply that these groundwaters inherit Cl^- from the recharge water. If this is the case, evapotranspiration was more substantial compared to the Macumba area because the salinities of these groundwaters were almost twice those measured in Mt. Dare and 3 O'clock. Alternatively, a near zero Cl isotope composition may be generated by adding Cl^- from a subsurface source, which also has a δ^{37}Cl value close to zero.

Raspberry and Freeling groundwaters also had Cl isotopic compositions close to SMOC. In Fig. 5 where δ^{37}Cl is plotted against Cl concentration, a correlation is observed for all but three groundwater samples, including Raspberry and Freeling. Both Raspberry and Freeling are located close to the southern transect. The groundwater samples from the southern transect showed a linear correlation between δ^{18}O and the Cl^- concentration (Love et al., 2000). Based on this correlation, the authors identified that evapotranspiration was the major process accounting for the fluctuation in the Cl^- concentrations (up to 2500 mg/L). The measured δ^{18}O and Cl^- concentrations of Raspberry and Freeling follow the same trend generated by the groundwaters from the southern transect, implying that these two samples may have undergone similar processes. The Cl isotope results provide an extra line of evidence to support evapotranspiration as the dominant process concentrating Cl^- along this transect.

5.1.3. Mixing of recharge with saline groundwater

A general increase in the Cl^- concentration was observed along the major flow directions, i.e., from Mt. Dare to Macumba in the Macumba area, and from Marys Well to Duckhole along the northern transect. Mixing of diluted recharge waters with saline groundwaters could be a potential mechanism accounting for the increase in Cl^-.

If mixing is the process responsible for the Cl^- variation between two groundwater end-members, a straight line should be generated on the δ^{37}Cl vs. 1/Cl diagram. For example, Eastoe et al. (2001) constructed several mixing trends on the δ^{37}Cl vs. 1/Cl diagram to explain the Cl isotopic compositions measured in formation waters from the Gulf Coast Basin. Hendry et al. (2000) applied this relationship to explain solute migration in a clay-rich aquitard system. Based on the distribution of Cl^-, Br^-, and Cl isotope ratios, Hendry et al. (2000) identified 5 Cl end-members. Linear relationships observed between end-members were thought to represent four mixing zones. Another successful application of the δ^{37}Cl vs. 1/Cl correlation can be found in Godon et al. (2004). The authors attributed the measured δ^{37}Cl and Cl^- concentration in interstitial fluids from mud volcanoes in the Barbados accretionary complex to mixing between seawater and two deep components. In their study, all the data points plotted inside the mixing lines defined by these three end-members.

To test the mixing hypothesis for the SW flow system of GAB, the possible correlation between δ^{37}Cl and 1/Cl was studied. Examination of the measured Cl isotope compositions reveals that the groundwater samples from the Macumba area may be most appropriate for use in the modeling (see Table 2). The southern transect had small data sets, with only two sample points. The Cl isotope ratio measured in four wells near two transects had only two distinctive values. Although eight samples were studied for the northern transect, the Cl isotope ratios fall mainly into two groups with the exclusion of Allandale: near zero (−0.1‰ to −0.3‰) and a highly negative value (−1.5‰). It is not possible to determine if the correlation is linear when there are only "two clusters" of data. In contrast, a large variation in δ^{37}Cl values was observed for groundwater samples from the Macumba area, and a gradual increase in the Cl concentration was measured in the flow direction. In the modeling, two samples from the northern transect (Watson and Duckhole), which are located further down gradient from Macumba, were also considered.

To construct a mixing curve, two end-members need to be defined. It is likely that the sample with the lowest Cl^- concentration and highest δ^{37}Cl value (close to SMOC) is most representative of the recharge water. The sample with highest Cl^- concentration and a highly depleted δ^{37}Cl value could be associated with the saline groundwater. Using these criteria, samples 3 O'clock and Macumba are chosen as the recharge and saline groundwater end-members, respectively. Modeling of mixing between these two end-members generates a straight line, as indicated by the mixing line on the δ^{37}Cl and 1/Cl diagram (Fig. 6). When the measured δ^{37}Cl values and Cl^- concentration of the groundwater samples are plotted on this diagram, they do not fall on the mixing line. For the same Cl^- concentration, much lower δ^{37}Cl would be expected to result from the mixing than were actually measured. This disagreement between the measured data and the modeling results indicates that mixing between dilute recharge water and saline groundwater is not likely to be the mechanism responsible for the increase in the Cl^-measured along the flow directions.

5.1.4. Addition of chloride from subsurface source

After ruling out salt dissolution, rainfall, and mixing as the dominant Cl^- sources for the majority of groundwater samples examined, the only possibility remaining is a subsurface source, possibly either the J-K aquifer or the Bulldog shale. For the Milk River aquifer, Fabryka-Martin et al. (1991) proposed diffusion of saline water from less permeable sedimentary rocks within the aquifer as the major source of Cl^-. Similar to the Milk River aquifer, low permeable units (e.g. clay, siltstone) are also present in the J-K aquifer. In this study, two rock samples from the J-K aquifer were leached

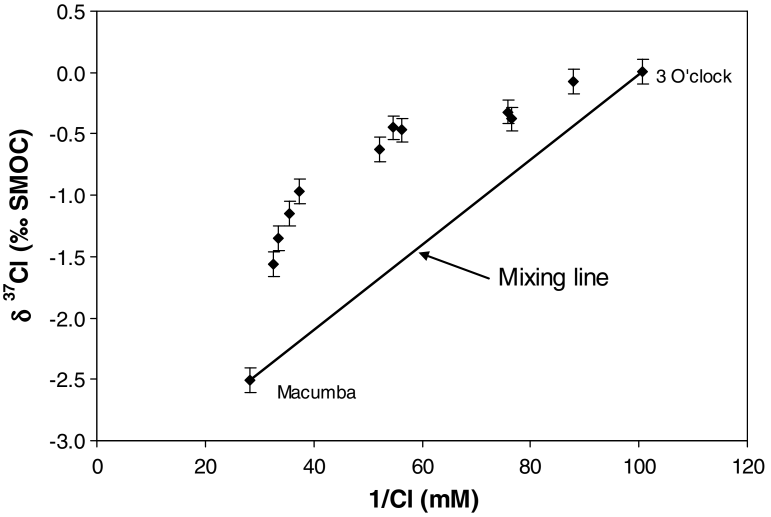

Fig. 6. Simulation of mixing between two end-members: 3 O'clock and Macumba, along with the measured sample points from the Macumba area.

for Cl^- isotope analysis. The $\delta^{37}Cl$ values of 0.2‰ and −1.8‰ were determined for Junction and Duckhole, respectively. However, it is not possible to determine if the aquifer is the source for Cl^- based on these $\delta^{37}Cl$ values. Lehmann et al. (2003) measured the concentrations of U and Th in the sandstone and shale retrieved from the J-K aquifer and the Bulldog aquitard of the study area, and used them to estimate the potential ^4He contribution of the sandstone to the groundwater. It was found that in situ production of He in the aquifer was too small to account for the ^4He concentrations measured in the groundwaters, implying the existence of an additional source. By comparing the $^3He/^4He$ ratios measured in the groundwater samples with those calculated for in situ production, they concluded that the source of the extra He was located in the Bulldog shale. Lehmann et al. (2003) further suggested that Cl^- was from the same source as He based on the linear relationship observed between $\delta^{37}Cl$ and ^4He.

If the concentration difference between two wells results solely from the addition of Cl^- from a subsurface source, the Cl isotope composition of the rock (Cl^- source) can be calculated based on the Cl^- concentrations and the $\delta^{37}Cl$ values measured in the groundwaters. The calculated rock signatures can then be compared with the measured values to determine the significance of this mechanism. In the calculation, the total Cl^- concentration measured in groundwater (C_t) is described using the following equation:

$$C_t = C_i + C_a \tag{1}$$

where C_i is the input of Cl^- from recharge water and C_a is the Cl^- being added from a subsurface source. Based on the mass balance, Cl isotope composition measured in the groundwater can be represented by

$$(\delta^{37}Cl)_{groundwater} = (C_i/C_t)(\delta^{37}Cl)_{recharge} + (C_a/C_t)(\delta^{37}Cl)_{rock} \tag{2}$$

where $(\delta^{37}Cl)_{groundwater}$ and $(\delta^{37}Cl)_{rock}$ are the Cl isotope ratios measured in groundwater and rock, respectively. The data set used in this calculation is the same as that used in modeling the mixing process, including 10 samples from the Macumba area and two from the northern transect (Watson and Duckhole). The chemical composition of sample 3 O'clock was assumed to represent the recharge water, with a $\delta^{37}Cl$ value of zero. The Cl^- concentration of the groundwater sample at each location was compared to the Cl^- from 3 O'clock, and the difference was attributed to addition from the subsurface source (C_a). The calculated $(\delta^{37}Cl)_{rock}$ values are plotted in Fig. 7, together with the measured $\delta^{37}Cl$ from leachates of the Bulldog shale.

The calculated rock signature for Junction was −1.3 ± 0.4‰, compared with the two measured values of 0.0‰ and −0.9‰ at depths of approximately 160 and 300 m, respectively. The more negative value measured at the greater depth is within the

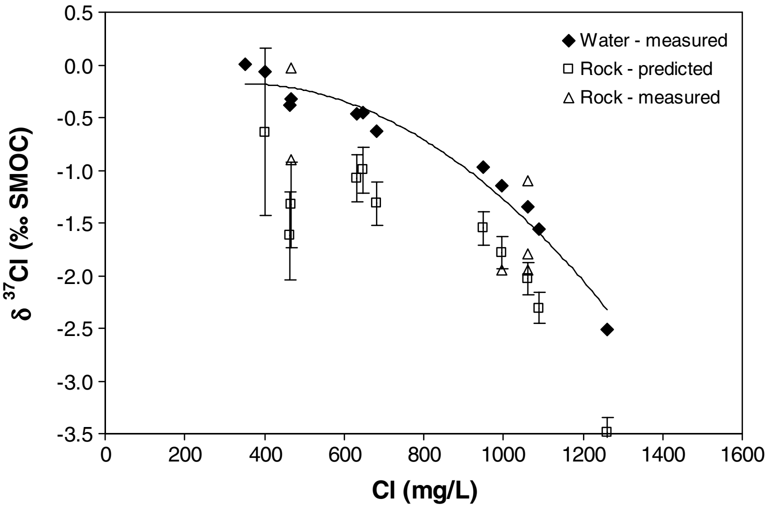

Fig. 7. A comparison of Cl isotopic compositions predicted for rock with those measured in the leachates of the Bulldog shale. $\delta^{37}Cl$ values of groundwater samples from the Macumba area were also plotted, with a regression line. The error bars for the predicted $\delta^{37}Cl$ are calculated assuming that the analytical precisions for Cl isotopic composition of groundwaters are ±0.1‰.

range of the predicted δ^{37}Cl. Excellent agreement between the measured and predicted δ^{37}Cl was found for Onqueedina, with values of −2.0‰ and −1.8 ± 0.2‰, respectively. Variations between −2.0‰ and −1.1‰ were found in the Duckhole rocks retrieved from different depths. The predicted δ^{37}Cl for the subsurface source was −2.0 ± 0.2‰. In general, the simulated δ^{37}Cl values for Cl^- addition from a subsurface source match well with the δ^{37}Cl measured in the Bulldog leachates. This agreement supports the hypothesis that the Cl isotope ratios measured in this set of groundwater samples are inherited from the overlying Bulldog shale. It is noted that the Cl isotope composition of the Bulldog shale at each location was calculated based on the assumption that addition of Cl^- from the aquitard only occurred at that specific location. As indicated by an increase in the Cl^- concentration, Cl^-has been gradually added to the groundwater along the flow paths.The calculated rock signatures therefore represent the average δ^{37}Cl value between the location simulated and 3 O'clock.

5.2. Possible mechanisms of chlorine isotope fractionation in aquitards

In the current study, three distinctive features of the Cl isotope ratios measured in the leachates of the aquitard rocks were observed: (1) all samples had negative δ^{37}Cl values, ranging between near zero to −2.0‰. Given that δ^{37}Cl values as low as −2.5‰ were measured in groundwaters, values below −2.0‰ are expected if the aquitard is the only subsurface source of Cl^-; (2) in the Macumba area, a spatial distribution in δ^{37}Cl may exist, decreasing downgradient from near the recharge area to Macumba (see Fig. 7); (3) variations in δ^{37}Cl were observed with depth. However, with only two or three sample points in each depth profile over a distance between 40 and 170 m, it is not possible to determine if these variations represent a systematic change in δ^{37}Cl as a function of depth.

Negative δ^{37}Cl values have been determined in pore waters associated with low permeability sediments in various geological settings. The negative signatures could be generated during diagenesis of sediments, such as those observed from mud volcanoes in subduction zones (Ransom et al., 1995; Spivack et al., 2002; Godon et al., 2004). Alternatively, they can also result from transport of Cl^- after the rock is formed. In the later case, diffusion is a process that has commonly been invoked to explain the negative Cl compositions observed in the field (Desaulniers et al., 1986; Eggenkamp et al., 1994; Groen et al., 2000; Arcuri and Brimhall, 2003). Two mechanisms have been proposed to explain highly negative δ^{37}Cl values generated during sediment diagenesis. Interactions between clay minerals and pore waters during sediment diagenesis and metamorphism were suggested to be the major processes responsible for these highly negative values (Ransom et al., 1995; Spivack et al., 2002). On the other hand, Godon et al. (2004) proposed ion filtration as a possible process to explain the negative δ^{37}Cl values measured in pore fluids. Ion filtration was believed to occur during compaction of the sediments, releasing a ^{37}Cl-enriched fluid. As a result, the residual fluid trapped in the increasingly compacted sediments is depleted in ^{37}Cl.

The Cl isotopic compositions measured in the leachates of the Bulldog shale may reflect the pore waters that reside in the shale, or may have been modified from the original values by various transport processes. Pore spaces were likely filled with seawater during sedimentation. It is not possible to generate the negative δ^{37}Cl values measured over a large scale through subsequent Cl^- transport processes such as diffusion or ion filtration. These processes would produce both positive and negative values if the original Cl isotope composition were close to zero. Similar to the Black Ridge sediments studied by Hesse et al. (2000), it is unlikely that interaction between hydrous minerals and water is responsible for the negative δ^{37}Cl values measured in this study. Hesse et al. (2000) presented three lines of evidence to support their arguments, including: (1) the absence of highly reactive volcanogenic detritus; (2) the unlikeliness of detrital clay minerals to undergo early diagenetic alteration; (3) the small amount of authigenic clay minerals relative to the overwhelming detrital background. These lines of evidence also apply well for the Bulldog shale examined in this study.

Chloride ions present in the pore waters of the Bulldog shale may have been transported through mechanisms such as advection, ion filtration, or diffusion. The ubiquitous presence of fractures in shale would allow leakage of groundwater from the shallow unconfined aquifer that overlies the Bulldog shale. If the groundwater had a δ^{37}Cl close to SMOC, progressive leaching of the pore water could result in an increase in δ^{37}Cl. Given that the extent of leaching of the pore water is likely higher near the recharge

Table 4
Ratio of subsurface addition of Cl^- to total Cl^- concentration (%) calculated using different $\delta^{37}Cl$ values for the Bulldog shale, southwestern Great Artesian Basin, Australia

Sample name	C_a/C_t (%)			
	$(\delta^{37}Cl) = -0.5‰$	$(\delta^{37}Cl) = -1.0‰$	$(\delta^{37}Cl) = -2.0‰$	$(\delta^{37}Cl) = -2.5‰$
Northern transect				
Marys Well	18	9	5	4
No. 2 Well	18	9	5	4
Midway	16	8	4	3
No. 1 Well	50	25	13	10
Oodnadatta TB1	52	26	13	10
Allandale	108	54	27	22
Watson Ck2	312	156	78	62
Duckhole	270	135	68	54
Southern transect				
Raspberry Ck.	20	10	5	4
Freeling	14	7	4	3

area, a $\delta^{37}Cl$ distribution pattern with higher $\delta^{37}Cl$ values close to the recharge area could result. However, this process is unlikely to occur in the Bulldog shale to a large extent due to the presence of an upward vertical hydraulic gradient across the Bulldog shale. Diffusion seems the most plausible mechanism for solute transport from the Bulldog shale to the groundwater. Love et al. (2000) evaluated the relative importance of diffusion and upward advection on the Cl^- transport through the Bulldog shale, and concluded that diffusion was responsible for the spatial variation in Cl^- observed. If diffusion is a dominant process, the Cl isotopic composition is expected to become more depleted with depth. This process, however, can not be evaluated based on the limited measurements of $\delta^{37}Cl$ on the Bulldog shale samples along each depth profile. More extensive study will be required to verify this hypothesis.

5.3. Implications of stable chlorine isotope results to ^{36}Cl dating

To apply the ^{36}Cl dating technique successfully, Cl^- must behave conservatively in the groundwater system, i.e. no Cl^- is added or removed from solution. If Cl^- concentration is modified after recharge, all the sources and sinks need to be quantified. Using Cl stable isotope ratios, this study has identified rainfall and subsequent evapotranspiration as the dominant source and concentrating process for Cl^- in groundwaters that have a $\delta^{37}Cl$ value close to SMOC. Subsurface addition of Cl^- from the pore water of the Bulldog shale by diffusion or/and mixing appears to be a significant source of Cl^- in groundwaters with negative $\delta^{37}Cl$ values.

If the Cl isotope composition of the subsurface source $(\delta^{37}Cl)_{rock}$ is known, the ratio of Cl^- from the subsurface source to the Cl^- concentration measured in groundwater (C_a/C_t) can be estimated using the following equation:

$$C_a/C_t = (\delta^{37}Cl)_{groundwater}/(\delta^{37}Cl)_{rock} \quad (3)$$

In this calculation, it is assumed that $\delta^{37}Cl$ of the recharge water is zero. Because the measured $\delta^{37}Cl$ were mainly between $-2.0‰$ and $-1.0‰$ for the Bulldog shale, the C_a/C_t ratios were calculated at the $(\delta^{37}Cl)_{rock}$ values of $-0.5‰$, $-1.0‰$, $-2.0‰$, and $-2.5‰$, respectively. The C_a/C_t ratios estimated for both the northern and southern transects are presented in Table 4.

For groundwaters from the northern transect that had a $\delta^{37}Cl$ value greater than $-0.3‰$ (i.e., Mary's Well, No. 2 Well, Midway, No. 1 Well, and Oodnadatta), marine aerosol input and subsequent evapotranspiration likely played a dominant role in concentrating Cl^-. For Oodnadatta groundwater, subsurface addition would account for 26% of the total Cl^- if the $\delta^{37}Cl$ of the rock were $-1.0‰$. If the subsurface source had a $\delta^{37}Cl$ value of $-2.0‰$, the percentage would drop to half. Based on the parameters measured for ^{36}Cl and ^{81}Kr dating, Lehmann et al. (2003) estimated the C_a/C_t ratio to be 8% for Oodnadatta. The dominance of evapotranspiration in these samples can also been seen in Fig. 8, where $\delta^{37}Cl$ is plotted against $^{36}Cl/Cl$. Substantial change in $^{36}Cl/Cl$ is observed for samples with a $\delta^{37}Cl$ value greater than $-0.3‰$, indicating insignificant contribution of Cl^- from subsurface sources. For samples with a highly negative $\delta^{37}Cl$ value, i.e. $-1.4‰$ for Duckhole and $-1.6‰$ for

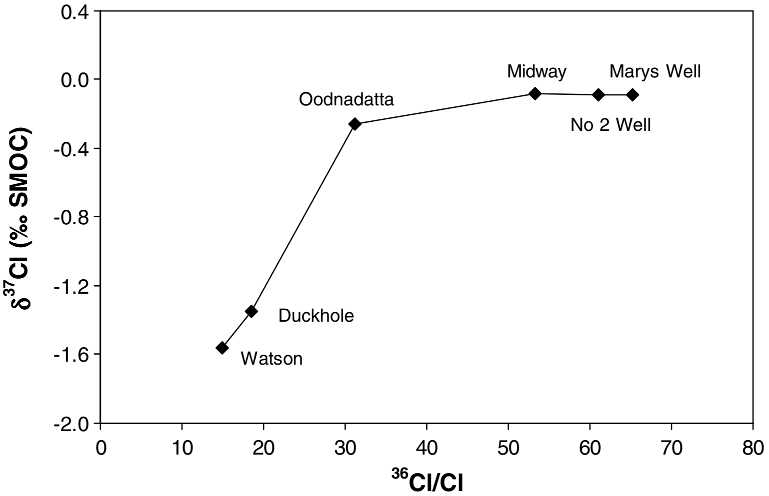

Fig. 8. δ^{37}Cl of groundwater from the northern transect vs. ^{36}Cl/Cl measured by Love et al. (2000).

Watson, subsurface addition becomes dominant. Using the $(\delta^{37}\text{Cl})_{\text{rock}}$ value of −2.0‰ measured in Duckhole, Cl$^-$ from the subsurface production is responsible for 70% of the total Cl$^-$, compared to 86% estimated by Lehmann et al. (2003). As a result of the high percentage of Cl$^-$ from subsurface sources, a near constant ^{36}Cl/Cl ratio was observed in these samples (Fig. 8).

Although the Cl$^-$ concentrations reached approximately 1000 mg/L or above, the groundwater samples from the southern transect seem to gain their salinity primarily through evapotranspiration. Subsurface sources account for less than 10% of Cl$^-$ assuming that the $(\delta^{37}\text{Cl})_{\text{rock}}$ value is −1.0‰ (Table 4). Lehmann et al. (2003) estimated that 18% of Cl$^-$ was from subsurface sources, which is similar to the value calculated assuming that the δ^{37}Cl of the subsurface source is −0.5‰. Evapotranspiration would increase both ^{36}Cl and total Cl$^-$ concentration, but the ratio of ^{36}Cl/Cl remains relatively constant. Therefore, the groundwater samples from the southern transect appear to be suitable for ^{36}Cl dating.

6. Summary and conclusions

A δ^{37}Cl range between near zero to −2.5‰ was determined in groundwater samples taken from the southwestern flow system of the GAB. A gradual decrease in δ^{37}Cl was observed along flow directions, whereas the Cl$^-$ concentration increased. In conjunction with other geochemical parameters, Cl isotope compositions were used to determine the relative importance of various processes that are responsible for the Cl$^-$ measured in groundwater.

A wide range of δ^{37}Cl between −0.6‰ and 0.3‰ measured in halite renders Cl isotope composition ineffective for distinguishing salt dissolution as a source of Cl$^-$. In this case, the Br/Cl ratio was used. The fact that the measured Br/Cl ratios are well above those of halite suggests that Cl$^-$ measured in groundwaters is not derived primarily from salt dissolution.

δ^{37}Cl values close to zero are expected for marine aerosols where there is no anthropogenic input. The subsequent evapotranspiration causes no Cl isotope fractionation in neutral to alkaline solutions as long as the Cl$^-$ concentrations are low enough that Cl$^-$ bearing minerals do not precipitate. Rainfall and subsequent evapotranspiration are responsible for the Cl$^-$ in the groundwater samples located close to the recharge area, and are also dominant along the southern transect.

The correlation between δ^{37}Cl and Cl$^-$ concentration was used to determine the importance of mixing between recharge water and saline groundwater. Poor comparison between the measured and simulated correlation curves discounts mixing as the process controlling Cl$^-$ concentrations.

δ^{37}Cl values were determined in the leachates of the Bulldog shale, ranging between near zero and −2.0‰. Based on δ^{37}Cl and Cl$^-$ concentrations measured in groundwaters, the Cl isotope compositions of the subsurface source were calculated. The calculated values agree well with measured δ^{37}Cl in the Bulldog leachates, suggesting that the Bulldog shale is the subsurface source.

Negative δ^{37}Cl values measured in the Bulldog shale are unlikely to result from the interaction between clay minerals and pore water due to the absence of volcanogenic detritus that readily undergoes early diagenetic alteration. Although Cl^- could be transported through advection and ion filtration, these mechanisms are not favored by the presence of a vertical hydraulic gradient in the aquitard. Diffusion is more likely the process through which the groundwaters are salinitized. However, detailed measurements of $\delta^{37}Cl$ values in rock samples are required in order to verify this hypothesis.

Groundwater samples taken along the southern transect are appropriate for ^{36}Cl dating because subsurface addition of Cl^- is insignificant. The Cl^- was concentrated mainly through evapotranspiration. For the northern transect samples, a portion of Cl^- was added from the aquitard. This portion was likely minor for groundwater samples with a $\delta^{37}Cl$ value of $-0.3‰$ or higher, whereas subsurface addition becomes dominant in samples that are highly depleted in ^{37}Cl. In the latter case, subsurface addition masked the $^{36}Cl/Cl$, resulting in constant $^{36}Cl/Cl$ ratio.

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