Geochemistry of ground waters from the Great Artesian Basin, Australia

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ABSTRACT


Ground waters from the confined Lower Cretaceous–Jurassic aquifer of the Great Artesian Basin, Australia (GAB) are characterised by Na–HCO₃ type waters throughout the eastern and central parts of the basin and Na–SO₄–Cl type waters in the western part. Sodium and bicarbonate increase in concentration from the northeastern margins to the southwestern discharge areas along the regional groundwater flowlines. A mass-balance and equilibrium model for major dissolved species and stable carbon isotopes of dissolved inorganic carbon show that the chemical trends observed are caused by mass transfer reactions involving cation exchange of Na for Ca–Mg, carbonate dissolution and reactions between Na and kaolinite to form Na-smectite. The stable carbon isotopic composition of dissolved inorganic carbon (DIC) increases from values of about −15‰ near the basin margins to −6‰ in the interior of the basin. An inverse relationship exists between δ¹³C and DIC indicating addition of enriched carbon as the ground waters move basinwards. A δ¹³C–δ¹⁸O mass balance indicates that the trend toward heavier δ¹³C values in the interior of the basin results from bacterial reduction of carbon dioxide to produce methane rather than dissolution of, and equilibration with, carbonate minerals. The GAB aquifer system is apparently open to CO₂ which is the product of in situ anaerobic fermentation producing CO₂ enriched in δ¹³C.

The chemical evolution of the major dissolved species and carbon isotope distribution in the eastern and central parts of the GAB can then be envisaged as an initial pCO₂ up to several orders of magnitude above atmospheric level is acquired within the recharge area by plant respiration and oxidation of organic matter in the soil zone. Initially, silicate and carbonate minerals may dissolve, at least in some parts of the basin, resulting in increased alkalinity, higher Ca and Mg concentrations, and a δ¹³C concentration of the DIC of around −12‰. Processes such as cation exchange of Na for Ca and Mg in addition to the removal of some Na by ‘reverse weathering’ which produces a Na smectite dominate in the interior of the GAB. The chemistry of ground waters derived from the western recharge areas is controlled by evaporite dissolution as indicated by very high Cl/Br ratios.
INTRODUCTION

Geochemical processes occurring within ground waters and reactions with aquifer minerals have a profound effect on water quality. Therefore, the evaluation of the importance of such processes is essential if groundwater resources are to be properly developed for human consumption and pastoral or mining activities. This paper investigates the possible physical and chemical processes affecting the major element and stable carbon isotopic composition of ground waters from the Great Artesian Basin (GAB) of Australia.

The GAB is located in the semi-arid and arid parts of eastern Australia and underlies about 22% ($1.7 \times 10^6$ km$^2$) of the Australian continent (Fig. 1). It is a confined groundwater basin composed of aquifers in continental quartzose sandstones with confining beds of partly marine mudstone and siltstone of Triassic, Jurassic and Cretaceous age up to 3000 m thick (Fig. 2). Recharge of ground water occurs mainly in the eastern marginal zone with some minor input from the western margin. Precipitation in the recharge area averages 600 mm year$^{-1}$ and is largely seasonal with relatively dry winters.

![Fig. 1. Location of the Great Artesian Basin, Australia (inset) and inferred flow lines based on potentiometric surfaces (after Habermehl, 1980). Recharge occurs mostly on the eastern and northeastern margins supplying water to the westward and southward flowing regimes. Some further recharge occurs in the western margins. Discharge via upward leakage takes place throughout the basin through artesian springs and by diffuse discharge in the southwestern marginal part of the basin.](image-url)
Fig. 2. Generalised cross-section of the Great Artesian Basin showing the Jurassic aquifer and the overlying confining bed and cretaceous aquifer. The section refers to the line A-A' (after Habermehl, 1980).
and wet summers. Large-scale groundwater movement is towards the south-western and southern margins (Fig. 1). Discharge occurs via upward leakage and through springs and diffuse discharge in the south-western and southern margins (Fig. 1). The potentiometric surface of the Lower Cretaceous–Jurassic aquifer system is above ground level throughout most of the basin. Aquifers from the Upper Cretaceous rocks have much lower water yields and greater salinity than water from the Lower Cretaceous–Jurassic aquifer system (hereafter termed the Jurassic aquifer system) and therefore are of lesser importance for exploitation. The geology and hydrogeology of the Great Artesian Basin is described in considerable detail in Habermehl (1980).

This paper deals exclusively with ground water collected from the widely exploited Jurassic aquifer system, in particular with water from the Hooray Sandstone and its equivalents which are highly productive, and the upper artesian aquifers in the GAB. The waters are dominated by Na⁺ and HCO₃⁻ throughout most of the basin with a general increase in total dissolved solids
from the northeastern and eastern margins towards the interior of the basin. Waters of predominantly Na–Cl type occur near the western marginal zone where recharge from the west dissolves evaporite minerals (Habermehl, 1980). Habermehl (1980, 1986) and Calf and Habermehl (1984) deal with some aspects of the hydrochemistry of the GAB ground waters in terms of general patterns throughout the basin. A discussion of the environmental isotope distribution in the ground waters by Airey et al. (1979) indicates that the waters are entirely of meteoric origin.

Nineteen chemical and isotopic analyses of ground water samples were obtained from existing flowing artesian water wells in the Jurassic aquifer of the GAB in 1985. Sample well localities for this study are shown in Fig. 3. We used a chemical and isotopic mass balance and equilibrium activity relationships to determine the types of mineral–water interactions that are likely to take place. Identification of solid mineral phases and their chemical compositions were carried out to verify whether the proposed chemical reactions derived from thermodynamic modelling are feasible. A $^{13}$C isotope and dissolved inorganic carbon mass balance places additional constraints on the proposed chemical reactions involving proton transfer reactions within the groundwater system.

ANALYTICAL METHODS

Water samples were collected in acid-washed Nalgene bottles from artesian wells that were flowing continuously and had been doing so for several years or decades. All sample bottles were flushed with several volumes of water before chemistry samples were taken. Separate 500-ml samples were taken for cations and anions and filtered immediately through 0.45-$\mu$m Millipore® filters and the cation aliquot acidified to pH < 1.5. Alkalinity samples were collected in 100-ml Wheaton® bottles to which 1 ml of saturated HgCl$_2$ solution was added, and a rubber septum was secured by an aluminium crimped seal. The pH was measured in the field using a portable Orion pH meter calibrated with two standard buffer solutions (pH values of 7 and 9).

Major cations were analysed by atomic absorption spectrophotometry. Sulphate, bromide and fluoride were determined on a Dionex® ion chromatograph. Chloride was determined separately by potentiometric titration with silver nitrate. Aqueous silica was analysed by atomic absorption following the method of Kiss (1982). Alkalinity was measured by a potentiometric Gran titration in the laboratory. Total dissolved inorganic carbon (DIC) was determined by calculation from pH and alkalinity data using the program PHREEQE (Parkhurst et al., 1980). For determination of $\delta^{13}$C$_{\text{DIC}}$, BaCl$_2$ and NaOH were added to about 250 ml of water to induce precipitation of dissolved CO$_2$ as BaCO$_3$. The precipitates were acidified in a vacuum line after
return to the laboratory and the evolved CO$_2$ determined for its isotopic composition on a modified Nuclide MS12 mass spectrometer. Precision for isotope analyses is nominally $\pm 0.1\%$.

RESULTS

Results of chemical and $\delta^{13}$C analyses of ground waters from the Jurassic aquifers in the Great Artesian Basin are presented in Table 1. The data are grouped into three transects (Fig. 3) which represent downgradient evolution from their respective recharge areas. The waters on our Line E transect (wells 78–92) are dominantly Na-HCO$_3$ type with total dissolved solids (TDS) contents ranging from 362 ppm in the northeastern zone to greater than 1600 ppm near the discharge areas in the western and southwestern portions of the basin. Wells 73–77, which lie on an east–west line towards the eastern side of the basin (Line A), tend to have higher TDS contents than those emanating from the northeastern part of the basin. They are characterised by higher Na, HCO$_3$ and Cl concentrations than the ground waters from Line E further to the north. Waters from the western transect, Line W (wells 93–98) are of the Na–Cl type and have much higher TDS contents (up to 5835 ppm) than the eastern transects.

Figure 4 shows the trends of chemical parameters and $^{13}$C along the three transects defined as Lines A, E and W (shown in Fig. 3) from near the inferred recharge areas towards the discharge area in the southwestern part of the basin. There is a general increase in dissolved solids concentration along all transects towards the interior of the GAB, which is a common feature of many large groundwater basins. Similarly Na content and alkalinity show similar increases to those of the TDS content and they dominate the TDS trend. Chloride increases gradually for the most part (except for the western transect) and increases by about a factor of three along Line E. There is a quite distinct separation of chloride concentration for the three transects and range over two orders of magnitude. Potassium mimics chloride to some extent as it shows a slight decrease along Line E and then some increase for the last four wells. Calcium and magnesium show a marked decrease to about 300 km then remain at very low concentrations except for Line A which shows a general increase, albeit at a low level. Alkalinity, DIC and $\delta^{13}$C show similar patterns for Line E as they increase steadily along the transect. Alkalinity and DIC concentrations are markedly higher for Line A than the other transects.

X-ray diffraction analysis of aquifer solid material was carried out to determine which minerals within the basin are likely to influence the water chemistry. Fifteen deep drill hole (petroleum exploration well) cores and cuttings of sandstones and confining mudstones show a uniform distribution
TABLE 1

Chemical and δ^13C analysis of ground waters from the Great Artesian Basin. The sample number refers to our internal code. The registered number is the Queensland Water Resources Commission Registered Bore number (73-86), and the abbreviated Registered Bore number of the South Australian Department of Mines and Energy (87-98). All results are quoted in millimoles, micromoles or milliequivalents per kilogram (as indicated). TDS is expressed as parts per million and is calculated by summing the ion data. Distance refers to the approximate distance of the well along a transect. SI calcite represents the saturation index of the solution with respect to calcite where negative numbers indicate undersaturation. The δ^13C is the carbon-13 composition of the DIC (CO₂ + HCO₃⁻) expressed in per mill notation relative to standard PDB.

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Fig. 4. (a)-(i) Plots of TDS, Cl, Na, K, Ca, Mg, alkalinity, DIC and $\delta^{13}$C along the three transects represented in Fig. 3. Note that TDS, Cl and Mg are displayed on a logarithmic scale.
TABLE 2

Average sandstone and shale composition from GAB core cuttings collected throughout the basin

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of predominantly quartz, kaolinite, illite and smectite with minor amounts of calcite and albite. Petrographic examination of core cuttings indicate that the plagioclase feldspars are completely sericitized but alkali feldspars and quartz are essentially unaltered. The chemical composition of the aquifer material (Table 2) verifies that the aquifer is highly altered and deficient in base cations. The organic carbon content of the sandstones is about 1% while CaCO₃ content ranges up to 3.5% by weight.

DISCUSSION

Increase in TDS downgradient

The increasing TDS content downgradient observed in the GAB may be caused by several processes. These include: (1) mixing of the dilute recharge waters with saline waters present within deeper parts of the basin; (2) ion-filtration through shale membranes; (3) dissolution of evaporites, carbonate minerals or incongruent dissolution of feldspars, micas or clay minerals.

The only saline waters that may influence GAB hydrochemistry are near the western margin where dissolution of halite and gypsum occur (see below) and potential leakage from above or below. Leakage is unlikely to occur from the overlying Cretaceous sequences because of the net upward head imposed by the Jurassic aquifer but diffusion of ions downwards against the hydraulic gradient may occur. The rate of upward movement of water exceeds the rate at which Cl and Na can diffuse downwards, hence the influence of more saline
water from the Upper Cretaceous aquifers must be considered to be slight. Saline waters from the marine Cretaceous mudstones may leak into the Jurassic aquifer, particularly near the discharge areas but it would not account for the overall chemical trends described above.

The GAB waters are pressurised in the interior of the basin (at more than 200 bar) and they are of meteoric origin as determined from stable isotopic composition of hydrogen isotopes in the water molecules (Airey et al., 1979). Using $^{36}$Cl and total chloride concentrations, Bentley et al. (1986) concluded that ion filtration does not occur in the GAB but that there is a contribution of ‘dead’ chloride in the eastern flow regimes, possibly from an underlying aquifer that contains connate water. We conclude that a combination of evapotranspiration within the recharge areas and mineral dissolution provide the most plausible mechanism for the chemical trends observed along Lines E and W. Evaporite dissolution and entrainment of more saline ground waters are not important contributors except in the western and southwestern margins of the basin.

Plotting the ion/Cl ratios as a function of distance along each transect allows us to delineate chemical processes that are not related to evapotranspiration variations during recharge because Cl is conserved during groundwater evolution throughout most of the GAB. Sodium/chloride ratios tend to be variable throughout the basin (Fig. 5(a)) but generally increase by a factor of about three. Sodium/chloride mole ratios are always greater than two (except for Line W), demonstrating that halite dissolution or mixing with
trapped seawater brines does not contribute to the increase in sodium observed here. The ratio of (Ca + Mg)/Cl decreases markedly for the first 300 km along transect E (Fig. 5(b)) but then remains at very low levels, therefore Ca and Mg are removed from solution during the first one-third portion of the transect.

Chloride/bromide ratios range over a factor of two for Lines E and A (Fig. 5(c)); however, all but one are within the range of values that could be derived from recharge of seawater-derived cyclic salt. The similarity of Cl/Br ratios for Lines A and E to those found in seawater (550–700) demonstrate that no evaporite dissolution has taken place which would generate Cl/Br mole ratios much greater than approximately 500–700. The high Cl/Br ratio measured at well 83 indicates that some mixing of waters has occurred between wells 82 and 83, possibly by upward leakage of Cl-rich water derived from the Lower Palaeozoic–Proterozoic Georgina Basin underlying the GAB. The eastern margin of the Georgina Basin is located in the area, and a fault structure is present in the GAB sequence in the region. Chloride/bromide ratios of groundwaters from the western margin are much greater than 1000 demonstrating that they are derived from evaporite dissolution.

Strontium/calcium ratios (Fig. 5(d)) show a general increase in Lines E and W which could be caused by loss of Ca via cation exchange. Precipitation of CaCO₃ is not possible because all but one of the waters from Line E are undersaturated with respect to CaCO₃ (Fig. 6).

Mineral–solution interactions

The types of mineral–solution reactions that may control the composition and trend of hydrochemical species in our transects A and E are cation exchange, dissolution of calcite or feldspars or reactions involving clay minerals. It is important to note that the three transects described above all
show different characteristics and therefore the types of chemical reactions need not operate to the same extent in all parts of the basin and therefore will be discussed separately.

We assume that chloride ions behave conservatively throughout Line E, with perhaps the exception of some addition of Cl-rich water between wells 82 and 83 (see above). Normalising all other chemical species to chloride allows us to evaluate the types of chemical processes affecting other dissolved species within the GAB that are not related to processes such as evapotranspiration.

Chloride concentrations in rainfall in regions, which are more than 100 km from the coast, fall into a narrow range of less than 1 to 5 ppm (Blackburn and McLeod, 1983). These concentrations are an order of magnitude or more lower than Cl⁻ concentrations in even the more dilute regional ground waters within the GAB (Table 1). Elevated chloride concentrations in the ground waters are probably caused by evapotranspiration during recharge and this evapotranspiration affects all ions equally. Cyclic wetting and drying in the unsaturated zone (e.g. Drever and Smith, 1978) within the recharge areas is not important because the recharge waters do not evaporate to dryness within the soil zone. This process can only fractionate sodium and chloride if halite forms in the soil zone, and this does not occur in the GAB recharge areas.

The types of reactions proposed for Line E must simultaneously satisfy the observed increases in Na, alkalinity and DIC and at the same time the decrease in Ca and Mg. Furthermore, the relatively conservative behaviour of aqueous silica must be accounted for in any reactions involving silicate minerals.

The release of Na, to the more dilute waters nearer the recharge areas may be accomplished by the following: (i) dissolution of Na bearing minerals (e.g. plagioclase or orthoclase); (ii) cation exchange which releases Na⁺ from clay minerals; (iii) conversion of a Na-smectite to kaolinite. Incongruent dissolution of albite releases Na and HCO₃⁻ into solution in an approximately 1:1 ratio according to the equation

\[
2\text{NaAlSi}_3\text{O}_8 + 11\text{H}_2\text{O} + 2\text{CO}_2 \leftrightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na} + 2\text{HCO}_3^- + 4\text{H}_4\text{SiO}_4^- \tag{1}
\]

or

\[
2.33\text{NaAlSi}_3\text{O}_8 + 8.64\text{H}_2\text{O} + 2\text{CO}_2 \leftrightarrow \text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 2\text{Na} + 2\text{HCO}_3^- + 3.32\text{H}_4\text{SiO}_4^- \tag{2}
\]

which also releases one equivalent of alkalinity for each equivalent of Na but also releases substantial amounts of dissolved silica for each mole of Na produced. Silica does not reach elevated concentrations anywhere in the GAB.
and the waters are well undersaturated with respect to amorphous silica. Precipitation of α-quartz is not likely to be achieved even over the very long water residence times within the deep aquifer. Furthermore, the Na/SiO₂ ratio actually increases along the transects which is the opposite of that predicted by the above equations.

Exchange of cations between the solution and clays (such as one Ca²⁺ for two Na⁺ ions) would increase Na relative to Ca but have no effect on alkalinity. Therefore, although cation exchange may be an important process, it cannot be the sole process responsible for the increase in Na and HCO₃⁻.

Dissolution of carbonates (calcite or dolomite) can occur within the GAB as the lower bicarbonate concentration waters are undersaturated with respect to calcite (Fig. 6, Table 1). Dissolution may take place via the reaction.

\[
\text{CO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \leftrightarrow 2\text{HCO}_3^- + \text{Ca}
\]  
(3a)

or:

\[
2\text{CO}_2 + \text{CaMg(CO}_3)_2 + 2\text{H}_2\text{O} \leftrightarrow 4\text{HCO}_3^- + \text{Ca} + \text{Mg}
\]  
(3b)

which produces Ca, Mg and HCO₃⁻. However, Ca and Mg decrease markedly with increasing TDS content and in fact never reach very high concentrations except in waters from Line E near the eastern margin.

Mass-balance calculations

We tested a model based on that proposed by Blake (1989) for the generation of waters high in NaHCO₃ in the Otway basin of southeast Australia. The model hypothesises a three-stage process involving: (1) release of Ca, Mg and HCO₃⁻ via carbonate dissolution; (2) cation exchange of Ca (and

<table>
<thead>
<tr>
<th>Mineral</th>
<th>H  (cal mol⁻¹)</th>
<th>G  (cal mol⁻¹)</th>
<th>log K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>-939.7</td>
<td>-886.3</td>
<td>2.59</td>
<td>Helgeson et al., 1978</td>
</tr>
<tr>
<td>Calcite</td>
<td>-288.8</td>
<td>-270.1</td>
<td>-8.48</td>
<td>Parkhurst et al., 1980</td>
</tr>
<tr>
<td>Na-beidellite</td>
<td>-1368.2</td>
<td>-1277.8</td>
<td>-7.9</td>
<td>Nesbitt, 1977</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-982.2</td>
<td>-905.6</td>
<td>-</td>
<td>Helgeson et al., 1978</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>-309.1</td>
<td>-276.2</td>
<td>10.38</td>
<td>Helgeson et al., 1978</td>
</tr>
<tr>
<td>Quartz</td>
<td>-217.65</td>
<td>-204.65</td>
<td>-4.01</td>
<td>Helgeson et al., 1978</td>
</tr>
<tr>
<td>Amorphous silica</td>
<td>-214.57</td>
<td>-202.89</td>
<td>-</td>
<td>Helgeson et al., 1978</td>
</tr>
</tbody>
</table>
Fig. 7. Activity–activity diagram depicting the stability field of Na minerals. Thermodynamic data for calculation of mineral stability fields are given in Table 3. The stability fields are given at 25°C while activities for dissolved species are at in situ groundwater temperatures (30–95°C). Within this temperature range the mineral–water stability fields do not change significantly from those denoted here. The waters appear to be at or near equilibrium with respect to kaolinite, and a Na-smectite. They are undersaturated with respect to amorphous silica and calcite and supersaturated with respect to quartz.

Mg) for Na on clay mineral sites; (3) back reaction of Na with kaolinite to produce a Na-bearing smectite. This would result in an increase in alkalinity through the dissolution of carbonates, exchange of Na for Ca to supply Na, and equilibrium controls on Na and SiO₂ by reaction of Na with kaolinite to form a Na-bearing smectite.

The reaction between sodium and kaolinite may take the general form

\[
3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{Na}^+ + 4\text{H}_4\text{SiO}_4 \rightarrow 3\text{Na}_{0.33}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + \text{H}^+ + 11.5\text{H}_2\text{O}
\]

(4)

The stoichiometry is such that one equivalent of Na is consumed for each equivalent of alkalinity consumed. The amount of H₄SiO₄ consumed depends somewhat on the amount of Si in the respective clays and need not be in the proportion given above but is somewhere between 1 and 4 moles depending on the stoichiometry of the clay minerals.

In the above scenario, no external source of CO₂ is required to dissolve CaCO₃ because the protons necessary for carbonate dissolution are derived from eqn. (4) above, proceeding to the right. Activities of ions calculated from the computer program PHREEQE (Parkhurst et al., 1980) are plotted on a mineral stability diagram for the Na–H–SiO₂ system in Fig. 7 using thermodynamic data in Table 3. Most of the waters are equilibrated with respect to kaolinite and a Na-mixed layer clay represented here by Na-beidellite. The Na concentration in these waters may therefore be controlled by equilibrium between kaolinite and a Na-smectite. Furthermore, Na-smectites are present
TABLE 4

Mass transfer (in mmol kg\(^{-1}\)) of Ca, Mg, alkalinity and Na from upgradient to downgradient wells as indicated. The calculations were done after normalising all data to chloride (see text). Positive numbers indicate flux from solid to solution and negative numbers indicate removal from the aqueous phase.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta\text{Ca (mmol kg}^{-1})</th>
<th>(\Delta\text{Mg (mmol kg}^{-1})</th>
<th>(\Delta\text{Alk (meq kg}^{-1})</th>
<th>(\Delta\text{Na (mmol kg}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
<td>Calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>78 → 79</td>
<td>-0.28</td>
<td>-0.55</td>
<td>-0.8</td>
<td>+0.41</td>
</tr>
<tr>
<td>79 → 81</td>
<td>-0.4</td>
<td>-0.85</td>
<td>+1.56</td>
<td>+3.76</td>
</tr>
<tr>
<td>81 → 82</td>
<td>-0.12</td>
<td>+0.01</td>
<td>+0.48</td>
<td>+0.89</td>
</tr>
<tr>
<td>82 → 83</td>
<td>-0.07</td>
<td>0</td>
<td>-4.65</td>
<td>-4.7</td>
</tr>
<tr>
<td>82 → 84</td>
<td>-0.05</td>
<td>0</td>
<td>-0.3</td>
<td>-0.1</td>
</tr>
<tr>
<td>84 → 85</td>
<td>+0.01</td>
<td>0</td>
<td>-3.0</td>
<td>-2.8</td>
</tr>
<tr>
<td>85 → 86</td>
<td>-0.02</td>
<td>0</td>
<td>+1.38</td>
<td>+1.5</td>
</tr>
<tr>
<td>86 → 87</td>
<td>-0.02</td>
<td>0</td>
<td>+1.11</td>
<td>+2.1</td>
</tr>
<tr>
<td>87 → 89</td>
<td>0</td>
<td>0</td>
<td>+4.5</td>
<td>+4.0</td>
</tr>
<tr>
<td>89 → 91</td>
<td>0</td>
<td>0</td>
<td>-3.6</td>
<td>-4.0</td>
</tr>
<tr>
<td>91 → 92</td>
<td>0</td>
<td>0</td>
<td>-4.0</td>
<td>-3.0</td>
</tr>
</tbody>
</table>

in much larger abundance in the aquifer than primary plagioclase (see above) and are much more reactive.

We performed mass-balance calculations along Line E to determine the relative importance of the above processes in controlling the major ion chemistry. The results are presented in Table 4 and were done in the following sequence to calculate the build-up of sodium:

1. Normalise all data in downgradient bore to \(\text{Cl}^-\) concentration in upgradient well.
2. Net Na gain via cation exchange and uptake of Na by Na-smectite equals:
   \[2 \times (\Delta\text{Ca} + \Delta\text{Mg}) + \Delta\text{HCO}_3^-\]
3. If \(\Sigma\text{Alk}\) loss is greater than \(2 \times (\text{Ca} + \text{Mg})\) loss then net Na loss to Na-smectite equals \(\Delta\text{Alk}\).
4. Compare calculated Na gain with normalised Na gain determined from the analytical data. The results (Table 4) show that the Na fluxes predicted by the mass-balance calculations are generally similar to that actually measured (after normalising to Cl). This suggests that the model adequately accounts for the distribution of the dissolved major ions observed as the GAB waters from Line E progress basinwards. Positive fluxes are the result of exchange of Na for Ca and Mg with some removal of Na via formation of a Na-smectite (reaction (4)). Negative fluxes suggest that either more Na is removed via the clay reaction than by cation exchange or that no cation exchange occurs and
that only eqn. (4) proceeds to remove Na from solution by conversion of kaolinite to Na-smectite.

From the results presented above, there is no a priori requirement for an external source of CO₂ to dissolve solid carbonate other than that present in the recharging water. If no additional CO₂ were to be acquired by the ground water during its traverse across the basin, then the pH would rise to values in excess of 8 or 9 because of consumption of CO₂. Removal of HCO₃ via conversion of kaolinite to a cation-bearing clay such as sodium-smectite involves transfer of hydrogen ion from clays to solution which conserves DIC in the waters but decreases alkalinity. A net increase in alkalinity can therefore only be accomplished by carbonate dissolution but maintaining high pCO₂ values must involve an external source of CO₂. Evidence for an external source of CO₂ is presented in the following section.

Carbonate chemistry and ¹³C

The components of the carbonate system and the ¹³C/¹²C ratio of total dissolved CO₂ are influenced by several processes within groundwater systems. Those processes which are likely to be most important within the GAB include CO₂ respiration by plant matter within the soil zone of the recharge areas, dissolution or precipitation of carbonate minerals such as calcite or dolomite, addition of CO₂ from degradation of organic matter within the aquifer, and methane production. Any other process that involves the transfer of protons, such as the hydrolysis reactions involving clay minerals, or the transfer of electrons by bacterially mediated redox reactions (e.g., sulphate reduction) will indirectly affect the carbonate system because addition or removal of hydrogen ions will perturb the CO₂ system and therefore indirectly promote calcite dissolution or precipitation. All components of the carbonate system, taken together with the stable carbon isotope distribution, can provide a constraint on the possible chemical processes occurring within the groundwater system and determine the role of CO₂ in these reactions.

There is a general increase in the alkalinity, DIC and δ¹³CDIC values with distance along Line E (Figs. 4(g)–4(i)) indicating addition of isotopically enriched DIC along Line E. Consider the case where CO₂ derived from oxidation of organic matter or plant root respiration in the recharge areas reacts with CaCO₃ according to eqn. (3a) (see above) to produce two equivalents of alkalinity for each net mole of DIC produced. If eqn. (3a) proceeds in strict stoichiometric proportions, the δ¹³CHCO₃ can be given by the expression:

\[
\delta^{13}C_{\text{HCO}_3} = \frac{\delta^{13}C_{\text{CO}_2} + \delta^{13}C_{\text{CaCO}_3}}{2}
\]  (5)
Fig. 8. $\delta^{13}C_{DIC}$ as a function of the inverse of DIC for ground waters from the GAB Jurassic aquifer. The trend of data represented by the diagonal line indicates addition of a $^{13}C$ enriched source of DIC with a $\delta^{13}C_{DIC}$ composition of about 0‰.

If the $\delta^{13}C$ concentration of CO$_2$ derived from plant respiration and degradation in the soil zone in semi-arid regions within the recharge areas of the GAB is estimated to be between $-20$ and $-24$‰ (Salamons and Mook, 1986) and the $\delta^{13}C$ concentration of CaCO$_3$ within the aquifer is between 0 and $-6$‰, which is the range for non-marine carbonates (Salamons and Mook, 1986), then the resultant bicarbonate produced in a closed system according to eqn. (5) would be approximately $-12$‰. Therefore, if only carbonate dissolution via addition of CO$_2$ was involved in adding DIC to the water, then the $\delta^{13}C$ concentration would evolve to about $-12 \pm 2$‰ given enough time or a sufficient amount of material and water residence time. Such a scenario could adequately explain the GAB $\delta^{13}C$ data for the first 600 km of the Line E transect and the data for Line W (Fig. 4(i)). However, this process does not explain the enriched $\delta^{13}C$ values measured for the last 600 km of Line E nor the enriched values in Line A.

On a plot of $\delta^{13}C$ values vs. the inverse of DIC concentration (Fig. 8) we observe two trends for the data. One group of points appear to be independent of DIC concentration at a $\delta^{13}C$ value of about $-12$ to $-14$‰. Another group of points define a linear trend with increasing $\delta^{13}C$ values as $1/DIC$ decreases. The latter linear trend indicates mixing of DIC derived from two end-members; one derived from dissolution of carbonate minerals and the other end-member having an isotopically enriched source with a $\delta^{13}C$ composition of around $-2$ to 0‰.

Processes which could provide DIC enriched in $^{13}C$ include:

(1) Exchange of carbon atoms between dissolved CO$_2$ and calcite which may ultimately result in a $\delta^{13}C$ concentration of dissolved HCO$_3^-$ which is close to that of the solid material, that is, about 0‰. However, isotopic
exchange would increase $\delta^{13}C$ concentration of the DIC without a concomitant increase in DIC concentration, therefore this process cannot be important in determining the observed trends.

(2) Preferential metabolism of $^{13}C$ enriched carbon by bacteria during oxidation of organic matter in a groundwater system (e.g. Chappelle et al., 1988). The magnitude of this enrichment is of the order of $-10$ to $-15\%_o$ for CO$_2$ relative to organic matter which would result in a $\delta^{13}C$ end-member composition of about $-12\%_o$; too light to explain the GAB data.

(3) Production of methane via CO$_2$ reduction:

$$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad (6a)$$

or by acetate fermentation:

$$2\text{CH}_3\text{O} \rightarrow \text{CH}_4 + \text{CO}_2 \quad (6b)$$

Both of these processes increase the DIC concentration and enrich the DIC in $^{13}C$ (Games et al., 1978; Whiticar et al., 1986). Carbon dioxide reduction also results in a net increase in DIC because the methane production step always accompanies CO$_2$ production via other anaerobic oxidation processes (Klass, 1984). The amount of CO$_2$ consumed to give methane is less than that produced by fermentative oxidation resulting in a net build-up of CO$_2$. In aquifers where the organic carbon content is low, the reduction step tends to dominate the production of methane (e.g. Grossman et al., 1989).

DIC with $\delta^{13}C$ compositions of more than 0%o have been recorded in groundwater systems (e.g. Barker and Fritz, 1981; Grossman et al., 1989) which indicates the importance of methanogenesis in the DIC mass-balance of many confined and phreatic groundwater systems. Free hydrogen, methane and other light hydrocarbons are present in most parts of the GAB (Habermehl, 1986), therefore these reactions must be taking place. The linear relationship seen in Fig. 8 then, can be explained by addition of CO$_2$ with an isotopic composition which is consistent with a combination of anaerobic fermentation and reduction of CO$_2$ to produce methane.

The relationship between alkalinity and DIC for the three transects (Fig. 9) can indicate the extent of open- or closed-system behaviour within the aquifer with respect to CO$_2$. Each of the transects show linear relationships, although with different gradients and for Lines A and E at least, more than 1 mole DIC is produced per equivalent of alkalinity produced. If carbonate dissolution was the only source of DIC to the ground waters, then the ratio of $\Delta$Alk : $\Delta$DIC would be about 2 : 1. However if some alkalinity is removed via production of one proton during the conversion of kaolinite to Na-smectite (eqn. (4)) then the ratio would approach 1 : 1. This value can only be achieved if there was no net production of Na.
Fig. 9. Alkalinity vs. DIC for all three transects show linear relationships with gradients ranging from 1 to 0.67. Lines A and E have more DIC added per equivalent of alkalinity added indicating a source of additional CO₂ that is not accompanied by generation of alkalinity.

Because anaerobic oxidation of carbon coupled with methanogenesis produces CO₂ with little or no concomitant increase in alkalinity, we should see more DIC than alkalinity produced as the waters evolve via this process. The added CO₂ induces the dissolution of carbonates which in turn increases alkalinity and DIC in a 2:1 ratio. We do observe that about 50% and 30% more moles of DIC are produced than equivalent of alkalinity for Lines E and A respectively (Fig. 9). Therefore, addition of CO₂ via fermentative bacterially mediated reactions is more important than carbonate dissolution throughout most of the GAB. This is particularly noticeable toward the basinward wells where in situ microbiologically mediated fermentation reactions become more dominant in producing the added DIC to the GAB waters.

CONCLUSIONS

The chemical evolution of the major dissolved species and carbon isotope distribution in the eastern and central parts of the GAB can then be envisaged as follows. An initial level of pCO₂ up to three orders of magnitude above atmospheric levels of pCO₂ is acquired by waters near the recharge area owing to plant respiration and oxidation of organic matter in the soil zone. Initially, silicate and carbonate minerals may dissolve, at least in some parts of the basin, resulting in increased alkalinity, Na, Ca and Mg concentrations and δ¹³C_{DIC} values around −12‰. As the waters progress basinwards, cation exchange of Na for Ca and Mg and subsequent reaction involving Na and kaolinite to produce Na-smectite exerts an important control on the distribution of dissolved species for a large part of the Great Artesian Basin. Clay mineral reactions buffer aqueous silica concentrations below amorphous SiO₂ saturation. Cation exchange and dissolution of carbonate minerals do not
appear to be important as the ground waters approach the discharge areas as there is net Na removal from the aqueous phase.

A dissolved inorganic carbon isotope mass balance indicates that the groundwater system is open to CO₂ and that addition of CO₂ is accomplished by fermentation processes occurring in situ. Some of the added CO₂ is a by-product of methanogenesis indicated by a δ¹³C enriched end-member for the DIC. The addition of CO₂ drives the carbonate dissolution reaction, thereby exerting an important control on the evolution of the Na-HCO₃ waters within the GAB.

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