International Journal of Coal Geology 289 (2024) 104535

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/coal

Geochemical tracers associated with methane in aquifers overlying a coal seam gas reservoir

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ARTICLE INFO

Keywords:
Great Artesian Basin
Surat Basin
Clarence-Moreton Basin
Methanogenesis
Coal bed methane

ABSTRACT

Understanding inter-aquifer connectivity or leakage of greenhouse gases and groundwater to aquifers overlying gas reservoirs is important for environmental protection and social licence to operate. Australia's Great Artesian Basin (GAB) is the largest artesian groundwater system in the world with groundwater extracted for agriculture, livestock, mines, energy, private or town water supply. Microbial coal seam gas (CSG) and production water are also extracted from the GAB. Here a range of groundwater tracers is used to investigate the potential for gas and groundwater connectivity between the CSG reservoir and aquifers.

The GAB aquifer and alluvium contained a range of methane concentrations (0.001 to 2100 mg/L) that exhibit an increase with depth and $\delta^{13}C$-CH_4. Aquifer and alluvium groundwater $^{87}Sr/^{86}Sr$ were in the range 0.7042 to 0.7082. CSG production waters however had non-radiogenic, distinctive $^{87}Sr/^{86}Sr$ signatures <0.7036, indicating a lack of significant groundwater leakage. One gassy aquifer bore with 160 mg/L methane conversely has $^{87}Sr/^{86}Sr$, $\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4 and $\delta^{13}C$-DIC values overlapping the CSG waters. In several aquifers $\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4 are sourced from windblown surface salts of inland Australian playa lakes in recharge waters. Bacterial sulphate reduction is additionally occurring in a regional aquifer. Cosmogenic isotopes and tritium show recent recharge and mixing with older groundwaters in several shallow aquifers.

Groundwater and gas signatures indicate that leakage of groundwater and methane from the CSG reservoir was not occurring in the majority of areas investigated here. Methane was consistent with in situ generation in shallow GAB aquifers by primary microbial CO_2 reduction or acetate fermentation. Connectivity of one alluvial bore and the underlying GAB aquifer could not be completely ruled out. Separately, one gassy Springbok GAB aquifer bore is either connected to the underlying CSG gas reservoir, or has in situ secondary microbial CO_2 reduction producing methane from interbedded coal within the aquifer. This study is relevant to other basins in Australia and internationally where gas is observed in aquifers that overly conventional, unconventional or coal seam gas reservoirs.

1. Introduction

Methane and the carbon cycle are gaining increasing attention both owing to the focus on lowering greenhouse gas emissions to mitigate climate change, and assessing the risk of gas in groundwater resources (IEA, 2023; IEEFA, 2023). Methane is ubiquitous in groundwater and some surface waters owing to microbial degradation of organic (Currell et al., 2017; Zhu et al., 2022). Natural and anthropogenic seeps of methane and other gases into aquifers and soils can also occur (Molofsky et al., 2016). This also has implications for the emission of methane to

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https://doi.org/10.1016/j.coal.2024.104535

Received 5 March 2024; Received in revised form 29 May 2024; Accepted 30 May 2024
Available online 31 May 2024

the atmosphere (Kulongoski and McMahon, 2019; Malerba et al., 2022; Rocher-Ros et al., 2023). The presence of methane in drinking water aquifers, however, continues to cause concern amongst landholders, especially in regions where gas is commercially extracted, and aquifers overlie coal seam gas (also known as coal bed methane), or conventional oil and gas reservoirs (Darrah et al., 2014; McMahon et al., 2018). Aquifers overlying shale reservoirs that are exploited for unconventional gas have been a major focus in the USA and Canada (Osborn et al., 2011). Multi isotope studies in the USA have found local occurrences of stray or fugitive gas leakage into aquifers and landholder water bores (Darrah et al., 2014), or surface water (Woda et al., 2020). Conversely other studies in the USA have found no evidence for leakage from gas reservoirs, with methane from natural biogenic sources (Nicot et al., 2017), from oxidised biogenic gas (Humez et al., 2019), or migration from deeper thermogenic sources (Bordeleau et al., 2021). This highlights the site-specific geological variability, and issues of well construction in causing potential leakage (Schout et al., 2018).

In Australia, and other countries such as the UK and France, exploration for unconventional gas from shales is a more recent occurrence (Innocent et al., 2021; Smedley et al., 2023). Several basins in Australia have produced conventional natural gas, or Coal Seam Gas (CSG, also known as coal bed methane), resulting in a few baseline studies on gas in overlying aquifers, or on gas leakage via faults into alluvium and surface waters (Banks et al., 2019; Currell et al., 2017; Iverach et al., 2020). The Surat Basin in Queensland, which is part of the GAB, is a major producer of CSG for domestic and international use (Hamilton et al., 2014; OGIA, 2019; Underschultz et al., 2018). CSG is produced from the Walloon Coal Measures (Fig. 1), and is gas that has mainly been generated via secondary microbial (bacterial) CO_2 reduction (Baublys et al., 2015; Golding et al., 2013). Dewatering the coal seams is generally employed to lower pressures for methane production, resulting in large volumes of produced water with potential implications for surface water and linked groundwater dependant ecosystems. The GAB contains various aquifers in sub basins across Queensland, the Northern Territory, New South Wales, and South Australia. The Surat Basin and Clarence-Moreton Basin are two of these sub-basins (Ransley et al., 2015). The overlying Condamine Alluvium and Condamine River forms part of Australia's largest surface water catchment, the Darling River Basin. Various landholders and industries extract groundwater from the GAB aquifers and the Condamine Alluvium, including feedlots, piggeries, agriculture, mines, power stations, town water supply, and domestic supply and irrigation (Frontier_Economics, 2016; Kent et al., 2020; OGIA, 2021). An estimated 180,000 people in regional Australia rely on the GAB groundwater (across all of the GAB); therefore, its water quality and groundwater protection is important (Balasooriya et al., 2023). Moreover, GAB groundwaters, and springs fed by the GAB aquifers, have cultural significance and supply water to Indigenous Australian communities, and also support unique and endangered groundwater dependant ecosystems (Frontier_Economics, 2016; Frontier_Economics, 2016; OGIA, 2016).

Similar to the examples from the USA, gas occurrences in shallow groundwater and surface water bodies are also present in the Surat and Clarence-Moreton basins with a long history of gas shows; for example, methane bubbling in the Condamine River, or landholder water bores going gassy resulting in pump cavitation or hazardous gas accumulation (personal communications, Surat Basin landholders). Several studies have previously shown conflicting conclusions that methane leakage does or does not occur from the Walloon Coal Measures CSG reservoir into the Condamine Alluvium (Iverach et al., 2017; Iverach et al., 2015; Owen and Cox, 2015; Owen et al., 2016; Pandey et al., 2020). While understanding the nature of gas within the Walloon Coal Measures has been the focus of previous work, other shallow GAB aquifers have generally lacked such studies. Previously a comparison of methane measurements in aquifers and CSG production waters was presented, along with the stable isotopes of methane and CO_2 within GAB aquifers and alluvium bores (Pearce et al., 2022c). The majority of methane in the GAB aquifer samples was generated via primary microbial CO_2 reduction and fermentation, different to the secondary microbial CO_2 reduction occurring in the CSG reservoir.

In the current study, a range of geochemical tracers including $^{87}Sr/^{86}Sr$, ^{14}C, ^{36}Cl, ^{3}H (tritium), $\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4 are used to understand if inter-aquifer groundwater and gas connectivity is occurring between the CSG reservoir and the aquifers, as well as to understand linked processes that may lead to changes in water chemistry and gas isotope compositions.

1.1. Geological setting

The GAB underlies ~1,700,000 square km's of Australia, containing an estimated 64,900 million megalitres of groundwater in sub-basins across four states. The Surat Basin forms the eastern edge of the GAB extending ~270,000 square km's across Queensland and northern New South Wales. Much of this is a semi-arid region, and therefore ecosystems and human activities are heavily reliant on groundwater. The area of interest here is approximately 200 km west/northwest of Brisbane. Major fault zones include the Hutton Wallumbilla (and associated smaller faults) (supplementary material), the Burunga-Leichardt Fault zone (north – south adjacent to the town of Miles), the Horrane Fault (below Dalby near Cecil Plains), and to the south the Moonie Goondiwindi fault zone (supplementary material). The Horrane Fault was recently reported to include faulting into the Walloon Coal Measures at ~50–600 m near the area of Cecil Plains where it acts as a lateral seal with a reported low level of connectivity to the overlying Condamine Alluvium (Pandey et al., 2020; Viljoen et al., 2020). The Surat Basin Precipice Sandstone, Hutton Sandstone, Walloon Coal Measures, Springbok Sandstone and Gubberamunda Sandstone are Jurassic age aquifers of the GAB (stratigraphic columns are shown in Supplementary material) (Hannaford et al., 2022; La Croix et al., 2020; Pearce et al., 2021a). The Surat Basin was recently postulated to be connected to the Clarence-Morton Basin to the east, where the Marburg Sandstone is the Hutton Sandstone equivalent in the Clarence-Moreton Basin (Fig. 1). The shallower Orallo Formation and Mooga Sandstone are early Cretaceous GAB aquifers. The Condamine Alluvium is Cenozoic and lies within a broad alluvial plain flanking the upper reaches of the Condamine River to the southeast of Chinchilla (Fig. 1, Fig. 2, and supplementary material). The alluvium is on average 20 to 30 m thick but increases to 150 m thick south of Dalby. Moving east from the Surat Basin towards the Clarence-Morton Basin, the Condamine Alluvium overlies the sub cropping Walloon Coal Measures (Fig. 1b, Fig. 2). Groundwater flow in the Condamine Alluvium is generally northwest (with the Condamine River) (Martinez et al., 2015; OGIA, 2019). Groundwater flow in the GAB aquifers is generally thought to be from recharge in the north and eastern margins to the southwest. However, flow paths are still under investigation, with components of flow identified east in the Precipice Sandstone to the Clarence-Moreton Basin, and north in the Hutton Sandstone to spring discharge in a river system (Hofmann et al., 2024; Hofmann et al., 2021; OGIA, 2016; Raiber and Suckow, 2017; Suckow et al., 2020). Owing to the extraction of coal seam gas and production water in the same region as various other industries and landholders, groundwater levels and water quality at bores are monitored within the Surat Cumulative Management area (OGIA, 2021). Many of the bores sampled in this study are part of the monitoring network through the Underground Water Impact Assessment.

CSG and production water are extracted from the Jurassic age Walloon Coal Measures in the Surat Basin within the GAB (Fig. 1, and supplementary material) (OGIA, 2019; Underschultz et al., 2018). The Walloon Coal Measures (also known as the Walloon Subgroup) are interbedded aquitards overlying the Durabilla Formation, with the Taroom Coal Measures underlying the Tangalooma Sandstone (see Figure 1b and the detailed stratigraphy in the supplementary material) (Baublys et al., 2021). The Juandah Coal Measures overly the Tangalooma Sandstone and are divided into the Lower and Upper Juandah

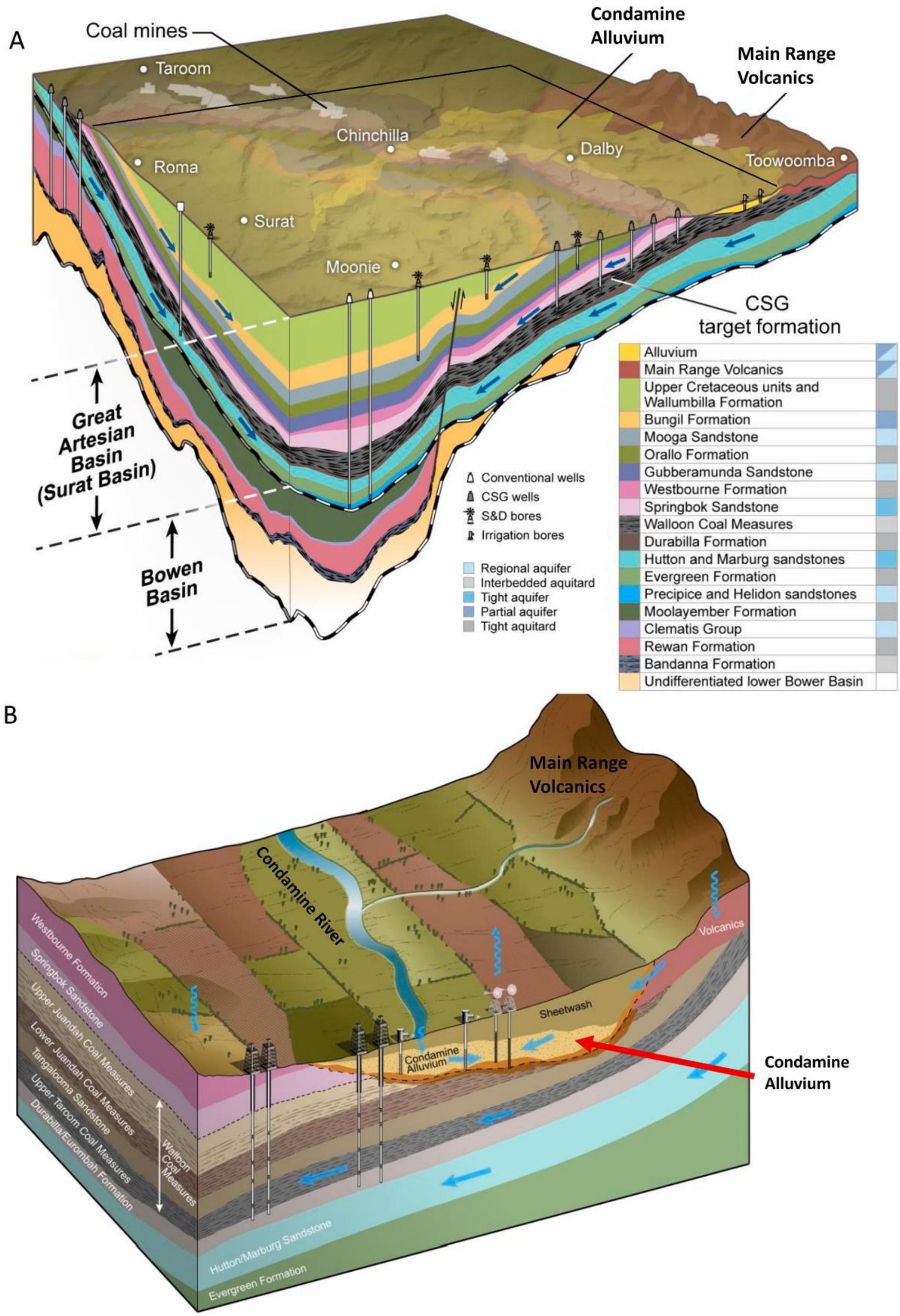


Fig. 1. A) Cross section of the Surat Basin aquifers of the Great Artesian Basin. B) Cross section showing the Condamine Alluvium and a more detailed view of the Walloon Coal Measures, modified after (OGIA, 2021).

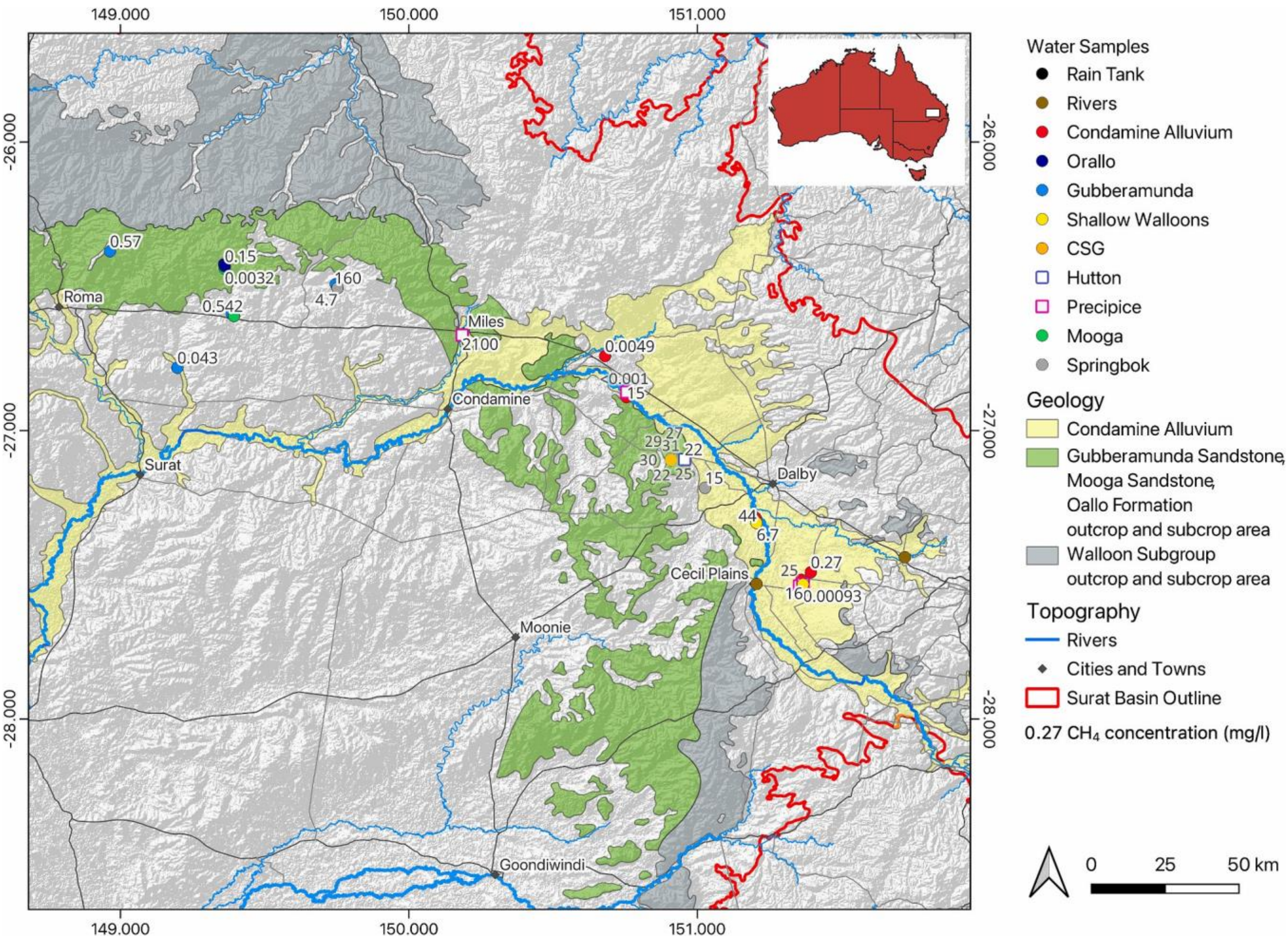


Fig. 2. Dissolved methane concentrations (mg/L) on an overview map of bores, CSG wells, and river sample positions. Note that several water bores were in close proximity to each other or nested. Full data are given in supplementary material. Inset is the study site position relative to Australia.

Coal Measures. The overwhelming majority of CSG production wells are completed over both the formations to maximise gas production (also known as co-produced gas and water) (Baublys et al., 2015). In some cases, such as the CSG wells sampled in this study, the production wells have been completed into one formation only. Coal seams comprise ~10% of the sequence and are laterally discontinuous, interbedded with sandstones, shales, mudstones, and siltstones (Hamilton et al., 2014; Pearce et al., 2022a).

2. Methods

Twenty groundwater bores were sampled between October 2019 and March 2021, including monitoring bores, landholder water bores, and town water supply bores (Fig. 2, note additional maps with individual labelled bores are also shown in supplementary material). Six CSG well production waters were also collected, along with samples from four rivers and creeks, four rainwater tanks and the water from one rainstorm in the region (all position data and meta data are given in supplementary material Table 1). The majority of bores were low flow N_2 pumped, with at least 3 bore volumes extracted until field parameters stabilised. Several bores had existing infrastructure or were artesian and were purged as above. CSG wells were actively pumping on arrival and production waters were purged prior to sampling. The pH, electrical conductivity (EC), dissolved oxygen (Do), temperature, and redox was measured in the field with a YSI multiprobe. Groundwaters were collected from gas tight connections to the pump or wellhead, in HDPE bottles or specific containers. Samples were chilled until analysis, except for Isoflask samples that contained a biocide. Major anions and cations (SO_4, Cl, alkalinity, Ca, Na, K, Mg) and mercury were analysed at ALS Environmental (Brisbane), with charge balances all within ±10%. Waters for analysis of minor and trace cations were filtered (0.45 µm) and acidified with ultra-pure nitric acid in the field, and analysed at the University of Queensland Environmental Geochemistry Laboratory. An Inductively Coupled Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima 8300 DV ICP-OES) was used to measure major and minor elemental concentrations of cations with an error of ~ < 5%. Trace and ultratrace elements were measured by an Inductively-Coupled Plasma Mass-Spectrometer (ICP-MS, Agilent 7900 ICP-MS with a collision cell) with errors <10%. Dissolved methane samples were collected in Isoflasks (Stratum Inc.) that were connected directly to the pump outlet or bore headworks to avoid contact with the atmosphere, and subsequently analysed at Stratum Reservoir (Molofsky et al., 2016). Samples for strontium isotope ($^{87}Sr/^{86}Sr$) analyses were collected in acid washed bottles, with waters filtered and acidified with ultra-pure nitric acid. Strontium isotopes were processed and analysed at the University of Queensland Radiogenic Isotope Facility (RIF). The analyses were run on a VG Sector 54 thermal ionization mass spectrometer (TIMS), with a three-sequence dynamic protocol. The USGS rock standards BHVO-2 and W2a were used with a 2 sigma better than 0.00002. Stable isotopes were run at the Stable Isotope Geochemistry Laboratory, The University of Queensland (UQ SIGL) (Pearce et al., 2022c; Pearce et al., 2023b). The $\delta^{13}C$ is reported as ‰ V-PDB, with $\delta^{18}O$ and $\delta^{2}H$ as ‰ V- SMOW. Note that stable isotopes of water, dissolved inorganic carbon (DIC), methane, and CO_2 were previously reported (Pearce et al., 2022c). Sulphate was extracted from groundwaters as $BaSO_4$ with $\delta^{18}O$- SO_4 and $\delta^{34}S$-SO_4 measured. An Elementar, Vario Isotope Cube Elemental Analyser coupled to a PrecisION isotope ratio mass spectrometer (EA-IRMS) was used to determine $\delta^{34}S$-SO_4 that was reported as ‰ VCDT. Calibration was performed via a 3-point normalisation using international silver sulphide standards IAEA–S1, S3 and sulphate NBS127 with S-MIF laboratory pyrite standard WD-11 analysed as an unknown. A Thermo TCEA was used for analysis of $\delta^{18}O$ in $BaSO_4$. International standards used were NBS127, SMOW and SLAP with a 3- point normalisation to the VSMOW-SLAP scale. The $\delta^{18}O$-SO_4 and $\delta^{34}S$-SO_4 were performed on a subset of samples with a sufficient dissolved SO_4 concentration for analysis. Of those groundwaters run for $\delta^{34}S$-SO_4, the Condamine Alluvium waters had sulphide concentrations <0.1 mg/L with no odour of H_2S detected during field sampling, so that the $\delta^{34}S$-SO_4 would not be affected by sulphide oxidation (field and analysis data are in supplementary material, Table S1) (Carmody et al., 1998). No odour of H_2S was detected during sampling the Mooga, Gubberamunda, Precipice (P17), and Orallo waters that were analysed. Filtered waters were kept chilled without exposure to air prior to analysis. The Precipice bore P17 field dissolved oxygen (Do) was 0.5 mg/l, although a trace of sulphide was detected, as well as in the Springbok S63 bore (see supplementary material).

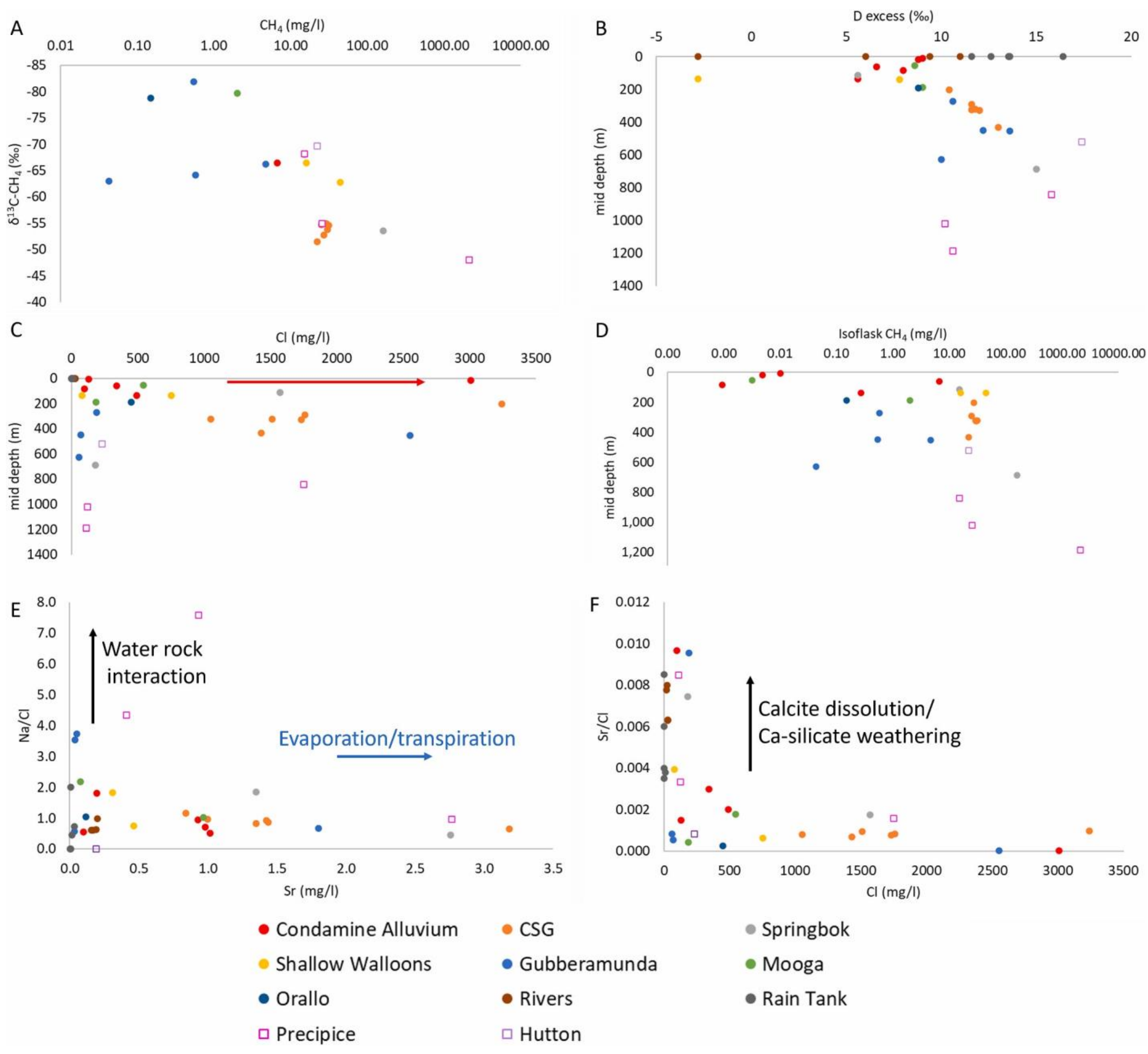

A
B
C
D
E
F
Water rock interaction
Evaporation/transpiration
Calcite dissolution/ Ca-silicate weathering
Condamine Alluvium
CSG
Springbok
Shallow Walloons
Gubberamunda
Mooga
Orallo
Rivers
Rain Tank
Precipice
Hutton

Fig. 3. A) Dissolved methane vs ^{13}C-CH_4. B) The δ^2H-H_2O or "D" excess vs depth. C) Concentration of Cl with bore screen sample depth below surface. The red arrow indicates the effect of (evapo)transpiration that has likely increased Cl in one Condamine Alluvium sample. D) Dissolved methane concentration (log scale, measured from Isoflask containers) with depth. E) Na/Cl vs Sr concentration. F) Sr/Cl vs Cl concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Tritium, cosmogenic isotopes $^{36}Cl/Cl$ and ^{14}C were collected in 1 l HDPE bottles by bottom filling, and allowed to overflow to avoid contact of the sample with the atmosphere, avoiding aeration or agitation of the samples, and filling with no headspace. Samples from a subset of bores were processed and analysed at the Australia's Nuclear Science and Technology Organisation (ANSTO). Groundwater DIC was converted to CO_2 and subsequently graphite for analysis of ^{14}C by accelerator mass spectrometry (AMS), with results expressed as pMC (Fink et al., 2004; Stuiver and Polach, 1977). $^{36}Cl/Cl$ was analysed at ANSTO by AMS (Wilcken et al., 2017). Tritium was measured at ANSTO by Liquid scintillation spectrometry conducted using a Perkin Elmer Quantulus after electrolytic enrichment. Tritium values are reported as Tritium units (TU) (Cendon et al., 2015´ ; Morgenstern and Taylor, 2009). Data, uncertainties and ANSTO ID codes are provided in Supplementary material.

3. Results and Discussion

3.1. Water chemistry, stable isotopes of waters, DIC, and $^{87}Sr/^{86}Sr$

The groundwaters and CSG production waters collected contained a wide range of dissolved methane concentrations (0.001 to 2100 mg/L) and salinities (EC 805 to 9970 µs/cm) (Fig. 2, Fig. 3, and supplementary material). A Precipice Sandstone bore, and a Springbok bore (bore S01), referred to as the gassy Springbok, contained particularly high methane concentrations. Most of the groundwaters are of Na-HCO_3 type, whereas the Condamine Alluvium, Condamine River and creek samples are Ca- Mg-Cl to Ca-Na-HCO_3 type (Piper, Schoeller and Durov plots are shown in supplementary material).

Methane concentrations showed no trend with Cl concentrations indicating that leakage of methane in saline water from deeper aquifers is minimal (supplementary material). Dissolved methane generally increases with bore screen depth, and as $\delta^{13}C$-CH_4 becomes more enriched (Fig. 3). More elevated Cl concentrations were present in the CSG production waters (1050 to 3240 mg/L), a Springbok Sandstone bore (S63, 1570 mg/L), Gubberamunda Sandstone bore (G01, 2550 mg/L), one Precipice Sandstone (P17, 1750 mg/L) and one Condamine Alluvium bore (C09A, 3010 mg/L), though Cl did not show a trend with depth (Fig. 3).

The stable oxygen and hydrogen isotopes of water ($\delta^{18}O$-H_2O and $\delta^{2}H$-H_2O) are indicators for evaporation, water-rock, gas interactions or microbial activity (Clark and Fritz, 1997). Climate conditions during recharge or rainfall amounts also affect the values. The aquifer $\delta^{18}O$- H_2O and $\delta^{2}H$-H_2O are generally more depleted with bore screen depth (supplementary material) and cluster along the global and local meteoric water lines. Precipice Sandstone ($\delta^{18}O$-H_2O -5.9 to − 6.7, and $\delta^{2}H$- H_2O -33 to − 43 ‰), Hutton Sandstone (− 6.8, − 37‰ respectively), CSG production waters (− 5.8 to − 7, and − 36 to − 43 ‰) and a gassy Springbok Sandstone bore (S01, − 8 and − 49‰) have the most depleted waters. The two Condamine River samples are more depleted in $\delta^{18}O$- H_2O and $\delta^{2}H$-H_2O (− 3.5 to − 4.5 and − 22 to − 25 ‰, respectively) than the Myall and Oakey Creeks (0.1 and − 0.8 for $\delta^{18}O$-H_2O, − 1.9 and 3 for $\delta^{2}H$-H_2O, respectively) with the Myall Creek showing an evaporative signature (appendix and supplementary material). Condamine River and rain samples are in agreement with previous data reported in the region (supplementary material) (Baublys et al., 2015; Martinez et al., 2015; Owen, 2016). One Walloons shallow water bore plots off the global meteoric water line indicating evaporation. The most enriched sample is the “Dalby rain storm” water collected during a thunderstorm with intense rainfall that formed inland. In arid or semi-arid regions such as the study area, small rainfall events have an enriched stable isotope composition since the droplets formed during condensation partially re- evaporate.

The deuterium (D) excess is defined as $\delta^{2}H – 8 \times \delta^{18}O$, where lower values can indicate processes such as evaporation of waters prior to recharge (Bershaw, 2018; Hughes and Crawford, 2012). The D excess of the groundwaters, CSG production waters, rain and river waters is plotted against depth in Fig. 3b. The above-mentioned Walloons shallow water bore CLJ18, and Myall Creek have D excess of − 2.8‰ consistent with evaporative processes occurring. The Condamine Alluvium bores have D excess of 5.6 to 9‰. The shallower Springbok bore S63 also has a low D excess of 5.6‰, and the deeper gassy Springbok S01 15‰. D excess of the Precipice Sandstone bores was 10.2 to 15.8, and the Hutton bore the highest at 17‰. The other GAB bores ranged from 7.8 to 13.6, the CSG production waters 10.4 to 13, the river waters 6 to 11, and rainstorm and raintank waters 11.6 to 16.4‰. The groundwater Na/Cl and Sr/Cl ratios were variable with two Precipice and two Gubberamunda groundwaters indicating greater water rock interaction, and several bore waters with calcite dissolution or Ca-silicate weathering (Fig. 3e,f).

The strontium isotope signatures indicate the origins of the waters, water-rock interactions, and aquifer mixing. Water-rock interactions result in groundwater signatures close to the aquifer rock (Raiber and Suckow, 2017). A map of $^{87}Sr/^{86}Sr$ isotope signatures is shown for sampled groundwaters and rivers in Fig. 4. The CSG production waters from the Walloon Coal Measures have low non-radiogenic $^{87}Sr/^{86}Sr$ signatures <0.7036 that are distinct from the other bore waters, and consistent with previous measurements in the Walloons Coal Measures (Fig. 5) (Baublys et al., 2019). Co-produced CSG production waters across the Surat Basin have been reported in the range $^{87}Sr/^{86}Sr$ = 0.70338 to 0.70456. Baublys and co-workers also reported both exchange and weak acid extracted $^{87}Sr/^{86}Sr$ from coals, calcite, and rock core of the Walloon Subgroup at 0.7033 to 0.7046. Baublys et al. (2019) previously attributed the non-radiogenic Sr to recharge via the Main Range Volcanics (Fig. 1), which consist of basalt with reported $^{87}Sr/^{86}Sr$ of 0.7049 to 0.7055, and also to silicate weathering and ion exchange in the Walloon Coal Measures (Baublys et al., 2019; Feitz et al., 2014). The CSG production waters also have positive $\delta^{13}C$-DIC 15.8 to 19.1 ‰ (Fig. 5a) consistent with secondary microbial CO_2 reduction forming methane during methanogenesis (Baublys et al., 2015; Golding et al., 2013). The gassy Springbok Sandstone bore, S01, also has a low non- radiogenic $^{87}Sr/^{86}Sr$ 0.7035 (Fig. 5) that is within the CSG production water range, and a positive $\delta^{13}C$-DIC of 16.3 ‰ consistent with strong methanogenesis. Exchange and weak acid extracted $^{87}Sr/^{86}Sr$ from a Springbok Sandstone core was previously also reported to have a low non-radiogenic signature at 0.7037 (Baublys et al., 2019). The majority of other groundwater samples have more depleted negative $\delta^{13}C$-DIC (− 5.9 to − 13.9‰) more consistent with recharge waters (Fig. 5a). Several Precipice, the Hutton, a shallow Walloons water bore, Mooga, and one Condamine Alluvium bore (C09A) waters are more enriched (− 4.2 to 7.1‰) in $\delta^{13}C$-DIC indicating calcite dissolution or methanogenesis occurring. The Condamine Alluvium bore C09A that only contained 0.005 mg/L methane, is the only Condamine Alluvium sample here that is saturated with respect to calcite (supplementary material). These other GAB aquifer bores (P17, H121, CUJ197, and M02) contain methane (2 to 44 mg/L) with isotopic signatures supporting the occurrence of in situ methanogenesis via primary microbial CO_2 reduction (appendix and supplementary material) (Pearce et al., 2022c). The Precipice bore, P, with 2100 mg/L methane and a positive $\delta^{13}C$-DIC of 5.8, has methane stable isotope signatures that are either consistent with secondary microbial CO_2 reduction or some mixing contribution from deeper thermogenic gas (Pearce et al., 2023b). The Precipice Sandstone is the basal aquifer of the Surat Basin, below the Walloon Subgroup CSG reservoir, with the Hutton Sandstone lying between (Fig. 1); therefore, deeper gas and/or in situ secondary microbial CO_2 reduction is the likely gas source in the Precipice (not CSG from the Walloon Subgroup).

The bore groundwaters from the Condamine Alluvium, shallow Walloons bores, Hutton, Gubberamunda, Mooga, Orallo, Precipice sandstones, and the Springbok Sandstone bore S63 are more radiogenic than the CSG production waters, with $^{87}Sr/^{86}Sr$ 0.7041 to 0.7083. The Gubberamunda, Orallo and Mooga samples from the Roma region also have low Sr concentrations (mean = 0.44 mg/L, median = 0.08 mg/L). The four river waters have a narrow range of $^{87}Sr/^{86}Sr$ from 0.7052 to 0.7056, and may have been influenced by flow originating over the Main Range Volcanics. The five rain waters have a wider range of $^{87}Sr/^{86}Sr$ from 0.7057 to 0.7081. Modern seawater $^{87}Sr/^{86}Sr$ is 0.709175; however since these samples were collected inland in a relatively arid region, the rain samples have likely been affected by non-radiogenic Sr from windblown dust or anthropogenic sources (N´egrel et al., 2007). The Precipice Sandstone bore waters are characterised by the most radiogenic strontium isotopic signatures (0.7062, 0.07063, 0.7083) (Fig. 5). The $^{87}Sr/^{86}Sr$ of whole rock core from the Precipice Sandstone has been

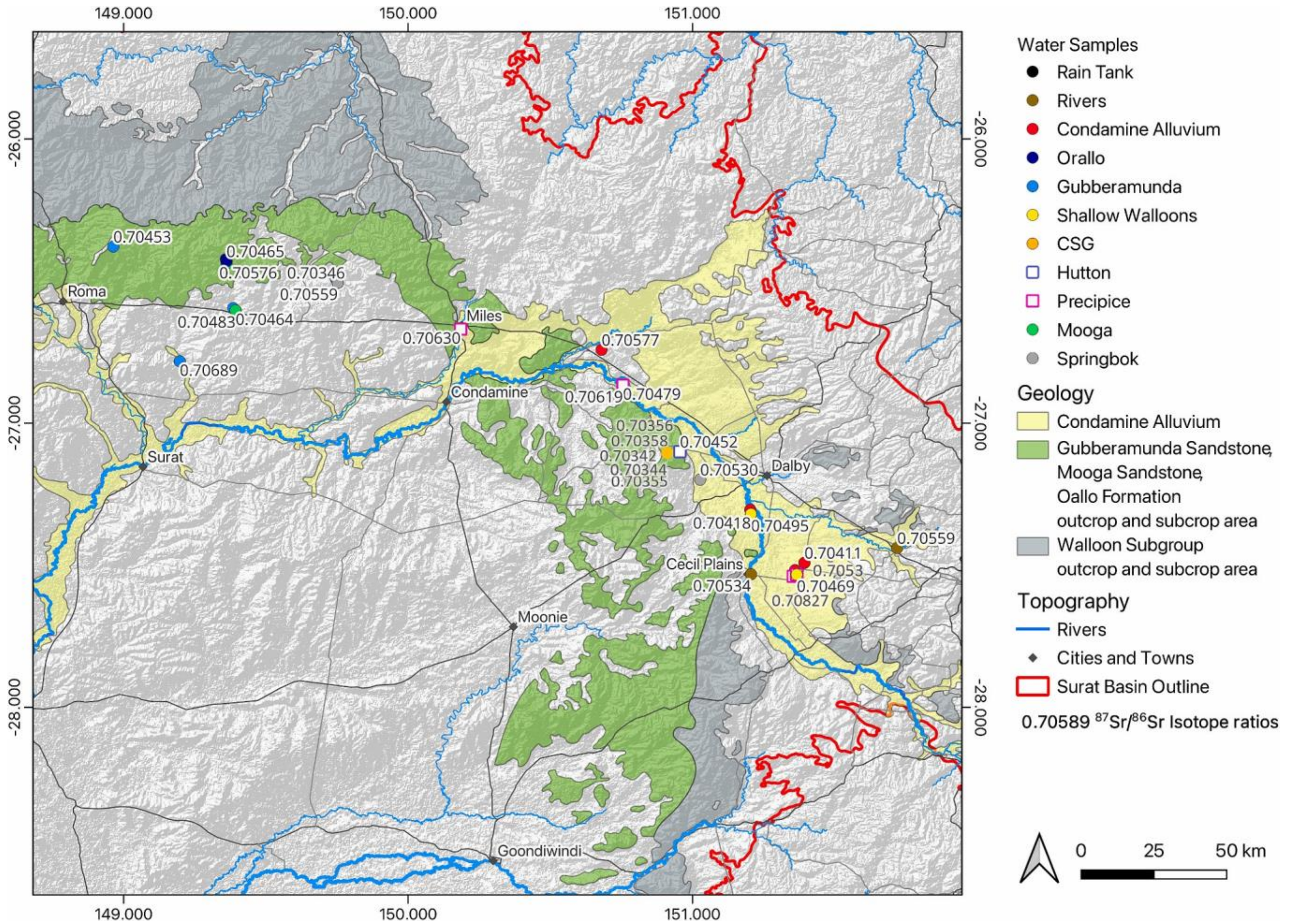


Fig. 4. Map showing the $^{87}Sr/^{86}Sr$ isotope ratios of bore groundwaters, CSG production waters, and river waters. Note many bores are nested, and one Condamine River sample is off the range of this map, see supplementary material. All data including rainwaters and positions are in the supplementary material.

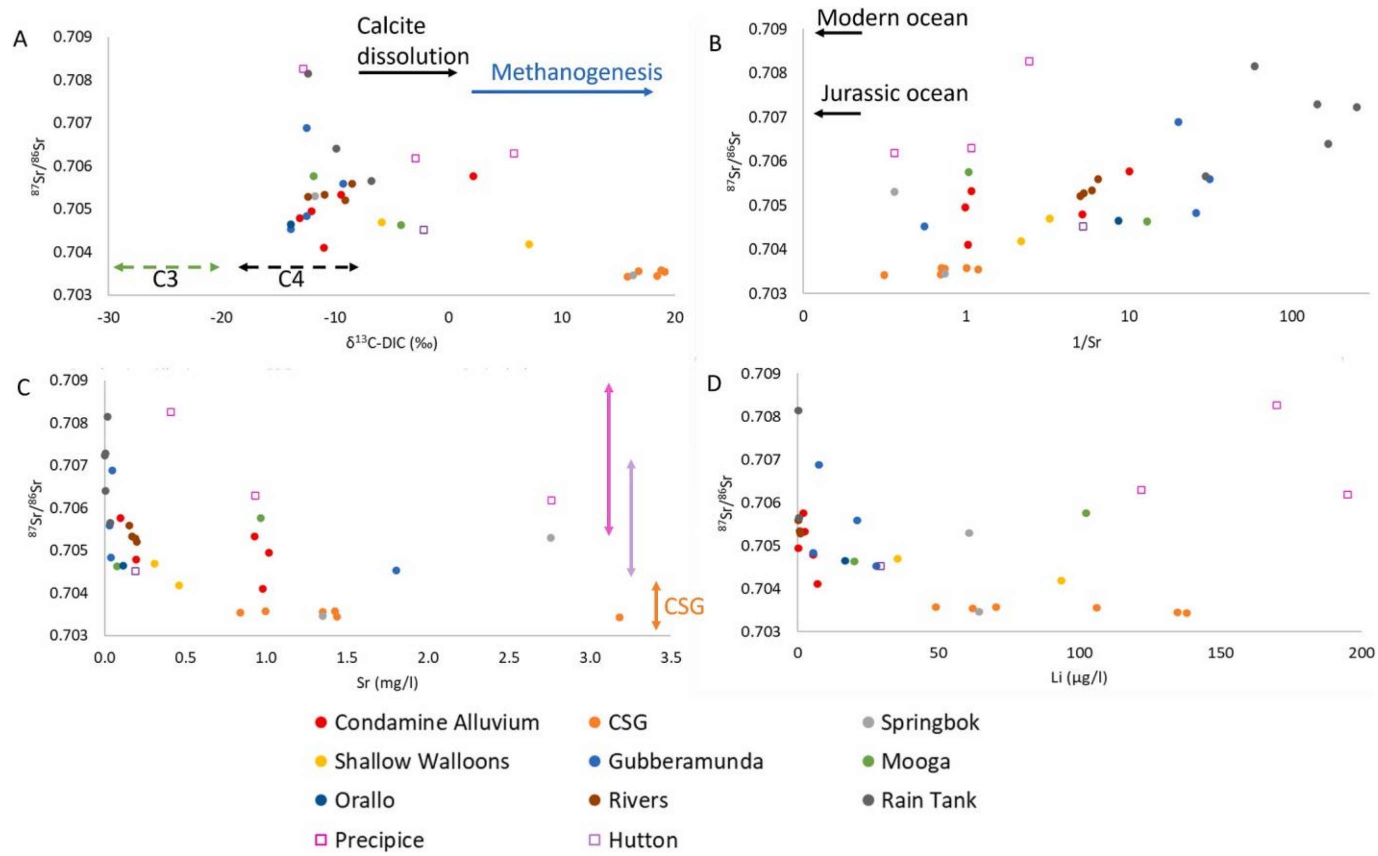
reported at 0.7117 to 0.7341, and Hutton Sandstone rock core at 0.7064 to 0.717, both higher than the groundwaters indicating they may not be in equilibrium with the rock (Hofmann et al., 2021) (Hofmann et al., 2024).

Rb and Li generally showed an increasing trend in all the groundwaters, consistent with Li usually sourced from dissolution of silicate minerals in freshwaters (supplementary material). The Precipice Sandstone waters had the highest Rb and Li concentrations (supplementary material, Fig. 5d, Fig. 6). Elevated concentrations of Li and B can also be tracers of hydrothermal activity (Godfrey et al., 2019). Evidence for the migration of hydrothermal fluids from depth especially around fault zones has been reported in the Precipice Sandstone. Therefore, it is possible that the relatively elevated Li in this deeper aquifer is also related to hydrothermal fluid migration (Golding et al., 2016; Pearce et al., 2023b; Underschultz et al., 2016). Li concentrations are also relatively elevated in the CSG production waters and several bores (shallow Walloons bore CUJ197, Mooga bore M15, and the gassy Springbok bore S01). Li concentrations are relatively low in the Condamine Alluvium and Gubberamunda groundwaters (Fig. 5d, Fig. 6). Incorporation of Li into secondary minerals, especially clays, can decrease Li/Na, as well as adsorption of B onto secondary minerals, especially clays, that can decrease B/Na (Godfrey et al., 2019). The low Li/Na and B/Na of the Condamine Alluvium waters are likely owing to Li and B incorporation and adsorption to clays formed through mineral weathering (Fig. 6). Overall groundwaters with higher dissolved methane concentrations contain higher Rb and Li concentrations, which reflects higher methane concentrations overall in deeper formations that have more evolved groundwaters where silicate weathering has occurred (supplementary material). Concentrations of other trace metals are presented in the supplementary material.

3.2. Stable isotopes of sulphate

The stable isotopes of dissolved sulphate were able to be measured on a subset of groundwater samples, and are combined in plots with previously reported data for interpretation (Feitz et al., 2014; Iverach et al., 2017). Of the groundwater bores sampled in this study, $\delta^{34}S\text{-}SO_4$ was 10.6 ‰ in a Gubberamunda and 10.7 ‰ in a Mooga bore; 16.4 ‰ for Condamine Alluvium C09A, 21.2 ‰ for Springbok S63, and 25.6 ‰ in the Orallo bore (Fig. 7, Appendix Table A1). One Precipice bore had much higher $\delta^{34}S\text{-}SO_4$ at 38.7 ‰. There are no evaporite sediments in the formations. Surface gypsum salts from Playa lakes around inland Australia have been reported with $\delta^{34}S\text{-}SO_4$ ~ 15.3 to 20.5 ‰, with higher values near the coastline (~21 ‰) decreasing inland (~14 ‰) (Chivas et al., 1991). The dissolved sulphate in the majority of the groundwaters are therefore dominated by sulphate aerosols sourced from surface salts in recharge waters. This is consistent with similar sources reported in the Murray Basin (Cartwright et al., 2006; Dogramaci et al., 2001). Similar processes with contributions from windblown dust from Playa lakes in the USA have also been documented (Mayo and Klauk, 1991; Ryu et al., 2002). The Gubberamunda Sandstone groundwaters plotted overall have enriched $\delta^{34}S\text{-}SO_4$ (Fig. 7) and a trend of increasing $\delta^{34}S\text{-}SO_4$ as the sulphate concentration decreases that suggests bacterial sulphate reduction is also occurring (Edraki et al., 2005; Innocent et al., 2021; Krouse and Mayer, 2000). These also plot on $\delta^{34}S\text{-}SO_4$ vs $1/SO_4$ with a trendline that has an intercept of $\delta^{34}S\text{-}SO_4 = 20.4$ ‰

Fig. 5. A) The $^{87}Sr/^{86}Sr$ signatures of bore groundwaters, CSG production waters, rivers and rain waters vs $\delta^{13}C$-DIC. The dashed arrows indicate general input $\delta^{13}C$- DIC ranges to soil carbon from C3 and C4 plants. Calcite dissolution and methanogenesis elevate $\delta^{13}C$-DIC. B) The $^{87}Sr/^{86}Sr$ signatures vs 1/Sr concentration (on a log scale to view the rainwaters), the isotope signatures of the Jurassic and modern ocean are also indicated. C) $^{87}Sr/^{86}Sr$ vs Sr concentration, the orange arrow indicates the $^{87}Sr/^{86}Sr$ isotope range of Walloon Coal Measures CSG production water previously published (Baublys et al., 2019). The pink and purple arrows indicate $^{87}Sr/^{86}Sr$ isotope ranges of Precipice and Hutton aquifer samples respectively across the southern Surat Basin from (Hofmann et al., 2021) and also from (Hofmann et al., 2024) note these arrows do not indicate the Sr concentration ranges. D) $^{87}Sr/^{86}Sr$ vs Li concentration. (For interpretation of the references to colour in this



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(supplementary material). This is consistent with a component of bacterial sulphate reduction occurring (Porowski et al., 2019; Zheng et al., 2019). Two of the Gubberamunda bores sampled in this study had stable gas isotopes indicating acetate fermentation (acetoclastic methanogenesis) also occurring, although methane concentrations were very low e.g. $\delta^{13}C$-CH_4–81.9 and − 64.2, $\delta^{2}H$-CH_4–335.7 and − 329.1 ‰ (appendix Fig. A1). There is no obvious increasing trend in $\delta^{34}S$-SO_4 as the sulphate concentration decreases for the Marburg or Condamine Alluvium bores plotted here. The Marburg Sandstone has an intercept of 9.9 ‰ which could be more consistent with a source from sulphate aerosols from inland surface salts in recharge waters (Feitz et al., 2014). The Condamine Alluvium only has three $\delta^{34}S$-SO_4 measurements, generally not enough to estimate the intercept or look at trends (Iverach et al., 2017). However, with caution, the source from the three bores on a plot of $\delta^{34}S$-SO_4 vs 1/SO_4 is $\delta^{34}S$-SO_4 = 16.6 ‰ that could be consistent with the sources from atmospheric inland sulphur aerosols in recharge waters as described above (supplementary material).

3.3. Cosmogenic Isotopes

Cosmogenic radioactive isotopes, radiocarbon ^{14}C and $^{36}Cl/Cl$ are generated in the atmosphere, and once the water infiltrates the subsurface the isotopes decay to lower values indicating longer residence times. Mean residence times of groundwater ~500 to 40,000 years can be estimated with ^{14}C, and $^{36}Cl/Cl$ for groundwaters >50,000 years (Clark and Fritz, 1997). However, the ^{14}C signature can also be lowered by a "dead" carbon source from calcite dissolution or methanogenesis (Baublys et al., 2021; Hofmann et al., 2024). Tritium indicates modern groundwater infiltration, relative to the longer time ranges provided by ^{14}C and ^{36}Cl. Fig. 7F, Fig. 8, Fig. 9, and Fig. 10 show the $^{36}Cl/Cl$, $\delta^{18}O$- H_2O, ^{14}C, and tritium signatures of the groundwaters, production waters, river and rainwaters. Ranges for previously reported CSG production waters and local rainwater are also shown in Fig. 9 (note the Condamine Alluvium groundwater stable water isotopes and ^{14}C are consistent with previous measurements) (Baublys et al., 2021; Owen, 2016; Scheiber et al., 2020). The CSG production waters, Precipice Sandstone, Hutton Sandstone and the gassy Springbok sandstone bore S01 generally have lower $^{36}Cl/Cl$ and ^{14}C pMC values indicating longer residence time groundwaters. These deeper aquifer samples may be approaching secular equilibrium. The $A^{36}Cl$ represent the concentration of ^{36}Cl atoms per litre and are therefore affected by evaporation or transpiration processes. Higher values indicate evaporation or evapotranspiration of recharge waters. A positive correlation of increasing $A^{36}Cl$ with increasing Cl concentration indicates evapotranspiration rather than groundwater mixing occurring. $A^{36}Cl$ of the CSG production waters ranges from 40 to 96 (x10^7), with shallow Walloons water bores having values of 10 and 26 (x10^7). Precipice Sandstone $A^{36}Cl$ values are 3, 4, and 88 (x10^7), with the Hutton 6 × 10^7 (Fig. 10, and supplementary material). The gassy Springbok bore S01 has a low $A^{36}Cl$ of 3 × 10^7.

The ^{14}C measurements of the bores with higher methane contents have likely been affected by the release of "dead" ^{14}C-free carbon from in situ methanogenesis (Cartwright et al., 2020). Owing to this, the uncertainty of the ^{14}C and $\delta^{13}C$-DIC in recharge waters in this arid environment, and the partial recharge of the alluvium by the river, a

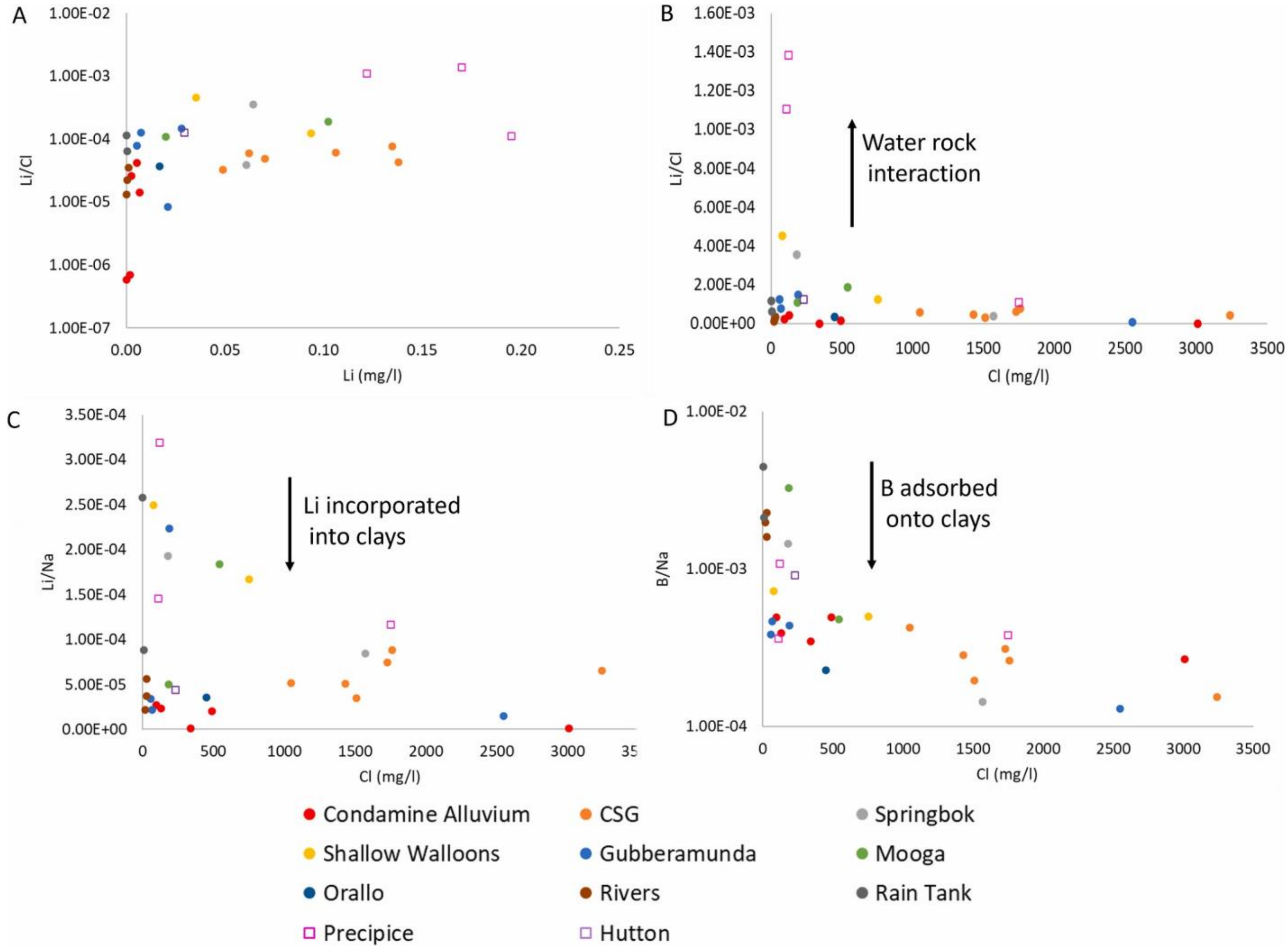


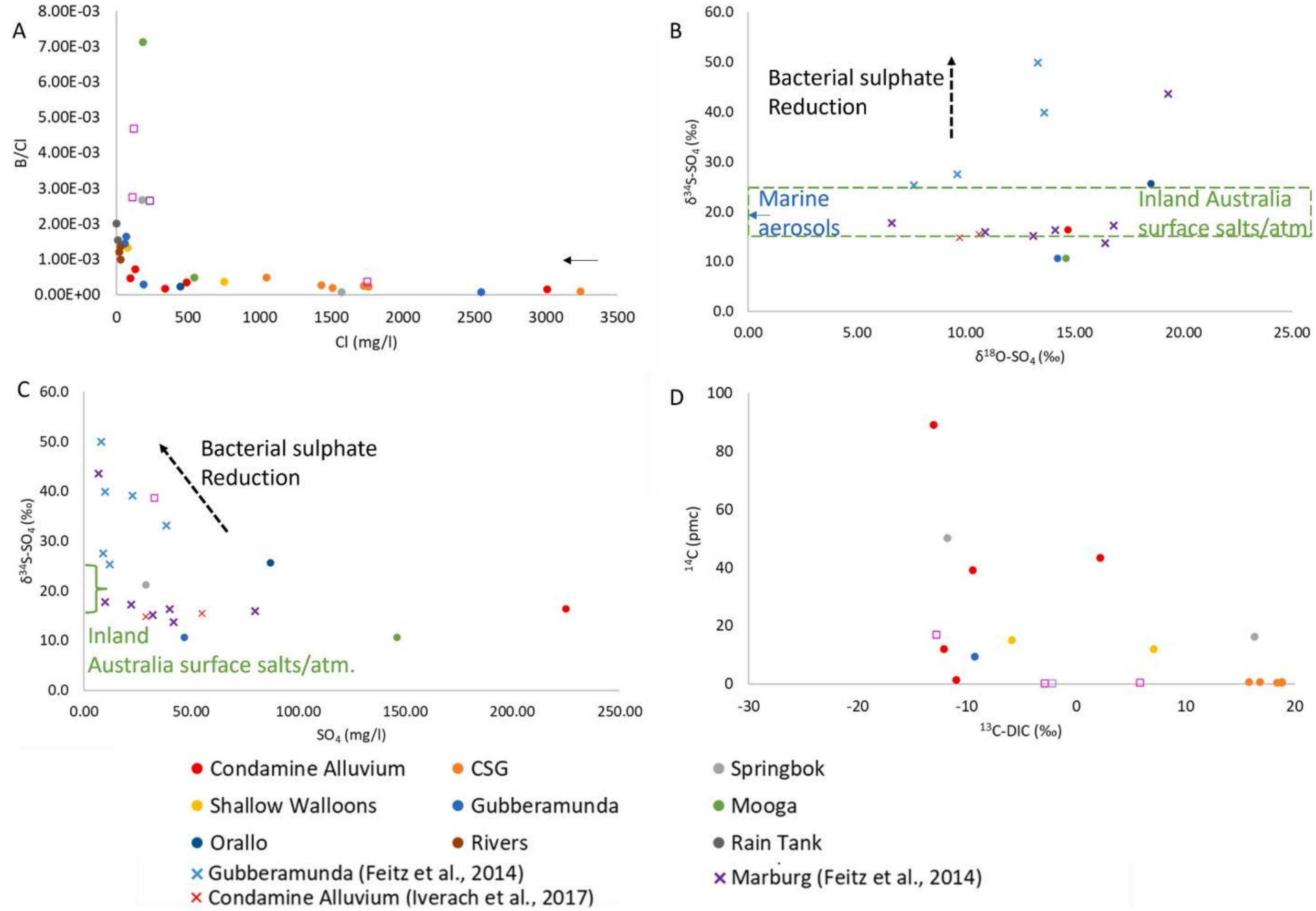
Fig. 6. A) The bore groundwater, CSG production water, river and rainwater Li/Cl (log scale) vs Li concentration. B) Li/Cl vs Cl concentration, where increasing Li/ Cl can indicate increasing water-rock interaction. C) Li/Na (log scale) vs Cl concentration, where decreasing Li/Na can indicate incorporation of Li into clays. D) B/Na (log scale) vs Cl concentration, decreasing B/Na can indicate B adsorption onto clays.

correction is not performed here to calculate residence times or ages (Cartwright et al., 2020; Cartwright et al., 2012).

The Condamine Alluvium samples have relatively higher $^{36}Cl/Cl$ from 72.7 × 10^{-15} to the modern value of 114 × 10^{-15}, with a wide range of ^{14}C of 1.3 to 89.2 pMC (Table A1). Bore C370A has a $^{36}Cl/Cl$ of 81 × 10^{-15}, but a very low ^{14}C of 1.3 pMC that could indicate groundwaters are almost ^{14}C dead (greater than ~35,000 to 40,000 years) or there is a source of dead ^{14}C-free carbon. Condamine Alluvium bore C370A has a low concentration of methane of 0.27 mg/L with SO_4 below detection, and is only slightly undersaturated with respect to calcite (supplementary material). Bore C195 has a $^{36}Cl/Cl$ of 80 × 10^{-15} and ^{14}C of 11.9 pMC. However, this bore has 6.7 mg/L dissolved methane and stable isotopes of methane and CO_2 consistent with in situ methanogenesis via primary microbial CO_2 reduction (appendix), that could be the source of dead ^{14}C-free carbon decreasing the ^{14}C value in this case. Condamine Alluvium samples overall show a positive correlation between $A^{36}Cl$ (15 to 384 × 10^7) and Cl concentrations (Fig. 10), indicating that evapotranspiration has occurred. One shallow Walloons water bore CLJ18, and a Springbok bore (S63) also have more recent recharge with $^{36}Cl/Cl$ 71 and 69 × 10^{-15}, respectively, and ^{14}C 50.1 and 15 pMC, respectively, indicating recharge within the ^{14}C age range (Fig. 8, Fig. 9, Fig. 10). Springbok bore S63 has a relatively high $A^{36}Cl$ of 190 × 10^7 indicating evapotranspiration, also consistent with the low D excess. Gubberamunda bore G01 also has a high $A^{36}Cl$ of 202 × 10^7. Several Condamine Alluvium bores, the two shallow Walloons water bores and a Springbok (S63) also have measurable tritium (up to 0.73 TU) indicating a component of recent recharge or mixing of two water sources (Fig. 9, Fig. 10D). One of the shallow Walloons bores with a $^{36}Cl/Cl$ of 20 × 10^{-15} and detectable tritium reflects mixing of older and recent recharged water and is likely to have been affected by poor well development or recent infiltration/contamination with evaporated surface water (personal communication with landholder).

The two Condamine River surface water samples and a local raintank have tritium of 1.5, 1.57, and 2.43 TU, respectively. The rainwater is consistent with tritium measurements at 2 to 3 Tu, (increasing with latitude) across Australia (Tadros et al., 2014). The Condamine Alluvium bores sampled here have tritium consistent with Iverach et al., who previously reported eighteen Condamine Alluvium irrigation bores to have a tritium range of 0.01 to 0.19 TU (Iverach et al., 2015). Recharge of the Condamine Alluvium has also been previously reported to be mainly through river flooding (with subsequent water-rock interaction or evapo-transpiration), with also a smaller component of recharge from volcanic aquifers (Scheiber et al., 2020). The Condamine River samples have $^{36}Cl/Cl$ values of 134.5 and 147 × 10^{-15}, with a raintank sample measured at 93.6 × 10^{-15} (Fig. 9, Fig. 10). Oakey Creek, however, has a very low $^{36}Cl/Cl$ value of 28 × 10^{-15} (Fig. 10) that could indicate connectivity to groundwater discharge or bank return flow (Baskaran et al., 2009; Hofmann, 2023). Martinez and co-workers previously identified connectivity with groundwater in other tributaries to the east of the Condamine Alluvium, including in the nearby Dalrymple Creek

Fig. 7. A) B/Cl vs Cl concentration. The arrow indicates the equivalent seawater value. B) The $\delta^{34}S$-SO_4 vs $\delta^{18}O$-SO_4 with general region associated with surface salts in Inland Australia in recharge waters. C) The $\delta^{34}S$-SO_4 vs SO_4 concentration. The reported value for surface salts in inland Australia is shown. Existing data for groundwaters from deeper Gubberamunda bores are also shown (crosses), along with those for Marburg Sandstone bores that are the equivalent of the Hutton Sandstone in the Clarence-Moreton Basin from (Feitz et al., 2014), and the Condamine Alluvium from (Iverach et al., 2017). Sulphide was below detection in the



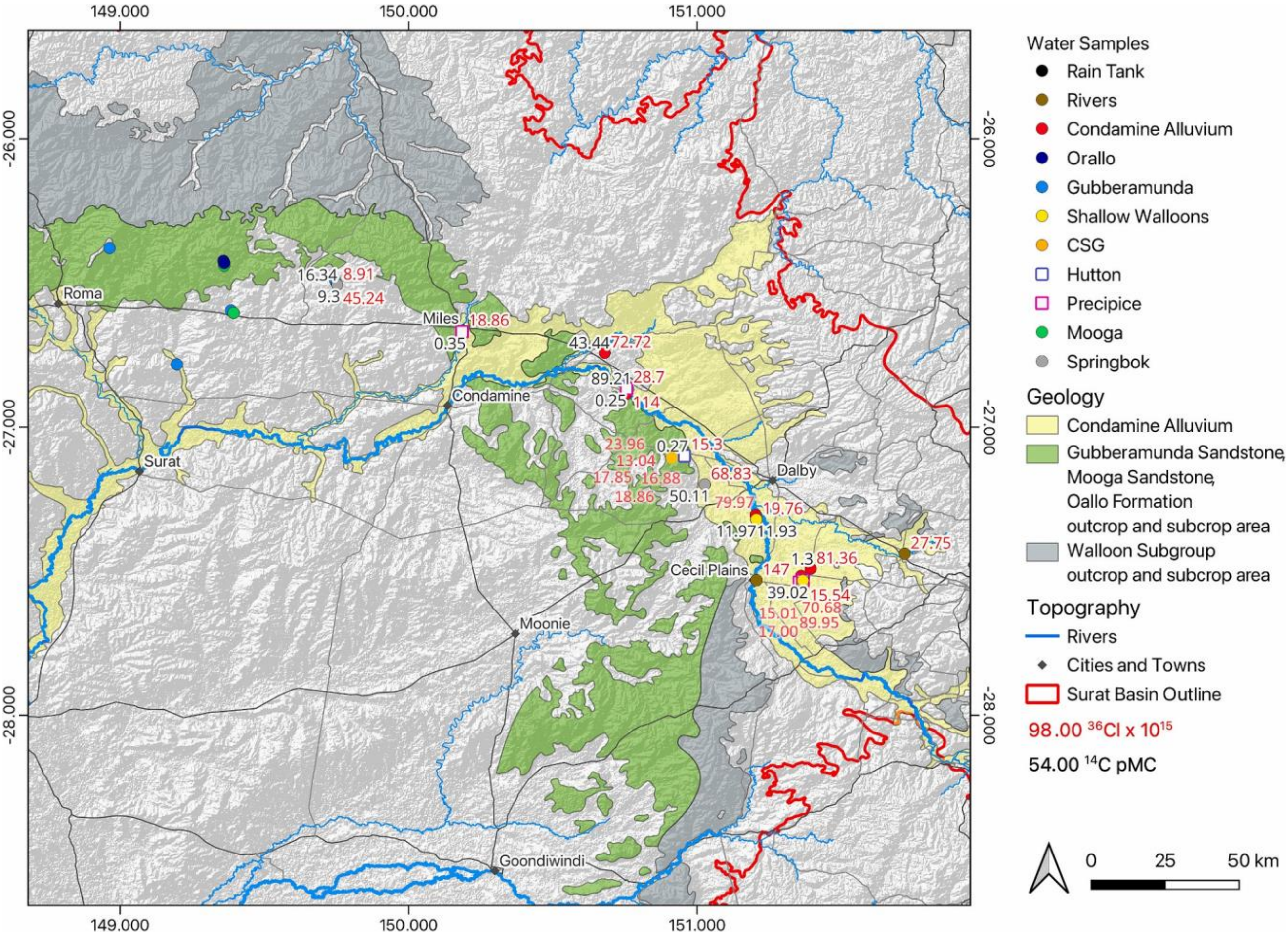
existing data. D) The ^{14}C of sampled waters vs $\delta^{13}C$-DIC.

(Martinez et al., 2015). They reported evidence for interaquifer (Marburg, Walloons, and Main Range Volcanic), Condamine Alluvium, and surface water connectivity. Geoscience Australia has also reported groundwater discharge to the Oakey Creek and Condamine Alluvium (Ransley et al., 2015). Other possibilities could be addition of a contamination source of Cl, however, the Cl concentration in Oakey Creek is not elevated compared to the other rivers. The Oakey Creek also has an enriched $\delta^{18}O$-H_2O signature, but the D excess does not indicate evaporation, and $A^{36}Cl$ is low at 1×10^7 that also does not indicate evaporation. The groundwater $^{36}Cl/Cl$ vs ^{14}C is shown in Fig. 10D,E including previous data for CSG production waters, and for the Gubberamunda, Mooga and Hutton aquifer groundwaters across the Surat Basin, and the Marburg Sandstone that is the Hutton equivalent in the Clarence-Moreton Basin (Baublys et al., 2021; Feitz et al., 2014). The previous data for the Gubberamunda and Mooga sandstones were generally from the south of the basin, further from recharge, with longer residence times.

3.4. Local Implications

The current study shows that signatures including Sr isotopes of aquifer groundwaters are distinct from the CSG reservoir indicating a lack of significant groundwater connectivity or leakage from the reservoir. Alluvium and shallower GAB aquifer bores show evidence for mixing of older and modern groundwater from meteoric recharge. In this inland arid region, windblown surface salts from Playa lakes control dissolved sulphate from recharge waters. In the important regional Gubberamunda and Marburg aquifers, however, bacterial sulphate reduction is additionally occurring. It was shown in a previous study (by the current study authors) that the majority of the shallow GAB aquifer samples collected had methane and CO_2 stable isotopes and fractionation factors consistent with primary microbial CO_2 reduction forming methane in situ within the aquifers (i.e. not from CSG leakage) (Fig. A1) (Milkov and Etiope, 2018; Pearce et al., 2022c). Two Gubberamunda samples, and a Shallow Walloons water bore, however, are indicative of acetate fermentation pathway producing methane in situ. Of the five Condamine Alluvium bores sampled, bore C195 has stable isotopes of methane, CO_2 and DIC (− 213, − 66.4, − 20.7, − 12.1 ‰ respectively) that plot within the regions for in situ primary microbial CO_2 reduction, forming methane in situ within the alluvium. The other four Condamine Alluvium bore samples have <0.27 mg/L dissolved methane (too low for methane isotopic analysis), and $\delta^{13}C$-CO_2 −16.8 to − 20.6 ‰ that is consistent with recharge sources. The CSG production waters have methane and CO_2 stable isotopes, and positive $\delta^{13}C$-DIC, consistent with methanogenesis via secondary microbial CO_2 reduction. The gassy Springbok Sandstone bore S01 has stable isotope signatures also indicative of secondary microbial CO_2 reduction. The Hutton and Precipice sandstones are deeper Jurassic aquifers, underlying the CSG reservoir. The Hutton bore, and one of the Precipice bores sampled here, have gas isotopic signatures consistent with in situ generation of methane via

Fig. 8. Map showing the groundwater, CSG production water and river water $^{36}Cl/Cl$ (x10^{15}) (labelled in red), and ^{14}C (pMC) labelled in black. Many bores were nested or in close proximity. Full data, including rainwater, are given in the supplementary material. (For interpretation of the references to colour in this figure



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primary microbial CO_2 reduction. The two other Precipice Sandstone bores have gases that plot in a mixed zone that could contain some methane from secondary microbial CO_2 reduction and/or thermogenic gas. Precipice bore P is also located near a major fault zone, and contains ethane, therefore likely has been influenced by historical migration of thermogenic gas up from the underlying Bowen Basin.

The $^{87}Sr/^{86}Sr$ signatures of the GAB aquifer and Condamine Alluvium groundwaters presented in this study are more radiogenic than the CSG production waters indicating a lack of significant aquifer and CSG reservoir groundwater connectivity. In isolation this does not preclude gas migration (without groundwater migration), hence the need for the combination with the gas signatures above. In contrast, the gassy Springbok Sandstone bore S01 has an overlapping $^{87}Sr/^{86}Sr$ signature with the CSG production waters, and with the Surat CSG production water range previously reported that could indicate groundwater migration (Baublys et al., 2019; OGIA, 2021). The Gubberamunda Sandstone and Condamine Alluvium bores sampled had low Li concentrations relative to the other aquifers and CSG production waters. Where Li/Cl and Li/B ratios indicate Li and B have been incorporated into clays formed by weathering.

Where $\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4 were able to be measured, they were mainly consistent with a source of sulphate from windblown aerosols of surface salts from inland Australia (Playa lakes) in recharge waters (Chivas et al., 1991; Dogramaci et al., 2001). The Gubberamunda Sandstone aquifer (and Marburg aquifer) groundwater $\delta^{34}S$-SO_4 became more depleted as sulphate concentration increased, indicating bacterial sulphate reduction was also occurring. The very low concentrations of dissolved methane in these aquifers are likely owing to competition of the sulphate reducing bacteria for substrates, outcompeting methanogenic bacteria.

The groundwater D excess can be lowered owing to evapotranspiration, and can be affected by differences in altitude, relative humidity, season (e.g. lower D excess during the summer), air mass trajectory, and precipitation recycling during recharge (Bershaw, 2018; Hollins et al., 2018). The D excess of precipitation in this region of Australia is reported at 11 to 15 ‰ (Hollins et al., 2018). Groundwater D excess can be subsequently elevated in the subsurface owing to hydrogenotrophic methanogenesis that preferentially uses ^1H and enriches residual D without changing O. The groundwater D excess is relatively more depleted in the Condamine Alluvium, shallow Walloons water bores, the shallow Springbok S63, and Mooga Sandstone. This supports evapotranspiration in these shallower aquifers, with an additional contribution from flood recharge of evaporated waters in the Condamine Alluvium (Scheiber et al., 2020). The Hutton bore, Precipice P17, and the gassy Springbok S01 have the most enriched D excess of the groundwaters sampled here, that have been elevated by the in situ occurrence of hydrogenotrophic methanogenesis, as supported by the stable isotope signatures of gases (appendix Fig. A1).

The deeper Jurassic aquifer bores in the Precipice Sandstone and Hutton Sandstone, the CSG reservoir production waters and one shallow Walloons bore have relatively low $^{36}Cl/Cl$ (Fig. 8, Fig. 9, Fig. 10). The gassy Springbok bore has the lowest value at 8.9×10^{-15}. The secular equilibrium, usually theoretically set to 5 half-lives, in other parts of the GAB (in the Algebuckina and Hooray sandstones) has been previously reported at ~5 to 10 ($\times 10^{-15}$) (Lehmann et al., 2003; Mahara et al., 2009; Suckow et al., 2018). Groundwaters sampled here in these deeper aquifers are likely reaching secular equilibrium. In the Condamine Alluvium samples groundwater ^{36}Cl activity ($A^{36}Cl$) has a positive correlation with Cl concentrations supporting the occurrence of evapotranspiration. The Condamine Alluvium groundwater $^{36}Cl/Cl$ ranges from 73×10^{-15} to the modern value of 114×10^{-15} showing much younger groundwaters. The Condamine Alluvium ^{14}C values, however, have heterogeneity with 1.3 to 89.2 pMC that could indicate longer residence time water close to the limit of ^{14}C or a source of dead carbon in two cases (Fig. 9, Fig. 10). Condamine Alluvium bore C370A has $^{36}Cl/Cl$ of 81.4×10^{-15} and a low ^{14}C of 1.3 pMC with tritium essentially at detection at 0.03 TU. The dissolved concentration of methane is very low at 0.27 mg/L indicating in situ methanogenesis is unlikely to be a strong source of dead carbon. While the methane concentration was too low to analyse the methane stable isotopes, the $\delta^{13}C$- DIC of − 11 ‰ and $\delta^{13}C$-CO_2 of − 18.1 ‰ do not indicate strong in situ methanogenesis or methane oxidation contributing dead carbon. The data reported here are also in good agreement with previous reported ^{14}C for Condamine Alluvium groundwater that was in the range 3.5 to 88.7 pMC reporting significant heterogeneity (Scheiber et al., 2020). Condamine Alluvium bore C195 also has ^{14}C of 11.9 pMC and a $^{36}Cl/Cl$ of 80×10^{-15}. C195 contains 6.7 mg/L of dissolved methane that has a $\delta^{13}C$-CH_4 −66.4‰, $\delta^{2}H$-CH_4 of − 213‰, and $\delta^{13}C$-CO_2 −20.7‰. This is interpreted as methane generated in situ within the Condamine Alluvium by primary microbial CO_2 reduction in the vicinity of this bore. The methane generation would contribute "dead carbon" that could be the reason for the low ^{14}C value. There is no clear evidence for leakage from the CSG reservoir into the Condamine Alluvium for the small number of Alluvium bores sampled in this study. However the possibilty that gas has migrated from the Shallow Walloons aquifer cannot be clearly ruled out. Monitoring bore C195 is reported to have a hydraulic gradient from the Shallow Walloons to the Condamine Alluvium, and hence the possibility of groundwater connectivity was reported by OGIA (OGIA, 2023). The closest Shallow Walloons bore CUJ197 that was sampled in the current study has a very similar ^{14}C of 11.97, but a lower $^{36}Cl/Cl$ of 19.67×10^{-15}. Shallow Walloons bore CUJ197 has a ^{13}C-CH_4 of − 63‰ (that could indicate in situ primary CO_2 reduction or acetate fermentation) but unfortunately the other stable isotopes of methane and CO_2 could not be measured (owing to low concentrations). Methane in Shallow Walloons bore CLJ18 had ^{13}C-CH_4 −66.4 and $\delta^{2}H$-CH_4 −280 ‰ indicating in situ acetate fermentation was producing methane. Owen et al. (2016) previously reported the presence of methane in 7 sampled "Shallow Walloons" Coal Measure bores that were not part of the CSG reservoir in the range $\delta^{13}C$-CH_4 −50.25 to − 78.11, $\delta^{2}H$-CH_4 −209.23 to − 310.13‰, showing that significant variability exists (Owen et al., 2016). Owen and co-workers argued that leakage from the underlying Shallow Walloon coal measures into the Alluvium was not occurring, although they only sampled four Alluvial bores. However, Iverach and co-workers reported evidence for migration of gas from the underlying

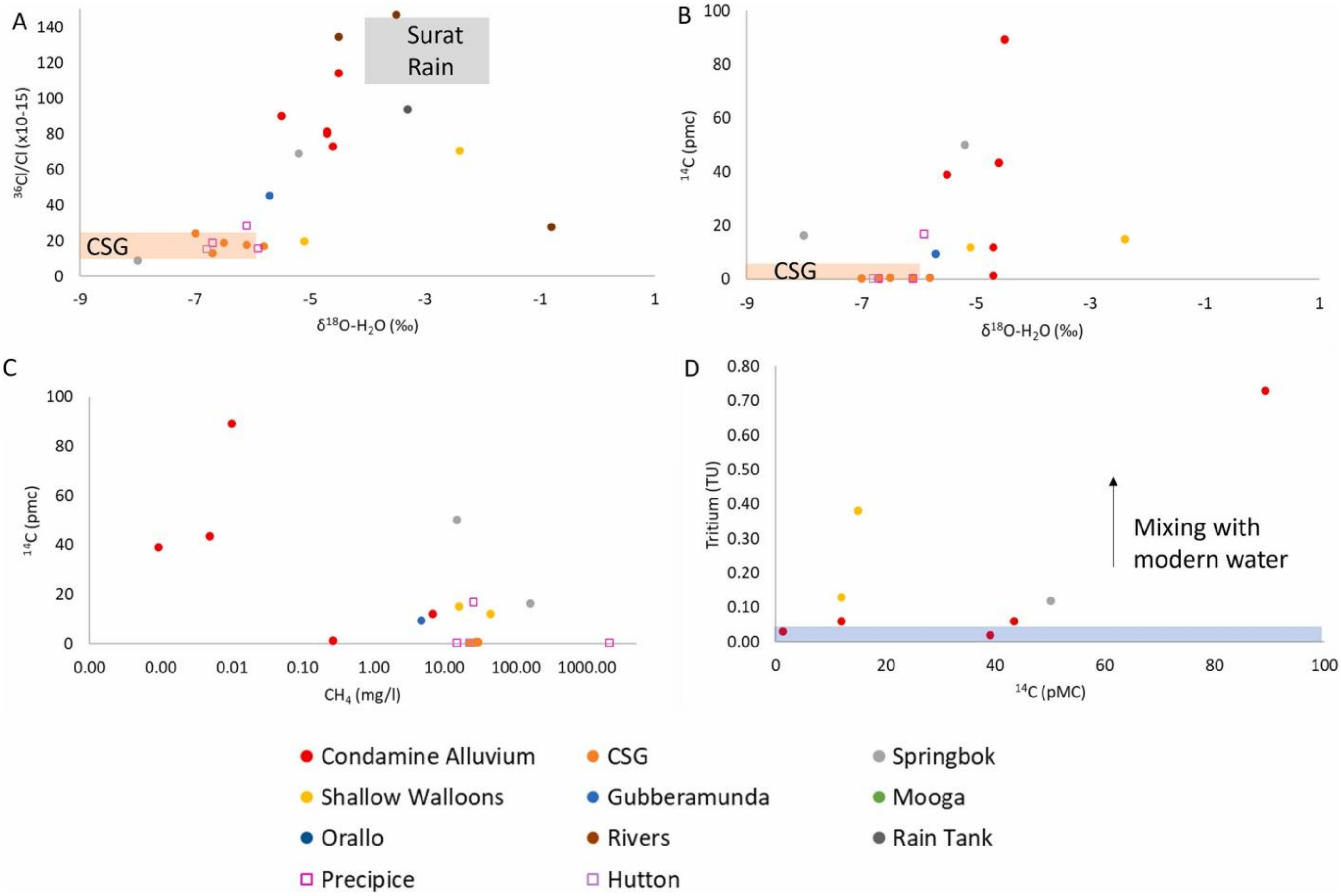

Fig. 9. A) Bore water and CSG production water $^{36}Cl/Cl$ vs $\delta^{18}O$-H_2O. The grey box indicates the reported values for rain (tanks) in the Roma, Miles, and Chinchilla region, Surat Basin, and the orange box the reported range for CSG production waters across the Roma, Chinchilla and Dalby regions from (Baublys et al., 2021). Note that more depleted rain $\delta^{18}O$-H_2O to ~ − 7 ‰ have also been reported. B) Bore water and CSG production water ^{14}C vs $\delta^{18}O$-H_2O. The orange box indicates the range for CSG production waters across the Roma, Chinchilla and Dalby regions from (Baublys et al., 2021(Owen, 2016)). C) The ^{14}C of sampled waters vs concentrations of dissolved methane (log scale). D) Tritium vs ^{14}C, where the blue box indicates where tritium is at the limit of meaningful detection. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

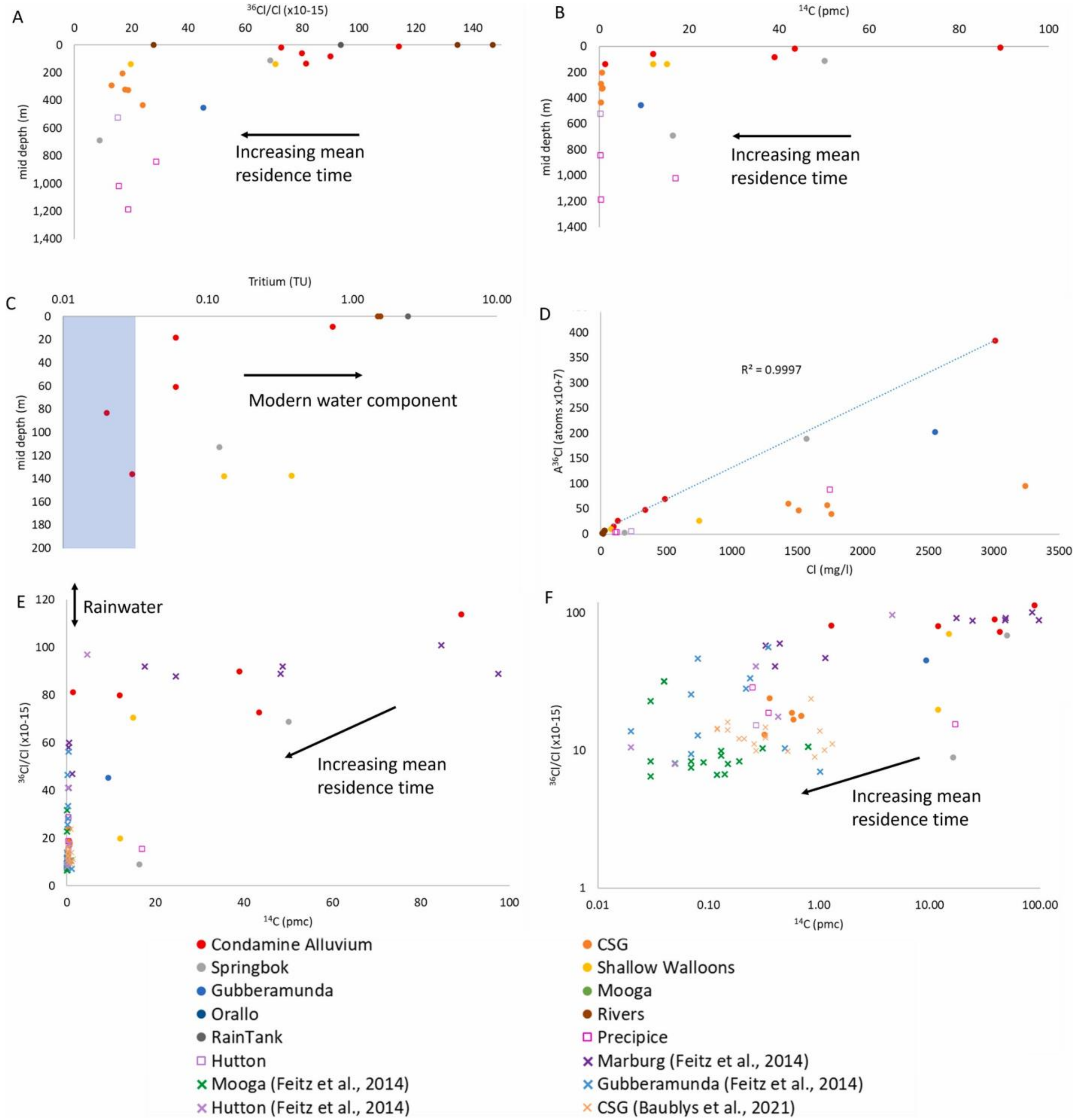

Fig. 10. A) The groundwater, produced water, rain and river water ^{36}Cl/Cl with mid screen sample depth. The more depleted river sample is Oakey Creek, the two more enriched river samples are Condamine River. B) The ^{14}C of groundwater and produced waters vs sample depth. C) Tritium of groundwaters, Condamine River samples and rain water vs sample depth (note the smaller depth scale compared to A) and B) for these shallow samples). The blue box indicates the limit of meaningful detection of tritium D) The A^{36}Cl vs Cl concentrations of waters. The correlation of Condamine Alluvium groundwaters is shown. E) The groundwater and produced water ^{36}Cl/Cl vs ^{14}C with existing data shown as crosses from (Baublys et al., 2021; Feitz et al., 2014). The rainwater range is from two reported Roma and Chinchilla rain samples (Baublys et al., 2021). F) The groundwater and produced water ^{36}Cl/Cl vs ^{14}C values shown on a log scale. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Walloon Coal Measures into the Condamine Alluvium in 19 sampled agricultural bores (Iverach et al., 2017; Iverach et al., 2015; Owen et al., 2016).

In this current study, the Condamine Alluvium was not intended to be the focus, where only five bores were sampled. Four of these bores did not have significant methane concentrations present, thus direct evidence of gas or groundwater leakage is not present. In the fifth bore, given the evidence above, the methane was likely generated in situ within the Condamine Alluvium but the possibility of gas movement from the Shallow Walloons aquifer remains. The Condamine Alluvium is a very heterogeneous aquifer, with ~8000 bores, and large volumes of groundwater extracted for irrigation and town water supply. Irrigation bores that continuously extract groundwater generally have long screens that may be more susceptible to drawing in gas; therefore the possibility of groundwater (and gas) migration in other regions of the broader Condamine Alluvium aquifer cannot be ruled out (Molofsky et al., 2021).

A subset of shallow bore waters were analysed for tritium; three of the Condamine Alluvium bores, the two Shallow Walloons bores, and the Springbok bore S64 have detectable tritium, indicating mixing with modern groundwaters. This is consistent with Condamine Alluvium partial recharge via connectivity to the Condamine River and flood event recharge.

The results of this study are generally consistent with the CSG reservoir groundwater being disconnected from the majority of overlying aquifer bore groundwaters of the GAB (Gubberamunda, Orallo, Mooga). This is also consistent with methane in the shallower GAB bores sampled in this study mainly being formed in situ within the aquifer via microbial CO_2 reduction or acetate fermentation (i.e. not from CSG leakage) (Pearce et al., 2022c). One gassy Springbok Sandstone bore (S01), that is in the aquifer directly overlying the CSG reservoir, however, has similar and overlapping signatures with the CSG production waters. The Springbok contains interbedded coal, and coal fines were observed during pumping of this gassy bore. Coal has been observed in the Springbok Sandstone formation (dispersed coals have also been observed in the deeper Jurassic aquifers, the Hutton Sandstone and Precipice Sandstone) (appendix, supplementary material) (Pearce et al., 2022a; Pearce et al., 2021a; Pearce et al., 2022b). Three scenarios are possible in the gassy Springbok bore S01: a) this bore is in a part of the Springbok Sandstone that is connected to the CSG reservoir via localised fault connectivity, b) the Springbok Sandstone contains coal in the vicinity of the bore S01 and methane is generated in situ within the Springbok Sandstone formation, but via the same processes as in the CSG reservoir (i.e. secondary microbial CO_2 reduction), or c) the bore is in a part of the Springbok Sandstone affected by CSG wells that have been completed across the Springbok Sandstone/Walloon Coal Measures boundary (OGIA, 2021, 2023). Owing to the transitional and erosional boundary between the Springbok and underlying CSG reservoir, the Walloons Coal Measures, the boundary has been picked differently by different stakeholders, resulting in some CSG wells reported to be completed partially into the Springbok Sandstone (OGIA, 2021, 2023). The bore S01 is a government monitoring bore that has been allocated a high confidence level of being completed in the upper Springbok Sandstone with good bore construction (according to OGIA); therefore the bore in itself is not likely to be completed into the underlying reservoir (OGIA, 2021, 2023). It is within the region of reported hydraulic head decline, and reported hydrocarbon indicators (Underschultz et al., 2016). This bore has also been recorded as 19.8 km from the closest CSG well. According to the regional geological models of OGIA, regions of the Springbok Sandstone are also predicted to have potential for cross fault leakage of groundwater. Although this bore is not specifically in a position predicted to have cross fault leakage, it is located near the Mimosa syncline (supplementary material). Thus, it is possible that free gas has migrated within the formation up dip.

3.5. Connectivity in the Surat Basin

In the USA and Canada, with the advent of shale gas, various studies have investigated potential migration of thermogenic gas into overlying aquifers. For example, stray gas was found to be more abundant in drinking water wells near to gas wells (Jackson et al., 2013). Those studies have focussed on differentiating thermogenic gas (from the shale gas reservoir) from biogenic gas that can be naturally occurring in aquifers. However, in Australia the connectivity of gas reservoirs to aquifers has received less attention. In addition, CSG is often biogenic in origin, making the differentiation of the reservoir gas more complicated (Faiz and Hendry, 2006). In the New South Wales Richmond River catchment, a CSG baseline study found up to 4.4 mg/L methane in aquifer and alluvial formations (Atkins et al., 2015). The methane had a biogenic isotopic signature with some methane oxidation occurring, but no correlation was found with distance to CSG exploration wells. Up to 30 mg/L dissolved methane was reported in aquifers of the Gippsland Basin, Victoria (Currell et al., 2017). Bacterial methanogenesis was identified, with carbonate reduction and acetate fermentation occurring in the shallower and deeper formations respectively. That study however was not focussed on connectivity. Iverach and co-workers found that groundwater and methane was leaking from coal seams and artesian formations of the GAB in the New South Wales Surat Basin into the Lower Namoi Alluvium (Iverach et al., 2020). Fault assisted leakage of groundwater and methane into an alluvial aquifer and the stream network was also separately identified in the Gloucester Basin in New South Wales (Banks et al., 2019).

In Queensland the CSG industry is expanding, especially in the Surat and Bowen Basins (Hamilton et al., 2020; Neininger et al., 2021; Underschultz et al., 2018). The majority of CSG in the Surat Basin is of microbial origin, where groundwater and gas studies have previously focussed on understanding the gas in the CSG reservoir (Baublys et al., 2015; Baublys et al., 2019; Boreham et al., 1998; Golding et al., 2013; Hamilton et al., 2014). One study investigated hydrocarbon indicators of historic migration in the Surat and Bowen basins via well completion reports and core data (e.g. mud gas logs, wireline analysis, or core and cutting staining and fluorescence shows) (Underschultz et al., 2016). Hydrocarbon indicators were identified in all formations, clustering around the major fault zones including the Moonie-Goondiwindi and Burunga-Leichhardt faults. Thermogenic gas was identified in the Walloon Coal Measures that had apparently migrated from below. Leakage of hydrocarbon indicators into the overlying Springbok Sandstone was also found on the NE edge of the Walloon Coal Measures. That study, however, did not investigate current day dissolved gas in the formations. Historic fault related fluid migration has also been reported in the GAB (Golding et al., 2016). A localised study, using several lines of investigation including pump tests, of the Walloon Coal Measures and Condamine Alluvium reported a low level of connectivity (Pandey et al., 2020). The hydrochemistry of the Condamine Alluvium was also separately investigated with salinisation reported to be via evapotranspiration, although inter aquifer connectivity and dissolved gas was not assessed (Owen and Cox, 2015). Two groups sampled groundwater and gas from the Condamine Alluvium, Shallow Walloons aquifer, and Walloon Coal Measures, with differing reports that localised connectivity or leakage was or was not occurring (Iverach et al., 2017; Iverach et al., 2015; Owen et al., 2016). The contradictory results are evidence of the heterogeneity of the Condamine Alluvium and localised differences.

The GAB is a vital water resource, therefore several recent studies have used hydrochemical and cosmogenic tracers to understand the connectivity within a formation and flow paths of key GAB aquifers within the Surat Basin (Habermehl, 2020). Raiber and co-workers have refined recharge and flow paths of the deeper Precipice Sandstone and Hutton Sandstone aquifers in the northern Surat Basin (Raiber and Suckow, 2017; Raiber, 2022; Suckow et al., 2020; Suckow et al., 2018). Groundwater flow to the south, with a component of flow connecting the adjacent Clarence-Moreton Basin was recently elucidated, with evidence for the overall lack of connectivity between the Hutton and Precipice Sandstones (Hayes et al., 2020; Hofmann et al., 2024). Recently Pearce demonstrated that gas in the Hutton Sandstone of the southern Surat Basin was mainly generated in situ via primary microbial CO_2 reduction (Pearce et al., 2023b). Whereas in the Precipice Sandstone in situ gas produced via microbial CO_2 reduction was mixed with early mature thermogenic gas. A likely source of the thermogenic gas was historic migration from the underlying Bowen Basin especially around major fault zones. In the Moonie Oil Field, the Precipice and Evergreen Formation host thermogenic gas, but microbial biodegradation is also occurring. Studies of gas and groundwater connectivity in the shallower GAB aquifers of the Surat Basin however has been generally lacking. Recent work by OGIA has identified potential localised fault connectivity between the Springbok and Walloons Coal Measures near the Kenya East gas field located between Tara and Chinchilla (OGIA, 2023). Other faults, such as the Horrane Fault near Cecil Plains, have been reported to act as a seal (Viljoen et al., 2020). Recently gas wetness parameters and stable isotope signatures showed that methane present in several shallow aquifer bores was generated via primary microbial CO_2 reduction, and acetate fermentation (Pearce et al., 2022c; Pearce et al., 2021b). This indicated that the gas had likely been generated in situ in the aquifers. A detailed understanding of the groundwater connectivity and processes however was lacking.

The current study shows that gas and groundwater had not migrated from the CSG reservoir into the GAB aquifer bores investigated here in the majority of cases. Strontium isotopes, and cosmogenic isotopes in combination with gas and water stable isotopes supported a lack of connectivity. In one Condamine Alluvium bore connectivity to the Shallow Walloons aquifer (not the CSG reservoir part) cannot be totally ruled out. In one gassy Springbok Sandstone bore, the aquifer directly overlying the reservoir, uncertainty remains. In locations where an aquifer contains coal and similar groundwater Sr isotope signatures to the gas reservoir, for example, or where methane concentrations are too low to enable certain isotope analyses, further lines of evidence (that are out of scope of this study) will be needed. Situations where the formation that contains the (gas) reservoir, is also used as an aquifer for water extraction (such as the Walloon Coal Measures) may also be complex. Further work is suggested to incorporate further lines of evidence over a wider bore sampling range, including microbial characterisation and noble gases. In the Surat Basin and Clarence-Moreton Basin, this could concentrate on the Condamine Alluvium including a wide range of irrigation bores and town water supply bores that are continuously pumped. In addition, the Shallow Walloons irrigation water bores are a suggested study target, and the Hutton Sandstone aquifer that is a high use aquifer for industry and landholders. Both these formations are predicted to be impacted by water drawdown in future that may release further in situ gas, or may be subject to dissolved or free gas migration (OGIA, 2021). GAB aquifers of the mid and southern Surat Basin such as the Gubberamunda and Mooga sandstones are heavily relied on by farms and private landholders, though they remain understudied. More broadly this study should be expanded in future to other regions and aquifers of the Surat Basin and the Bowen Basin, other parts of the GAB, and to shale gas exploration regions such as in the Northern Territory or Cooper Basin (Pearce et al., 2023a). This study is relevant to other regions in Australia and internationally where aquifers with various users overly CSG reservoirs (also known as coal bed methane reservoirs), conventional gas reservoirs, or shales that are or will be stimulated for unconventional gas. In addition, the data on gas isotopic signatures will be useful in identifying methane emission sources, that are becoming a hot topic worldwide.

4. Conclusions

- The CSG production waters and one gassy Springbok aquifer bore have low, non-radiogenic, distinctive $^{87}Sr/^{86}Sr$ signatures, and enriched ^{13}C-DIC, compared to the aquifers and alluvium. Indicating a lack of significant groundwater connectivity between the CSG reservoir, and the GAB or alluvium in the regions studied.
- The CSG wells and gassy Springbok aquifer bore have the longest residence time groundwaters. The CSG reservoir samples and a gassy Springbok aquifer bore also have relatively higher Li and B content than overlying aquifer and alluvium groundwaters.
- The Condamine Alluvium bores sampled here have more radiogenic $^{87}Sr/^{86}Sr$ than the CSG reservoir production waters, indicating a lack of groundwater connectivity, and lower Li and B from incorporation into clays via mineral weathering.
- The deep Precipice Sandstone aquifer groundwaters sampled here are characterised by high Li and Rb concentrations, and the most radiogenic $^{87}Sr/^{86}Sr$.
- Dissolved sulphate in groundwaters where $\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4 were able to be measured, is consistent with a source in recharge waters from surface salts (Playa lakes) in inland Australia. • The Gubberamunda aquifer samples have $\delta^{34}S$-SO_4 and $\delta^{18}O$-SO_4 signatures consistent with the occurrence of bacterial sulphate reduction. Methane and water stable isotopes show acetate fermentation occurring in situ in several of the Gubberamunda bores sampled in this study with fresher groundwaters closer to recharge.
- Cosmogenic isotopes and tritium indicate mixing of the older groundwater with younger waters in the Shallow Walloons water bores and a shallow Springbok bore.
- Condamine Alluvium groundwaters show evidence of more recent recharge and shorter residence time waters with mainly very low methane content. Methane in one Condamine Alluvium bore was consistent with in situ primary microbial methane generation within the Alluvium. However the possibility that the gas had migrated from the underlying Shallow Walloons aquifer (not the CSG reservoir part) could not be completely ruled out.
- A gassy Springbok Sandstone bore contained secondary microbial methane, and various isotope signatures overlap with the CSG reservoir. Therefore, connectivity is possible in this case. The Springbok Sandstone contains coal (with coal fines observed from this gassy bore). This may indicate that the gas in gassy Springbok bore (S01) is generated from interbedded coals within the Springbok Sandstone via the same processes (secondary CO_2 reduction) as the underlying CSG reservoir, and therefore the gas and groundwater have overlapping signatures with the CSG production waters. Alternatively, leakage from the reservoir may be occurring in or proximal to this bore.
- The majority of GAB bore groundwaters sampled from aquifers in this study support a lack of connectivity with the CSG reservoir, and methane generation in situ in the aquifers by microbes. However, where aquifers contain coal lenses for example, differentiation becomes more complex and two potential explanations may remain.
- In the current energy transition, with the increased reliance on gas, and the advent of new subsurface technologies such as CO_2 storage, hydrogen storage, and compressed air or thermal energy storage, understanding aquifer and reservoir connectivity will become increasingly important.

CRediT authorship contribution statement

J.K. Pearce: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **H. Hofmann:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **K. Baublys:** Writing – review & editing, Validation, Investigation, Formal analysis. **D.I. Cendon´**: Conceptualization, Methodology, Investigation, Formal analysis; Writing – review & editing. **S.D. Golding**: Conceptualization, Supervision, Writing – review & editing, Funding acquisition. **S.J. Herbert:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Z. Bhebhe:** Writing – review & editing, Investigation, Formal analysis, Data curation. **A. Nguyen:** Writing – review & editing, Formal analysis, Data curation. **P. Hayes:** Writing – review & editing, Supervision, Project administration, Investigation, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: P Hayes reports financial support was provided by Arrow Energy Pty Ltd. P Hayes reports financial support was provided by APLNG. P Hayes reports financial support was provided by SANTOS. S Golding reports financial support was provided by National Energy Resources Australia. The funding bodies had no influence in the study design; in the collection, analysis, and interpretation of data; in the writing of the paper; and in the decision to submit the paper for publication.

S.J. H. and Z.B. are employed by Arrow Energy.

Data availability data is in the supplementary material

Acknowledgments

The feedlot and private landholders, town water bores, CSG companies, mines and power plants, and the regional government and council staff are thanked for enabling access to their water bores.

This research has been conducted with the support of the UQ Centre for Natural Gas industry members – APLNG, Arrow Energy, and Santos. The information, opinions and views expressed in this manuscript do not

Appendix A. Appendix

necessarily represent those of the University of Queensland, the UQ Centre for Natural Gas or its constituent members or associated companies. National Energy Resources Australia (NERA) also provided funding for this research. Degan Wye is thanked for assistance in the field. Jianxin Zhao and Nicole Leonard are thanked for assistance with strontium isotope analyses. Matthias Raiber is acknowledged for helpful discussions and general collaboration on the GAB. Steve Flooks and Chris HarrisPascal are thanked for helpful discussions and collaboration.

The authors acknowledge the support of the Australian Nuclear Science and Technology Organisation ANSTO in providing access to instruments, capabilities and facilities used in this study via proposals AP12539, AP13019, and AP15196. Financial support for the Centre for Accelerator Science, at ANSTO, through the Australian National Collaborative Research Infrastructure Strategy (NCRIS) is acknowledged.

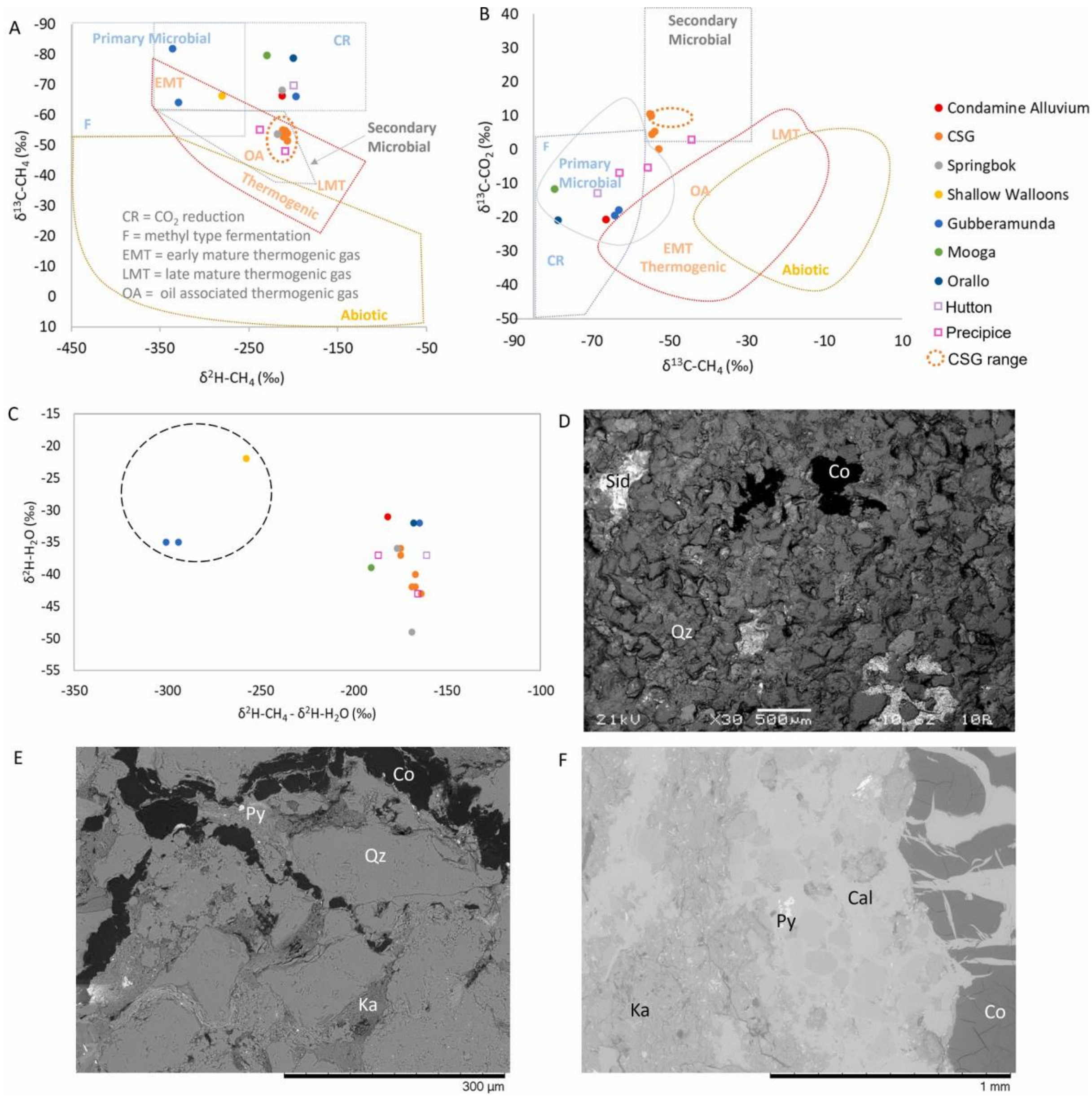

Fig. A1. A) The $\delta^{13}C$-CH_4 vs $\delta^{2}H$-CH_4 for the groundwater and CSG production waters. B) The $\delta^{13}C$-CO_2 vs $\delta^{13}C$-CH_4 modified after (Pearce et al., 2022a).. The regions are shown from (Milkov and Etiope, 2018). The CSG range orange dashed circle is existing data across the Surat Basin from (Baublys et al., 2015). C) The $\delta^{2}H$- H_2O vs $\delta^{2}H$-CH_4 - $\delta^{2}H$-H_2O where two Gubberamunda samples and a Shallow Walloons bore sample with lower $\delta^{2}H$-CH_4 - $\delta^{2}H$-H_2O, circled, are consistent with acetate fermentation, and the others with CO_2 reduction pathways producing methane. D) Example of coal in the Hutton Sandstone, scanning electron microscope (SEM) image. E) SEM of coal in the upper Precipice Sandstone. F) SEM of coal and calcite cements in the Springbok Sandstone. Co = coal, Qz = quartz, Sid = siderite, Py = pyrite, Ka = kaolinite, Cal = calcite.

Table A1

Groundwater bore isotopic data. All data, meta data, and bore information are given in Supplementary material Table S1, S2. Methane, carbon dioxide and water stable isotopes were previously published in Pearce et al., 2023.

bore	$\delta^{13}C$-DIC	$\delta^{18}O$-H_2O	$\delta^{2}H$-H_2O	D excess	^{14}C -DIC	$^{36}Cl/Cl$ (x10_^{15})	^{13}C-CH_4	$\delta^{13}C$-CO_2	$\delta^{2}H$-CH_4	$^{87}Sr/^{86}Sr$	tritium	^{34}S-SO_4	^{18}O-SO_4	Formation
	VPDB ‰	VSMOW ‰	VSMOW ‰	‰	pMC		VPDB ‰	VPDB ‰	VSMOW ‰		tritium ratio TU	VCDT ‰	VSMOW ‰	
G06 − 12.5 − 6 − 38 10 − 63 − 17.9 0.706889 Gubberamunda M15 − 11.9 − 5.7 − 37 8.6 − 20.7 0.705762 10.7 14.6 Mooga														
O01	− 13.9	− 5.1	− 32	8.8			− 78.7	− 20.8	− 200	0.704651		25.6	18.5	Orallo
M02	− 4.2	− 6	− 39	9			− 79.7	− 11.6	− 230	0.704637				Mooga
G04	− 12.5	− 5.9	− 35	12.2			− 81.9		− 335.7	0.704835				Gubberamunda

(*continued on next page*)

Table A1 (*continued*)

bore	$\delta^{13}C$-	$\delta^{18}O$-	$\delta^{2}H$-	D	^{14}C	$^{36}Cl/Cl$	^{13}C-	$\delta^{13}C$-	$\delta^{2}H$-CH4	$^{87}Sr/^{86}Sr$	tritium	^{34}S-	^{18}O-SO4	Formation

	DIC VPDB ‰	H_2O VSMOW ‰	H_2O VSMOW ‰	excess ‰	-DIC pMC	(x10–15)	CH_4 VPDB ‰	CO_2 VPDB ‰	VSMOW ‰		tritium ratio TU	SO_4 VCDT ‰	VSMOW ‰	
G02	− 13.9	− 5.7	− 35	10.6			− 64.2	− 19.4	− 329.1	0.704529		10.6	14.2	Gubberamunda
S01	16.3	− 8	− 49	15	16.3	9	− 53.6		− 218	0.703459				Springbok
G01	− 9.3	− 5.7	− 32	13.6	9.3	45	− 66.2		− 197	0.705588				Gubberamunda
C195	− 12.1	− 4.7	− 31	6.6	11.9	80	− 66.4	− 20.7	− 213	0.70495	0.06			Condamine Alluvium
CUJ197	7.1	− 5.1	− 33	7.8	12.0	20	− 62.8			0.704185	0.13			Shallow Walloons Upper Juandah
S63	− 11.8	− 5.2	− 36	5.6	50.1	69	− 68.1		− 213	0.705302	0.12	21.2		Springbok
C17	− 9.5	− 5.5	− 36	8	39.0	90		− 16.8		0.70533	0.02			Condamine Alluvium
CLJ18	− 5.9	− 2.4	− 22	− 2.8	15.0	71	− 66.4		− 280	0.704693	0.38			Shallow Walloons Lower Juandah
C370A	− 11	− 4.7	− 32	5.6	1.3	81		− 18.1		0.704108	0.03			Condamine Alluvium
C09A	2.2	− 4.6	− 28	8.8	43.4	73		− 20.6		0.705766	0.06	16.4	14.7	Condamine Alluvium
C16	− 13.1	− 4.5	− 27	9	89.2	114		− 20.3		0.704792	0.73			Condamine Alluvium
P17	− 2.9	− 6.1	− 33	15.8	0.25	28.7	− 68.2	− 8.3		0.706186		38.7		Precipice
P20	− 12.8	− 5.9	− 37	10.2	17	15.5	− 55	− 5.5	− 224	0.708265				Precipice
H121	− 2.2	− 6.8	− 37	17.4	0.27	15.3	− 69.7	− 12.2	− 198	0.704521				Hutton
P	5.8	− 6.7	− 43	10.6	0.35	18.9	− 48	0.8	− 209	0.706298				Precipice

Table A2

CSG production water, river and rainwater isotopic data. All data and bore information are given in Supplementary material Table S1. Water and methane stable isotopes were previously published in Pearce et al., 2023.

bore	$\delta^{13}C$-DIC VPDB ‰	$\delta^{18}O$-H_2O VSMOW ‰	δ^2H-H_2O VSMOW ‰	D excess ‰	^{14}C pMC	$^{36}Cl/Cl$ (x10–15)	^{13}C CH_4 VPDB ‰	$\delta^{13}C$-CO_2 VPDB ‰	δ^2H-CH_4 VSMOW ‰	$^{87}Sr/^{86}Sr$	tritium ratio TU	^{34}S-SO_4 VCDT ‰	^{18}O-SO_4 VSMOW ‰	Formation
Da8T	18.8	− 6.1	− 37	11.8	0.7	18	− 55	10.6	− 212	0.703579				CSG Taroom
Da37T	19.1	− 6.7	− 42	11.6			− 54.6	4.6	− 211	0.703547				CSG Taroom
Da30T	18.8	− 7	− 43	13	0.4	24	− 51.5		− 207	0.703579				CSG Taroom
Da44	18.4	− 6.7	− 42	11.6	0.3	13	− 54.7	9.9	− 209	0.703442				CSG Juandah
Da22	15.8	− 5.8	− 36	10.4	0.6	17	− 52.8	0.1	− 211	0.703427				CSG Juandah
Da12T	16.8	− 6.5	− 40	12	0.6	19	− 53.8	5.4	− 207	0.703556				CSG Taroom
Condamine River W	− 12.4	− 4.5	− 25	11		135				0.705283	1.5			Condamine River Warwick
Condamine River CP	− 10.9	− 3.5	− 22	6		147				0.705339	1.57			Condamine River Cecil plains
Oakey Creek	− 8.5	− 0.8	3	9.4		28				0.705588				Oakey Creek
Myall Creek	− 9.1	0.1	− 1.9	− 2.8						0.705211				Myall creek
Rain Kogan	− 6.8	− 3.3	− 10	16.4		94				0.705651				Wambo FL rain tank
Rain Grassdale	− 12.4	− 3.2	− 12	13.6						0.708148	2.43			Grassdale FL rain tank
Dalby rain	− 9.9	1	21	13.6						0.706402				Dalby rain storm
Chincilla rain		− 3.2	− 14	11.6						0.707293				Chinchilla rain tank

Millmerran rain	− 2.7	− 9	12.6	0.707235	Milmerran rain tank

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coal.2024.104535.

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