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The University of Queensland Surat Deep Aquifer Appraisal Project (UQ-SDAAP)

Scoping study for material carbon abatement via
carbon capture and storage

Supplementary Detailed Report

Mineralogy, geochemical CO₂-water-rock reactions and
associated characterisation

30 April 2019

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1. Executive summary

This report focuses on predicted kinetic geochemical CO₂-water-rock reactions. These predictions rely on mineral and porosity data from drill core. Existing data was obtained from mainly the northern region, and additionally a well in the southern region of the Basin to build predictions. The northern region was more data rich. The southern region is more well core and data sparse with the exception of the Moonie oil field. Additional drill core samples were collected from archived well core of Moonie and from the Southwood 1 well to the north of the Moonie fault zone. The core samples were characterised for porosity and pore throat distribution by mercury injection, mineral, and metal content to build geochemical models to predict local CO₂-water-rock reactions and their potential effect on reservoir scaling, changes to porosity and formation water pH, and mineral trapping of CO₂. For the northern region, our work has predicted low likelihood of scaling in the Blocky Sandstone Reservoir, with the lowest pH predicted owing to the low buffering capacity of the sandstone and formation water. Mineral trapping was predicted in the Transition Zone with pH buffered by reaction of carbonates, plagioclase and chlorite mainly. The Blocky Sandstone Reservoir sampled in the Moonie field well core has different mineralogical characteristics to wells in the northern region. Here, CO₂-water-rock predictions indicate a minor alteration of plagioclase and K-feldspar to kaolinite, chalcedony and ankerite in cleaner Moonie sandstones, with additional precipitation of smectite in clay rich sandstones. Formation water pH was buffered between 5 and 6 by dissolution of calcite or siderite cements, and additionally a more buffering formation water. Sampled core has also shown evidence of previous natural CO₂ and hydrothermal fluid alteration, fractured quartz grains, and fracture fills with mineral trapping as carbonates. This type of natural analogue data is vital to validate long term predictions. It could additionally indicate the potential for fracture flow in the Moonie Sands for example. New drill core and characterisation of existing core or cuttings is still required in the future for the southern and central Surat Basin region.

2. Introduction

For carbon storage projects, as CO₂ is injected into geological formations it displaces some of the fluids (normally formation water) that are residing in the pore space. Water is, to a certain extent, soluble in supercritical CO₂ and supercritical CO₂ is soluble in water. This creates a complex dynamic area at the interface of the injected CO₂ and the indigenous formation water. As supercritical CO₂ dissolves in formation water it forms carbonic acid lowering the pH. This can result in its reactivity to minerals within the rock matrix, especially carbonate minerals. Calcite, for example, has the fastest dissolution kinetics. Dissolution and precipitation of minerals can modify the formation water chemistry, buffer the pH, and may modify for example porosity and permeability. Precipitation of carbonate minerals is a process that traps some of the injected CO₂ in mineral form. Precipitation in the reservoir or other related processes such as movement of fine particles if occurring too close to the injection well may scale or clog the reservoir and cause reduced injectivity. The potential CO₂ reactivity of various rock types is dependent on parameters such as mineral content. CO₂-formation water- rock geochemical modelling requires data on the mineral content, porosity, temperature and water chemistry, therefore these parameters were analysed for the UQ-SDAPP project in regions where data or core samples were available. The injection models presented in other chapters indicate that there is potential for some CO₂ to migrate into the Transition Zone. It was considered important therefore, for geochemical modelling to include the Blocky Sandstone Reservoir, Transition Zone and Ultimate Seal strata. This is not suggesting that CO₂ will migrate into the Ultimate Seal, but is considering the potential reactivity if CO₂ were to interact with the Ultimate Seal rocks. A range of possible lithologies were simulated so that findings may be generalised or give insights to other areas.

3. Methods

UQ-SDAAP used pre-existing data and collected new information on the rock mineralogy and rock properties, the formation water chemistry, and the distribution of temperature and pressure. This was accomplished with a number of laboratory-based methodologies for the strata making up the Blocky Sandstone Reservoir, Transition Zone, and Ultimate Seal from across the UQ-SDAAP study area.

Mineralogy and rock properties

Pre-existing mineralogical information was available and used to populate geochemical models where possible. However, this was largely limited to well core from the northern region, and in some cases limited only to the Blocky Sandstone Reservoir (Lower Precipice Sandstone). In addition to this data, core was sampled from Southwood 1, Moonie 22, Moonie 31, Moonie 33, Moonie 38, GSQ Chinchilla 4, and West Wandoan 1 wells drilled in the Surat Basin (Table 1). All of the following depths described in this report refer to “core measured depth” in metres.

*Table 1 Drill core sample data from the three zones in each well used in the study. Existing data used in this study marked as E, and new data collected as N. *Note: more existing data was available, see text.*

Well	Blocky Sandstone Reservoir	Transition Zone	Ultimate Seal	Existing/New data
Reedy Creek MB3-H	11	10	0	E
Condabri MB9-H	3	2	0	E
GSQ Chinchilla 4	3	8	4	E/N
West Wandoan 1*		3	1	N
GSQ Roma 8		9	3	E
Moonie 38	2	3	0	N
Moonie 22	1	0	0	N
Moonie 31	1	4	0	N
Moonie 33	0	2	0	N
Cabawin 1	6	4	0	E
Southwood 1	0	6	0	N

Mercury injection porosimetry (MICP) performed on selected core samples (21) provided porosity and pore throat distributions. QEMSCAN was performed on 15 selected thin sections to provide quantitative estimates of mineral amounts. QEMSCAN is an automated scanning mineral quantification method based on comparing the chemical composition of the minerals to a database (Golab et al. 2010). It produces both a quantified mineral content and images showing the mineral distribution and associations. Scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) was performed separately in backscatter electron detection (BSE) mode on 28 polished thin sections and 5 core blocks with a TM3030. A Bruker EDS was used to detect minor minerals, semi quantitative composition, textures, porosity, clay habit, and weathering, to supplement the other model input data. The most important minerals to capture from a CO₂-

water-rock reaction point of view, even when present in trace amounts, are generally carbonates - especially the most reactive, calcite. Even trace amounts of these, can significantly buffer the pH. Sulphides are additionally important. In some cases, these and trace carbonates can only be detected by direct SEM observations and inferred from rock digestion. Total acid digestions were performed on 11 core samples from the Southwood 1 and Moonie 38 wells to determine the total content of various metals and arsenic (As) for comparison to guidelines and existing data.

Formation water chemistry and temperature

The formation water chemistry is typically a poorly characterised parameter because of the lack of data and the poor quality of data that is available. There are a number of processes that occur when sampling water either from a petroleum well or a groundwater bore. As the sample is brought to surface the pressure and temperature changes and the sample degasses, causing the chemistry to change. If a rigorous sampling procedure and sample preservation procedure is not followed, there is a high chance of sample contamination. In addition, typically not all parameters such as minor or trace cations (e.g. Al) were measured or reported. For these reasons, it is difficult to obtain an accurate distribution of water chemistry for an aquifer using historical data. As an alternative, the data from the most closely sampled formation water can be equilibrated with the rock matrix mineralogy using a geochemistry model to provide an estimated water chemistry.

Kinetic geochemical models

Kinetic geochemical models were calculated using the react module of Geochemist Workbench 9 (GWB), with the thermodynamic database based on EQ3/6 as described in detail in public domain literature (Bethke & Yeakel 2012; Delany & Lundeen 1989; Pearce et al. 2015). An equilibrated initial water chemistry from local measured formation water data and a water-rock ratio based on porosity was used (Feitz 2014; Prommer et al. 2016). A fugacity of CO₂ for a reservoir pressure (12 MPa to 20 MPa) and temperature (60 to 80°C) was calculated using Duan & Sun 2003. The pressure and temperature was based on downhole measurements from well completion reports where available. In some cases, a lower CO₂ fugacity, where stated, was used to simulate the impact of a reaction on the edge of the plume where the concentration of dissolved CO₂ was lower (assumed to be 50% of the full fugacity). Additionally, a lower temperature (e.g. 10°C less than the base case) was tested in some cases under reservoir cooling conditions (injected CO₂ is normally cooler than the formation temperature). Models were generally run for 30 years. Selected models were also run for 100 or 1000 years, with either the injected reservoir CO₂ fugacity, or at half of the value to simulate the edge of the plume. Minerals were input as script files for acid, neutral and basic mechanisms. Some ~42 different input mineral compositions were run for different conditions. The mineralogical input was based on the pre-existing or measured data from drill core and supplemented with the SEM-EDS observations of minor minerals and semi quantitative compositions where available. Mineral and porosity input data from core samples from the GSQ Chinchilla 4 well was obtained from Farquhar et al. 2015; Pearce et al. 2015 and Pearce et al. 2019 in prep. Existing data was also used as input for Reedy Creek MB3-H, Condabri MB9-H, Roma 8 and Cabawin 1 (APLNG 2013; Grigorescu 2014; Haese et al. 2014; Prommer et al. 2016). Selected drill core depths characterised in the UQ-SDAAP project from Southwood 1 or Moonie 38 wells were also geochemically modelled. In accordance with the available drill core observations and previous characterisation, a Fe-rich chlorite (Fe:Mg 3:1) was used (Farquhar et al. 2015; Pearce et al. 2016). Input ankerite had a Ca_{0.5}Fe_{0.35}Mg_{0.15} composition, and siderite a Fe_{0.9}Mg_{0.1} composition. However, in the Ultimate Seal complex (ironstone) core samples, generally an Fe-siderite +/- Mn was observed to be present and hence and Fe-siderite was used as input. Mineral input data (Table 2) is from the compilation of Palandri & Kharaka 2004, except siderite and ankerite which is from Steefel 2001, Illite from Köhler et al. 2003, and chlorite based on Lawson et al. 2007 and Köhler et al. 2003, also described previously in (Pearce et al. 2015). In general, several simulations were run for each drill core sample mineralogy. An initial run was used to identify precipitating or saturated minerals and these were

subsequently allowed or suppressed based on knowledge from general experimental and natural analogue data.

Table 2 Geochemical modelling parameters used for models, where K is the rate constant, E_a is the activation energy, n is a power term, Γ is the pre-exponential nucleation factor (Pearce et al. 2015).

Mineral	K25 (acid)	E_a (acid)	n	K25 (neut)	E_a (neut)	K (precip)	T
	mol/cm ² /s	kJ/mol		mol/cm ² /s	kJ/mol	mol/cm ² /s	
Quartz				1.70E-17	68.7	K(diss)	2.00E+10
K-feldspar	8.71E-15	51.7	0.5	3.89E-17	38	K(diss)	2.00E+10
Albite	6.92E-15	65	0.457	2.75E-17	69.8	K(diss)	2.00E+10
Andesine	1.32E-13	53.5	0.54	3.39E-16	57.4	K(diss)	2.00E+10
Kaolinite	4.90E-16	65.9	0.777	6.61E-18	22.2	K(diss)/10	2.00E+10
Illite/muscovite	1.91E-16	46	0.6	8.91E-20	14	K(diss)	2.00E+10
Smectite	1.05E-15	23.6	0.34	1.66E-17	35	K(diss)	2.00E+10
Biotite	1.45E-14	22	0.525	2.82E-17	22	K(diss)	2.00E+10
Fe-Mg-Chlorite	1.62E-14	25.1	0.49	1.00E-17	94.3	K(diss)	2.00E+10
Calcite	5.01E-05	14.4	1	1.55E-10	23.5	K(diss)	1.00E+10
Ankerite	1.59E-08	45	0.9	1.26E-13	62.76	K(diss)/1e5	3.00E+10
Siderite	1.59E-08	45	0.9	1.26E-13	62.76	K(diss)	2.00E+10
Fe-oxide	4.07E-14	66.2	1	2.51E-19	66.2	K(diss)	1.00E+10

Reactive surface areas were determined with the geometric method of White 1995, and modified according to general SEM observations of the minerals in the core (e.g. cementing phases had lower available surface areas than framework grains). In general, owing to a clay coating of grains, reactive surface areas at the reservoir scale are lower and were therefore upscaled with the methods detailed by Pearce et al. 2015, 2018b. Reactive surface areas for framework grains were generally 1-30, clays 70-150, and carbonate cements 0.01 – 0.05. Trace amounts of minerals such as rutile, apatite, zircon were not included in models owing to their low expected reactivity based on previously published CO₂-water-rock experiments of GSQ Chinchilla 4 and West Wandoan 1 core (Farquhar et al. 2015; Pearce et al. 2015; Pearce et al. 2018b). Coal was also not included.

4. Results

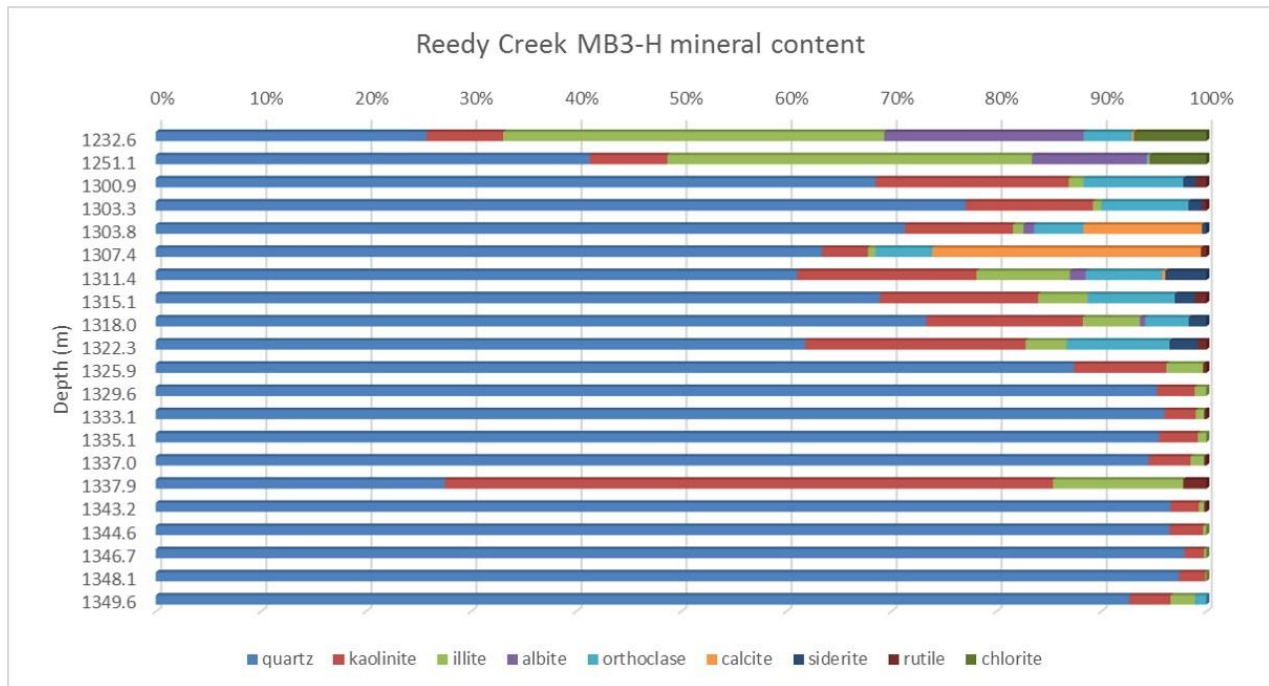
The results of the geochemical modelling are grouped according to the UQ-SDAAP project model sectors (La Croix et al. 2019a). The geological facies and stratigraphy referenced here are described in detail in the facies prediction from well logs as outlined in La Croix et al. 2019a, b, c, d.

4.1 Managed aquifer recharge sector

Reedy Creek MB3-H Well

Existing mineralogical data was available for the Reedy Creek MB3-H Well core from the Blocky Sandstone Reservoir (Lower Precipice Sandstone) and part of the Transition Zone (Upper Precipice Sandstone and Evergreen Formation) only as shown in Figure 1 (APLNG 2013; Prommer et al. 2016).

Figure 1 Mineral content with depth in the Reedy Creek MB3-H well core Blocky Sand Reservoir and Transition Zone.



Examples of geochemical model outputs over a 30-year simulation for the Reedy Creek MB3-H Well Blocky Sandstone Reservoir S1 facies are shown in Figure 2, where negative delta minerals indicates mineral dissolution and positive values, precipitation. Mineral alteration was minimal owing to the high quartz content and low reactivity. The pH decreased to ~ 4 and remained low as there was also little buffering capacity in the formation water. Small increases in dissolved silica and potassium were predicted owing to the minor dissolution of K-feldspar or illite.

Over the 30-year CO₂ reaction simulation, the predicted pH in the Transition Zone was buffered to up to 5.2 (Figure 3 and Figure 4) through dissolution of minerals including chlorite, calcite, siderite, and plagioclase. Generally, siderite re-precipitated along with ankerite, kaolinite or smectite (beidellite).

Figure 2 Geochemical modelling of Reedy Creek MB3-H well mineralogies from the Blocky Sandstone Reservoir S1 facies. (A-C) The mineralogy at 1349.6 m, change in minerals, pH and water chemistry over 30 years, and (D) change in minerals for a different sample mineralogy from 1337.9 m.

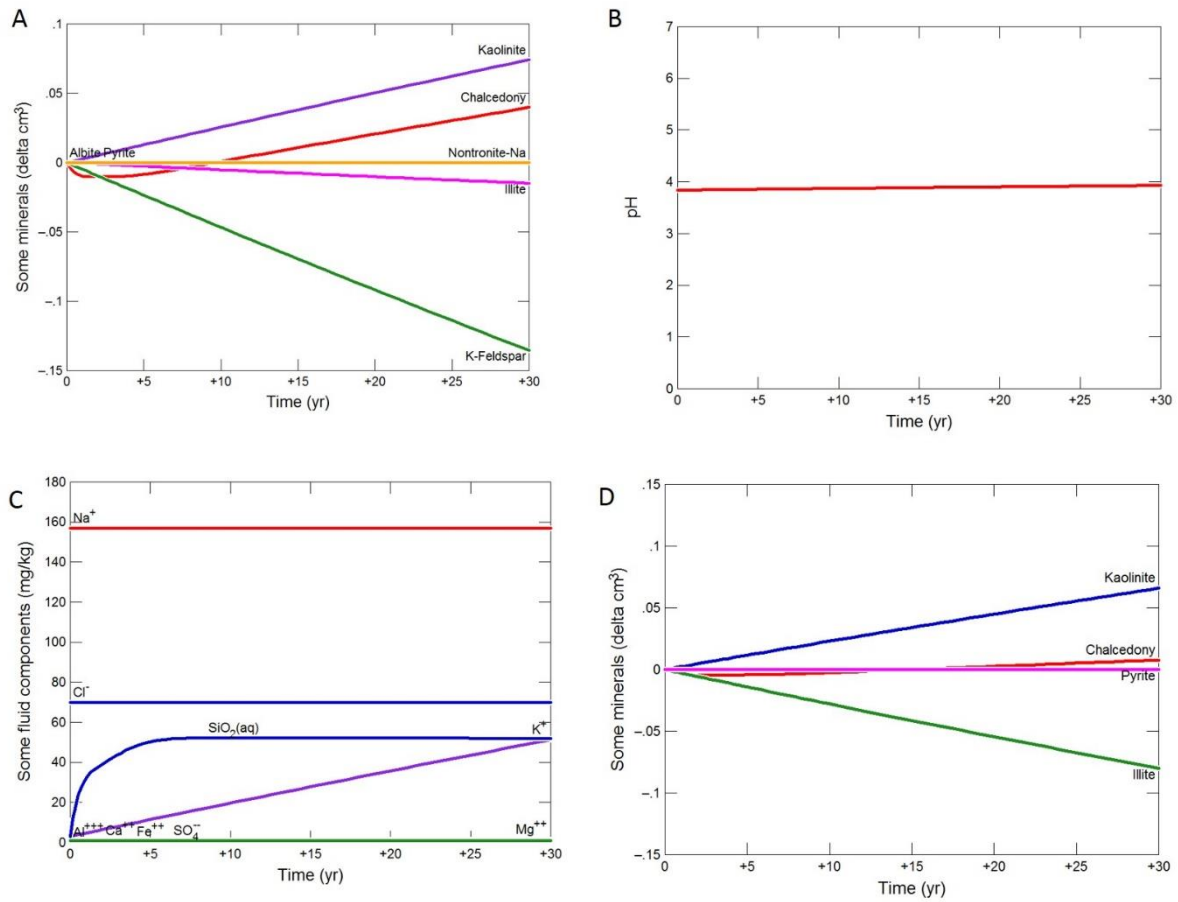


Figure 3 Geochemical modelling of Reedy Creek MB3-H well mineralogies from the Transition Zone S2 facies. (A-C) at 1318.0 m change in minerals, pH and water chemistry over 30 years, and (D) change in minerals in a different sample mineralogy from 1311.4 m.

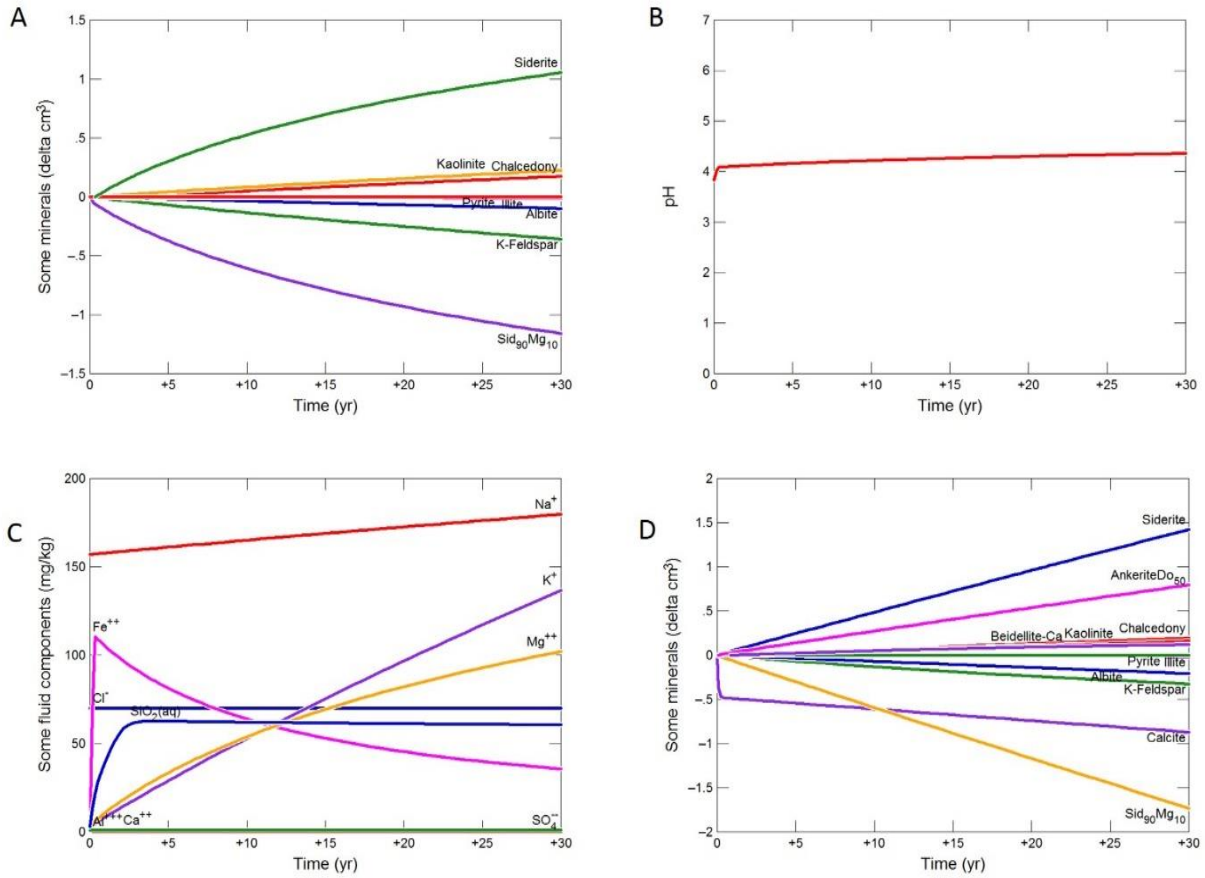
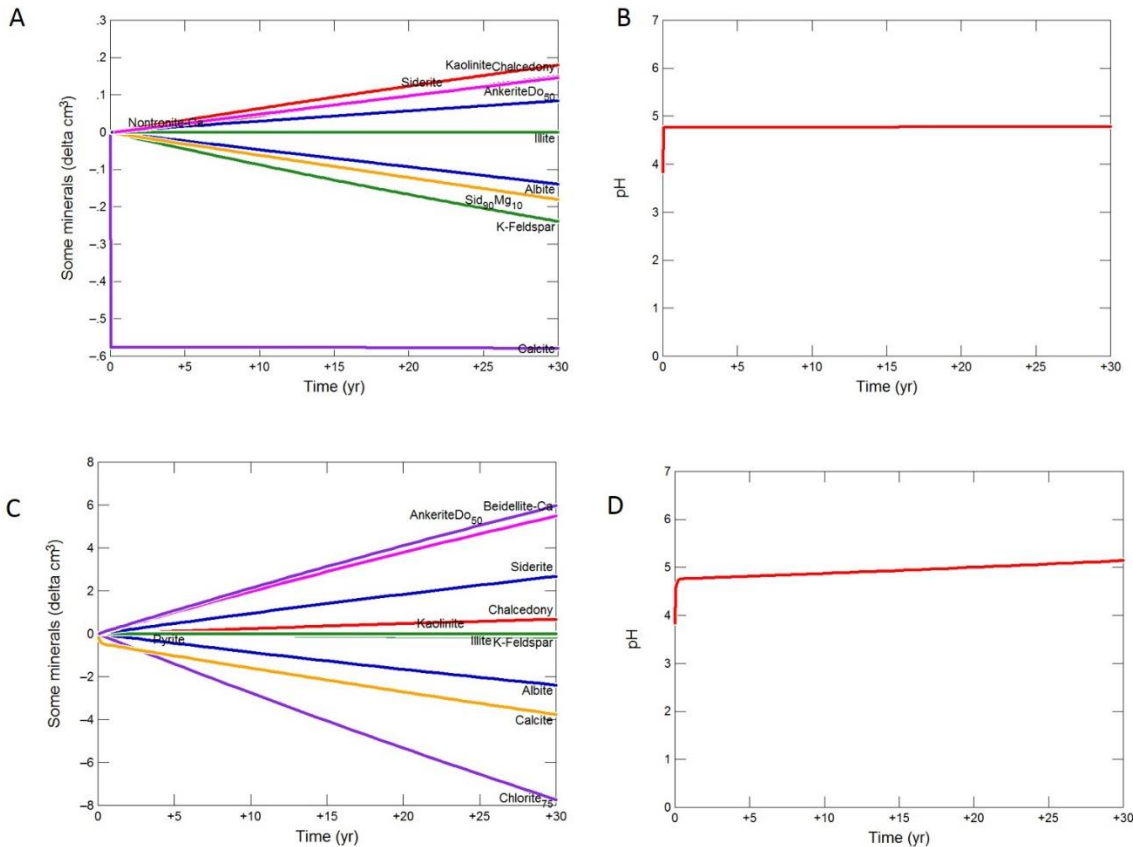


Figure 4 Geochemical modelling of Reedy Creek MB3-H well mineralogies from Transition Zone SM1 facies, (A-B) at 1251 m change in minerals and pH over 30 years, and (C-D) from 1232.6 m.



Condabri MB9-H well

Some existing mineralogical data was also available for the Condabri MB9-H drill core from the Basement, Blocky Sandstone Reservoir (Lower Precipice Sandstone) and part of the Transition Zone (Upper Precipice Sandstone) only (APLNG 2013). The two Basement samples contained high portions of kaolinite, illite, feldspar and siderite, the Blocky Sandstone Reservoir samples were again quartz rich with minor kaolinite, and the two Transition Zone samples contained high proportions of kaolinite, illite, feldspar and calcite (Figure 5).

The published formation water chemistry had a higher buffering capacity, and the pH in the model of the Blocky Sandstone Reservoir 1300.0 m S1 facies remained at ~ 4.9, with essentially no mineral reaction (Figure 6). The result was the same for the 1513.1 m sample mineralogy. The pH was however buffered slightly higher to 5 and 5.05 for the Transition Zone sample reactions of the SM3 facies at 1476.0 m and M1 facies at 1460.7 m.

Figure 5 Mineral content with depth in the Condabri MB9-H well core Basement, Blocky Sandstone Reservoir and Transition Zone.

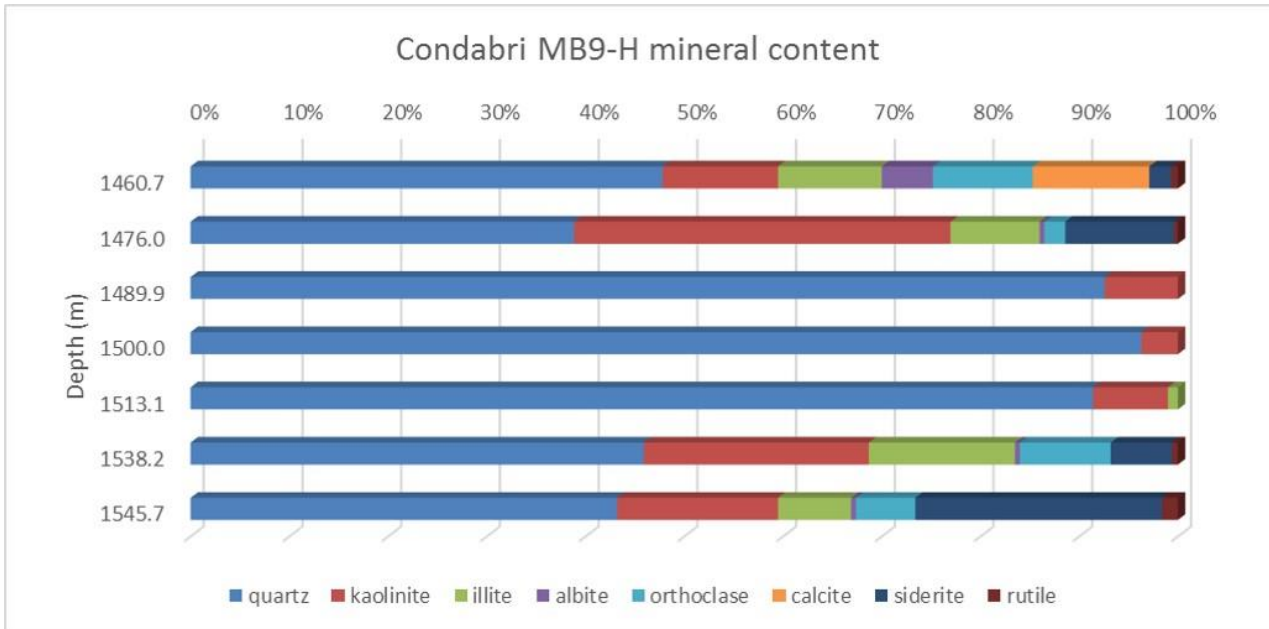
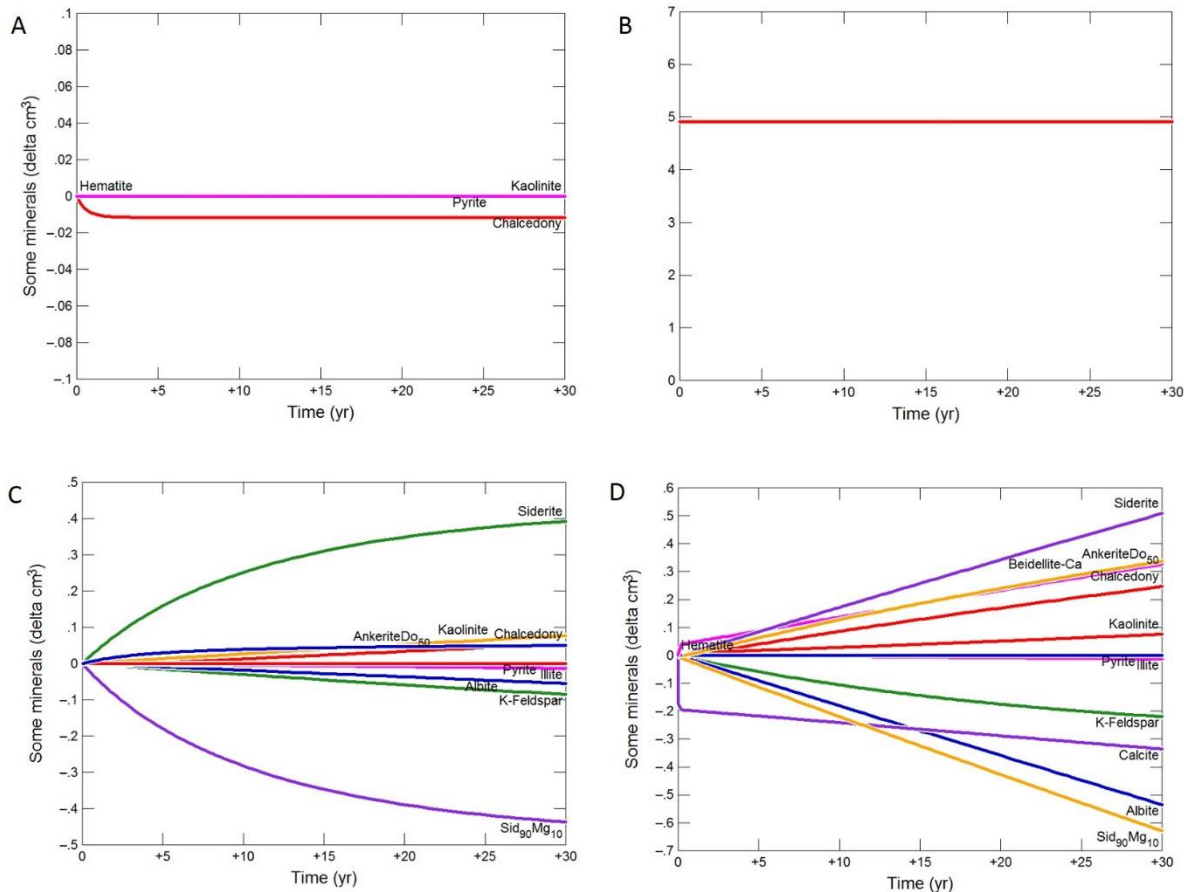


Figure 6 Geochemical modelling of Condabri MB9-H well mineralogies from (A-B) the Blocky Sandstone Reservoir 1500.0 mS1 facies, showing change in minerals and pH over 30 years. (C) Transition Zone SM3 facies 1476.0 m core change in minerals, and D) change in minerals in the M1 facies at 1460.7 m.



GSQ Chinchilla 4 well

Existing quantified mineralogical data (and porosity data) for core from the GSQ Chinchilla 4 well was used by Farquhar et al. 2015, Pearce et al. 2015 and Pearce et al. 2019 in prep. This was one of the wells with the most drill core samples characterised in detail through all three zones, the Blocky Sandstone Reservoir, Transition Zone, and Ultimate Seal (Figure 7). SEM-EDS was performed on thin sections of core as available for various facies to supplement the model input (Pearce et al. 2019 in prep). Figure 8 and Figure 9 show examples of SEM images of drill core from the Blocky Sandstone Reservoir, Transition Zone, and Ultimate Seal. In general, the geochemical predictions for the Blocky Sandstone Reservoir reaction (S1 facies at 1192.9 m and 1197.7 m) was similar overall to Reedy Creek MB3-H and Condabri MB9-H, with low mineral reactivity. The pH after 30 years of simulation was ~ 4.6, and after 1000 years was 4.8. Overall, no mineral trapping was predicted for this facies over 30 years, with 1.2 kg/m³ CO₂ mineral trapping potential over 1000 years.

Assuming a low CO₂ fugacity to simulate the edges of the plume or areas of lower dissolved CO₂, a pH of 4.7 was predicted after 30 years. Separately assuming the temperature could be lowered by cooling to 50°C, the simulated pH was 4.5, only slightly lower than the base-case of 4.6 after 30 years. To separately test the effect of a different water chemistry (given existing uncertainties with the available data), the more buffering

water chemistry from Condabri MB9-H was also used in a simulation which resulted in a pH of 4.9 after 30 years, somewhat higher than the base-case of 4.6.

The Transition Zone had more variable mineralogy and reactivity, for example the core from ~1154.0 m (O2 facies) contained a relatively high proportion of feldspar, calcite, kaolinite and chlorite. Mainly chlorite and calcite reacted over the 30 year simulation to form ankerite, siderite and smectite and the pH was buffered to 5.2. The S2 facies at 1138.2 m contained 5 % carbonate cements (calcite, siderite and ankerite) and the pH was buffered by their dissolution to 5.1 after 30 years simulation. Additionally, assuming a low CO₂ fugacity to simulate the edges of the plume, or areas of lower dissolved CO₂, the pH was predicted to reach 5.5. An SM3 facies from 1115.0 m containing feldspars and clays including chlorite, and traces of calcite, buffered pH to 5.4. Chlorite, plagioclase and calcite altered to ankerite, siderite and smectite. Overall, the CO₂ mineral trapped in ankerite and siderite (taking into account any lost through dissolution of calcite etc.) was 1.1 kg/m³ after 30 years of simulation for the sample at 1138.2 m and 2.6 kg/m³ after 1000 years simulation. For the sample mineralogy at 1154.0 m, which contained a higher portion of chlorite (~ 9%) to provide Fe cations, 2.6 kg/m³ of CO₂ was mineral trapped as siderite and ankerite after 30 years simulation.

The Ultimate Seal O3 facies had variable reactivity (but overall little net change as siderite dissolved and subsequently re-precipitated) with pH buffered to 4.7-5.3 (Figure 10).

Figure 7 Mineral content with depth in the GSQ Chinchilla 4 well core Blocky Sandstone Reservoir, Transition Zone, and Ultimate Seal.

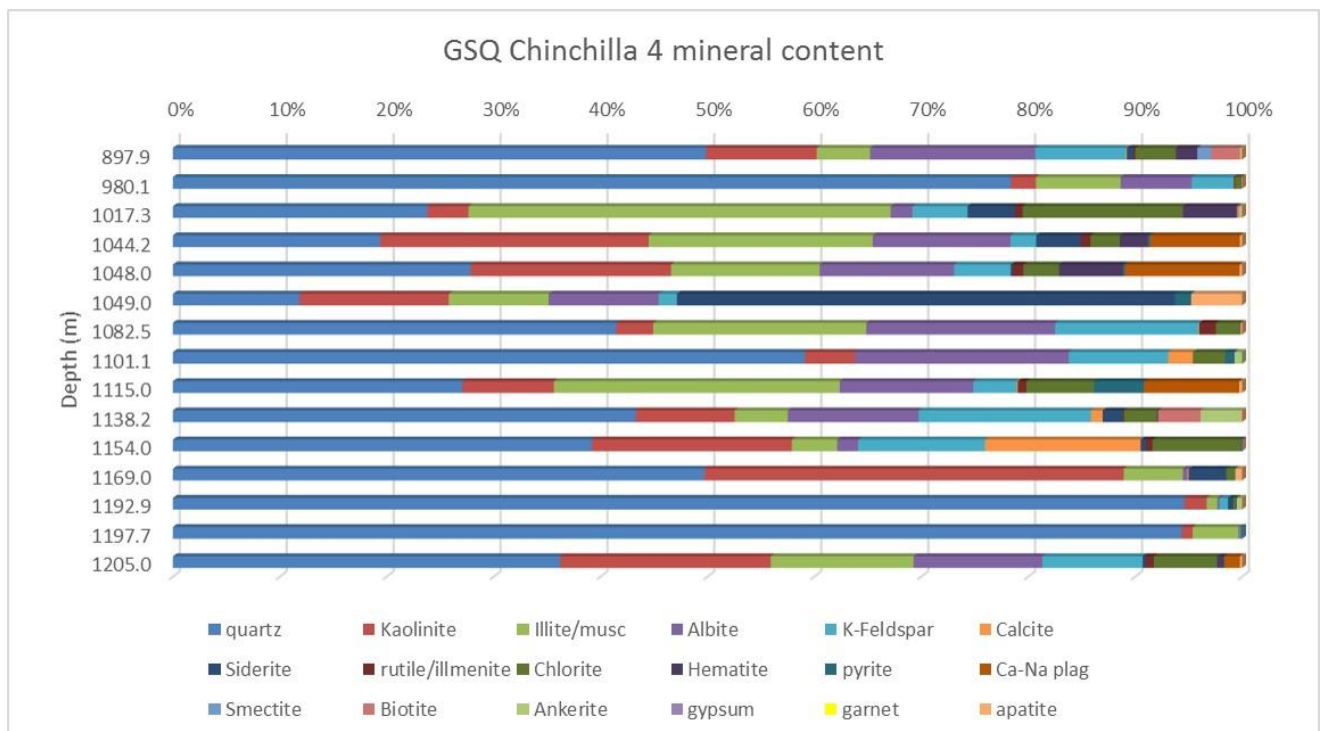


Figure 8 GSQ Chinchilla 4 well core examples of SEM images. (A) Blocky Sandstone Reservoir S1 facies at 1197.7 m: note dark areas are open porosity, and inset S1 facies at 1207.5 m shows pore rimming and bridging kaolinite. (B) Transition Zone with kaolinite filling porosity in S2/SM2 facies at 1182.5 m, (C) Transition Zone SM3 facies at 1126.0 m with calcite cement, (D) Transition Zone SM1 facies at 1101.1 m, (E) shows chlorite in the Transition Zone S2 facies at 1053.0 m. F) Shows siderite (bright areas) and coal (black) in the Ultimate Seal M1 facies at 1017.3 m. Ka = kaolinite, KF = K-feldspar, Cal = calcite, Chl = chlorite, Sid = siderite.

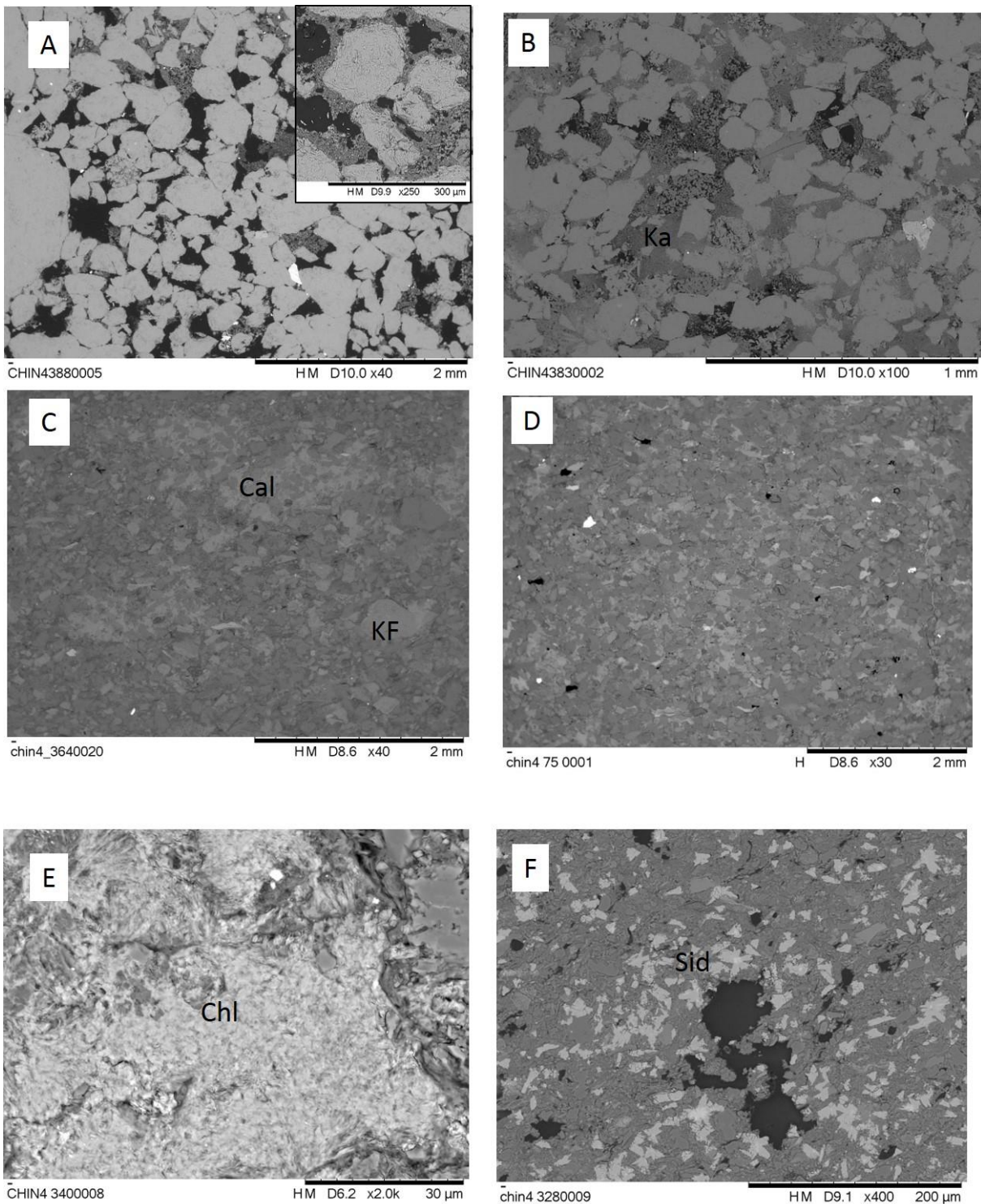


Figure 9 GSQ Chinchilla 4 well SEM images of core examples where (A-B) show clay hosted porosity in illite and kaolinite of the M1 facies at 992.3 m, (C) S2 facies at 980.1 m, (D) shows K-feldspar altered to kaolinite generating porosity at 980.1 m. Ka = kaolinite, KF = K-feldspar.

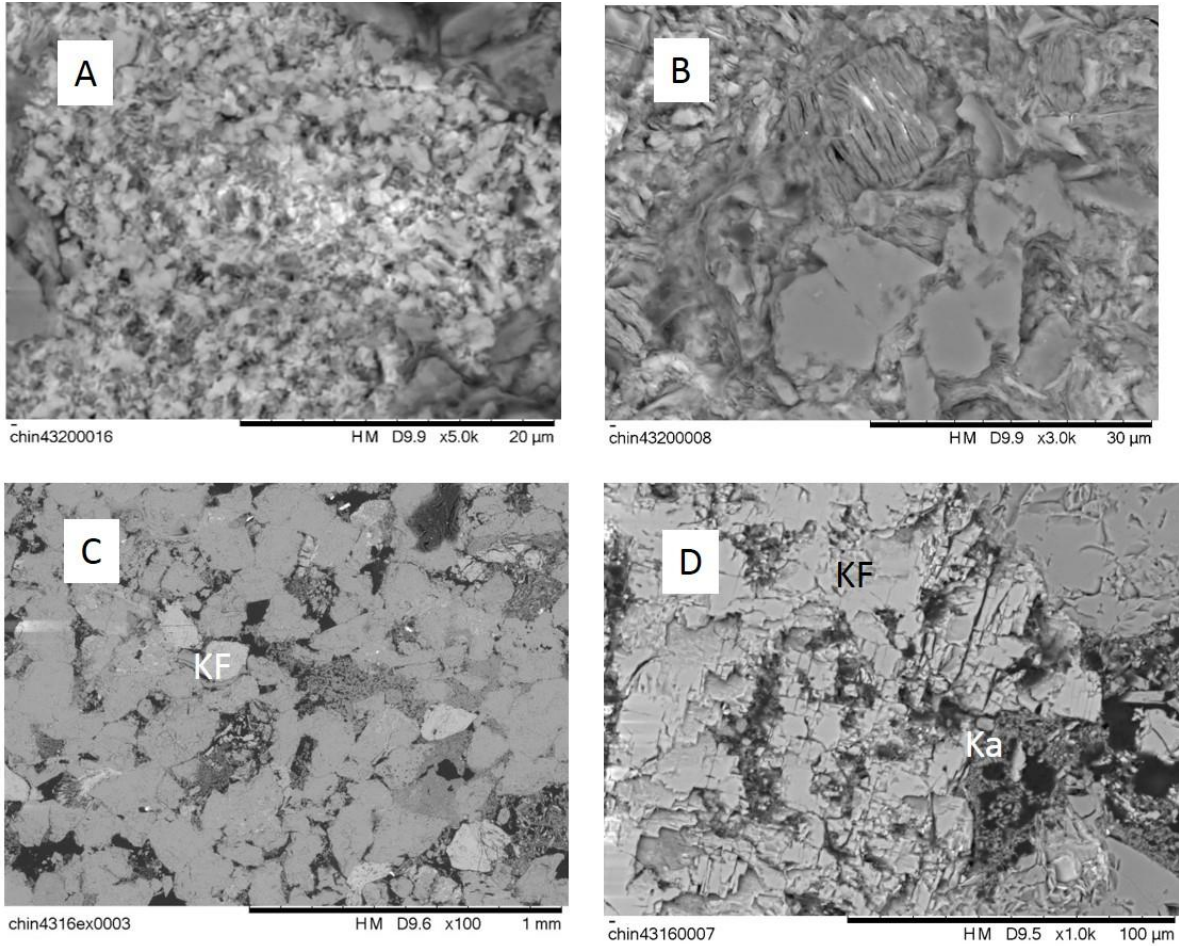
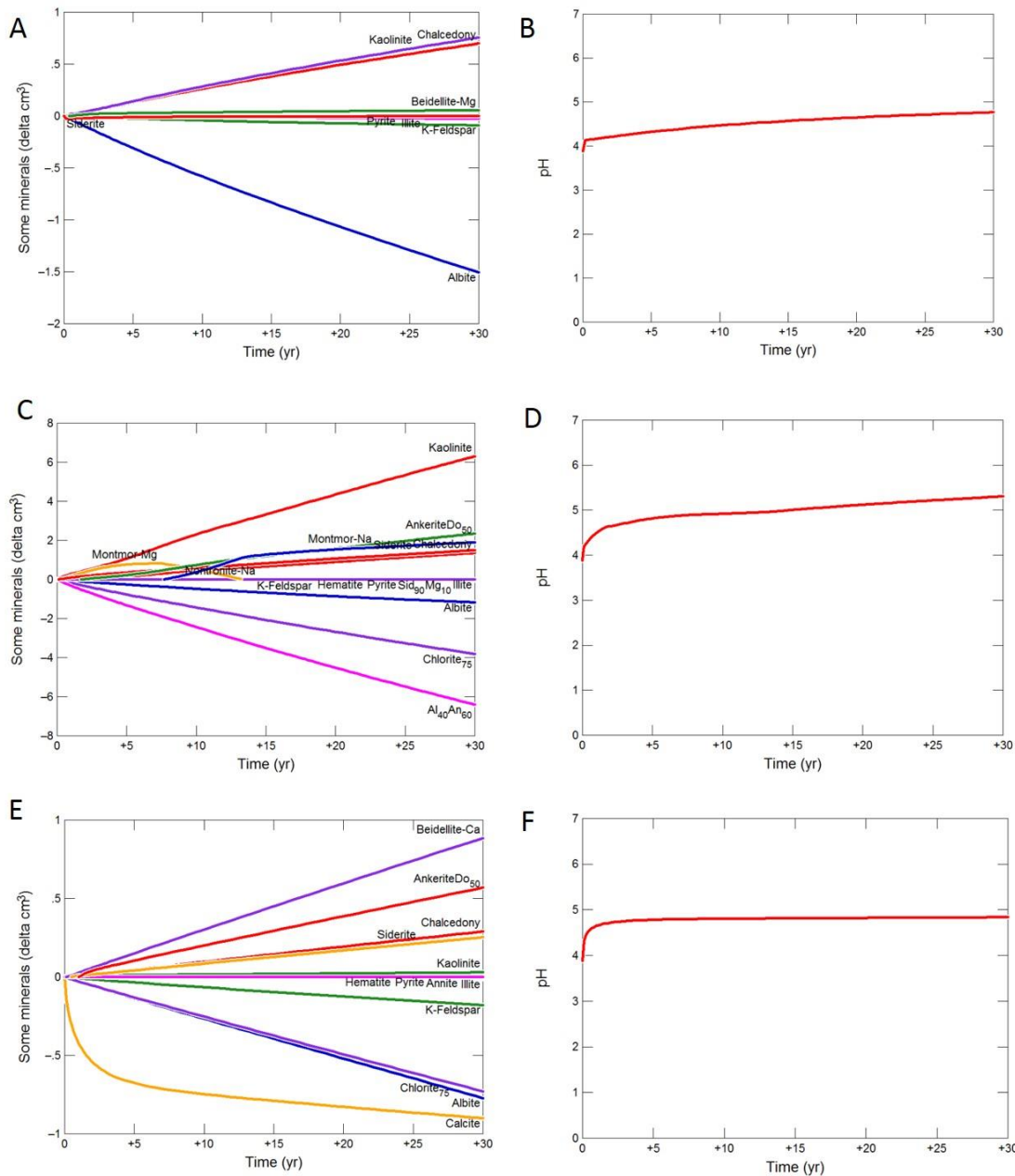


Figure 10 Geochemical modelling of the GSQ Chinchilla 4 well mineralogies from the Ultimate Seal (A-B) O3 facies at 1049.0 m showing a change in minerals and pH over 30 years simulation, (C-D) O3 facies at 1048.0 m, (E-F) are for samples from the S2 facies at 980.1 m.



West Wandoan 1 well

Geochemical modelling has been performed elsewhere in the Surat Basin through ANLEC R&D projects for core from the West Wandoan 1 well in the Blocky Sandstone Reservoir and Transition Zone using similar methodologies (Kirste et al. 2017; Pearce et al. 2018a). Therefore, only limited work was performed on core from this well in the UQ-SDAAP project to avoid repetition.

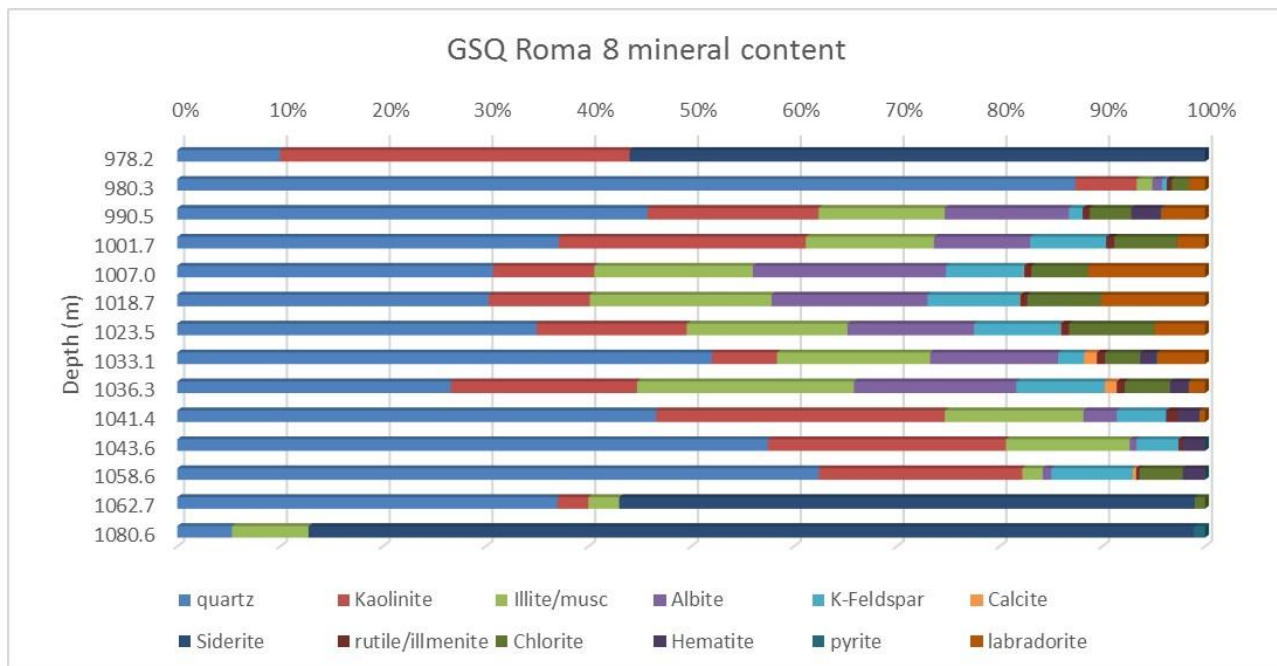
Since calcite cemented lithologies are the most reactive to CO₂, calcite cemented core from the Transition Zone (Evergreen Formation) from 1056.0 m (S3 facies) was characterised, experimentally reacted, and geochemically modelled, along with feldspar-rich and mudstone lithologies from 1043.0 m (S3 facies) and 981.0 m (SM2 facies). These results were published in Pearce et al. 2018b. In addition, owing to the small number of available core samples from the Ultimate Seal in general, one from this well was characterised. This core from 1017.0 m contained chlorite, siderite cements and apatite cement with secondary textures and veins. The porosity was 10%, however the pore throat diameters were small <1 µm, with the majority ~0.01 µm (similar to an Ultimate Seal core from GSQ Chinchilla 4 1033.0 m).

GSQ Roma 8 well

Newly defined stratigraphy from UQ-SDAAP shows that the GSQ Roma 8 well occurs to the west of the Blocky Sandstone Reservoir pinch out, but does intersect the Transition Zone and Ultimate Seal. It is included here to give further evidence to its lack of a Blocky Sandstone Reservoir, and also to assess its response to CO₂ reaction in the Transition Zone.

Existing mineralogical data was available for GSQ Roma 8 core from the Basement and Transition Zone. Mineralogical data was also available up to and including the Ultimate Seal (Haese et al. 2016). Comparing the mineral content in GSQ Roma 8 (Figure 11) to other wells, including Condabri MB9-H and Reedy Creek MB3-H shown above, it is clear that the quartz content is much lower in the Transition Zone sands (previously assigned to the Precipice Sandstone by Ziolkowcki et al. 2014 (~ 1058 – 1036 m)), and more consistent with the clay and feldspar rich Transition Zone sands in other northern wells (facies S2, SM1/S4, SM1). This independently confirms the stratigraphic nomenclature defined by UQ-SDAAP is consistent and predictive.

Figure 11 Mineral content with depth in the GSQ Roma 8 well core from Basement, Transition Zone, and Ultimate Seal.



Even though the core in GSQ Roma 8 is not part of the main reservoir considered in this project, the reactivity of several depth sections were geochemically modelled and presented here to compare their dissolved CO₂ reactivity to similar core from other wells.

The CO₂ reactivity of various facies of the Transition Zone are shown in Figure 12. These are variable with calcite, chlorite and plagioclase dissolution where present, and over the 30-year simulation the pH is buffered between 4.3 and 5.1. Siderite, ankerite and smectite are precipitated in two cases, for reactions of the S2 facies at 1058.6 m 1.2 kg/m³ of CO₂ is mineralogically trapped after 30 years simulation.

The geochemical model outputs for reaction of the Basement and the Ultimate Seal are shown in Figure 13 and Figure 14. The highly siderite cemented mineralogies have little overall net mineral change as siderite is dissolved and reprecipitated. For the Ultimate Seal SM2 and S2 facies, chlorite and plagioclase were altered to siderite, ankerite, smectite and kaolinite, and pH was buffered to 4.7-5.

Figure 12 Geochemical modelling of GSQ Roma 8 well mineralogies from the Transition Zone (A-B) S2 facies at 1058.6 m change in minerals and pH over 30 years simulation. (C-D) SM1/S4 facies at 1043.6 m. E-F) SM1 facies at 1036.3 m.

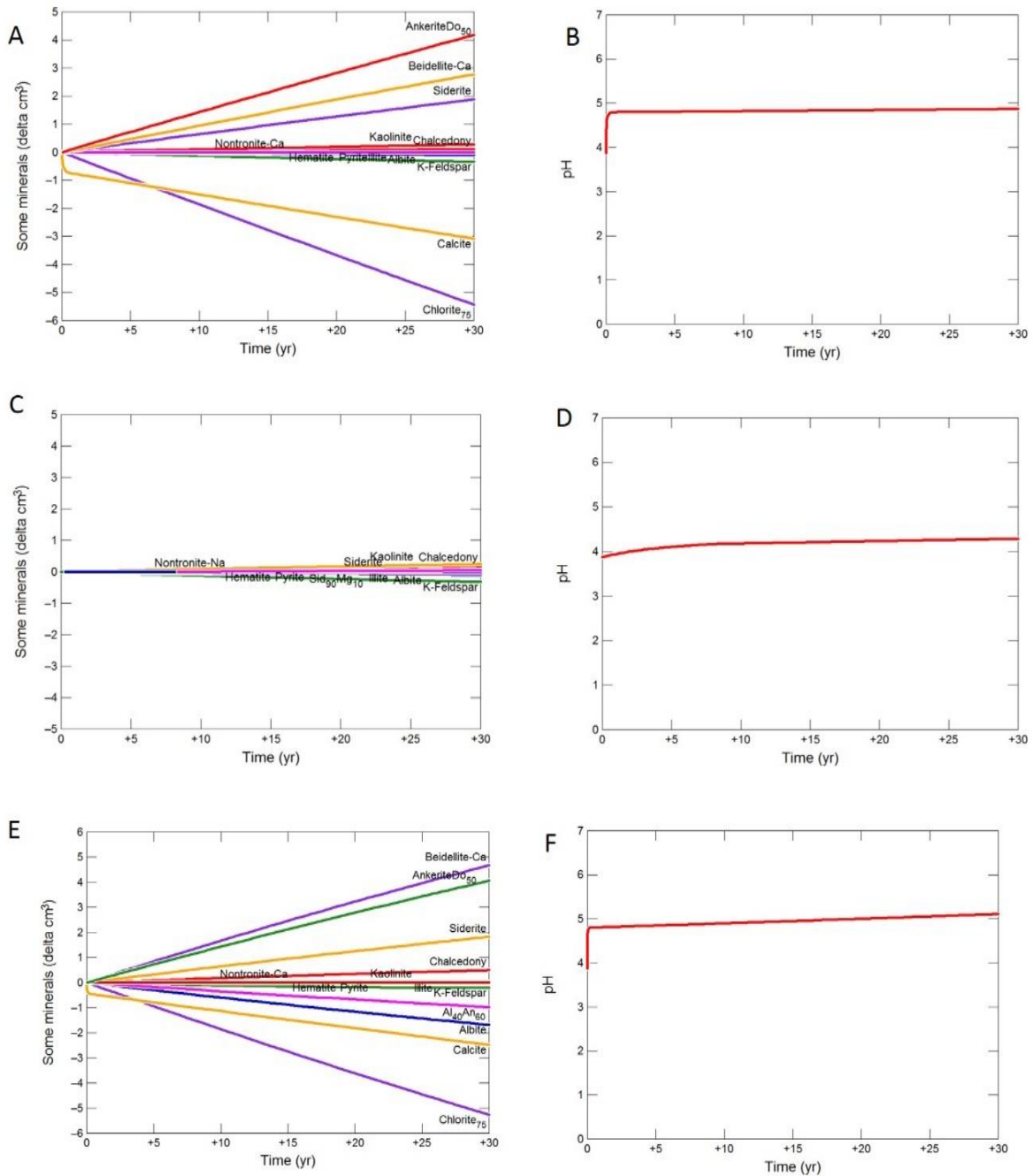


Figure 13 Geochemical modelling of GSQ Roma 8 well mineralogies from (A-B) the Basement 1080.6 m change in minerals and pH over 30 years, (C-D) a different mineralogy at 1062.7 m.

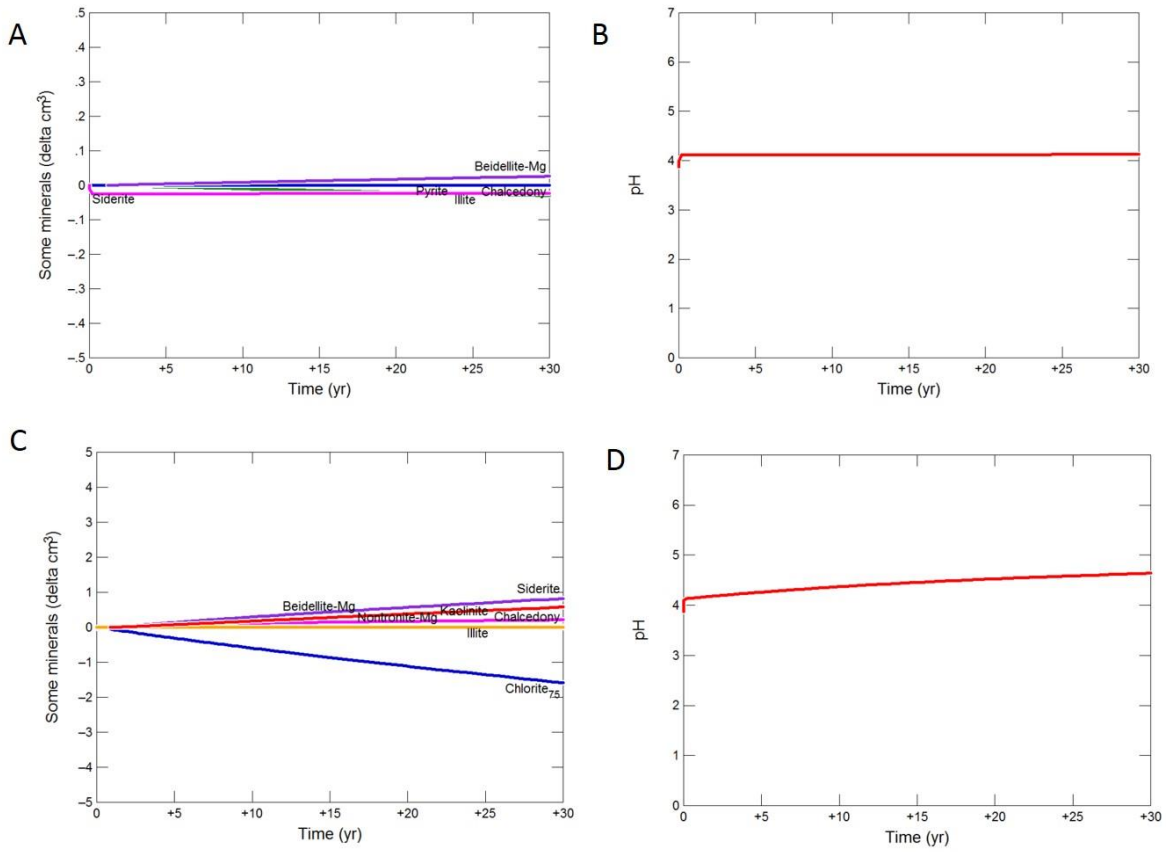
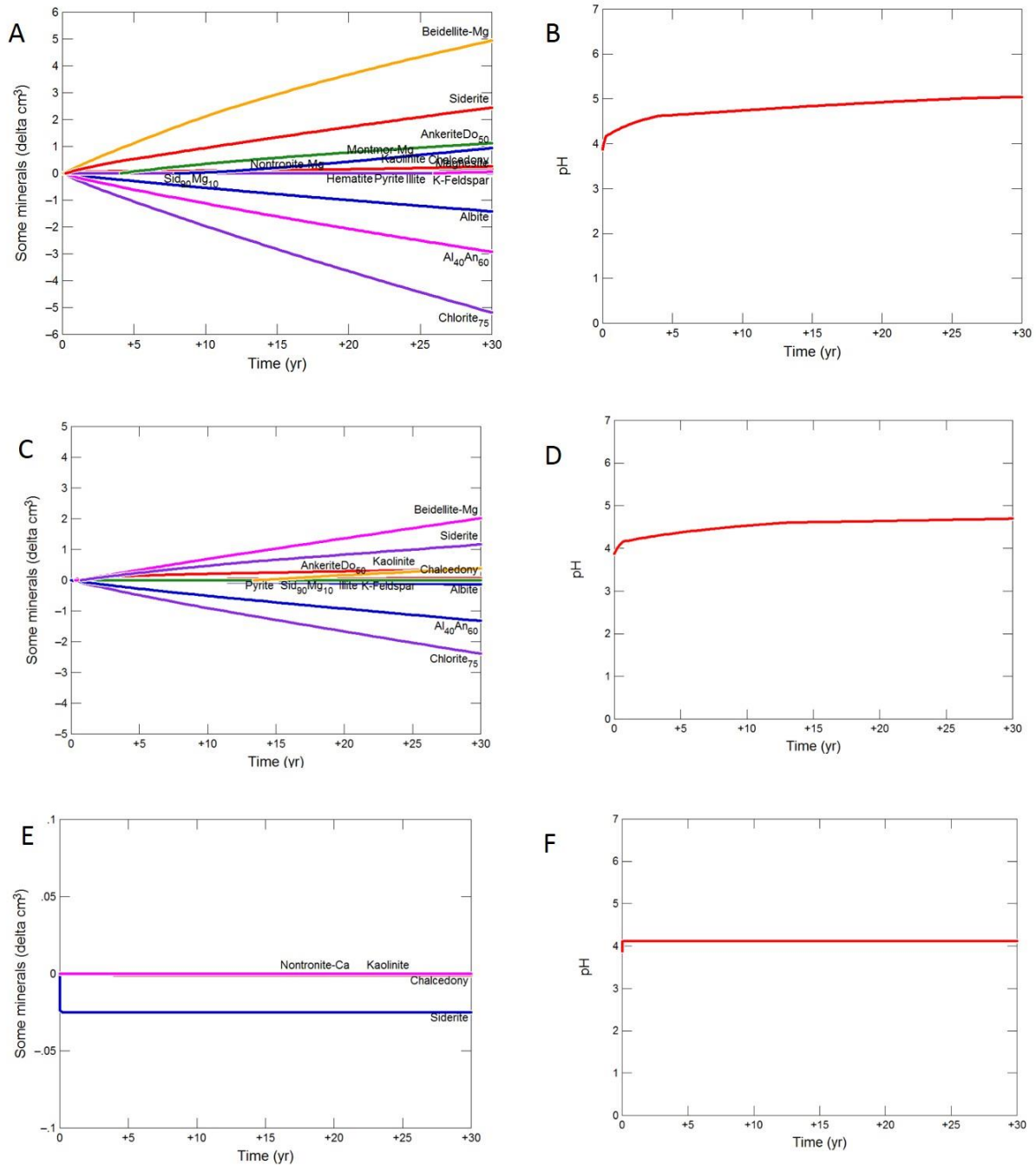


Figure 14 Geochemical modelling of GSQ Roma 8 well mineralogies from Ultimate Seal (A-B) SM2 facies at 990.5 m showing change in minerals and pH over 30 years, (C-D) S2 facies at 980.3 m, and (E-F) reaction of the O3 facies 978.2 m.



4.2 Moonie sector

Moonie 38 well

Five samples of drill core from the Moonie 38 well Blocky Sandstone Reservoir (called the 58 Sand in the well completion report) and Transition Zone (called the 56 Sand in the well completion report) were characterised for minerals (Figure 15, Figure 16). Only two samples were characterised from the Blocky Sandstone Reservoir, so limited conclusions can be drawn. However, they contained less quartz content and more feldspar than those sampled from the Blocky Sandstone Reservoir of the MAR area. The feldspar was often corroded/altered and quartz grains were sometimes fractured or compacted. The Moonie 38 well Blocky Sandstone Reservoir pore throat distributions represent a much broader range of values between 0.01 and 100 μm , whereas those published from the Blocky Sandstone Reservoir of the MAR area wells (e.g. GSQ Chinchilla 4, West Wandoan 1, Woleebee Creek GW4) had mainly sharp distributions of large pore throats around 100 μm (Pearce et al. 2019; Pearce et al. 2019 in prep). This may indicate that the high porosities and permeabilities in the Moonie area Blocky Sandstone Reservoir sands are partly fracture controlled.

Figure 15 Mineral content with depth in the Moonie 38 well core for the Blocky Sandstone Reservoir (58 Sands, deeper two samples) and Transition Zone (56 Sands).

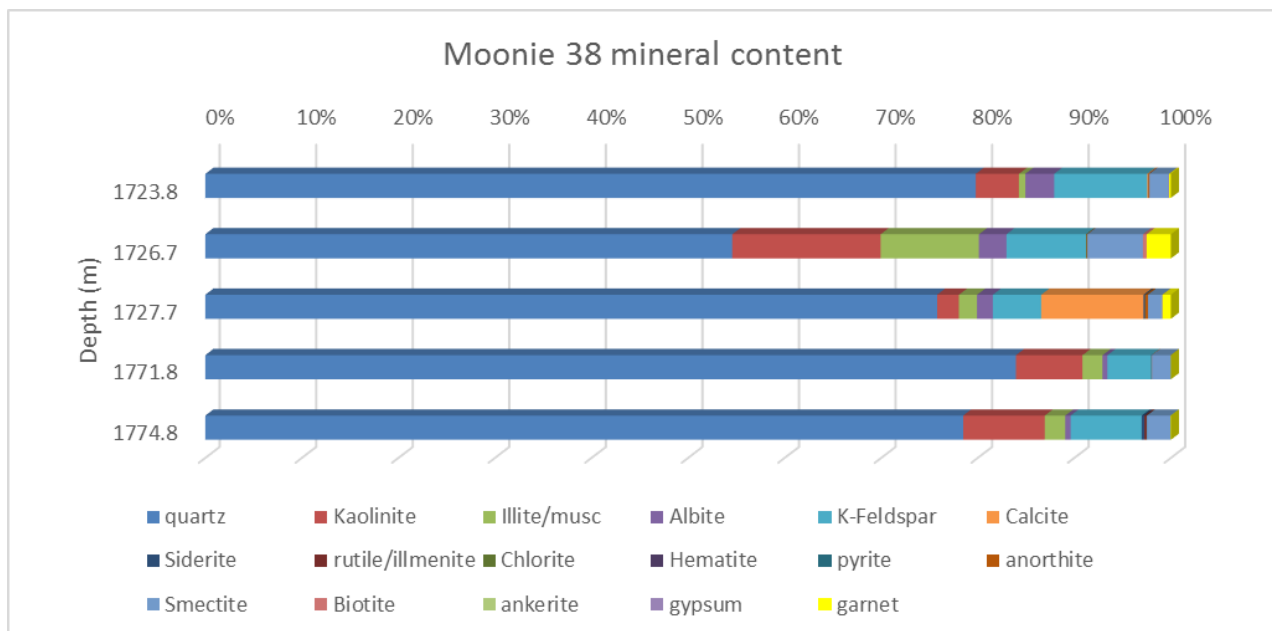
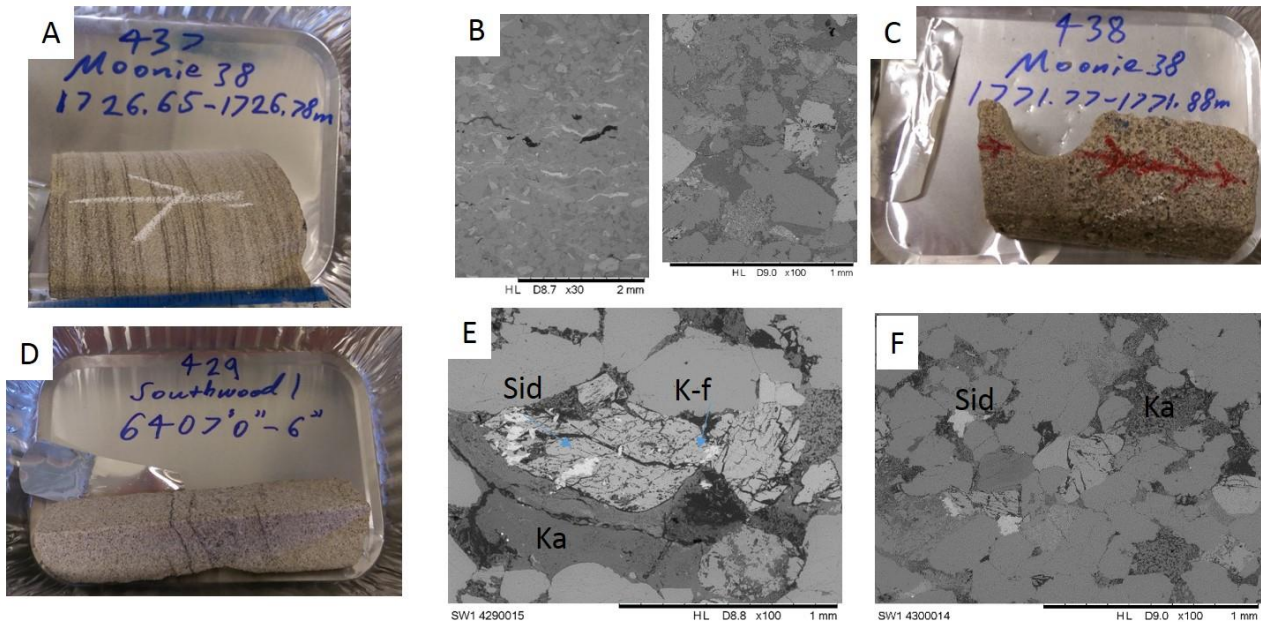


Figure 16 Photos and SEM examples of sampled core from the Moonie 38 and Southwood 1 wells. (A) and (B) Moonie 38 Transition Zone (56 sands) at ~ 1726.7 m. (C) Moonie 38 Blocky Sandstone Reservoir (58 sands) 1771.8 m. (D) and (E) Southwood 1 Transition Zone 1952.9 m. (F) Southwood 1 Transition Zone 1955.0 m. Sid = siderite, K-f = K-feldspar, Ka=kaolinite.



Geochemical modelling of the Moonie 38 well Blocky Sandstone Reservoir sample from 1771.8 m resulted in a pH of 4.8 after 30-years simulation and 5.0 after 1000 years. For lower fugacity of CO₂ simulations e.g. the edges of the plume, the pH was 5.3 after 1000 years (Figure 17). The higher Na-bicarbonate content formation water in the Transition Zone (56 Sands) buffered pH to higher values along with dissolution of minerals. For the more reactive Transition Zone samples, the calcite cement dissolution at 1727.7 m quickly buffered pH to 4.9 after 30 years simulation, 5.0 after 100 years, and 5.3 after 1000 years. The low fugacity model predicted a pH of 5.7 after 1000 y. The quartz rich 1723.8 m mineralogy (and 1726.7 m) buffered pH to 4.9 after 30 y, 5.0 after 100 years, and 5.3 after 1000 years. The low fugacity model had a predicted pH of 5.6 after 1000 years.

Moonie 22, Moonie 31 and Moonie 33 wells

Sandstones and mudstone core samples from the Moonie 22, 31 and 33 wells were additionally sampled for MICP. The Moonie 22 well sample from 1772.0 m and the Moonie 31 well sample from 1786.0 m from the Blocky Sandstone Reservoir also appeared (via SEM) to contain a higher portion of K-feldspar and clay than the Blocky Sandstone Reservoir samples from the MAR wells in the north. They also had wider pore throat distributions than the MAR area wells, being more similar to those from Moonie 38 (Figure 18). Several Moonie 31 well mudstone core samples from between the 56 and 58 Sands Facies SM1 and SM2 of the Transition Zone, had very small pore throat radii, e.g. Moonie 31 1724.0 m, Moonie 31 1765.0 m, and Moonie 31 1768.0 m (Figure 18). Only the mineral content in Moonie 31 1724.0 m and Moonie 31 1768.0 m were quantified. They contained 36-50% quartz and 40% clays. Their pore throat distributions were similar to those measured from two Ultimate Seal samples from the West Wandoan 1 and GSQ Chinchilla 4 wells (Figure 18 lower panel).

Figure 17 Predicted change in minerals and pH for the Moonie 38 well core samples over 1000 years simulation, with lower CO₂ fugacity (saturation) e.g. representing the edge of the plume. (A-B) Blocky Sandstone Reservoir (58 Sands) 1771.8 m change in minerals and pH, (C-D) Transition Zone (56 Sands) 1727.7 m change in minerals and pH, and (E-F) Transition Zone (56 Sands) 1723.8 m change in minerals and pH.

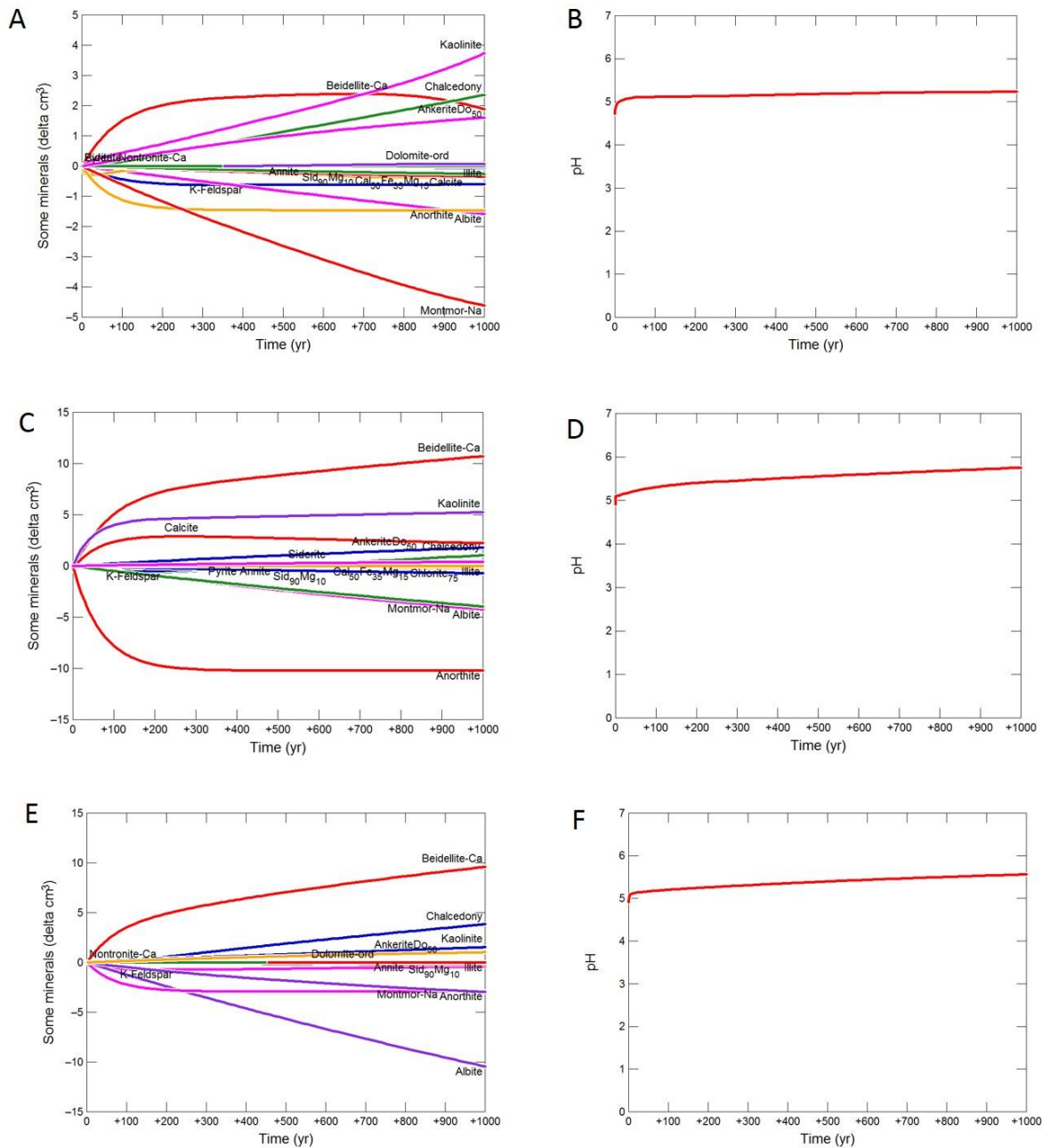
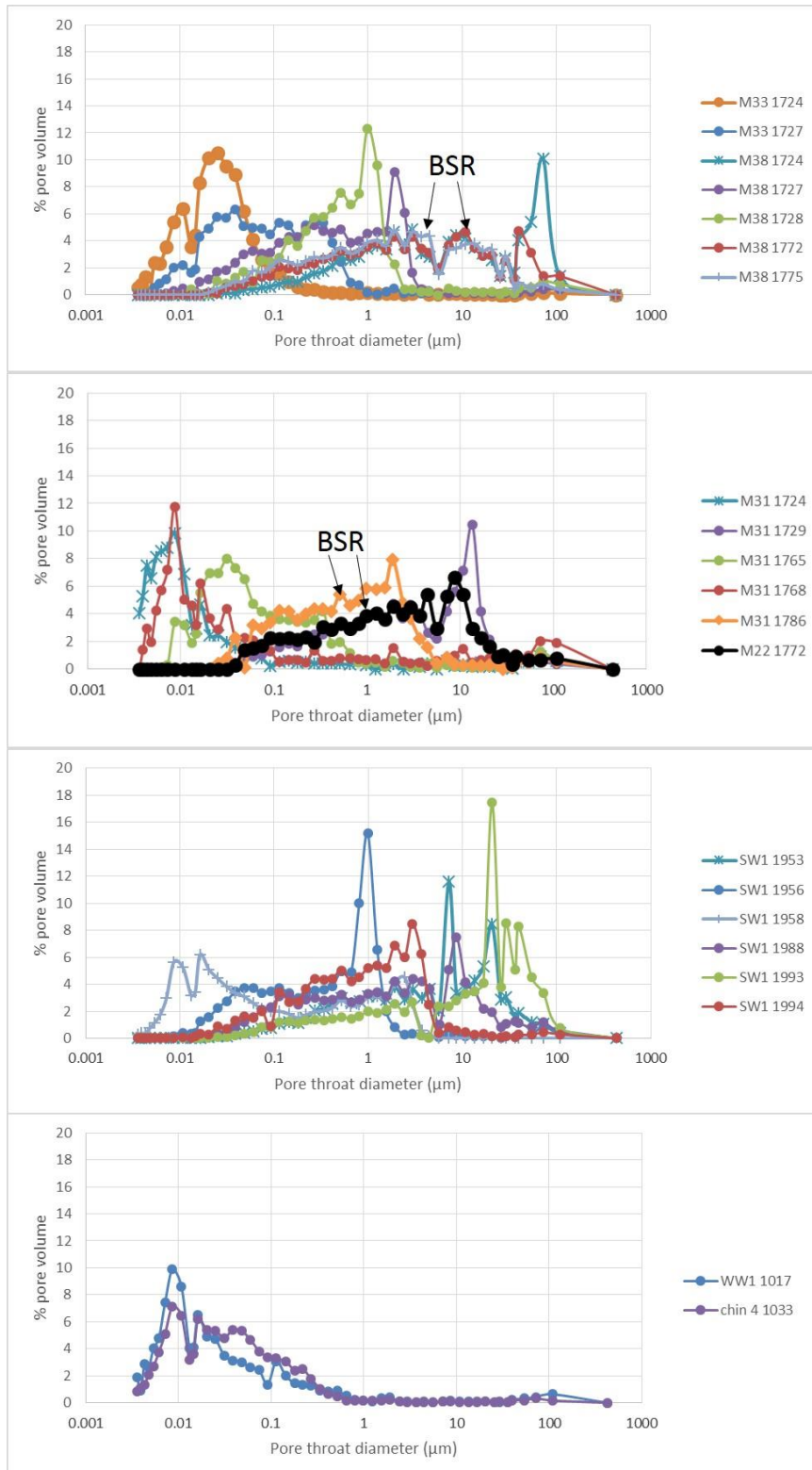


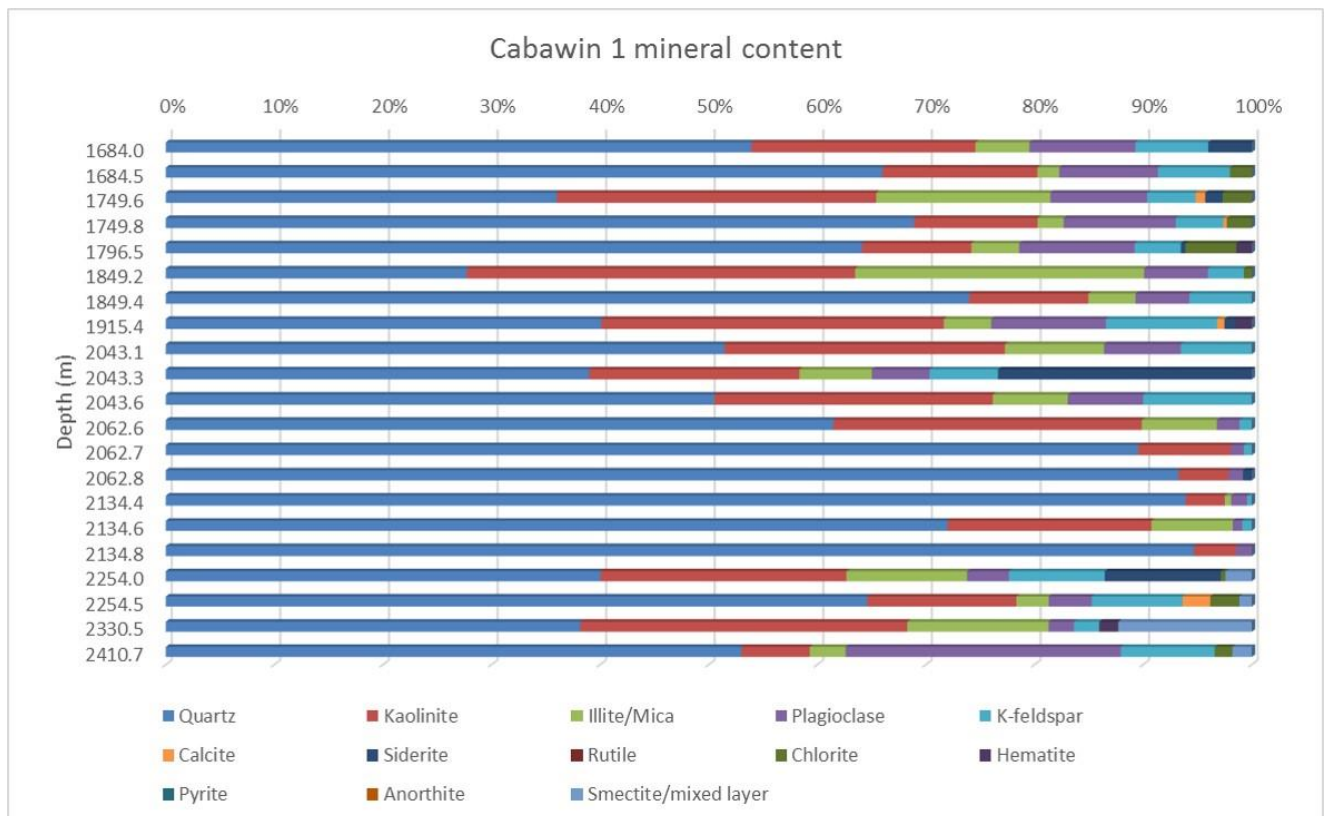
Figure 18 MICP pore throat distributions measured for core samples from the Moonie 33, Moonie 38, Moonie 31, and Moonie 22 wells (M33 etc.). Samples are from the Transition Zone except those marked at the Blocky Sandstone Reservoir (BSR). Southwood 1 well samples SW1 are from the Transition Zone, and two Ultimate Seal core samples from the West Wandoan 1 (WW1) and GSQ Chinchilla 4 (Chin 4) wells labelled by depth in m (rounded to nearest m).



4.3 Meandara sector

Geochemical modelling for the Meandara sector was performed using existing data available from the Cabawin 1 well as shown in Figure 19 (Grigorescu 2014). Models were run for two Blocky Sandstone Reservoir mineralogies (2134.4 and 2062.7 m). These showed low reactivity to CO₂ with the predicted pH after 30 years at 4.4- 4.5. A siderite cemented Transition Zone sample from ~2043.3 m buffered pH to 4.9 with dissolution and reprecipitation of siderite, and additional precipitation of kaolinite and smectite. The sample from 1915.4 m contained 10% albite, 1% siderite and 0.7% calcite and was predicted to quickly buffer pH to 4.7 after 8 days through dissolution of the calcite. After 30 years, pH reached 5 with smectite, kaolinite, and ankerite precipitated. Further details have been documented in the project publications (Pearce et al. 2018b, 2018c).

Figure 19 Mineral content with depth in the Cabawin 1 well Basement, Blocky Sandstone Reservoir, Transition Zone, and base of the Hutton Sandstone.

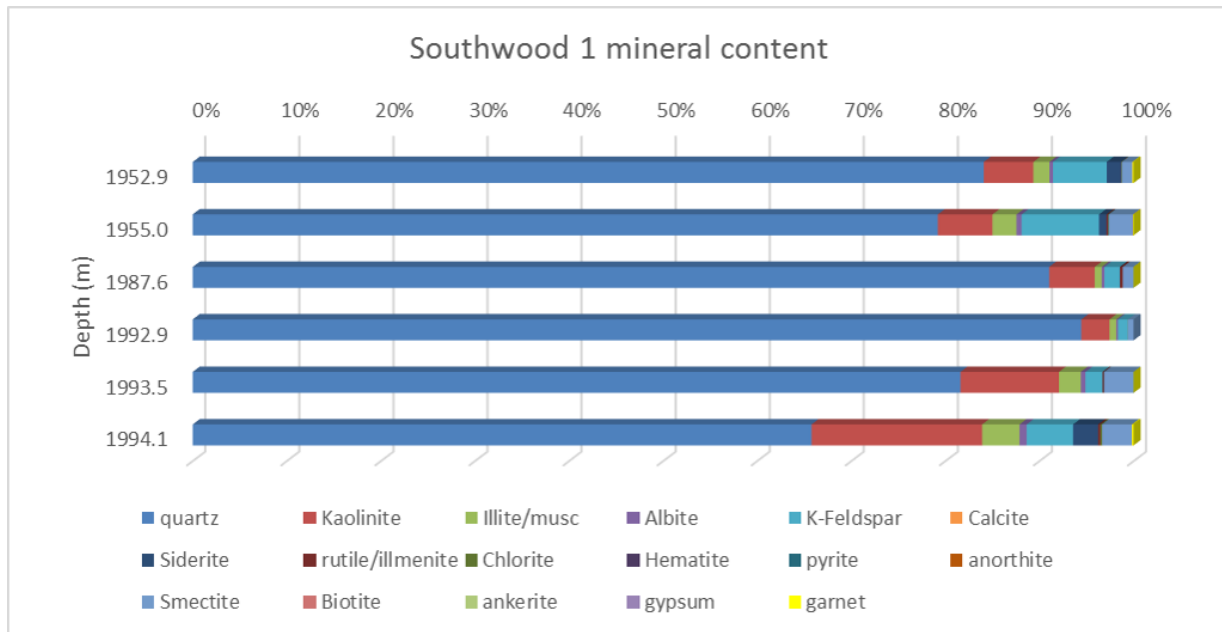


Southwood 1 well

A limited amount of drill core was available from the Southwood 1 well located in the Transition Zone. The mineral content of six sampled core depths is shown in Figure 20. Note a mudstone layer at ~1958.0 m was also present; this was sampled for seal capacity measurements by MICP but its quantified mineral content was not determined. The sandstones are quartz rich compared to other well core from the Transition Zone. Note, this may be influenced by the sections that were cored and available not being statistically representative, or it may be that the Transition Zone near Southwood 1 well is geologically different. Many of the cores had small amounts of siderite disseminated through them visible by eye, and several had naturally fractured quartz grains and corroded feldspar e.g. (Figure 16). Note this well is near the Moonie Goondiwindi fault zone.

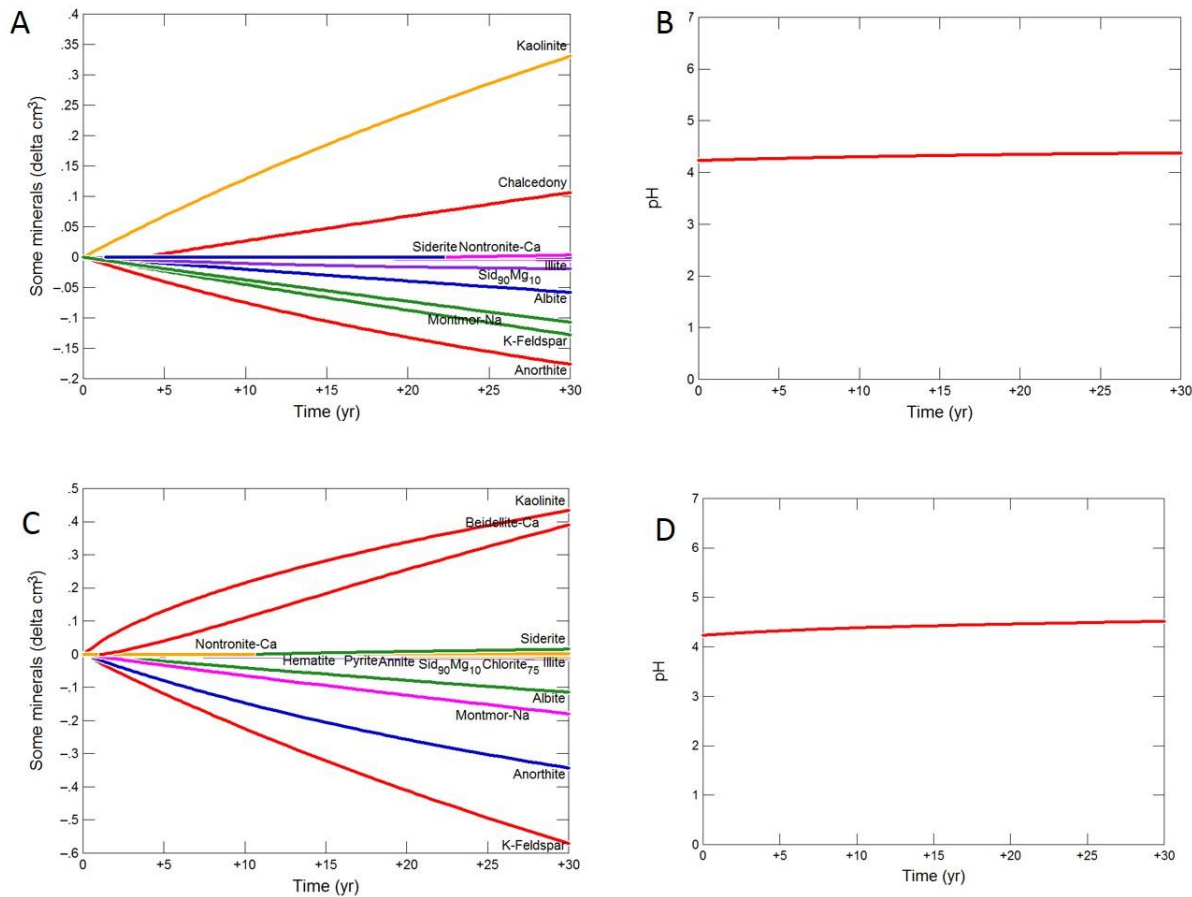
The most quartz rich core also had the largest pore throats, though like the other samples in the Transition Zone, it had a wide distribution of pore throat sizes or even bimodal distributions (Figure 18).

Figure 20 Mineral content with depth in the Southwood 1 well Transition Zone.



Geochemical modelling was performed for the most quartz rich sandstone at 1992.9 m, and the sandstone from 1952.9 m, which contained minor siderite cements (along with kaolinite, illite and feldspar). Both had low reactivity and pH remained low at 4.4-4.5 after 30 years simulation (Figure 21), 4.5-4.7 after 100 years, 4.8-4.9 after 1000 years. The low fugacity simulations (edges of the plume) were pH 5-5.2 after 1000 years simulation.

Figure 21 Predicted change in minerals and pH over 30 year's reaction simulation of Southwood 1 core from the Transition Zone: (A) and (B) sample from 1992.9 m, (C) and (D) sample from 1952.9 m.



4.4 Heavy metals data summary

The Blocky Sandstone Reservoir (Precipice Sandstone) is a Great Artesian Basin (GAB) aquifer with multiple users. An appraisal program will need to demonstrate that injection will not cause permanent damage to water resources (Risk register R28), or affect other users. An assessment of the likelihood for metals or metalloids e.g. arsenic or lead to be released to groundwater at concentrations exceeding existing native levels or drinking water, livestock, or agriculture guidelines (e.g. Pearce et al. 2018) is out of the scope of this report. The existing publicly available data for the total metal content of drill core is discussed along with new data.

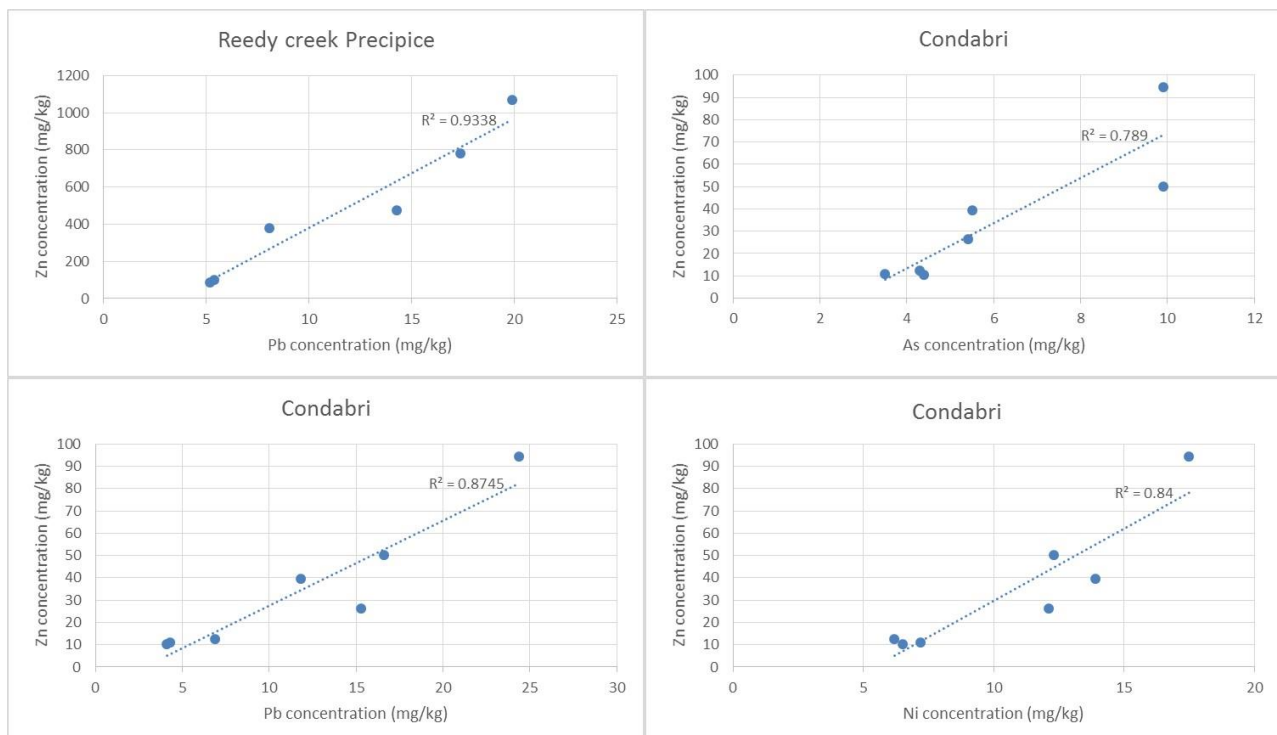
Available data for metals was very limited. Of the available data for total metal content in drill core, Reedy Creek MB3-H core from the Blocky Sandstone Reservoir had the highest concentrations of several regulated metals (compared to publically available data for GSQ Chinchilla 4, West Wandoan 1, and the core analysed here as part of the UQ-SDAAP) (APLNG 2013; Pearce 2016). In the Reedy Creek MB3-H drill core analysis it reported arsenic (As) and chromium (Cr) concentrations exceed sediment low trigger guidelines (ANZECC ARMCANZ 2000), and zinc (Zn) and mercury (Hg) exceeded high trigger guidelines (ANZECC ARMCANZ 2000; Table 3. Lead (Pb) and zinc were correlated indicating similar source minerals e.g. sulphides (Figure 22). This is consistent with the reported initial MAR water injection trials with release of arsenic exceeding

drinking water guidelines, including from oxidation of sulphide minerals (Prommer et al. 2016). In the Condabri MB9-H core chromium, cadmium (Cd) and antimony (Sb) exceeded low trigger guidelines (APLNG 2013; Prommer et al. 2016). Arsenic, lead and nickel (Ni) are also correlated, indicating potentially similar source minerals.

Table 3 Low and high sediment trigger guidelines (ANZECC ARMCANZ 2000).

Metal(loid)	ISQG low trigger value mg/kg	ISQG-high mg/kg
Sb	2	25
Cd	1.5	10
Cr	80	370
Cu	65	270
Pb	50	220
Hg	0.15	1
Ni	21	52
Ag	1	3.7
Zn	200	410
As	20	70

Figure 22 Metal correlations in the Reedy Creek MB3-H well core and Condabri MB9-H well core for the Blocky Sandstone Reservoir.



A limited number of drill cores from the Moonie 38 and Southwood 1 wells were analysed for total metals as part of the UQ-SDAAP project (Figure 23). The Moonie 38 well Transition Zone (56 Sands) cores had generally higher concentrations of metals overall than the Blocky Sandstone Reservoir (58 Sands) cores. However, they did not exceed sediment low trigger guidelines (ANZECC ARMCANZ 2000). The Southwood 1 well Transition Zone cores had comparatively low concentrations of metals overall; they also did not exceed sediment trigger guidelines. While this is initially favourable, further work is needed to assess the potential for metals to be released to formation water at concentrations exceeding drinking water, agriculture or stock guidelines (Table 4) and their potential to persist or affect other groundwater users. If metals are present in carbonate minerals (e.g. calcite or siderite) or acid reactive sulphides (e.g. sphalerite) and these dissolve, some may be released, or additionally released through desorption processes. However, if metals are in more stable framework minerals, they may not dissolve. In addition, any mineral precipitation may re-sequester metals over time. Further characterisation, experiments and modelling work would be needed, including characterising natural analogues for metal sequestration. More broadly, it is unclear if there is good data control on the regulated metal content of core in certain areas, e.g. if they are present in hydrothermal minerals associated with local faulting but no core is available. Further work is suggested on characterising metals within and dating secondary minerals associated with fault zones and fault rock for comparison.

Figure 23 An example of selected heavy metals in core at different depths from the Moonie 38 well Blocky Sandstone Reservoir (58 sand, 2 deeper samples) and Transition Zone (56 sand), and from the Southwood 1 well core Transition Zone.

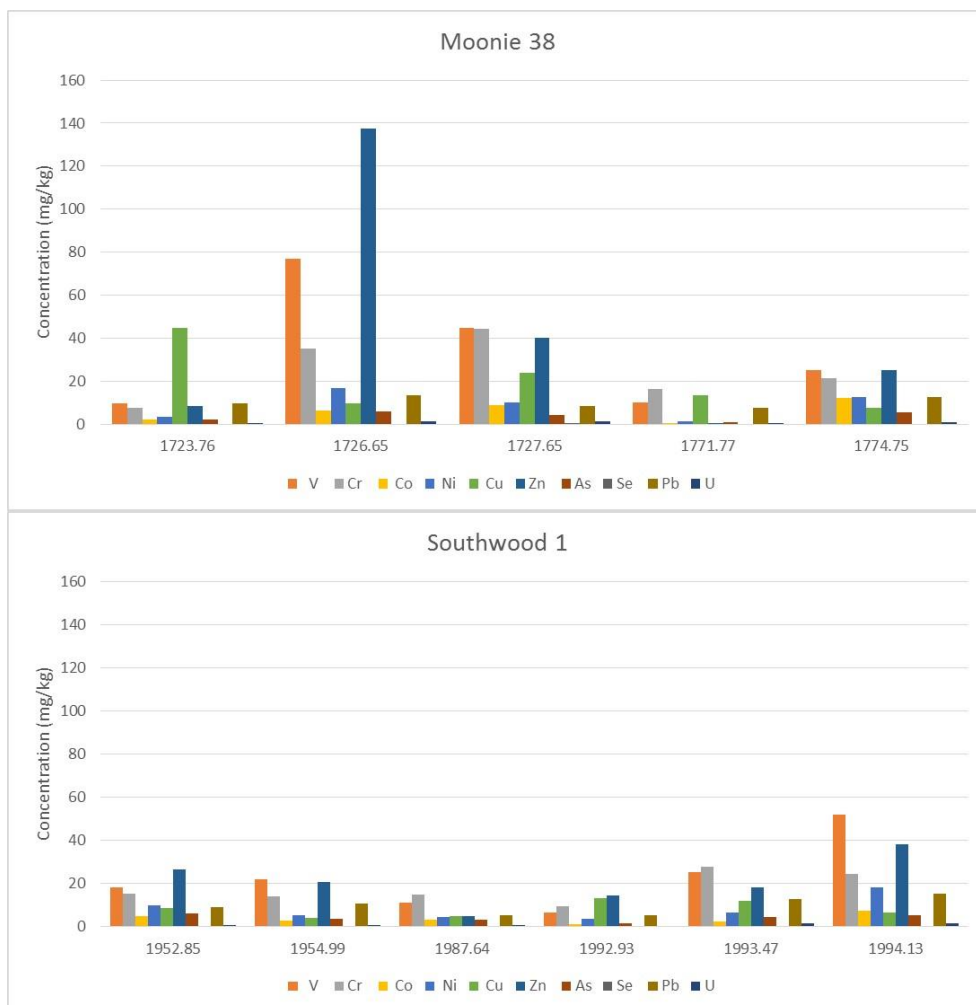


Table 4 Australian drinking water guidelines for human aesthetic and health, and low risk trigger values for livestock. Concentrations are in mg/l, electrical conductivity (EC) is $\mu\text{S}/\text{cm}$, from NHMRC 2011 and ANZECC & ARM CANZ 2000.

	Ag	Al	As	Ba	B	Be	Ca	Cd
Aesthetic		0.2						
Health	0.1		0.01	2	4	0.06		0.002
Cattle							1000	
Sheep							1000	
Stock		5	As(V) 0.5-5		5		1000	0.01
	Cr	Cu	Fe	Pb	Mg	Mn	Hg	Mo
Aesthetic		1	0.3			0.1		
Health	0.05	2		0.01		0.5	0.001	0.05
Cattle		1			600			
Sheep		0.4			600			
Stock	Cr(VI) 1	0.4-5		0.1	2000		0.002	0.15
	Ni	Se	Sb	Na	U	Zn	SiO ₂	
Aesthetic				180		3	80	
Health	0.02	0.01	0.003		0.017			
Cattle								
Sheep								
Stock	1	0.02			0.2	20		
	pH	TDS	EC					
Aesthetic	6.5-8.5	1200						
Health								
Cattle		7000- 10000						
Sheep		13000						
Stock			2985 – 7463					
Note	9.2 tolerated	<600 good quality						

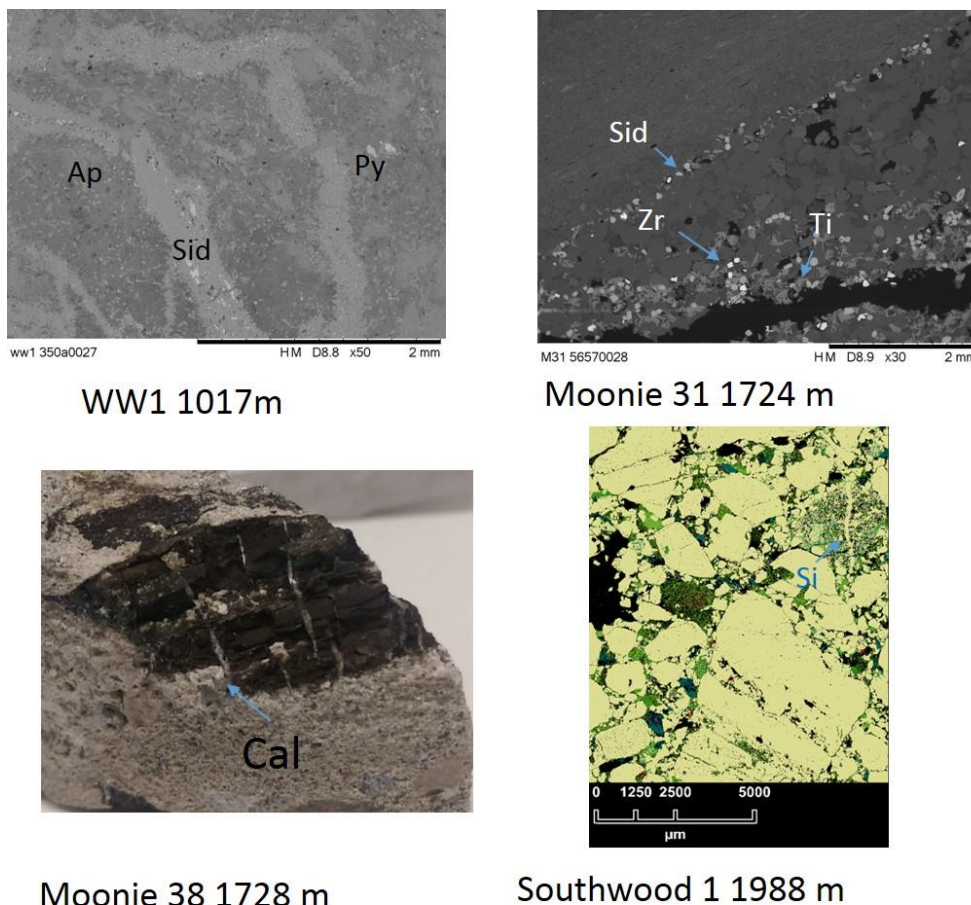
4.5 Core evidence for existing natural fractures and natural CO₂ alteration

Various drill cores sampled showed evidence of natural fractures, fracture fills of carbonate minerals and presence of hydrothermal minerals that could be related to previous natural CO₂ alteration (natural analogues). Examples of this were found in the Transition Zone (Evergreen Formation) and Ultimate Seal (Westgrove Ironstone Member) in the GSQ Chinchilla 4 and West Wandoan 1 wells, parts of the Moonie 38 well Transition Zone, the mudstones in the Transition Zone (between the 58 and 56 Sands) of the Moonie 31 well, calcite cemented zones in the Moonie 22 well, and the Southwood 1 Transition Zone core (Figure 24).

Natural fracture fill minerals include siderite, calcite, Ti-oxides, apatite, pyrite, silica, and barite cements. Fractured quartz grains in the Southwood 1 (e.g. Figure 24) and various Moonie wells could indicate potential for fracture flow, given the relatively high permeabilities in the Moonie reservoir sands (58 and 56 sands).

Natural analogue data is useful to understand processes over geological timescales and essential to validate geochemical model outputs. For example, alteration processes predicted in this chapter include plagioclase and chlorite conversion to siderite and ankerite. This is consistent with observations in natural systems with high CO₂ content (Higgs et al. 2015; Watson et al. 2004).

Figure 24 Examples of natural mineral trapping alteration and natural fractures in core from the West Wandoan 1 well (WW1) Ultimate Seal, Moonie 31 and 38 wells Transition Zone, and Southwood 1 well Transition Zone. Ap = apatite, Sid = siderite, Py = pyrite, Zr = zircon, Ti = Ti-oxide cement, Cal = calcite, Si = silica cement.



5. Implications

Overall, the drill core characterisation and geochemical CO₂-water-rock modelling indicates that the Blocky Sandstone Reservoir has a low likelihood of plugging or scaling through mineral precipitation, however this is mainly based on data from the MAR sector. The Transition Zone is variable in porosity and mineral composition and, where present, carbonate minerals can be dissolved. In modelling predictions, minerals such as plagioclase and chlorite were altered to ankerite and siderite that allowed mineral trapping of CO₂. This is consistent with general natural analogue observations internationally. Regions with higher chlorite content for example have a higher mineral trapping potential. Smectites were also formed, and these have the potential to re-seal the pore space of the Transition Zone or Ultimate Seal, with overall no predicted significant net change in porosity. In addition, smectite may adsorb CO₂ and enhance trapping.

Drill core mineral characterisation data for the GSQ Roma 8 well supports the lack of a Blocky Sandstone Reservoir (S1 facies) west of the mapped pinch out. Here the sands are part of the Transition Zone. A limited number of samples from the Blocky Sandstone Reservoir in the Moonie 38, Moonie 22 and Moonie 31 wells' core data (Moonie Sector) appear different in character to the Blocky Sandstone Reservoir in the MAR sector northern wells. The Blocky Sandstone Reservoir in the Moonie 38, Moonie 22 and Moonie 31 wells' core samples contain more feldspar and clay (illite, kaolinite), less visible open pores, and the pore throat distributions are broader including smaller radii associated with clays. Even though total porosities of Moonie Blocky Sandstone Reservoir core measured here are in the range 12-15%, a lot appears to be clay porosity.

Evidence of natural fractures, fractured quartz grains, or previous hydrothermal fluid movement were present in several Moonie and Southwood 1 wells' core samples (along with the Ultimate Seal in several MAR sector Northern wells). Given the high reported bulk permeabilities in the Moonie reservoir sands (e.g. 58 and 56 Sands), it is possible that these are influenced by fracture permeability. The Southwood 1 well Transition Zone core samples also appeared different to those in the MAR sector northern wells, being more quartz rich and containing small amounts of disseminated siderite cements, and fractured quartz grains.

Formation water pH was predicted to be lowered by the dissolved CO₂, however the pH was in many cases subsequently buffered to higher values by mineral dissolution, especially in the presence of calcite, or additionally by the formation water in areas of higher buffering capacity (e.g. near the Condabri MB9-H well, or in the Moonie field). The generated pH was in the range of 4-5 for the Blocky Sandstone Reservoir mineralogy at Reedy Creek MB3-H, GSQ Chinchilla 4, and the quartz rich transition zone of the Southwood 1 well for example. The pH was more buffered in general in the Transition Zone (the northern MAR sector wells), which contained more reactive minerals than the Blocky Sandstone Reservoir. In the Condabri MB9-H and Moonie 38 well simulation results for the Blocky Sandstone Reservoir, the pH was in the range of 5-6, partly owing to the higher buffering capacity of the local formation water. Note that in some cases, data was missing for the formation water chemistry and assumptions were made, or the closest available bore data was used. The Southwood 1 and GSQ Roma 8 well simulation predictions were somewhat limited by this. One uncertainty is the degree of cooling which will occur on CO₂ injection; this has been observed through several field studies to be generally greater than that predicted through injection modelling studies (e.g. the CO2CRC Otway projects, Aquistore). The reduced temperature region in the plume has also been observed to persist over time in field studies. Further geochemical modelling to test the sensitivity of reactivity to different degrees of cooling is suggested.

Other existing core and cuttings in the southern and central region of the Surat Basin may be available for characterisation, for example the Tara 1 well, Tasmania 1 well, and additional Moonie wells to constrain uncertainty. The Ultimate Seal characterisation data in the southern region for example is lacking. Geochemical models can be improved and validated with experimental CO₂-formation water-rock data, which is also suggested in future studies. These can be coupled with before and after reaction porosity-permeability or rock strength studies to determine changes. Experiments on an appropriate range of lithologies are suggested e.g. quartz rich Blocky Sandstone Reservoir, calcite cemented, clay rich or siderite cemented Transition Zone or Ultimate Seal core. Existing data for total concentrations of heavy metals (e.g.

lead, arsenic) in drill core was extremely limited. Where existing data was available or measured in the UQ-SDAAP project, heavy metal concentrations in core were variable by location and lithology. Core from the Reedy Creek MB3-H well had the highest concentrations of regulated metals including arsenic, chromium, zinc and mercury, which exceeded trigger guidelines in the Blocky Sandstone Reservoir. The reason for this (e.g. proximity to fractures/hydrothermal minerals) is unknown. Further core characterisation, experiments and predictions are out of the scope of this study, but would be necessary to determine if metals could potentially be mobilised into and persist in formation water at concentrations in excess of drinking water or agriculture guidelines. Additionally, data for the local formation water chemistry in the Precipice Sandstone aquifer and overlying aquifers is generally lacking, especially in the southern parts of the UQ-SDAAP study area where new data is needed for input and comparison interpretations.

As mentioned in the introduction, formation water can dissolve into the supercritical CO₂ plume. This wet supercritical CO₂ has been shown in various studies, including one with the Surat Basin core, several experimental studies in the USA, and a natural analogue study in New Zealand that also showed reactivity to rock forming minerals (Higgs et al. 2015; Miller et al. 2013; Pearce et al. 2016). The potential effects of wet supercritical CO₂ on altering properties of Surat Basin cap-rocks or seal lithologies may merit further experimental study. This would be most pertinent when site-specific data are acquired.

6. References

- ANZECC & ARMCANZ (2000), Australian and New Zealand guidelines for fresh and marine water quality - Volume 1 Version 2000 ed. Australian and New Zealand Environment and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand.
- APLNG (2013), Australia Pacific LNG Upstream Phase 1, Reedy Creek Aquifer Injection Management Plan – Precipice Sandstone, Report, Q-4255-95-MP-004.
- Bethke CM & Yeakel S (2012), The Geochemist's Workbench (Version 9.0): Reaction modelling guide, p ed. Aqueous Solutions, LLC, Champaign Ill, pp 96.
- Delany JM & Lundeen SR (1989), The LLNL thermodynamic database, Lawrence Livermore National Laboratory Report, UCRL-21658.
- Duan Z & Sun R (2003), An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar, *Chemical Geology*, vol 193, pp 257-271.
- Farquhar SM, Pearce JK, Dawson GW, Golab A, Kirste D, Biddle D & Golding SD (2015), A fresh approach to investigating CO₂ storage: Experimental CO₂-water-rock interactions in a freshwater reservoir system, *Chemical Geology*, vol 399, pp 98-122.
- Feitz AJ, Ransley TR, Dunsmore R, Kuske TJ, Hodgkinson J, Preda M, Spulak R, Dixon O & Draper J (2014), Geoscience Australia and Geological Survey of Queensland Surat and Bowen Basins Groundwater Surveys Hydrochemistry Dataset (2009-2011).
- Golab AN, Knackstedt MA, Averdunk H, Senden T, Butcher AR, Jaime P (2010), 3D porosity and mineralogy characterization in tight gas sandstones, *The Leading Edge*, vol 29, pp 1476-1483.
- Grigorescu M (2011), Mineralogy of the north-eastern Bowen Basin and north-eastern Surat Basin, Queensland, Queensland Geological Record.
- Haese R, Frank A, Grigorescu M, Horner KN, M, KD, Schacht U, Tenthorey E (2016), Geochemical impacts and monitoring of CO₂ storage in low salinity aquifers, 3-1110-0088, CO₂CRC report RPT15-5328 for ANLEC R&D.
- Higgs KE, Funnell RH, Reyes AG (2013), Changes in reservoir heterogeneity and quality as a response to high partial pressures of CO₂ in a gas reservoir, New Zealand, *Marine and Petroleum Geology*, vol 48, pp 293-322.
- Kirste D, Pearce J & Golding S (2017), Parameterizing Geochemical Models: Do Kinetics of Calcite Matter? *Procedia Earth and Planetary Science*, vol 17, pp 606-609.
- Köhler SJ, Dufaud F & Oelkers EH (2003), An experimental study of illite dissolution kinetics as a function of pH from 1.4 to 12.4 and temperature from 5 to 50°C, *Geochimica et Cosmochimica Acta*, vol 67, pp 3583-3594.
- La Croix A, Wang J & Underschultz J (2019), *Integrated facies analysis of the Precipice Sandstone and Evergreen Formation in the Surat Basin*, The University of Queensland Surat Deep Aquifer Appraisal Project – Supplementary Detailed Report, The University of Queensland.
- La Croix A, Wang J, Gonzalez S, He J, Underschultz J & Garnett A (2019), *Sequence stratigraphy of the Precipice Sandstone and Evergreen Formation in the Surat Basin*, The University of Queensland Surat Deep Aquifer Appraisal Project – Supplementary Detailed Report, The University of Queensland.
- La Croix A, He J, Wang J & Underschultz J (2019), *Facies prediction from well logs in the Precipice Sandstone and Evergreen Formation in the Surat Basin*, The University of Queensland Surat Deep Aquifer Appraisal Project – Supplementary Detailed Report, The University of Queensland.

- La Croix A, Hannaford C & Underschultz J (2019), *Palynological analysis of the Precipice Sandstone and Evergreen Formation in the Surat Basin*, The University of Queensland Surat Deep Aquifer Appraisal Project – Supplementary Detailed Report, The University of Queensland.
- Lowson RT, Comarmond MCJ, Rajaratnam G, Brown PL (2005), The kinetics of the dissolution of chlorite as a function of pH and at 25°C, *Geochimica et Cosmochimica Acta*, vol 69, pp 1687-1699.
- Miller Q.R.S, Thompson CJ, Loring JS, Windisch CF, Bowden ME, Hoyt DW, Hu JZ, Arey BW, Rosso KM & Schaefer HT (2013), Insights into silicate carbonation processes in water-bearing supercritical CO₂ fluids. *International Journal Greenhouse Gas Control*, vol 15, pp 104-118.
- NHMRC (2011), Australian Drinking Water Guidelines Paper 6 National Water Quality Management Strategy, National Health and Medical Research Council, National Resource Management Ministerial Council, Commonwealth of Australia, Canberra.
- Palandri JL, Kharaka YK (2004), A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling, USGS Open File Report 2004-1068, pp 64.
- Pearce JK, Kirste DM, Dawson GW, Farquhar SM, Biddle D, Golding S, Rudolph V (2015), SO₂ Impurity Impacts on Experimental and Simulated CO₂-Water-Reservoir Rock Reactions at Carbon Storage Conditions, *Chemical Geology*, vol 399, pp 65-86.
- Pearce JK, Dawson GW, Law ACK, Biddle D, Golding SD (2016), Reactivity of micas and cap-rock in wet supercritical CO₂ with SO₂ and O₂ at CO₂ storage conditions, *Applied Geochemistry*, vol 72, pp 59-76.
- Pearce JK, Kirste DM, Dawson GW, Golding S (2018), Mobilisation and fate of heavy metals by the GHG stream, Milestone 5 West Wandoan 1 experimental results and reactive transport modelling, Report for ANLEC R&D, 7-0115-0236.
- Pearce J & Dawson G (2018b), Experimental Determination of Impure CO₂ Alteration of Calcite Cemented Cap-Rock, and Long Term Predictions of Cap-Rock Reactivity, *Geosciences*, vol 8(7), pp 241; <https://doi.org/10.3390/geosciences8070241>.
- Pearce J, Kirste DM, Dawson GW, Altaf I, Golding S, Underschultz J (2018c), Geochemistry of storing CO₂ and NO_x in the deep Precipice Sandstone, Proceedings of the Australian Exploration Geoscience Conference, Sydney, 18- 21 Feb, https://doi.org/10.1071/ASEG2018_TechnologyCO2.
- Pearce JK, Dawson GW, Golab A, Knuefing L, Sommacal S, Rudolph V, Golding SD (2019), A combined geochemical and μ CT study on the CO₂ reactivity of Surat Basin reservoir and cap-rock cores: Porosity changes, mineral dissolution and fines migration, *International Journal Greenhouse Gas Control*, vol 80, pp 10-24.
- Pearce et al. (2019 in prep), Long term CO₂ reactivity of low salinity sandstone reservoir, transition zone and seal lithologies.
- Prommer H, Rathi B, Donn M, Siade A, Wendling L, Martens E, Patterson B (2016), Geochemical Response to Reinjection, Final Report for GISERA, CSIRO, Australia, CSIRO.
- Steeffel CI (2001), GIMRT, version 1.2: Software for modeling multicomponent, multidimensional reactive transport, User's Guide, UCRL-MA-143182, Livermore, California, Lawrence Livermore National Laboratory.
- Watson MN, Zwingmann N, Lemon NM (2004), The Ladbroke Grove-Katnook carbon dioxide natural laboratory: A recent CO₂ accumulation in a lithic sandstone reservoir, *Energy*, vol 29, pp 1457-1466.
- White AF (1995) Chemical weathering rates of silicate minerals in soils, *Reviews in Mineralogy and Geochemistry*, vol 31, pp 407-461.
- Ziolkowski V, Hodgkinson J, McKillop M, Grigorescu M, McKellar JL (2014), Sequence stratigraphic analysis of the Lower Jurassic succession in the Surat Basin, Queensland—preliminary findings. Queensland

Minerals and Energy Review Series. Queensland Minerals and Energy Review Series, Department of Natural Resources and Mines, Queensland.



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