

Geochemistry of storing CO₂ and NO_x in the deep Precipice Sandstone

J. K. Pearce^{1*}, D. Kirste², G.K.W. Dawson¹, I. Altaf³, S.D. Golding¹, J. Undershultz⁴

¹School of Earth and Environmental Sciences, University of Queensland, Australia. *j.pearce2@uq.edu.au ²Department of Earth Sciences, Simon Fraser University, Canada. ³School of Chemical Engineering, University of Queensland, Australia. ⁴UQ-Energy Initiative, University of Queensland, Australia.

SUMMARY

The Precipice Sandstone in the Surat Basin is being appraised for CO₂ geological storage owing to its high porosity and permeability and expected high injectivity. Generally it is quartz rich with variable kaolinite, however detailed characterisation of core shows that it contains minor to trace amounts of potentially reactive minerals including carbonates, plagioclase, chlorite, and muscovite, increasing towards the overlying Evergreen Formation top seal. The Evergreen Formation is mineralogically more variable with interbedded low porosity and permeability mudstones, fine-grained sandstones, and calcite cemented zones. Comparative kinetic geochemical modelling of the CO₂ reactivity of four example core mineralogy's indicates that the Evergreen Formation is potentially more reactive than the Precipice Sandstone especially for calcite or siderite containing zones. Dissolution of calcite and siderite favourably buffer acidity, with predicted precipitated minerals including siderite, kaolinite, ankerite, and smectites. Recent data from capture technologies has reported that CO₂ from coal combustion may retain NO_x impurities in the form of NO. Simulations with addition of 30-100 ppm NO indicated the generated pH is similar to pure CO₂ after 30 years but with additional precipitation of Fe-rich smectites predicted. Geochemical reactivity of core affects predicted pH and the dissolution or precipitation of minerals which could permanently trap CO₂ or dynamically change porosity and permeability.

Key words: CO₂ storage, NO_x, Precipice Sandstone, Hutton Sandstone, Evergreen Formation, Surat Basin

INTRODUCTION

Geological storage of carbon dioxide (CO₂) is one potential way to mitigate emissions contributing to climate change (IPCC 2005). CO₂ is captured from point sources such as coal fired power plants and injected into suitable formations such as a sandstone reservoir with high porosity and permeability, overlain by a low permeability cap-rock seal to prevent vertical migration. Usually reservoirs are selected at depths >800 m to maintain supercritical CO₂. Injected supercritical CO₂ can dissolve into formation water subsurface to form carbonic acid (Dawson et al., 2015). The lowered solution pH induces mineral dissolution, especially for carbonates or reactive silicates, and subsequently mineral precipitation can occur (Farquhar et al., 2015; Higgs et al., 2015). Captured CO₂ streams may contain impurities gases including N₂, CH₄, NO_x, SO_x or O₂ (Talman 2015). Injection of less pure CO₂ streams has been proposed to potentially decrease the cost of capture through avoidance of installing deSO_x or deNO_x technology. However, NO_x, SO_x and O₂ have been shown to have higher reactivity to rock (Pearce et al., 2015; Pearce et al., 2016; Turner et al., 2016).

The Surat Basin, Queensland, Australia, has been selected as having high prospectively for CO₂ storage (Hodgkinson et al., 2010; 2012). The proposed reservoir is the Precipice Sandstone with fresh to brackish formation water, overlain by the Evergreen Formation regional seal, and above the Hutton Sandstone aquifer (Figure 1) (Ziolkowski et al., 2014). To avoid potential water resource conflicts, injection into the Precipice Sandstone in deeper parts of the basin containing brackish formation water may be favourable.

METHOD AND RESULTS

Publicly available literature including journal publications, industry, agency, and government reports were interrogated for mineralogical data on the Precipice Sandstone and Evergreen Formation of the Surat Basin, with a focus on deeper wells near the centre of the basin. This study sought to undertake a holistic approach from different types of data. Available data included quantitative core sample mineral contents by X-ray diffraction (XRD) or QEMSCAN, relative mineral contents from core Hylogger data, and core elemental content from X-ray fluorescence (XRF) or core fusion or digestion data. The Cabawin 1 well (150.1905472, -27.4945361) was the deepest with available quantitative mineralogical data (XRD) for several depth sections of the Precipice Sandstone, Evergreen Formation and Hutton Sandstone (Grigorescu 2011a). Four mineralogy's are shown in Figure 1, quartz rich Precipice Sandstone containing siderite (2061.6 m), clay rich Precipice Sandstone (2134.4 m), siderite rich Evergreen Formation (2043.1 m), and clay rich Evergreen Formation containing calcite and siderite. Since techniques such as XRD and QEMSCAN typically cannot detect or quantify minerals in quantities less than 2-5%, petrological descriptions or scanning electron microscopy (SEM-EDS) data was also used to supplement and constrain minerals. Direct core imaging techniques such as SEM-EDS are also useful to give textural relationships, indicative metal contents (e.g. Fe or Mg rich chlorite), observe porosity and organic matter, and estimate mineral reactive surface areas (Pearce et al., 2015, White 1995). Figure 2 shows examples of core SEM-EDS images from our own work, note available core from wells located to the north were used as this data from Cabawin 1 well was not available, in future it would be preferable to take images from the same core. SEM-EDS surveys in back scatter electron mode were performed on core blocks with methods published previously (Dawson 2015, Pearce et al., 2015, Pearce et al., 2016). Major minerals included quartz, kaolinite, K-feldspar, plagioclase, chlorite, illite, calcite or siderite/ ankerite. Trace amounts of pyrite and chlorite were observed in the Precipice Sandstone, where chlorite and siderite contained both Fe and less Mg (Figure 2). Ti-oxides and organic matter were also present, along with zircon, and apatite. Plagioclase was generally present as both albite and a Ca-Na-plagioclase. Available information on Precipice Sandstone,

Evergreen Formation, and Hutton Sandstone experimental reactivity to CO₂ with water, low salinity brine or synthetic groundwater was also used to inform potentially reactive minerals, along with knowledge from national and international studies, especially natural analogue observations (i.e. natural CO₂ accumulations) of dissolution and precipitation to constrain models. Figure 3 shows examples of the release of dissolved Ca, Si, Fe, and S to solution from mineral dissolution during experimental CO₂-water-rock reactions of Precipice Sandstone, Evergreen Formation, and Hutton Sandstone cores (Farquhar et al., 2015). Dissolved Ca concentration is higher on dissolution of calcite from calcite cemented cores, Si is higher from cores containing chlorite, Fe is higher from cores containing siderite or chlorite, S is also released from cores containing pyrite or sphalerite. Evidence of plagioclase dissolution was also observed. Geochemical modelling was performed with the React module of Geochemist Workbench software version 9 (Bethke and Yeakel 2012). Methods were similar to those published previously (Pearce et al., 2015), with the majority of kinetic and thermodynamic data from Palandri and Kharaka 2004 input via mineral scripts. Mineral contents were based on the four Cabawin 1 well depth sections (Figure 1) with addition of traces of pyrite and chlorite (Grigorescu 2011a). Plagioclase was assumed to be albite for simplicity, siderite and chlorite containing Fe and Mg were used based on observations and previous work, chalcedony was input for quartz, and illite for mica (or as a proxy for muscovite). Mineral reactive surface areas were based on core observations previously modified for experimental observations and upscaled for reservoir based on previous work with framework grains 10 g/m², clays 70 g/m², and 0.05 g/m² for carbonates which were generally pore filling cements with limited accessibility (Kirste et al., 2015, 2017, Pearce et al., 2015, White 1995). Water volume was determined for pore volume based on reported porosities from other wells (Golab et al., 2015a, 2015b), with water chemistry (TDS 5800) from Feitz et al., (2014), consistent with Grigorescu (2011b). Models were run for 30 years at 70 °C with a CO₂ fugacity for 200 bar (Duan and Sun 2005, Hodgkinson et al., 2010, Hodgkinson and Grigorescu 2012, Raza 2009). The Precipice Sandstone 2061.6 m mineralogy was also run with 30 or 100 ppm NO added. The 2061.6 mineralogy was separately run for a temperature of 60 °C assuming injection of CO₂ could cool the immediate reservoir by an unknown amount which would decrease reaction rates.

Predicted reaction of the quartz rich Precipice Sandstone 2061.6 m resulted in dissolution of all minerals but mainly siderite and albite, with precipitation of siderite, and kaolinite (Figure 4). After 30 years, 2.4 % of the original siderite content in the core dissolved and 0.8% of the total albite content. Formation of carbonic acid decreased the pH which was only buffered slightly to 4.46 by mineral dissolution after 30 years. At 60 °C, less siderite dissolved with the resulting pH slightly lower at 4.4 after 30 years. For reaction of the Precipice Sandstone 2034.4 m core (not shown), albite (0.8% of the total), chlorite, K-feldspar (0.3% of the total), illite and pyrite dissolved, with kaolinite and siderite precipitation (mineral trapping). The pH was slightly lower at 4.4 after 30 years as siderite was not present originally in the core to dissolve and buffer the acidity.

The Evergreen Formation 2043.1 m contained 23% siderite and on reaction with dissolved CO₂ mainly siderite dissolution occurred followed by re-precipitation of Fe or Fe-Mg siderite (Figure 5). Only 0.65% of the original albite content dissolved, with precipitation of kaolinite and also smectite clay (beidellite) predicted. The lowered pH was buffered more strongly by siderite dissolution increasing gradually to 4.85 after 30 years. Evergreen Formation 1915.4 m contained 1% siderite and 0.7% calcite, with a relatively high albite content of 10.6% (Figure 1). On reaction with dissolved CO₂, pH was quickly buffered by dissolution of calcite to 4.65 after 8 days, and increased to 4.96 after 30 years (Figure 6). Siderite dissolved and re-precipitated, smectite clay (beidellite and nontronite), ankerite and kaolinite were also predicted to precipitate.

Predicted results of reaction of Precipice Sandstone 2061.6 m with CO₂ and 30 ppm NO was similar to the pure CO₂ case, with pH buffered to 4.46 after 30 years, but with goethite hematite slightly under saturated. With the addition of 100 ppm NO, resulting pH was 4.45, with hematite closer to saturation but not predicted to precipitate, however Fe-rich smectite nontronite was predicted to precipitate.

CONCLUSIONS

The geochemical reactivity of the modelled Evergreen Formation mineralogy's was generally higher than the Precipice Sandstone owing to the higher siderite, calcite and albite contents. The lower reactivity of the Precipice Sandstone indicates permeability is less likely to decrease through mineral precipitation; however we cannot predict the potential for fines migration clogging pores without experimental studies. The Evergreen Formation has low permeability so limited fluid infiltration, but the predicted higher reactivity of the Evergreen Formation indicates favourable pH buffering and precipitation of carbonates and clays at the base. Even small amounts of calcite were predicted to have fast pH buffering. The precipitation of clays in pore throats has the potential to decrease permeability or self-seal cap-rock, this deserves future work. The precipitation of minerals such as siderite, ankerite, kaolinite and smectite is consistent with observations from natural analogues (Higgs et al., 2013, 2015, Watson et al., 2004). Addition of 100 ppm NO in the CO₂ did not affect predicted pH after 30 years reaction of the quartz rich Precipice Sandstone, although precipitation of nontronite (Fe-rich smectite) was predicted. Experiments at reservoir conditions have shown CO₂-NO slightly lowers pH over 1 month time scales and is more reactive to minerals in Precipice Sandstone core than pure CO₂. Precipitation of Fe-rich material including Fe-hydroxide and potentially fine grained Fe-rich clays was observed after 1 month of experimental NO-CO₂ reaction of Precipice Sandstone (Figure 2) (Turner et al., 2016). The comparative geochemical modelling has shown that the local mineralogy can have a strong effect on the resulting pH after CO₂ injection, and on dissolution and precipitation of minerals. More detailed modelling is suggested in future for different sites in the Surat Basin. Investigating the potential for clay fines migration or pore throat clogging is also suggested which may be favourable in the case of permeability reduction in cap-rocks but could be unfavourable if reservoir permeability were decreased. This work was limited by the lack of detailed data available on core from several areas of the Surat Basin, core SEM-EDS, petrography and metal content characterisation is needed in future, along with experimental studies of changes to core rock mechanical properties and permeability on CO₂ water reaction.

ACKNOWLEDGMENTS

We acknowledge assistance and access to publically available data sets from M. Grigorescu, L. Turner, and S. Farquhar. For their contribution and support, UQ would like to acknowledge: Commonwealth Government of Australia; ACA Low Emissions Technology Pty Ltd (ACALET).

REFERENCES

- Bethke, C.M. and Yeakel, S., 2012. The Geochemist's Workbench (Version 9.0): Reaction modeling guide. Aqueous Solutions, LLC, Champaign, Ill., 96 p.
- Dawson, G.K.W., Biddle, D., Farquhar, S.M., Gao, J., Golding, S.D., Jiang, X., Keck, R., Khan, C., Law, A.C.K., Li, Q., Pearce, J.K., Rudolph, V., Watson, A. and Xing, H., 2015a. Achieving Risk and Cost Reductions in CO₂ Geosequestration through 4D Characterisation of Host Formations, University of Queensland report for ANLEC R&D, 7-1110-0101.
- 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*, 193(3-4): 257-271.
- Farquhar, S.M., Pearce, J.K., Dawson, G.K.W., Golab, A., Kirste, D., Biddle, D. and Golding, S.D., 2015. A fresh approach to investigating CO₂ storage: Experimental CO₂-water-rock interactions in a freshwater reservoir system. *Chemical Geology*, 399:98-122.
- Feitz, A.J., Ransley, T.R., Dunsmore, R., Kuske, T.J., 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). Geoscience Australia, Canberra Australia. <http://dx.doi.org/10.4225/25/5452D04771CCF>.
- Golab, A., Arena, A., Khor, J., Goodwin, C., Young, B., Carnerup, A. and Hussain, F., 2015a. Milestone 1.4 Final report of RCA and SCAL data on plugs from West Wandoan-1 Well, FEI Lithicon, Report for ANLEC R&D.
- Golab, A., Knuefing, L., Goodwin, C., Sommacal, S., Carnerup, A., Dawson, G., Pearce, J.K. and Golding, S.D., 2015b. Milestone 5.7: Final report on geochemical reactivity studies of core material using ScCO₂, Lithicon FEI, Report for ANLEC R&D.
- Grigorescu, M., 2011a. Mineralogy of the north-eastern Bowen Basin and north-eastern Surat Basin, Queensland. Queensland Geological Record. Queensland Geological Record.
- Grigorescu, M., 2011b. Jurassic groundwater hydrochemical types, Surat Basin, Queensland - a carbon geostorage prospective, Queensland Geological Record 2011/05.
- Higgs, K.E., Funnell, R.H., Reyes, A.G., 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*, 48(0): 293-322.
- Higgs, K.E., Haese, R.R., Golding, S.D., Schacht, U., Watson, M., 2015. The Pretty Hill Formation as a natural analogue for CO₂ storage; an investigation of mineralogical and isotopic changes associated with sandstones exposed to low, intermediate and high CO₂ concentrations over geological time. *Chemical Geology*, 399: 36-64.
- Hodgkinson, J., Preda, M., Hortle, A., McKillop, M., Dixon, O. and Foster, L., 2010. The potential impact of carbon dioxide injection on freshwater aquifers: the Surat and Eromanga Basins in Queensland 9781921489570, Dept. of Employment, Economic Development and Innovation, Geological Survey of Queensland, Brisbane.
- Hodgkinson, J. and Grigorescu, M., 2012. Background research for selection of potential geostorage targets—case studies from the Surat Basin, Queensland. *Australian Journal of Earth Sciences*, 60(1): 71-89.
- IPCC (Intergovernmental Panel on Climate Change) 2005. Special Report on Carbon Dioxide Capture and Storage. Cambridge University Press, Cambridge, UK, and New York, NY, USA.
- Kirste, D.M., Pearce, J.K., Golding, S., Frank, A., 2015. Reactive transport modelling of CO₂ with SO₂ and O₂ as impurities for geological storage: Upscaling from the benchtop to the reservoir, Goldschmidt, Prague, CZ.
- Kirste, D., Pearce, J., Golding, S., 2017. Parameterizing Geochemical Models: Do Kinetics of Calcite Matter? *Procedia Earth and Planetary Science*, 17: 606-609.
- Palandri, J.L. and Kharaka, Y.K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. USGS Open File Report 2004-1068, USGS Open File Report 2004-1068.
- Pearce, J.K., Kirste, D.M., Dawson, G.K.W., Farquhar, S.M., Biddle, D., Golding, S. and Rudolph, V., 2015. SO₂ Impurity Impacts on Experimental and Simulated CO₂-Water-Reservoir Rock Reactions at Carbon Storage Conditions. *Chemical Geology*, 399: 65-86.
- Pearce, J.K., Golab, A., Dawson, G.K.W., Knuefing, L., Goodwin, C. and Golding, S.D., 2016. Mineralogical controls on porosity and water chemistry during O₂-SO₂-CO₂ reaction of CO₂ storage reservoir and cap-rock core. *Applied Geochemistry*, 75: 152-168.
- Raza, A., Hill, K.C., Korsch, R.J., 2009. Mid-Cretaceous uplift and denudation of the Bowen and Surat Basins, eastern Australia: relationship to Tasman Sea rifting from apatite fission-track and vitrinite-reflectance data. *Australian Journal of Earth Sciences*, 56(3): 501-531.
- Talman, S., 2015. Subsurface geochemical fate and effects of impurities contained in a CO₂ stream injected into a deep saline aquifer: What is known. *International Journal of Greenhouse Gas Control*, 10.1016/j.ijggc.2015.04.019.
- Turner, L.G., Pearce, J.K., Golding, S.D., Myers, G.A., Morgan, Q., 2016. Experiments and geochemical simulations of co-injection of CO₂, SO₂ and NO University of Queensland, Report for ANLEC R&D, 7-0314-0229.
- Watson, M.N., Zwingmann, N., Lemon, N.M., 2004. The Ladbroke Grove-Katnook carbon dioxide natural laboratory: A recent CO₂ accumulation in a lithic sandstone reservoir. *Energy*, 29(9-10): 1457-1466.
- White, A.F., 1995. Chemical weathering rates of silicate minerals in soils. *Reviews in Mineralogy and Geochemistry*, 31(1): 407-461.
- Ziolkowski, V., Hodgkinson, J., McKillop, M., Grigorescu, M. and McKellar, J.L., 2014. Sequence stratigraphic analysis of the Lower Jurassic succession in the Surat Basin, Queensland—preliminary findings., Queensland Minerals and Energy Review Series, Department of Natural Resources and Mines, Queensland.

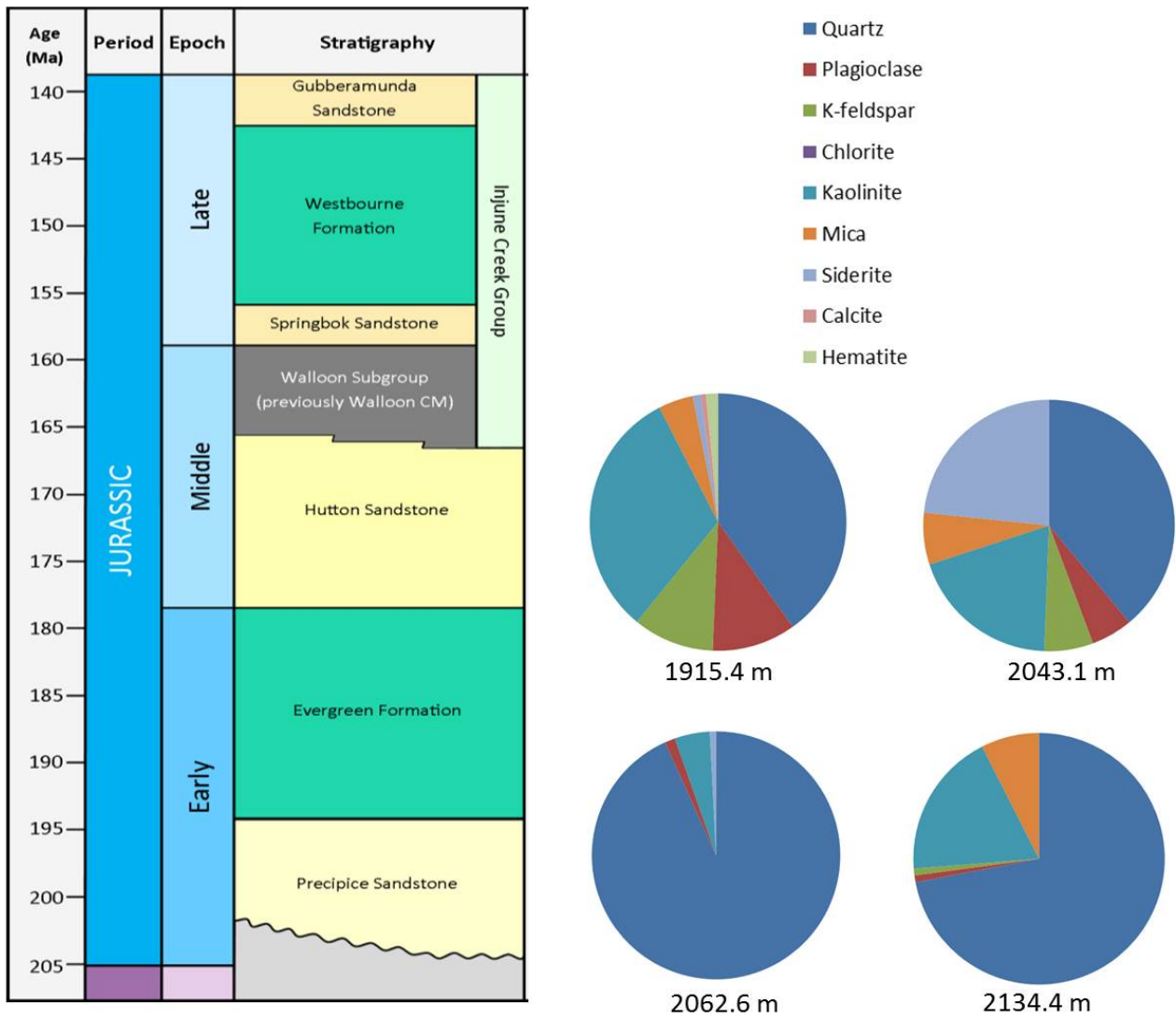


Figure 1: Generalised stratigraphy of the Surat Basin, where the Precipice Sandstone is the proposed storage reservoir, and the Evergreen Formation the proposed seal. The Boxvale Sandstone and Westgrove Ironstone member are within the Evergreen Formation. Modified from (Farquhar et al., 2015; Pearce et al. 2015). Examples of major minerals in cores from the Cabawin 1 well core (created from data in Grigorescu 2011a).

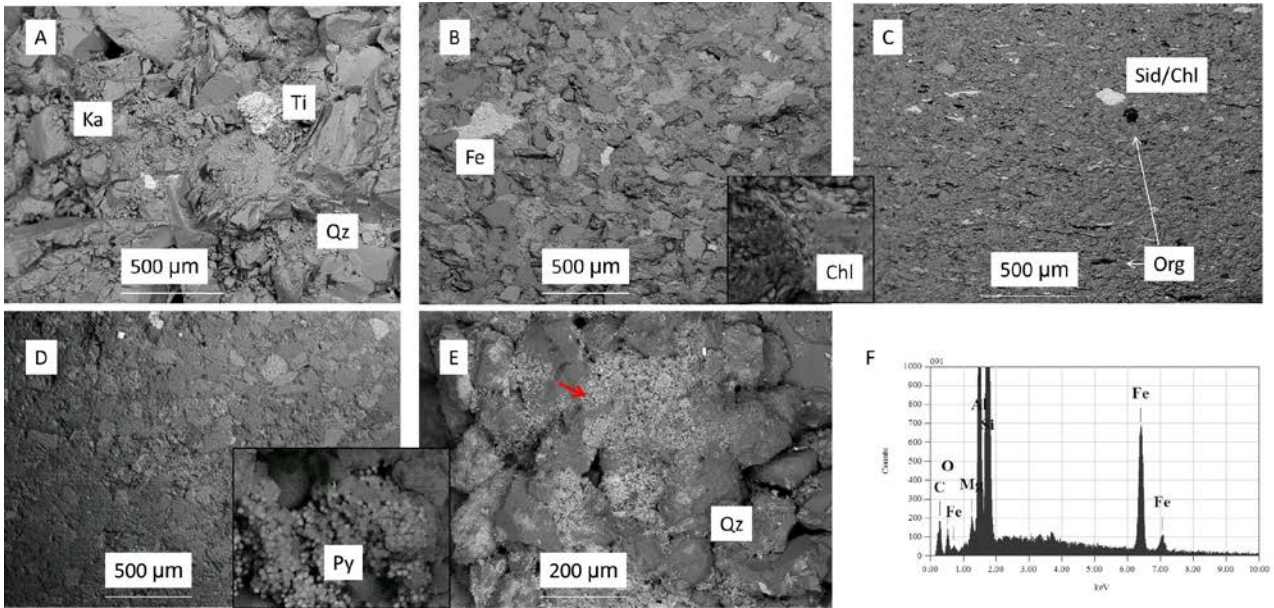


Figure 2: SEM-EDS image examples of minerals, grain size, pores and textures in a) quartzose Precipice Sandstone, b) feldspar rich Precipice Sandstone, inset Fe-rich chlorite (image width 100 μm), c) Evergreen Formation shale, d) Plagioclase rich Evergreen Formation, inset pyrite in Precipice Sandstone (image width 30 μm), e) Fe-rich precipitates (red arrow) on Precipice Sandstone after CO₂-NO reaction, f) EDS spectrum of Fe-Mg-chlorite in Evergreen Formation core. Qz = quartz, Ka= kaolinite, Ti = Ti-oxide, Fe = Fe-oxide, Sid = siderite, Chl = chlorite, Org = organic matter, Py = pyrite. From samples of Chinchilla 4 and West Wandoan 1 well cores.

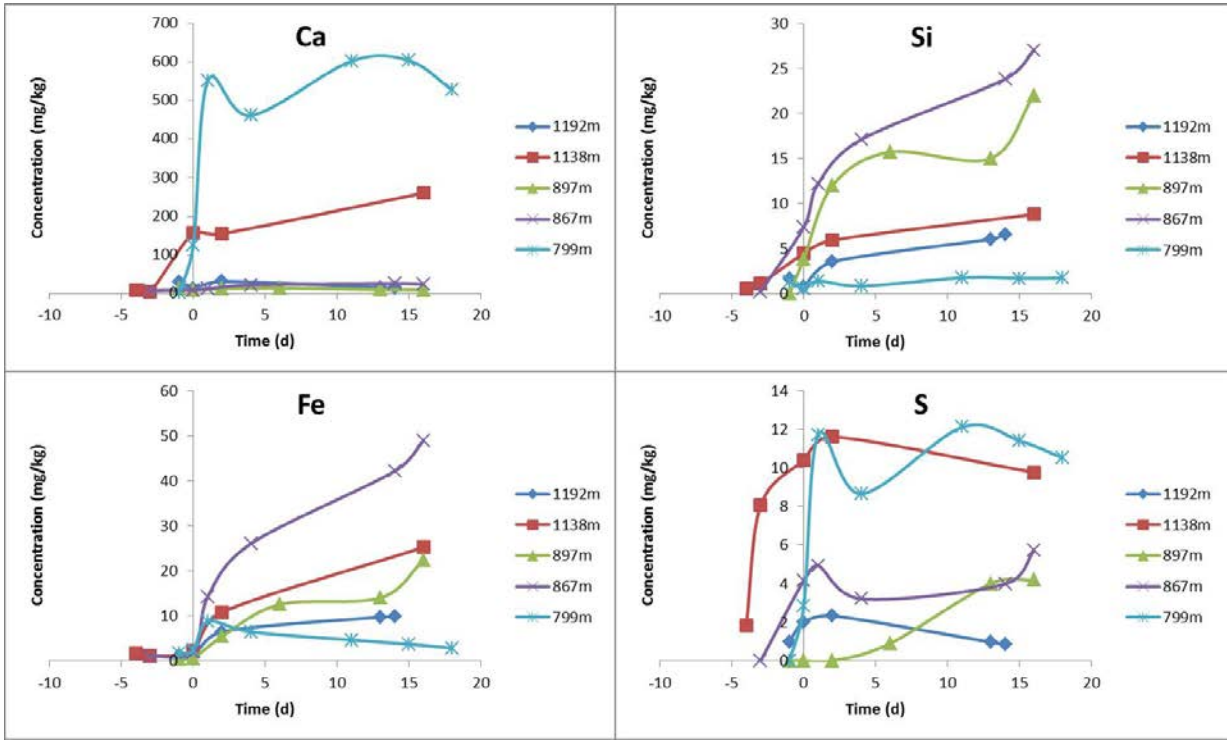


Figure 3: Experimentally measured dissolved Ca, Si, Fe, and S released to solution from mineral dissolution during CO₂-water reaction of rock core from different depths of the Chinchilla 4 well (created from data in Farquhar et al., 2015). CO₂ was injected at time zero. 1192m is a quartzose Precipice Sandstone, 1138m is a feldspar rich Precipice Sandstone, 897m is Evergreen Formation shale, 867m is a feldspar rich Hutton Sandstone, 799m is a calcite cemented Hutton Sandstone.

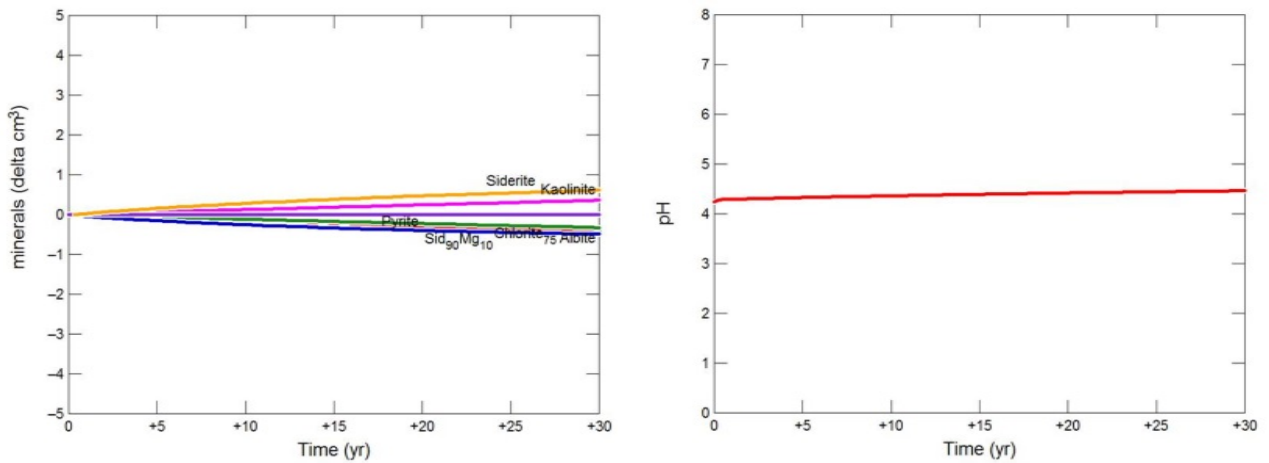


Figure 4: Kinetic geochemical model output for reaction of the Precipice Sandstone 2062.6 m mineralogy with CO₂ for 30 years, with predicted change in minerals (-ve indicates net dissolution), and predicted solution pH. Note Sid₉₀Mg₁₀ is a siderite with Fe:Mg content 9:1.

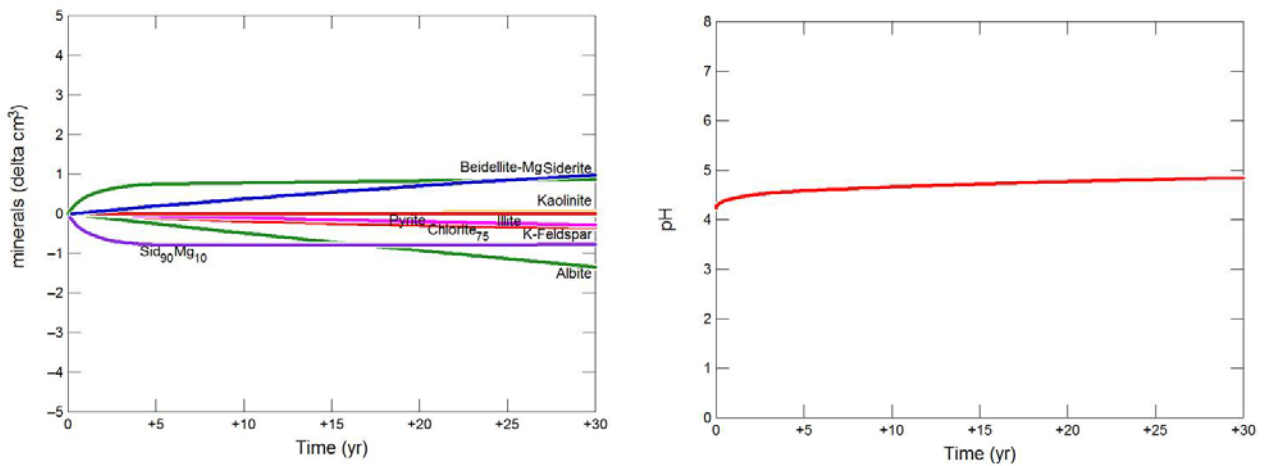


Figure 5: Kinetic geochemical model output for reaction of the Evergreen Formation 2043.1 mineralogy with CO₂ for 30 years, with predicted change in minerals (-ve indicates dissolution), and predicted solution pH. Beidellite is a smectite.

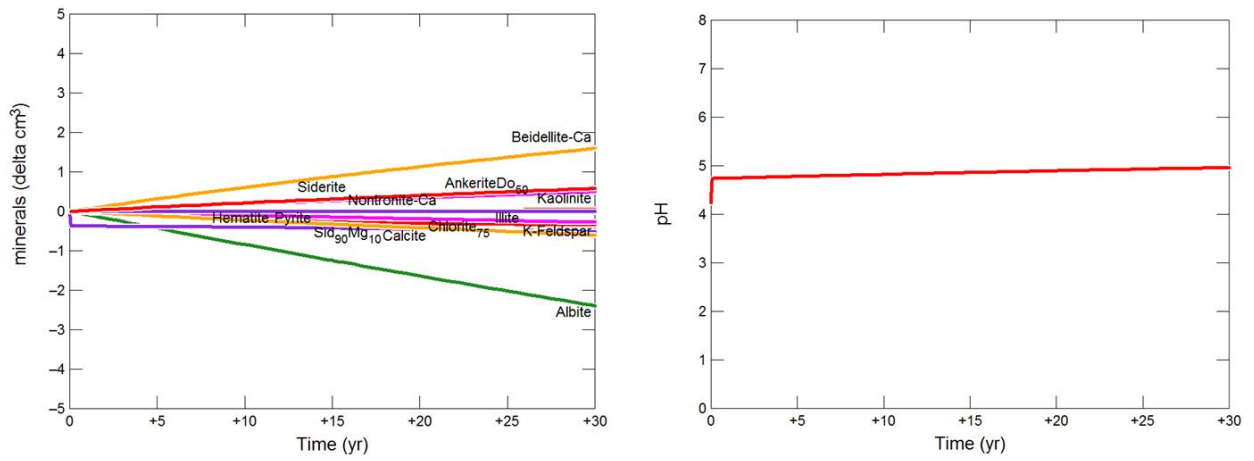


Figure 6: Kinetic geochemical model output for reaction of the Evergreen Formation 1915.4 m mineralogy with CO₂ for 30 years, with predicted change in minerals (-ve indicates dissolution), and predicted solution pH. Note the large apparent change in albite reflects the relatively high albite content. Beidellite and nontronite are smectites.