

Geochemistry of storing CO₂ and NO_x in the deep Precipice Sandstone

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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 more variable, with interbedded low porosity and permeability mudstones, fine-grained sandstones, and calcite cemented zones. Injected CO₂ dissolves into formation water forming carbonic acid. The geochemical reactivity of drill core samples affects the predicted pH and the dissolution or precipitation of minerals which could permanently trap CO₂ as carbonates such as siderite, or dynamically change porosity and permeability altering CO₂ migration.

Comparative kinetic geochemical modelling of the CO₂ reactivity of four representative mineralogies from drill core samples from deeper parts of the central basin indicates that the Evergreen Formation is potentially more reactive to CO₂ than the Precipice Sandstone, especially for calcite or siderite containing zones. In the Precipice Sandstone small amounts of albite and siderite dissolved with traces of siderite and kaolinite precipitated. Dissolution of calcite and siderite in the Evergreen Formation favourably buffered acidity, with predicted precipitated minerals including siderite, kaolinite, ankerite, and smectites. The geochemical models indicate overall changes to porosity are however minor.

Recent data from capture technologies has reported that CO₂ from coal combustion may retain NO_x impurities in the form of NO. Simulations with the addition of 30-100 ppm NO in the CO₂ stream indicated the generated pH in the quartz rich Precipice Sandstone is similar to that on injection of pure CO₂ after 30 years. The precipitation of Fe-rich smectite clays was additionally predicted.

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 a suitable reservoir such as a sandstone formation 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). Precipitation of carbonate minerals such as calcite, siderite or ankerite can favourably permanently trap the injected CO₂. Captured CO₂ streams may contain impurities including N₂, CH₄, NO_x, SO_x or O₂ (Talman 2015). Injection of low purity CO₂ streams has been proposed to potentially decrease the cost of capture through avoidance of installing deSO_x or deNO_x technology in Australia. However, co-injected NO_x, SO_x and O₂ have been shown to have higher reactivity to rock than pure CO₂ when dissolved in formation water (Pearce et al., 2015; Pearce et al., 2016; Turner et al., 2016). Assessing the potential geochemical impacts of these impurity gases is also necessary.

The Surat Basin in Queensland, Australia, has been selected as having a high prospectively for CO₂ storage (Hodgkinson et al., 2010; 2012). The proposed reservoir is the Precipice Sandstone with fresh to brackish formation water, this is 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

Publically available literature including journal publications, industry, agency, and government reports were examined 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 from drill core included quantitative mineral contents by X-ray diffraction (XRD) or QEMSCAN, relative mineral contents from core Hylogger data, and major element content from X-ray fluorescence (XRF), fusion or digestion data. The Cabawin 1 well (150.1905472, -27.4945361) was the deepest, with available quantitative mineralogical data (XRD) for several depth intervals of the Precipice Sandstone, Evergreen Formation and Hutton Sandstone (Grigorescu 2011a). The mineralogy of four representative samples are shown in Figure 1: quartz rich Precipice Sandstone containing siderite (2062.6 m), clay rich Precipice Sandstone (2134.4 m), siderite rich Evergreen Formation (2043.1 m), and clay rich Evergreen Formation containing calcite and siderite (1915.4 m).

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). Since SEM-EDS data was not available from the Cabawin 1 well, available drill cores from wells Chinchilla 4 and West Wandoan 1, located to the north, were used. Figure 2 shows examples of SEM-EDS images from our own work on drill core from the wells Chinchilla 4 and West Wandoan 1. SEM-EDS surveys in back scatter electron mode were performed on drill core blocks with methods published previously (Dawson 2015, Pearce et al., 2015, Pearce et al., 2016). Major minerals in the Precipice Sandstone included quartz and kaolinite, with moderate to minor K-feldspar, albite, chlorite, illite, calcite or siderite/ankerite. Trace amounts of pyrite, Ti-oxides, zircon, and apatite were also observed. In the Evergreen Formation the identities of minerals were similar but with a lower proportion of quartz, and higher proportion of feldspar, clays and carbonate minerals. Plagioclase was generally present as both albite and a Ca-Na-plagioclase in the Evergreen Formation. Trace amounts of pyrite, sphalerite, Ti-oxides and organic matter were also present, along with zircon, and apatite. In EDS analysis of both the Precipice Sandstone and Evergreen Formation chlorite and siderite were both Fe rich but also contained Mg (Figure 2).

The above data, along with knowledge from national and international studies, and especially natural analogue observations (i.e. natural CO₂ accumulations) of dissolution and precipitation was used to constrain models. 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 identify potentially reactive minerals. 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 drill cores (Farquhar et al., 2015). Dissolved Ca concentration is higher on dissolution of calcite from calcite cemented cores, Si is higher from drill cores containing chlorite, Fe is higher from drill cores containing siderite or chlorite, S is also released from drill 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 samples (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 drill core observations previously modified for experimental observations and upscaled for the reservoir scale 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 fluid 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) based on data 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 2062.6 m mineralogy was also run with 30 or 100 ppm NO added to the CO₂. The 2062.6 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. A decrease of 10 °C is based on data from water injection into the Precipice Sandstone.

Predicted reaction of the quartz rich Precipice Sandstone 2062.6 m with dissolved CO₂, resulted in slight dissolution of all minerals but mainly siderite and albite. Precipitation of trace amounts of siderite (mineral trapping) and kaolinite (Figure 4) was also predicted. 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. Kaolinite precipitation was predicted with also siderite precipitation permanently trapping CO₂. 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 2062.6 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 and 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 the Fe-rich smectite nontronite was predicted to precipitate.

CONCLUSIONS

The geochemical reactivity of the modelled Evergreen Formation sample mineralogies from the Cabawin 1 well drill core 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 clogging of pores by clay fines migration 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. 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 stream 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.

Limitations to the results presented here included a lack of detailed data available on drill core from deeper central areas of the Surat Basin. Drill core SEM-EDS, petrography and metal content characterisation is needed in future, along with experimental studies of changes to drill core rock mechanical properties and permeability on CO₂ – formation water reaction.

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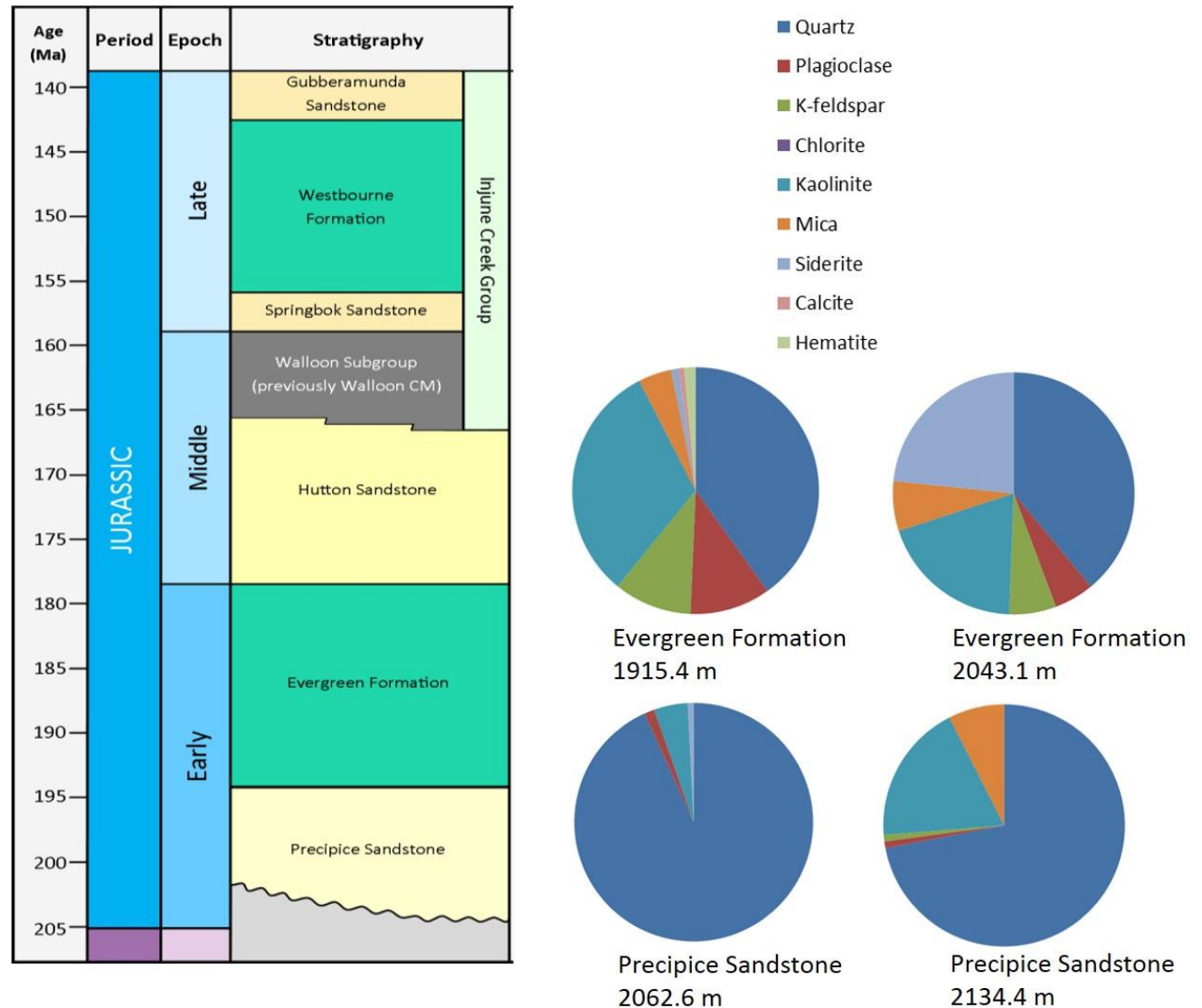


Figure 1: Generalised stratigraphy of the Surat Basin, where the Precipice Sandstone is the proposed storage reservoir, and the Evergreen Formation the proposed seal. Modified from (Farquhar et al., 2015; Pearce et al. 2015). Examples of major minerals in samples from the Cabawin 1 well core (created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

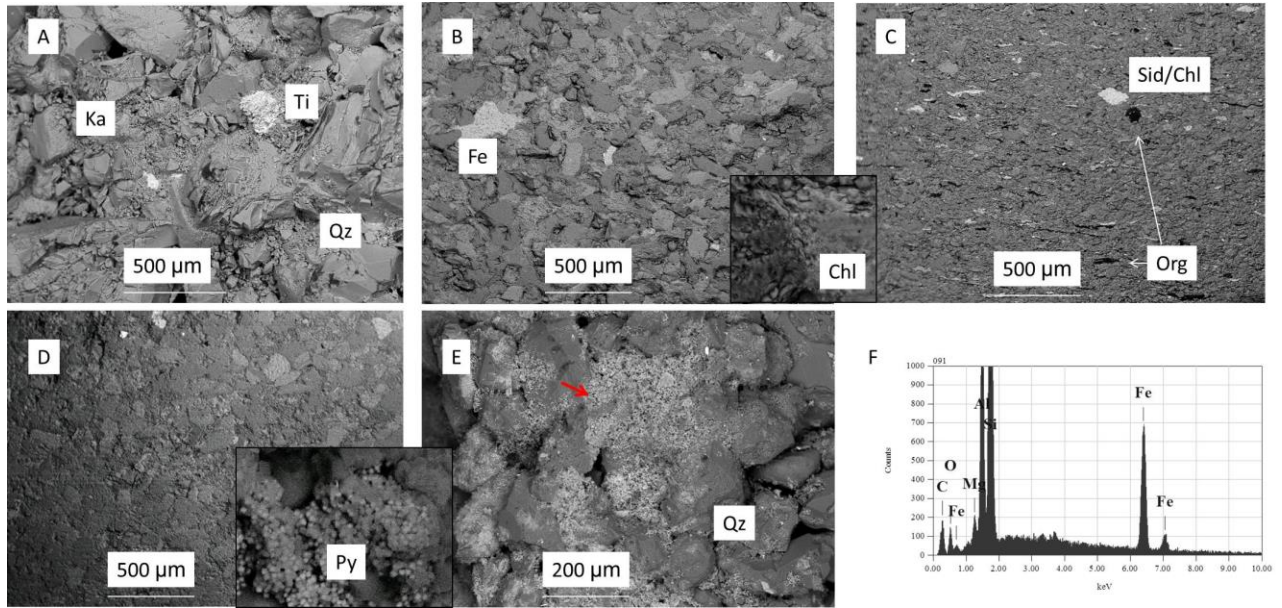


Figure 2: SEM-EDS image examples of minerals, grain size, pores and textures in a) quartzose Precipice Sandstone, b) feldspar rich Precipice Sandstone, inset Fe-rich chlorite (image width 100 μm), c) Evergreen Formation shale, d) Plagioclase rich Evergreen Formation, inset pyrite in Precipice Sandstone (image width 30 μm), e) Fe-rich precipitates (red arrow) on Precipice Sandstone after CO_2 - 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.

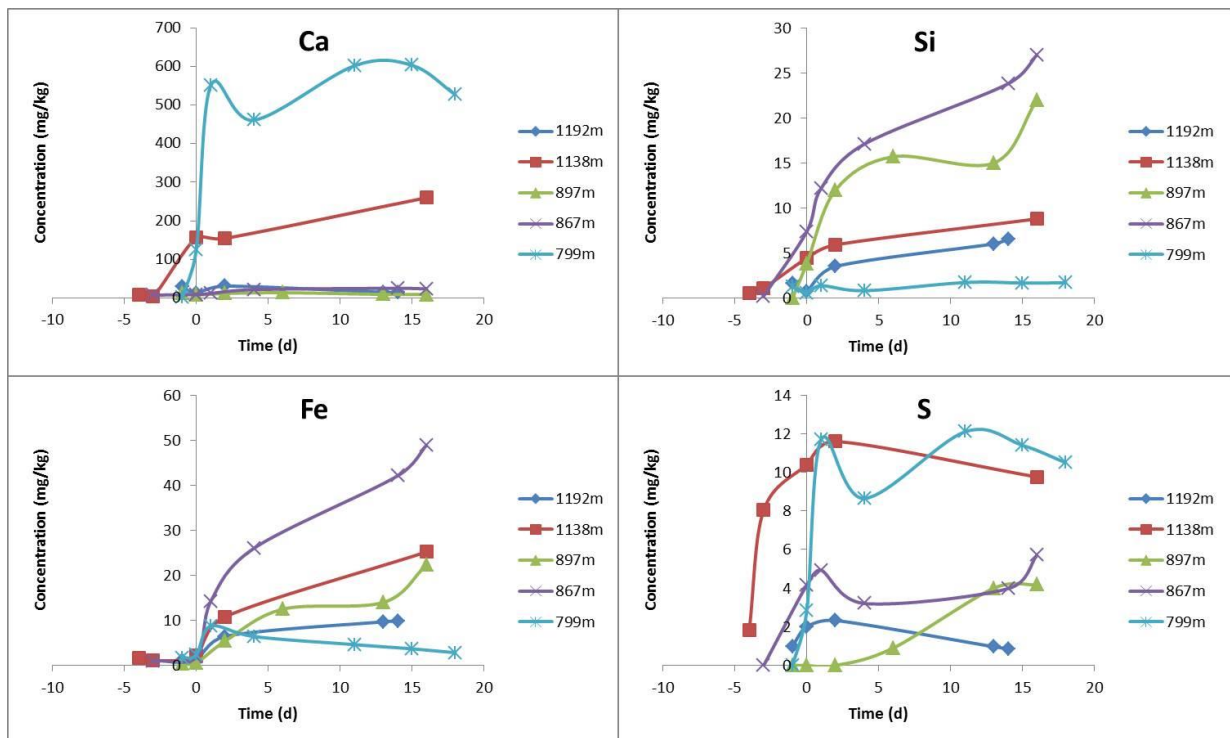


Figure 3: Experimentally measured dissolved Ca, Si, Fe, and S released to solution from mineral dissolution during CO_2 -water reaction of rock core from different depths of the Chinchilla 4 well (created from data in Farquhar et al., 2015). CO_2 was injected at time zero. 1192m is a quartzose Precipice 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.

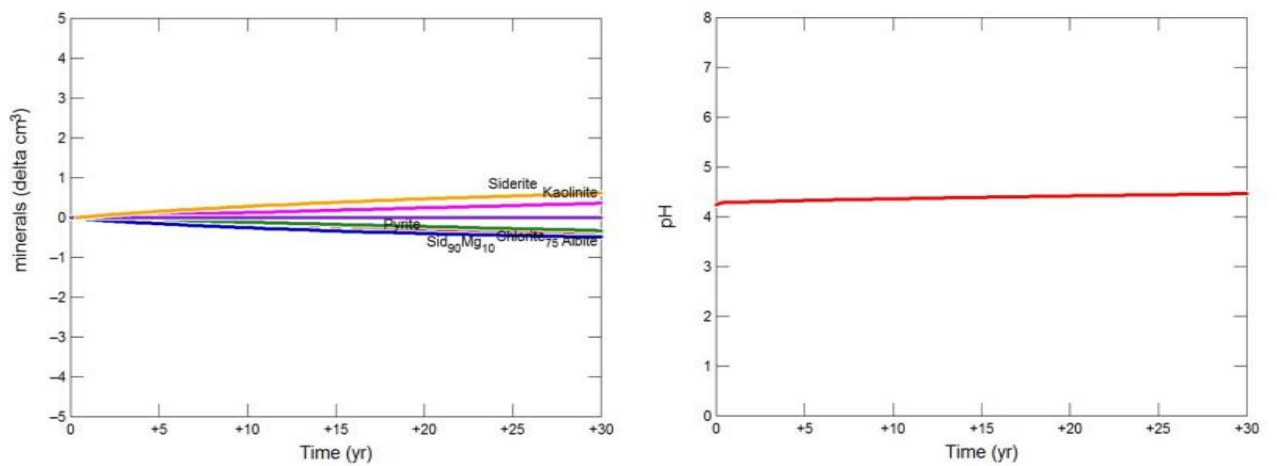


Figure 4: Kinetic geochemical model output for reaction of the Precipice Sandstone 2062.6 m mineralogy with CO₂ for 30 years, with predicted change in minerals (-ve indicates net dissolution), and predicted solution pH. Note Sid₉₀Mg₁₀ is a siderite with Fe:Mg content 9:1.

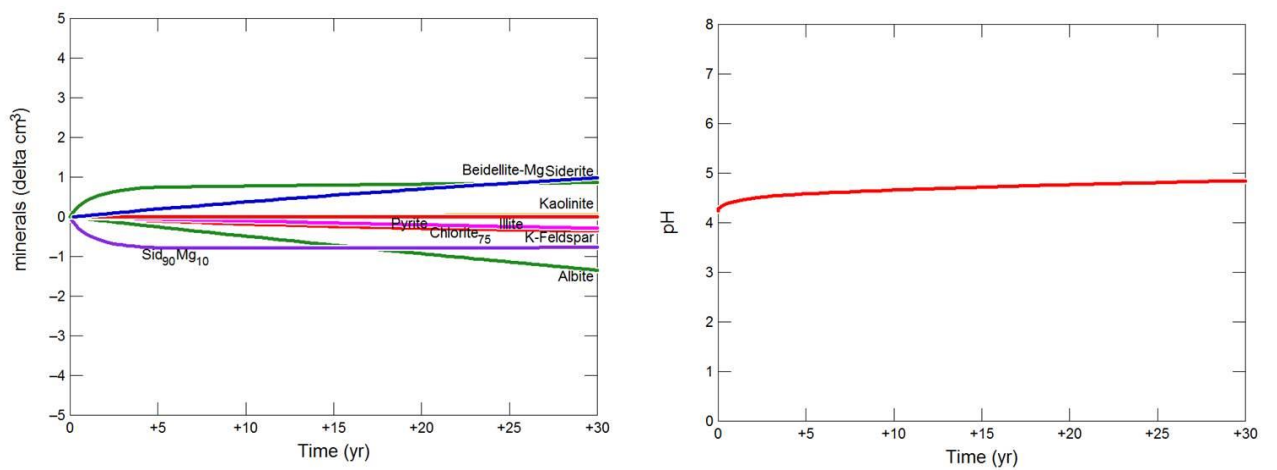


Figure 5: Kinetic geochemical model output for reaction of the Evergreen Formation 2043.1 mineralogy with CO₂ for 30 years, with predicted change in minerals (-ve indicates dissolution), and predicted solution pH. Beidellite is a smectite.

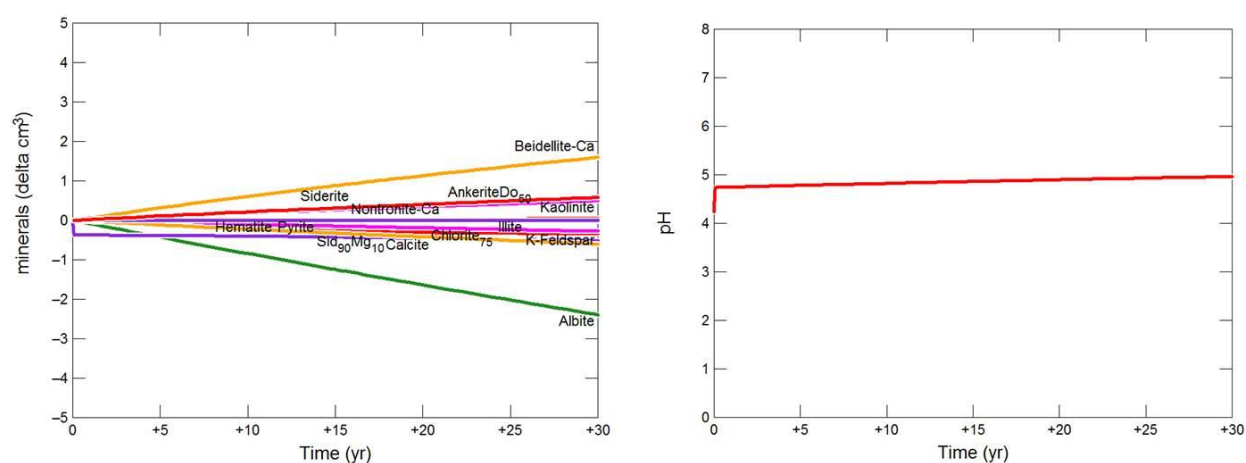


Figure 6: Kinetic geochemical model output for reaction of the Evergreen Formation 1915.4 m mineralogy with CO₂ for 30 years, with predicted change in minerals (-ve indicates dissolution), and predicted solution pH. Note the large apparent change in albite reflects the relatively high albite rock content.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