Assessing geochemical reactivity during CO_2 geological storage: an example from the Surat Basin

J K Pearce
University of Queensland
j.pearce2@uq.edu.au

G K W Dawson
University of Queensland

S D Golding
University of Queensland

D Kirste
Simon Fraser University

G Southam
University of Queensland

D Paterson
Australian Synchrotron

F Brink
Australian National University

V Rudolph
University of Queensland

SUMMARY

CO_2 storage is part of the transition to lower emissions; however, it necessitates a geochemical assessment of potential site-specific impacts. Injected CO_2 will dissolve into formation water and the resulting acidification can induce mineral dissolution and precipitation, alteration of porosity and permeability, or mobilisation of metals to groundwater. Reactivity can depend on several factors including the captured gas stream composition, and mineralogical content. We present a comprehensive assessment methodology with a focus here on understanding metal mobilisation. Drill core samples are characterised for minerals, poro-perm, and for metals via total digestions; sequential extractions; and synchrotron X-ray Fluorescence Microscopy. Drill cores are reacted at reservoir conditions with pure CO_2 and the specific greenhouse gas stream, e.g., CO_2-SO_x-NO_x-O_2. Kinetic geochemical models are then history matched to experimental data that ultimately are inputs to a reactive transport model. The Surat Basin Precipice Sandstone is undergoing feasibility studies as a CO_2 storage reservoir, and an example from a storage site assessment is presented here. The Evergreen Formation is the overlying cap-rock, and the Moolayember Formation underlies the reservoir. The lower Precipice Sandstone is quartz-rich while the upper Precipice Sandstone, and the Evergreen and Moolayember formations are mineralogically diverse with higher feldspar, clay, and carbonate content. Dissolved elements Ca, Mg, Mn, Sr, and Ba increased in experiments from reaction of trace amounts of carbonates. Generally dissolved Fe, Pb, As, Cr, Se increased and subsequently decreased in concentration indicating adsorption and precipitation. Kinetic reaction path modelling demonstrated that carbonate minerals and chlorite are the main minerals reacting. The presence of O_2 and rapid Fe mobilisation results in the precipitation of Fe-oxyhydroxides that act as a sink for Fe and provide new adsorption sites for sequestering a proportion of the trace metals. In the longer term, CO_2 mineral trapping as ankerite at the reservoir-seal interface additionally traps metals.

**Key words:** carbon storage, CCUS, Surat Basin, geochemistry, Bowen Basin.

INTRODUCTION

Carbon dioxide geological storage traditionally involves the injection of a captured CO_2 stream into a suitable reservoir underground such as a deep saline aquifer, depleted oil and gas reservoir or coal seam. In the case we discuss here CO_2 is injected ~1-2 km deep into a sandstone reservoir. A seal or cap-rock complex with low porosity and permeability structurally prevents migration. In Australia several low salinity aquifers have been previously proposed as reservoirs, since these may have other uses in other areas it is important to understand any potential impacts to rock properties or water resources and if these stay within the expected areas. Appraisals for CO_2 storage will be site specific and involve multiple components, this paper focuses on CO_2 rock reactivity aspects.

A demonstration scale CO_2 injection trial was proposed in the Surat Basin in the Glenhaven area near Wandoan for the feasibility of geological storage (Figure 1). More recently larger scale storage is proposed in the southern Surat Basin west of Moonie (that is separate to proposed Moonie oil field EOR/storage). The Precipice Sandstone is the proposed reservoir, the Evergreen Formation is the seal, and the Moolayember Formation underlies the reservoir (Figure 1).
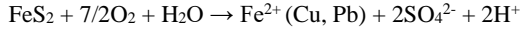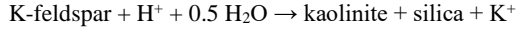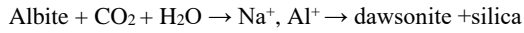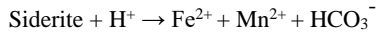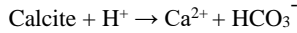
Injected CO_2 dissolves in formation water, and the resulting acidification can induce rock reactions. Industrial captured CO_2 streams can contain other gases e.g. SO_2, O_2, NO_x that can cause higher acidification. Storage hubs may contain a mixture of gas stream compositions e.g. from power plants, blue hydrogen production, direct air capture, cement, steel or ammonia production. Injected CO_2 can dissolve in formation water lowering pH:

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$
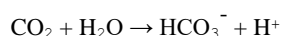
Captured CO_2 impurities such as SO_2, NO_x, O_2 can form stronger acids:

$$SO_2 + H_2O + 0.5O_2 \rightarrow H_2SO_4$$
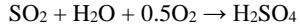
The reaction of minerals including carbonates, silicates and sulphides can result in the release of ions and metals:

$$Calcite + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

$$Siderite + H^+ \rightarrow Fe^{2+} + Mn^{2+} + HCO_3^-$$

$$Albite + CO_2 + H_2O \rightarrow Na^+, Al^+ \rightarrow dawsonite + silica$$

$$K\text{-feldspar} + H^+ + 0.5\,H_2O \rightarrow kaolinite + silica + K^+$$

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} (Cu, Pb) + 2SO_4^{2-} + 2H^+$$

Silicates such as chlorite, anorthite, olivine may dissolve releasing Fe, Ca, Mg etc. these can combine with dissolved CO_2 to form carbonates mineral trapping the CO_2. Mineral reactions have the potential to change rock properties (e,g, strength, porosity/permeability), water quality, trapping of CO_2, and corrode old wellbores etc.
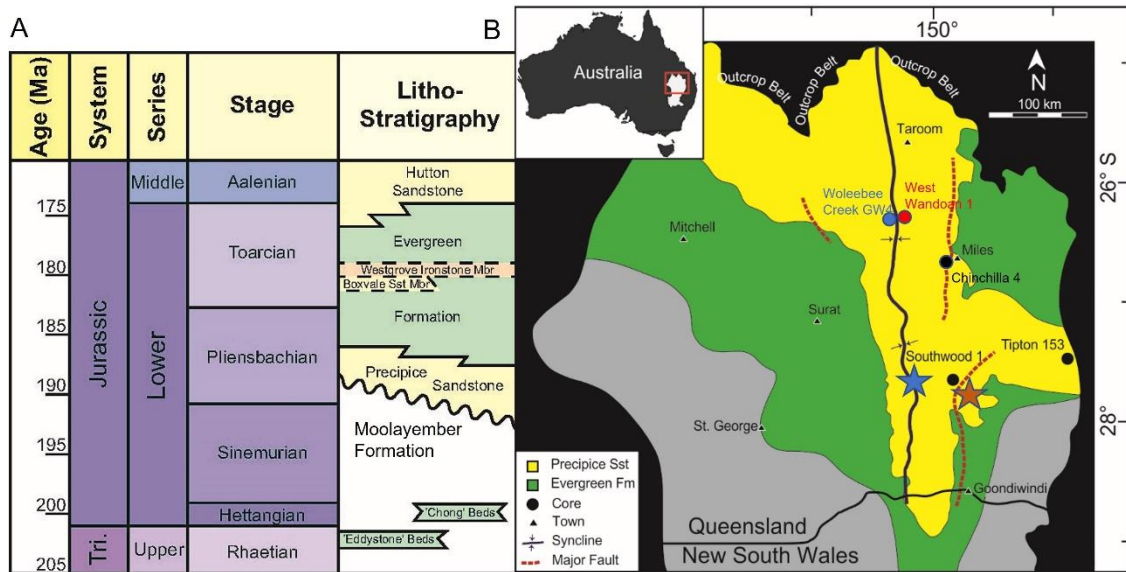

Figure 1. A) Stratigraphy showing the Precipice Sandstone reservoir and overlying Evergreen Formation seals. The Moolayember Formation of the Bowen Basin underlies the Precipice Sandstone. B) Map showing the Surat Basin with the West Wandoan 1, Woleebee Creek GW4, and Chinchilla 4 wells. Stars indicate other potential storage sites. Modified after LaCroix et al., 2019.

DRILL CORE CHARACTERISATION METHODS

Reservoir, seal and basement drill cores from various depths were sampled from the West Wandoan 1, Woleebee Creek GW4 and Chinchilla 4 wells. A wide range of sample depths and lithology types were selected, only a subset are discussed here. Mineral characterisation was performed with X-ray diffraction (XRD), and QEMSCAN (Figure 2, 3, 4). Cores were also subject to total acid digests for rock core total metal content, and sequential extractions of metals loosely bound vs those in carbonates etc. Synchrotron X-ray fluorescence microscopy (XFM) was performed at the Australian Synchrotron on selected thin sections prepared on quartz slides to determine metals in specific mineral phases, with the general methods described previously (Pearce et al., 2021, 2022a,b). Porosity was measured by mercury injection capillary porosimetry (MICP) or by micro-CT (Golab et al., 2015), and permeability with low pressure N_2. Minor mineral compositions and morphologies were surveyed with scanning electron microscopy (SEM-EDS).

CO2-WATER-ROCK EXPERIMENT METHODS

Supercritical CO_2 (SO_x, NO_x, O_2) - water - rock reactions were performed at reservoir conditions in a Parr reaction rig that has been described in detail previously (Pearce et al., 2015). The core sample in a low salinity synthetic formation water was first pressurised with inert N_2 gas at 60°C and 12 MPa to determine the water-rock changes (negative time in Figure 3). Reactors were subsequently pressurised with the gas mixture (time zero in Figure 3). Changes to rock surfaces were detected with SEM-EDS performed before and after the CO_2 reactions. Waters from experiments were sampled during the reactions. Analysis of reaction waters was performed including pH and electrical conductivity. Reaction waters were filtered and acidified with ultra-pure nitric acid and analysed for any dissolved elements and trace metals. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) and inductively coupled plasma-mass

spectrometry (ICP-MS) were preformed at the University of Queensland Centre for Geoanalytical Mass spectrometry (UQ CGMS) Environmental Geochemistry Laboratory (EGL). The characterisation and experimental results were subsequently history matched with kinetic geochemical reaction path modelling predictions using Geochemists Workbench with similar methods to those previously described (Golding et al., 2019; Kirste et al., 2017, 2019; Pearce et al., 2015). Mineral scripts were constructed containing specific metal compositions from the characterisation data. History matched reaction path experiments were then upscaled to the reservoir. The upscaled reaction path models were input to reactive transport models (Golding et al., 2019; Kirste et al., 2017, 2019).

MINERALOGY AND METALS

The lower Precipice Sandstone reservoir is generally quartz-rich with open porosity and minor kaolinite (Figure 2,3,4). Porosity in the West Wandoan 1 lower Precipice Sandstone cores was 13 to 25 %, and 8% in a mudstone layer. The upper Precipice Sandstone and the Evergreen Formation were more diverse with porosity in the range 0.1 to 25 %. These consisted of interbedded sandstones, mudstones and carbonate cemented sandstones and were mineralogically diverse with higher feldspar, clay, and carbonate content (Figure 2,3,4). The Moolayember Formation samples consisted of carbonate cemented (siderite, ankerite, dolomite) sandstones and mudstones with interbedded coals and heavy minerals (Figure 4,5). The different cores contained a wide range of different metal contents and concentrations (Golding et al., 2019). From synchrotron XFM, elements such a Mn were hosted in siderite and chlorite mainly, with Zn in sphalerite mainly, and Ba concentrated in barite (Figure 5). From sequential extractions As was loosely bound, but also observed in XFM hosted in minerals such as sulphides. Pb was concentrated in sulphides and monazite, and also sequential extractions and experiments indicated it was also in carbonate cements.
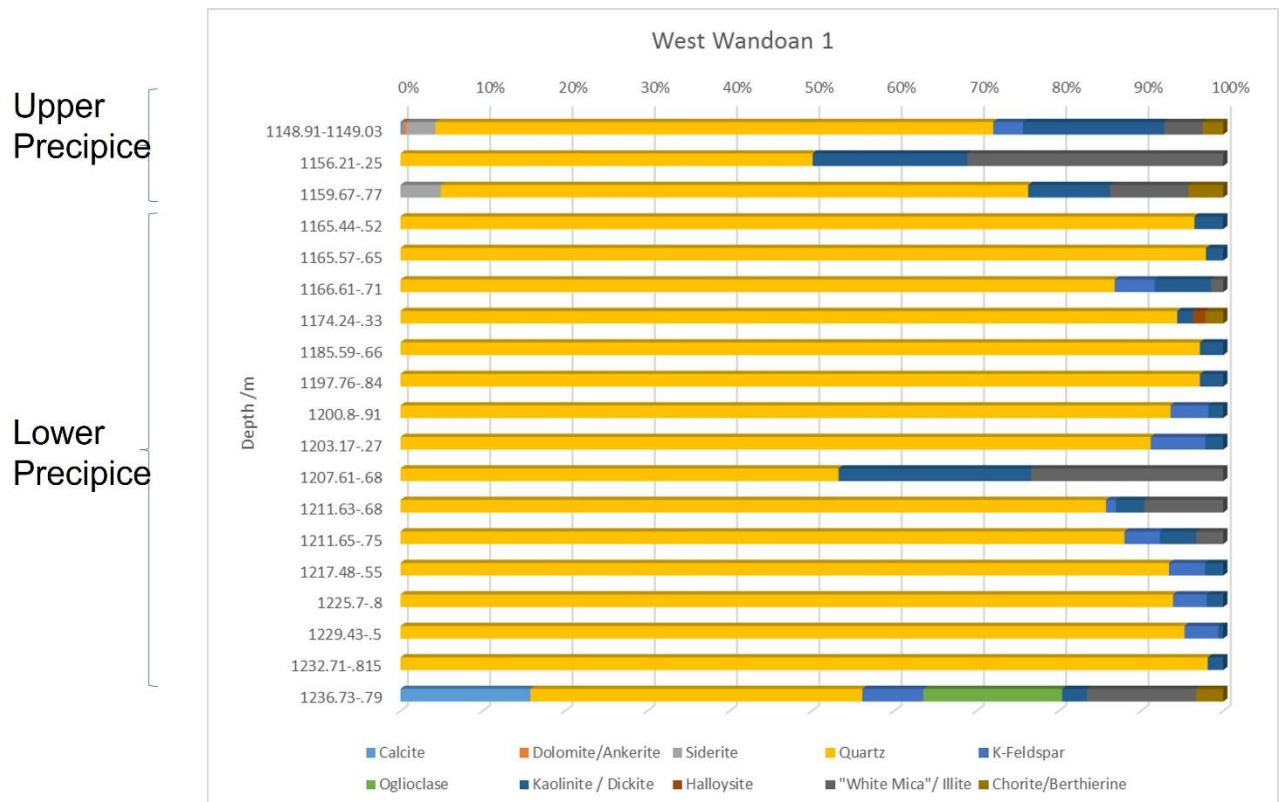

Figure 2. Examples of West Wandoan 1 well lower and upper Precipice Sandstone core mineral content by depth section (m).
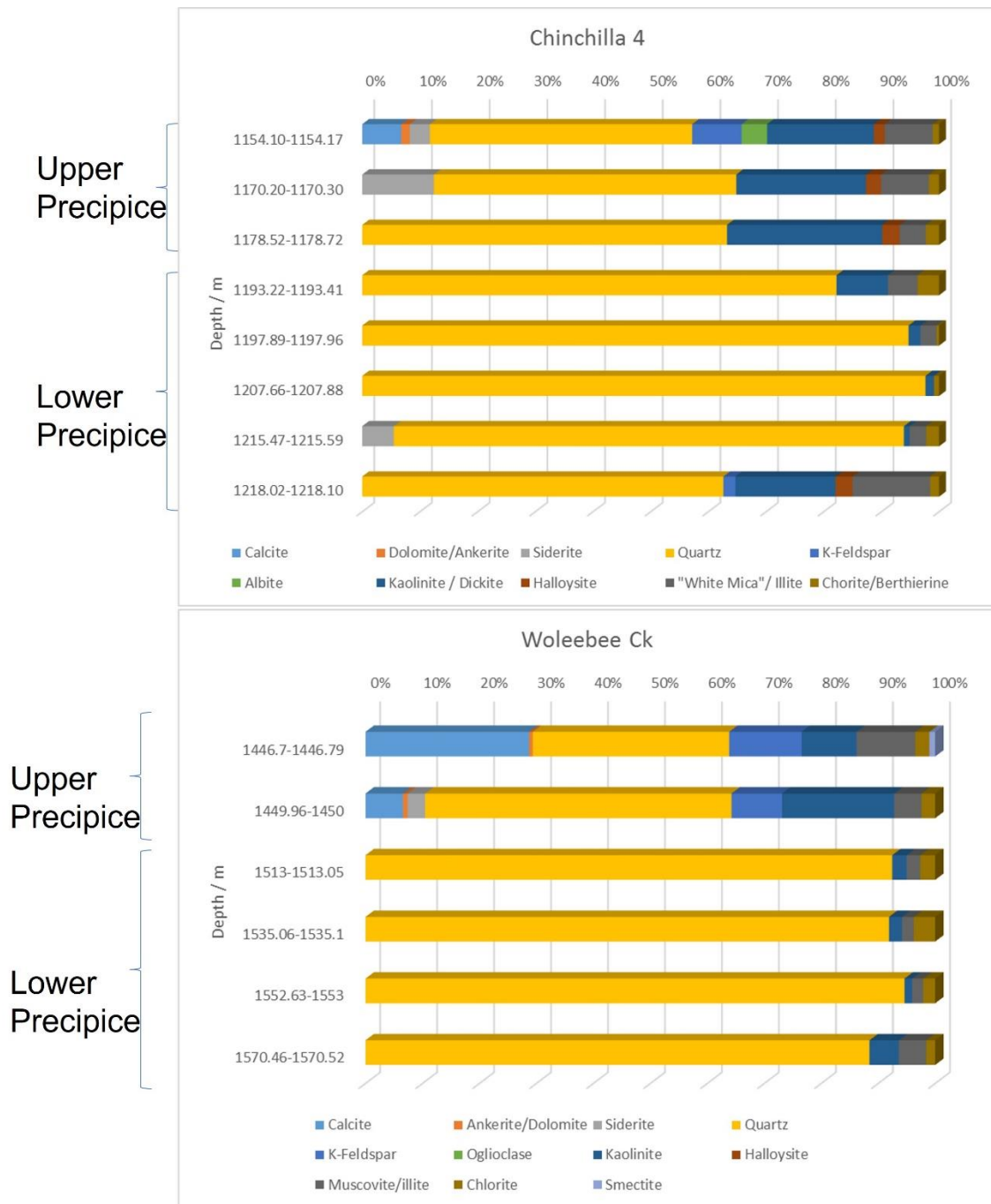
Figure 3. Examples of Chinchilla 4 and Woleebee Creek GW4 well lower and upper Precipice Sandstone core mineral content by depth section (m).

CO₂-SOx-NOx-O₂-WATER-ROCK EXPERIMENTS AND MODELS

Dissolved elements released in experiments were variable with rock mineralogy. Dissolved elements including Ca, Mg, Mn, Sr, and Ba increased in experiments from reaction of carbonate minerals (Figure 6a). Generally dissolved Fe, Pb, As, Cr, Se increased and subsequently decreased in concentration indicating subsequent adsorption and precipitation (Figure 6b-d). In strongly carbonate cemented core the release of metals such as Pb was relatively low. Generally, As was released prior to CO₂ stream injection in experiments from desorption and ion exchange. After reactions SEM showed the dissolution of calcite and siderite (Figure 6e), corrosion of feldspars, chlorite, and sulphides, and movement of clays. In carbonate rich rocks less corrosion of silicate minerals was observed owing to the buffering of pH. Fine-grained Fe-rich iron oxide minerals were precipitated in experiments owing to the presence of O₂. Carbonate cements including calcite and ankerite were also precipitated in some Moolayember Formation reactions. Kinetic reaction path modelling demonstrated that carbonate minerals and chlorite are the main minerals reacting. The presence of O₂ and

rapid Fe mobilisation resulted in the precipitation of Fe-oxyhydroxides that acted as a sink for Fe and provided new adsorption sites for sequestering a proportion of the released trace metals. In the longer term, CO_2 mineral trapping as ankerite at the reservoir-seal interface additionally trapped metals in the reaction transport model, where metal release was restricted to the injected CO_2 plume (Golding et al., 2019; Kirste et al., 2017, 2019).

CONCLUSIONS

- The lower Precipice Sandstone is a suitable quartz rich reservoir that has lower reactivity in terms of dissolution/precipitation of minerals and porosity changes, which is favourable. The lowered pH and dissolution of minor amounts of carbonate, clays and sulphides however contributed in CO_2 stream reaction experiments to initial release of some trace metals. A portion of these subsequently decreased via precipitation of Fe-rich oxide minerals and adsorption.
- In the upper Precipice, Evergreen and Moolayember formations dissolution of calcite and siderite cements, corrosion of feldspars, chlorite, and sulphides occurred in CO_2 stream experiments. Subsequent precipitation of Fe-rich oxides and carbonates re-sequestered metals and CO_2.
- A multi-pronged methodology contributed to the construction of robust geochemical models used in site assessments. Drill core was very variable in mineral content therefore characterisation and experiments on a range of core depths and lithologies was needed to capture heterogeneity.
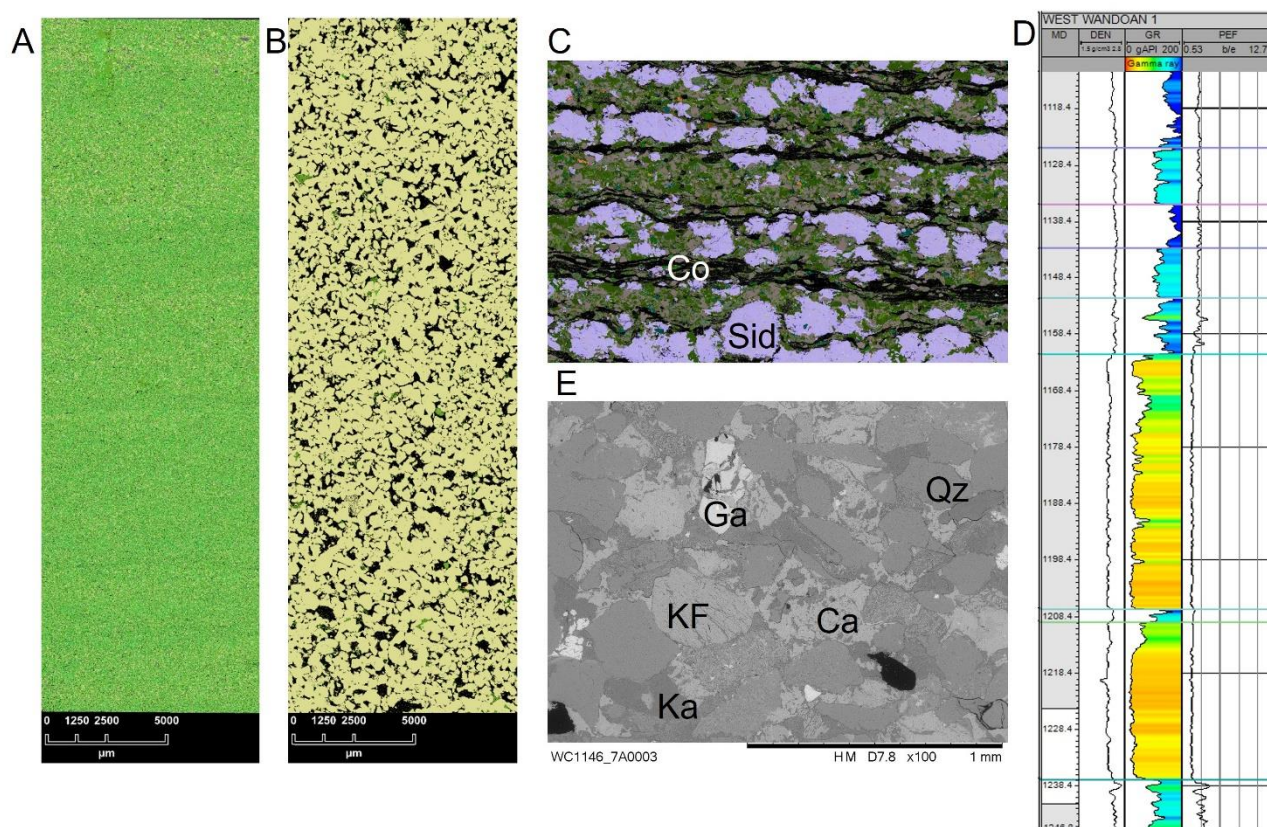

Figure 4. A) QEMSCAN image of an Evergreen Formation seal example of a clay-rich (green) mudstone. B) QEMSCAN image of a Precipice Sandstone reservoir core with quartz grains (yellow) and open porosity (black). C) QEMSCAN image of a Moolayember Formation core example. Siderite cements (purple) and coal (black) are interbedded with clay-rich mudstone. D) West Wandoan 1 well log over part of the Evergreen Formation, Precipice Sandstone and Moolayember Formation. E) SEM image of a calcite cemented Woleebee Creek GW4 well upper Precipice Sandstone sample. Qz = quartz, Ca = calcite, KF = K-feldspar, Ka = kaolinite, Ga = garnet.

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QEMSCAN was performed at the ANU Centre for Advanced Microscopy (CAM). SEM-EDS was also performed at the UQ Centre for Microscopy and Microanalysis.
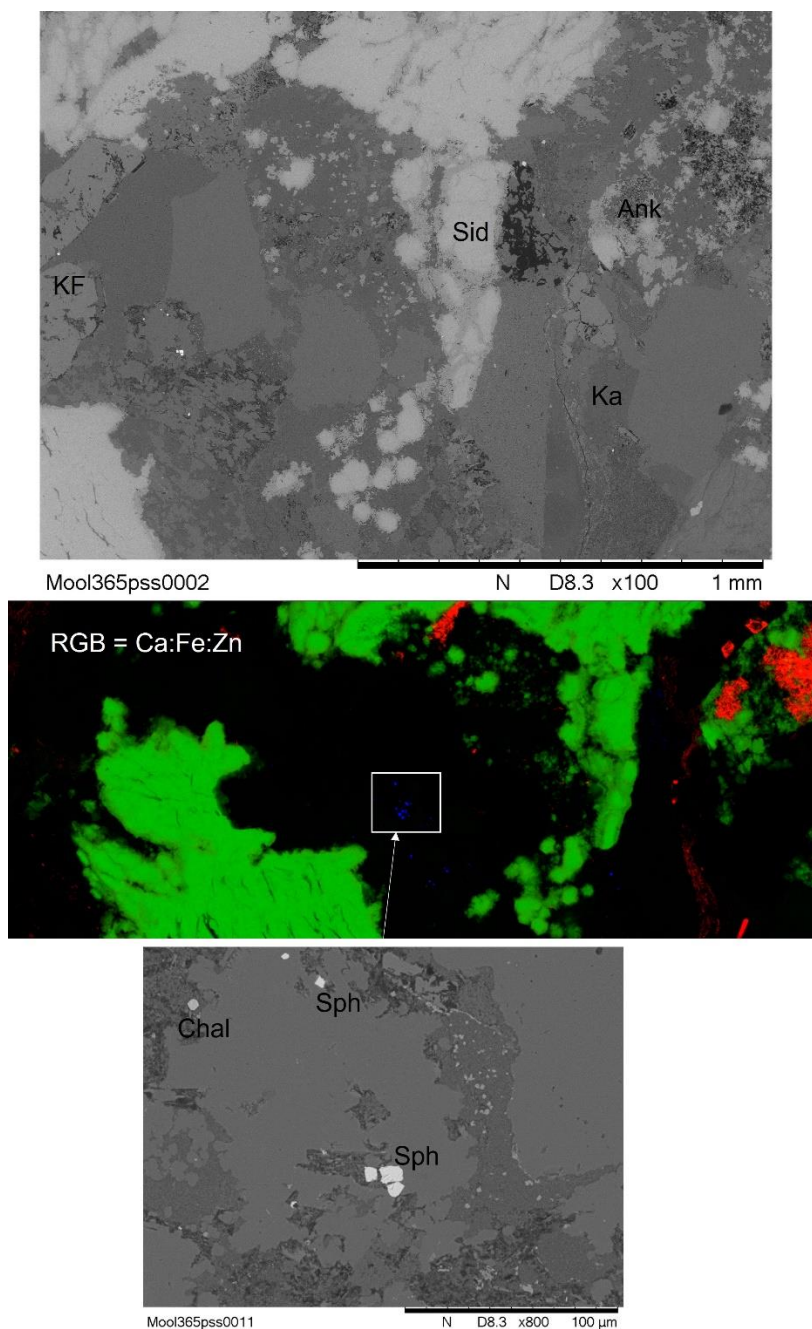

Figure 5. SEM and XFM red:green:blue images of a siderite cemented Moolayember Formation sample. Red = Ca, green = Fe, blue = Zn. Sid = siderite, Ank = ankerite, KF = K-feldspar, Ka = kaolinite, Sph = sphalerite, Chal = chalcopyrite.
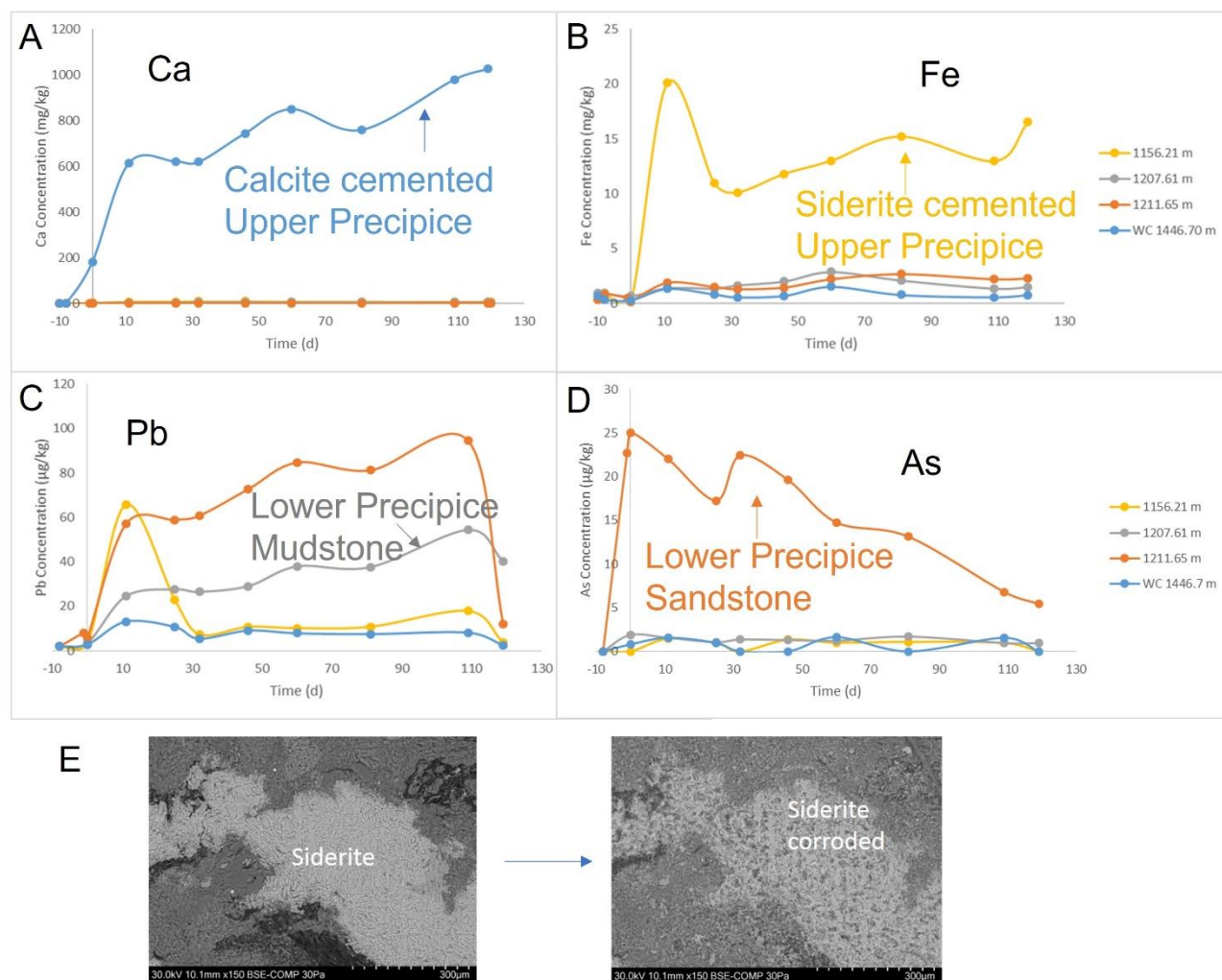
Figure 6. A) to D) Dissolved Calcium (Ca), iron (Fe), lead (Pb) and arsenic (As) during CO₂-SO₂-NO-O₂ water rock reactions of West Wandoan 1 and Woleebee Creek GW4 core. Negative time indicates before CO₂ injection (at time zero). E) SEM image of siderite before reaction, and corroded after reaction.

REFERENCES

Golab, A., Arena, A., Sommacal, S., Goodwin, C., Rajan, P., Dodd, N., Khor, J., Deakin, L., Zhang, J., Young, B., Carnerup, A., 2015. Milestone 2.9: Final report of digital core analysis results for plug samples from West Wandoan-1 Well. FEI-Lithicon, Report for ANLEC R&D.

Golding, S.D., Pearce, J.K., Dawson, G.K.W., Kirste, D.M., 2019. ANLEC Project 7-1115-0236: Mobilisation and Fate of Heavy Metals Released by the GHG Stream, Report for ANLEC R&D.

Kirste, D., Pearce, J., Golding, S., 2017. Parameterizing Geochemical Models: Do Kinetics of Calcite Matter? Procedia Earth and Planetary Science 17, 606-609.

Kirste, D., Pearce, J.K., Golding, S.D., Dawson, G.K.W., 2019. Trace element mobility during CO2 storage: application of reactive transport modelling. E3S Web Conf. 98, 04007.

La Croix, A.D., Wang, J., He, J., Hannaford, C., Bianchi, V., Esterle, J., Undershultz, J.R., 2019. Widespread nearshore and shallow marine deposition within the Lower Jurassic Precipice Sandstone and Evergreen Formation in the Surat Basin, Australia. Marine and Petroleum Geology 109, 760-790.

Pearce, J.K., Kirste, D.M., Dawson, G.K.W., Farquhar, S.M., Biddle, D., Golding, S., Rudolph, V., 2015. SO2 Impurity Impacts on Experimental and Simulated CO2-Water-Reservoir Rock Reactions at Carbon Storage Conditions. Chem. Geol. 399, 65-86.

Pearce, J.K., Brink, F., Dawson, G.W., Poitras, J., Southam, G., Paterson, D.J., Wolhuter, A., Underschultz, J.R., 2021. Core characterisation and predicted CO2 reactivity of sandstones and mudstones from an Australian oil field. International Journal of Coal Geology, 103911.

Pearce, J.K., Dawson, G.W., Southam, G., Paterson, D., Kirste, D., Golding, S.D., 2022a. Metal Mobilization From CO2 Storage Cap-Rocks: Experimental Reactions With Pure CO2 or CO2 SO2 NO. Frontiers in Energy Research 10.

Pearce, J.K., Dawson, G.W., Golding, S.D., Southam, G., Paterson, D.J., Brink, F., Underschultz, J.R., 2022b. Predicted CO2 water rock reactions in naturally altered CO2 storage reservoir sandstones, with interbedded cemented and coaly mudstone seals. International Journal of Coal Geology 253, 103966.