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# Impure $CO_2$ reaction of feldspar, clay, and organic matter rich cap-rocks: Decreases in the fraction of accessible mesopores measured by SANS

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## ABSTRACT

During $CO_2$ geological storage, low porosity and permeability cap-rock can act as a structural trap, preventing $CO_2$ vertical migration to overlying fresh water aquifers or the surface. Clay and organic matter rich shales, fine-grained sandstones and mudstones often act as cap-rocks and may contain substantial sub-micron porosity. $CO_2$-brine-rock interactions can open or close pore throats through dissolution, precipitation or migration of clay fines or grains. This could affect $CO_2$ migration if the porosity is accessible, with unchanging or decreasing accessible porosity favourable for trapping and integrity. Two cap-rock core samples, a clay and organic-rich mudstone and a more organic-lean feldspar-rich fine grained sandstone, from a well drilled for a $CO_2$ storage feasibility study in Australia were experimentally reacted with impure $CO_2$ (+ $SO_2$, $O_2$) and low salinity brine at reservoir conditions. Mercury injection capillary pressure indicated that the majority of pores in both cores had pore throat radii ~ 5–150 nm with porosities of 5.5–8.4%. After reaction with impure $CO_2$-brine the measured pore throats decreased in the clay-rich mudstone core. Dissolution and precipitation of carbonate and silicate minerals were observed during impure $CO_2$ reaction of both cores via changes in water chemistry. Scanning electron microscopy identified macroporosity in clays, mica and amorphous silica cements. After impure $CO_2$-brine reaction, precipitation of barite, Fe-oxides, clays and gypsum was observed. Ion leaching from Fe-rich chlorite was also apparent, with clay structural collapse, and fines migration. Small-angle neutron scattering measured the fraction of total and non-accessible pores (~10–150 nm radii pores) before and after reaction. The fraction of pores that was accessible in both virgin cap-rocks had a decreasing trend to smaller pore size. The clay-rich cap-rock had a higher fraction of accessible pores (~0.9) at the smallest SANS measured pore size, than the feldspar rich fine-grained sandstone (~0.75). Both core samples showed a decrease in SANS accessible pores after impure $CO_2$-water reaction at $CO_2$ storage conditions. The clay-rich cap-rock showed a more pronounced decrease. After impure $CO_2$-brine reaction the fraction of accessible pores at the smallest pore size was ~0.85 in the clay-rich cap-rock and ~0.75 in the feldspar-rich fine-grained sandstone. Reactions during impure $CO_2$-brine-rock reaction have the potential to close cap-rock pores, which is favourable for $CO_2$ storage integrity.

## 1. Introduction

Carbon dioxide storage in siliciclastic reservoirs generally involves injection into a high porosity and permeability "reservoir". Low porosity and permeability overlying cap-rocks or seals, which are generally clay-rich shale, mudstone or siltstone, structurally trap the $CO_2$ preventing or slowing migration (Gaus, 2010). Because $CO_2$ dissolves in formation water to produce carbonic acid, which reacts with some rock forming minerals(Kaszuba et al., 2013), gas-water-rock reactions may increase and subsequently decrease rock porosity; often the clay-rich cap-rock contains minerals that are more geochemically reactive than those in the target reservoir (Farquhar et al., 2015). Over short time periods, mineral dissolution may increase porosity, but over longer time periods, migration of fines and mineral precipitation, including mineral trapping of $CO_2$ as carbonates, may decrease cap-rock porosity or permeability (Higgs et al., 2013; Higgs et al., 2015; Watson et al., 2004).

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Several studies of mineral weathering or natural analogues of $CO_2$ storage have shown porosity decreases through carbonate and clay precipitation, especially at the reservoir-seal interface (Higgs et al., 2013; Navarre-Sitchler et al., 2013). Recently micro computed tomography (CT) has been used as an automated technique to characterise reservoir and cap-rock porosity down to the micron scale (Farquhar et al., 2015; Golab et al., 2015c; Golab et al., 2010; Pearce et al., 2016b; Wunsch et al., 2014). Experimental $CO_2$-water-rock reactions have been shown to result in changes to (micro) CT resolvable porosity, especially through dissolution of calcite cements over the time scale of weeks (Dávila et al., 2016). However micro CT generally does not resolve the estimated 80% of nanometer scale porosity in shales or mudstones (Curtis et al., 2010). Changes in porosity will be most important when pores are open and interconnected or "accessible" to migrating gas and brine; therefore characterising changes to cap-rock accessible pore fraction in the nanometer size range is needed. Small-angle neutron scattering (SANS) with contrast matching can measure both the total and inaccessible pores in the nanometer size region, and has recently been applied to characterising organic matter rich gas shales and sandstones as well as coal (Bahadur et al., 2015; Clarkson et al., 2013; Melnichenko et al., 2012; Ruppert et al., 2013).

$CO_2$ streams injected subsurface from industrial sources such as coal post combustion capture or oxy-fuel firing, cement or steel processing plants may contain ancillary flue gases or impurities including Ar, $N_2$, $CH_4$, $SO_2$, NOx ($NO_2$, NO), $O_2$ (Porter et al., 2015; Talman, 2015). In Australian and UK power plants, the relatively low S and N content of coal means historically desulfurization of flue gas has not been necessary. Co-injecting impurities with the $CO_2$ in geological storage has been suggested to reduce the cost of $CO_2$ capture by avoiding installing deSOx and deNOx technology (Glezakou et al., 2012). Several authors have shown that dissolved $SO_2$, $O_2$ and NOx are more reactive than $CO_2$ to rock through the formation of strong sulphuric and nitric acids (Dawson et al., 2015b; Knauss et al., 2005; Palandri and Kharaka, 2005; Pearce et al., 2015a; Pearce et al., 2015b). However, relatively few studies have investigated the impacts of impurity gases (Gaus, 2010). Co-injection of $SO_2$ (and $O_2$) with $CO_2$ has been predicted in geochemical modelling studies and observed in laboratory experiments to result in the precipitation of sulphate and oxide minerals, e.g. hematite or gypsum/anhydrite (Lu et al., 2014; Pearce et al., 2016b; Shao et al., 2014; Xu et al., 2007). Co-injection has the potential to plug pores and decrease accessible porosity effectively self-sealing the cap-rock. The precipitation of Fe-oxides, sulphides, and sulphates such as gypsum or anhydrite with carbonate minerals and clays, has been observed in natural analogue studies of $CO_2$ accumulation and leakage. For example, gypsum, hematite and pyrite precipitation has been reported in fractures at a natural $CO_2$ accumulation in Green River, Utah (Chen et al., 2016; Kampman et al., 2014; Wigley et al., 2012). Chopping and Katzuba have shown that anhydrite and pyrite precipitated in pore space and fractures in the presence of natural supercritical $CO_2$ and dissolved sulphate and sulphide in the Madison Limestone, Wyoming (Chopping and Kaszuba, 2012; Kaszuba et al., 2011).

The Evergreen Formation overlies the Precipice Sandstone, a proposed low salinity $CO_2$ storage reservoir in the Surat basin, Queensland, Australia (Fig. 1) (Farquhar et al., 2013; Hodgkinson and Grigorescu, 2012). The Evergreen Formation, the storage cap-rock, consists of quartzoze sandstone interbedded with siltstone, shale and carbonaceous mudstone of variable porosity and permeability, with reported average porosity 15 ± 6%, and average horizontal permeabilities of 87 ± 246 mD (Kellett et al., 2012). Several cores from the GSQ Chinchilla- 4 well and West Wandoan 1 well were recently determined to have porosities in the range 4.6–21.5% and permeabilities of $< 0.1$ mD (Farquhar et al., 2015; Golab et al., 2015c).

The purpose of this study was to determine if pores in cap-rock cores from a well drilled for a $CO_2$ storage feasibility study in the Surat Basin, Australia, become opened or closed through the interaction with impure $CO_2$–brine. Small angle neutron scattering was used to determine the change in accessible pores before and after reaction with impure $CO_2$ (+ $SO_2$ and $O_2$) and low salinity brine at reservoir conditions. Complementary scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), mercury injection capillary pressure (MICP), and experimental water chemistry aid interpretation by detecting mineral habit, macroporosity, mesoporosity, mineral dissolution or precipitation and physical rock changes.

## 2. Materials and methods

Two whole core depth sections of the Jurassic Evergreen Formation from the West Wandoan 1 well, Surat Basin, Queensland, Australia, were sampled at depths of 1043.70–1043.77 m and 981.24–981.31 m (well position: latitude − 26.181622, longitude 149.812422). The well core has been described elsewhere (Golab et al., 2015a). An interlaminated black carbonaceous silty mudstone and very fine-grained sandstone was selected from 981.24 m (referred to as 981 m) with additional adjacent samples collected for additional analyses. The core at 1043.70 m depth (referred to as 1043 m), a fine-grained sandstone with mud rip-up clasts, was also sampled, and exhibited a courser grain size than the 981 m core and was plagioclase feldspar rich. Petrography of the cores has been detailed elsewhere (Dawson et al., 2015a).

The mineralogy of the core samples 981 m and 1043 m is shown in Table 1 from data reported previously (Dawson et al., 2015a; Golab et al., 2015b; Golab et al., 2015c). SEM-EDS performed in this study confirmed that Fe-rich, Mg-poor chlorite was present in both samples. Organic matter and minerals present in minor to trace amounts identified in SEM-EDS include, apatite, Ti-oxide, monazite, zircon, barite, sphalerite, and calcite/ankerite ± Mn. Petrography of the same core section reported elsewhere also identified Fe-oxides (Dawson et al., 2015a). Sample 981 m contained a higher amount of organic matter than 1043 m as indicated by the higher loss on ignition (LOI) (Table 1) (Ross and Bustin, 2009).

In the Evergreen 1043 m sub-sample minor to trace components observed in SEM-EDS performed in this study include organic matter (visibly less than Evergreen 981 m), barite, monazite, apatite, zircon, Ti-oxide, sphalerite and pyrite. EDS confirmed the presence of Fe-rich, Mg-poor chlorite. XRD reported elsewhere detected the presence of $\sim < 5\%$ illite and Fe-oxides (Dawson et al., 2015a).

The core samples 1043 m and 981 m were reacted in a batch reactor system at reservoir in situ conditions of 60 °C and 12 MPa for 28 days. Core sub-samples were immersed in 100 ml of 1500 ppm NaCl low salinity brine and pressurised with an inert gas, $N_2$, for 4 days to equilibrate the rock and fluid and provide baseline water samples. A 1500 ppm NaCl low salinity brine was used to replicate a simplified formation water representative of the injection reservoir (Hodgkinson and Grigorescu, 2012). Subsequently, the $N_2$ was depressurised and a gas mixture consisting of 0.2% $SO_2$, 2% $O_2$ and a balance of 97.8% $CO_2$ was injected into the reactors. The reactions then proceeded for 28 days. This gas mixture is representative of an average possible gas stream from oxyfuel capture (Talman, 2015). The gas stream composition planned to be injected in the field was not known at the time of this study, but is now expected to contain lower concentrations of impurity gases. The batch reactors were based on unstirred Parr reactors with thermoplastic liners to prevent fluid corrosion, the reactor design has been described in detail elsewhere (Pearce et al., 2016a; Pearce et al., 2015a). Virgin and reacted core samples, designated as 1043 m and 981 m, and 1043 mR and 981 mR respectively, were prepared for SANS measurements by hand polishing subsplit core samples to 15 mm width discs on the face perpendicular to the bedding plane. Discs were polished to 1 mm thickness ± 0.2 mm. SEM-EDS images were obtained for pre and post reaction samples. Pre and post reaction images were obtained in the same position where possible on reacted unpolished blocks to directly identify dissolution or precipitation of minerals. SEM-EDS was also performed on the polished discs to identify minor mineral phases, organic matter, mineral habit and visible porosity (JEOL