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# **Fluid flow and CO<sub>2</sub>-fluid-mineral interactions during CO<sub>2</sub>-storage in sedimentary basins**

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## **Abstract**

Modelling the progress of geochemical processes in CO<sub>2</sub> storage sites is frustrated by uncertainties in the rates of CO<sub>2</sub> flow and dissolution, and in the rates and controlling mechanisms of fluid-mineral reactions that stabilise the CO<sub>2</sub> in geological reservoirs. Dissolution of CO<sub>2</sub> must be controlled by the complexities of 2-phase flow of CO<sub>2</sub> and formation brines and the smaller-scale heterogeneities in the permeability in the reservoirs which increase the fluid contact areas. The subsequent fluid mineral reactions may increase storage security by precipitating CO<sub>2</sub> in carbonate minerals but the consequences of fluid-mineral reactions on caprock rocks or potential leakage pathways up fault zones are less certain as the CO<sub>2</sub>-charged brines may either corrode minerals or decrease permeabilities by precipitating carbonates.

Observations from CO<sub>2</sub>-injection experiments and natural analogues provide important constraints on the rates of CO<sub>2</sub> and brine flow and on the progress of CO<sub>2</sub> dissolution and mineral-fluid reactions. In these experiments brines in contact with the propagating plume appear to rapidly saturate with CO<sub>2</sub>. Dissolution of the CO<sub>2</sub> drives the dissolution of oxide and carbonate minerals, on times scales of days to weeks. These reactions buffer fluid pH and produce alkalinity such that carbonate dissolution moves to carbonate precipitation over time-scales of weeks to months. The dissolution of Fe-oxide grain coatings and the release of Fe to solution is important in stabilizing insoluble Fe-Mg-Ca carbonate minerals but the rate limiting step for carbonate mineral precipitation is the transport of CO<sub>2</sub>-charged brines and silicate mineral dissolution rates. Observations from CO<sub>2</sub>-EOR experiments and natural analogues suggest that the silicate mineral dissolution reactions are initially fast in the low pH fluids surrounding the CO<sub>2</sub> plume but that reaction progress over months to years drives minerals towards thermodynamic equilibrium and dissolution rates slow over 2-5 orders of magnitude as equilibrium is approached. The

sluggish dissolution of silicate minerals is likely to preside over the long-term fate of the CO<sub>2</sub> in geological reservoirs. Observations from injection experiments and natural analogues suggest that the potentially harmful trace elements mobilized by the drop in pH are immobilized as adsorbed and precipitated phases as fluid pH is buffered across mineral reaction fronts.

There are very few observations of caprock exposed to CO<sub>2</sub>-rich brines. Preliminary examination of core recently recovered from scientific drilling of a natural CO<sub>2</sub> accumulation in Utah suggests that the diffusion of CO<sub>2</sub> into reservoir caprocks drives dissolution of Fe-oxides but subsequent precipitation of carbonate minerals likely retards the diffusion distance of the CO<sub>2</sub>. At this site thin siltstone layers are shown to be effective seals to the CO<sub>2</sub>-charged fluids, which has significant implications for the long term security of CO<sub>2</sub> in geological reservoirs.

## 1 Introduction

Carbon capture and storage equipped power generation from fossil fuels needs to form a significant fraction of new power generation capabilities by 2035 to satisfy global energy needs while limiting the rise in atmospheric CO<sub>2</sub> and mitigating potential climate instabilities (Metz et al., 2005). Such geological storage in saline aquifers and depleted oil and gas reservoirs represents a practical and safe method of CO<sub>2</sub> disposal as demonstrated by the several current large-scale injection programs (e.g. Hosa et al., 2011) and the retention of CO<sub>2</sub> in natural geological reservoirs for millions of years (e.g. Zhou et al., 2012). Secure long-term storage in geological reservoirs must be demonstrated to satisfy operational and regulatory criteria, public acceptance, and auditing of carbon credits for the stored CO<sub>2</sub>. Regulation requires, for example, ‘that the stored CO<sub>2</sub> will be completely and permanently contained’ (EU DIRECTIVE 2009/31/EC). Uncertainty over the security of storage is seen as a major risk factor which has significant impact on the overall costs (e.g. DECC (UK Department of Energy and Climate Change), 2012).

Geological carbon storage involves separating CO<sub>2</sub> at power stations or other industrial plants, compressing it and injecting it into permeable strata at depths where it remains in a dense supercritical state (Fig. 1). Previously exploited oil and gas fields and saline aquifers offer the most storage potential (Hendriks et al., 2004). Injection into, and reaction with, basaltic or peridotitic rocks is also being explored as alternative sites in appropriate settings, where the CO<sub>2</sub> is often pre-dissolved in water prior to injection (e.g. Newark, Assayag et al., 2009; CarbFix, Gislason et al., 2010; Keleman & Matter, 2008). At the pressure and temperatures in most potential storage sites, the CO<sub>2</sub> is less dense than formation brines and will rise. Secure storage therefore requires that the CO<sub>2</sub> is trapped under an impermeable caprock. Major concerns include; 1) that the CO<sub>2</sub> may exploit permeable pathways such as faults to escape upwards; 2) the acid fluids formed when the CO<sub>2</sub> dissolves

in formation brines may corrode caprocks or fault seals, allowing CO<sub>2</sub> to migrate upwards; 3) changes in stress related to injection may fracture caprocks; 4) carbonate mineralization in faults and fractures may generate stresses by the force of crystallization, inducing leakage; 5) migrating CO<sub>2</sub>-charged brines might mobilise trace metals and organic compounds and contaminate overlying potable aquifers; 6) displacement of brines distant from the injection site may contaminate overlying aquifers and; 7) CO<sub>2</sub> storage reservoirs will be hard to monitor to verify that the stored CO<sub>2</sub> remains in place.

Several processes may act to further stabilise the CO<sub>2</sub> trapped by geological structures (Fig 2; Metz et al., 2005). In residual trapping, between 10 and 35% of the pore space is occupied by CO<sub>2</sub> after a CO<sub>2</sub> plume has passed, held immobile by capillary forces (Bachu and Bennion, 2009). The fraction of CO<sub>2</sub> so trapped depends both on the magnitude of the residual CO<sub>2</sub> saturation and on the volume of the reservoir swept by the CO<sub>2</sub> plume (Hesse et al., 2008). Dissolution trapping occurs as CO<sub>2</sub> dissolves into formation brines and is facilitated by large brine-CO<sub>2</sub> contact surface areas, the negative buoyancy of CO<sub>2</sub>-saturated brine and density driven convective mixing. Ionic trapping of dissolved CO<sub>2</sub> as bicarbonate ions and its subsequent trapping as precipitated carbonate minerals result from reaction between CO<sub>2</sub>-bearing brines and the reservoir rock and are therefore dependent on the rates of dissolution trapping, on the flow paths of the CO<sub>2</sub>-saturated brines and on the kinetics of subsequent fluid-mineral reactions.

There are a number of potentially significant consequences of fluid-mineral reactions.

1) The rapid mineral dissolution, especially of carbonates, may corrode caprocks, wellbores and fault seals, potentially leading to migration of CO<sub>2</sub> into overlying formations, 2) carbonate precipitation in caprocks may reduce their permeability, stabilising storage, 3) mineral dissolution or precipitation in reservoirs may alter the permeability and the flow of CO<sub>2</sub> and CO<sub>2</sub>-saturated brines and 4) sequestration of CO<sub>2</sub> into carbonate minerals may

contribute to the long-term storage security. The general impacts of CO<sub>2</sub>-injection on fluid-rock reactions are reviewed in Gaus (2009).

The nature and especially the rates of the geochemical processes in CO<sub>2</sub> storage reservoirs are very poorly constrained. This arises from a combination of factors: 1) there are a limited number of anthropogenic CO<sub>2</sub> injection experiments and their short duration, combined with the difficulty of observing dissolution and mineral reactions and the sluggish nature of these reactions, results in a very limited observational data base. 2) A key process, the rate of dissolution of CO<sub>2</sub> in the brine, will be strongly moderated by reservoir heterogeneities on scales less than ~ 10 m which is below that resolvable by remote observation. 3) The kinetics of fluid-mineral reactions are often not well known and there are order-of-magnitude discrepancies between reaction rates determined in the laboratory and those recovered from natural field settings (e.g. White and Brantley, 2003). 4) Monitoring the progress of CO<sub>2</sub> dissolution by direct sampling of CO<sub>2</sub>-rich fluids is complicated by the limited sampling opportunities and CO<sub>2</sub> degassing as samples are collected.

In this paper we review the state of knowledge of these fluid flow and geochemical processes and how understanding of these processes might be improved. Theoretical modelling of the flow of CO<sub>2</sub> and brine in potential CO<sub>2</sub> storage sites combined with prediction of the nature and rates of fluid-fluid and mineral-fluid reactions from laboratory experiments and imaging of two-phase flow in rock core provide a framework in which to evaluate the observations from field sites. These predictions are compared with the results of completed or on-going CO<sub>2</sub> injection experiments and studies of natural analogues. In particular we focus on the results from small scale CO<sub>2</sub>-injection experiments at Frio, Texas and on-going CO<sub>2</sub>-EOR projects in Canada and the USA and present initial results from our work on a CO<sub>2</sub>-EOR project (Salt Creek, Wyoming). We present preliminary results from scientific drilling of a natural CO<sub>2</sub> accumulation at Green River, Utah. An important

conclusion of the work is that monitoring the geochemical evolution of brines provides a unique set of constraints on the complex interactions of CO<sub>2</sub> flow, fluid-fluid and fluid-mineral reactions in the reservoirs. We conclude that, if these processes, including the critical impact of small scale heterogeneities on flow and reaction in the reservoirs, are to be quantified it will be essential to carry out additional experiments to sample, analyse and model the geochemical evolution of the brines.

## **2 Modelling of Flow and Reaction**

### **2.1 Flow and dissolution of CO<sub>2</sub> in brine**

The progress of fluid-fluid and fluid-rock reactions in geological storage sites will critically depend on the flow of CO<sub>2</sub> in the reservoir and the dissolution of CO<sub>2</sub> into formation brine and flow of the CO<sub>2</sub>-rich brines. CO<sub>2</sub> has limited solubility and is therefore immiscible in formation brines, and is typically the non-wetting phase. Its flow is therefore dependent on the complex multiphase flow properties of the reservoir rocks. Important consequences of such multiphase flow are (Jacob, 1972): 1) that the injected CO<sub>2</sub> will only occupy a fraction of the pore space depending on the pore structure, capillary pressure and flow dynamics, 2) the effective permeability of the formation to CO<sub>2</sub> reduces rapidly with decreasing saturation of the CO<sub>2</sub> ('relative permeability'), 3) caprocks with very small pores and permeabilities will have high capillary entry pressures, increasing their effectiveness as seals (Bildstein et al., 2010), 4) where brines replace a migrating CO<sub>2</sub> plume a significant fraction of the CO<sub>2</sub> remains trapped in the porosity by capillary forces (Hesse et al., 2008) and 5) formation pressures and two phase flow effects in less permeable reservoirs may require injection pressures sufficiently high so as to induce brittle deformation facilitating CO<sub>2</sub> escape (Rutqvist et al., 2007).

Supercritical CO<sub>2</sub> at reservoir conditions is less dense and an order-of-magnitude less viscous than brines. The flow of supercritical CO<sub>2</sub> into brine filled pore-space will depend on

capillary pressure and phenomena related to the relative permeability of brine filled pores to CO<sub>2</sub> and the brine-CO<sub>2</sub> viscosity contrast and interfacial tension (Fig 3; e.g. Bachu and Bennion, 2008). Generally, the brine-CO<sub>2</sub> viscosity contrast and CO<sub>2</sub>-brine interfacial tension decrease with increasing pressure, and increase with increasing temperature and salinity such that a given brine-saturated rock becomes more permeable to CO<sub>2</sub> at higher pressures, or lower temperatures and salinity (Bachu and Bennion, 2009). These relative permeability phenomena strongly influence the amount of residual CO<sub>2</sub> trapping; with higher permeability to CO<sub>2</sub> tending to lead to higher residual CO<sub>2</sub> saturation and greater amounts of residually trapped CO<sub>2</sub>. However, these multiphase flow processes are complex and this description is a simplified one, and ultimately the overall amount of residually trapped CO<sub>2</sub> will be dependent on the macroscopic structure of the growing CO<sub>2</sub> plume.

Injected CO<sub>2</sub> will rise through reservoirs until it reaches impermeable horizons, where it will flow laterally and the CO<sub>2</sub> front will tend to finger (Homsy, 1987). In geological reservoirs the innate heterogeneity of reservoir permeabilities will undoubtedly dominate and accentuate the structure of the resulting fingering. The overall flow of the light supercritical CO<sub>2</sub> from injection wells will be dominated by viscous and buoyancy forces that drive the spread of CO<sub>2</sub> as a gravity current and these have been modelled by a range of approaches including a variety of analytical solutions (Golding et al., 2011; Lyle et al., 2005; Nordbotten et al., 2005; Vella and Huppert, 2006) to full numerical simulations (Chadwick and Noy, 2010; Pruess, 2004).

Seismic reflection images of the CO<sub>2</sub> injection operation at Sleipner illustrate the characteristics of the flow of injected CO<sub>2</sub> and the complexities which arise from reservoir heterogeneity (Arts et al., 2004; Chadwick et al., 2008). Here the CO<sub>2</sub> was injected near the base of the ~ 200 m thick permeable Utsira Sand which contains a number of thin and probably discontinuous ~ 1 m thick mudstones, and is overlain by the several hundred metres

thick Nordland Shale. The thin mudstones were predicted to retard the flow of the injected CO<sub>2</sub> (Zweigel et al., 2000) and seismic reflection profiles taken periodically since injection started in 1996 nicely illustrate this, with 8 horizons retarding CO<sub>2</sub> flow within the reservoir (Fig. 4).

Analytical modelling of sharp-interface axisymmetric gravity flows (Lyle et al., 2005) predicts that the CO<sub>2</sub> will rise and spread out under impermeable caprocks and that the radius of an axisymmetric accumulation will increase as the square-root of time. This relationship is preserved in models which allow for capillarity (Golding et al., 2011). Although the layer radii derived from seismic reflection surveys at Sleipner in 1999, 2001 and 2002 satisfy such a relationship (Bickle et al., 2007), with planforms moderated by topographic infilling (Boait et al., 2012; Singh et al., 2010), subsequent surveys show that lower layers apparently start to shrink and dim by 2004 and the seismic dimming extends to the upper layers by 2008 (Fig 4b; Boait et al., 2012). Shrinkage of the lower layers maybe due to increased migration of the CO<sub>2</sub> through the lower layers as CO<sub>2</sub> completely penetrates the thin mudstones and migration rates increase markedly due to expulsion of the more viscous water, increased CO<sub>2</sub> saturation and removal of the capillary pressure at the CO<sub>2</sub>-brine interface (Boait et al., 2012; Chadwick and Noy, 2010). However, Boait et al. (2012) argue that much of the dimming results from a reduction in seismic velocity contrast between the CO<sub>2</sub> plumes and brine which contains widely dispersed residually trapped CO<sub>2</sub>. Irrespective of the precise cause of the layer dimming it likely reflects either a flow or trapping process that has increased CO<sub>2</sub>-brine contact area and therefore dissolution rates.

Dissolution of CO<sub>2</sub> into formation brine is an important stabilising mechanism, as saturated brines with between 2 to 5 wt% CO<sub>2</sub> (depending on pressure, temperature and salinity) have negative buoyancy, compared to CO<sub>2</sub>-poor brines. Where CO<sub>2</sub> dissolves at the base of a trapped CO<sub>2</sub> plume, sinking plumes of the denser brine set up convective circulation

(Ennis-King and Paterson, 2005; Riaz et al., 2006), that can lead to enhanced rates of CO<sub>2</sub> dissolution (Ennis-King and Paterson, 2005; Neufeld et al., 2010; Yang and Gu, 2006). Neufeld et al., (2010) have shown that the rate of convective circulation and dissolution of CO<sub>2</sub> is governed principally by the velocity of the sinking plumes. In the high permeability Utsira Sand at Sleipner, Neufeld et al. (2010) estimate that 10% of the annually injected mass of CO<sub>2</sub> was being dissolved six years after injection commenced, a fraction that should increase with time as the CO<sub>2</sub> plumes spread.

Diffusion of CO<sub>2</sub> in brine is a relatively sluggish process and after a year CO<sub>2</sub> would only penetrate ~ 25 cm into static brine (Fig. 5). However, Taylor dispersion (Taylor, 1953) at high flow rates may lead to broadening of the diffusive fringe and to an increase in the effective diffusion coefficient up to 15 times that of molecular diffusion (Backhaus et al., 2011). In addition, a combination of complex macroscopic flow paths, such as in the Sleipner example, sub-metre bedding-scale heterogeneities in permeability and flow, and convective circulation of the denser, CO<sub>2</sub>-saturated brines are all expected to cause large increases in the surface area of CO<sub>2</sub> in contact with brine, enhancing dissolution (MacMinn et al., 2011). The nine CO<sub>2</sub> layers in Sleipner increase the basal contact areas between CO<sub>2</sub> and brine by about an order-of-magnitude over that occupied by a single layer at the top of the reservoir. Bedding-scale heterogeneities of flow and pore-scale complexities arising from capillarity will further increase the contact areas but without a better constraint on these processes it is impossible to quantify this increase.

Whilst important information about the macroscopic flow of CO<sub>2</sub> can be gained from experiments like Sleipner, further small-scale CO<sub>2</sub> injection experiments are required to test models, theories and predications about the complexities of flow. In-situ geophysical and geochemical observation of the growth and development of fingering, the brine-CO<sub>2</sub> interface and mobility of dense CO<sub>2</sub>-saturated brines is critical to predict the subsequent rates of fluid-

fluid and fluid-mineral reactions that determine the long-term fate of the CO<sub>2</sub>.

## 2.2 Controls on fluid-fluid and fluid-rock reactions

### 2.2.1 CO<sub>2</sub>-Brine Phase Relationships

CO<sub>2</sub> will be injected in a supercritical state to minimise storage volume. The critical point of CO<sub>2</sub> is at 7.4 MPa and 31°C and injection at depths below ~800m will maintain this phase stability. Suitable storage sites may occupy reservoirs significantly beneath this depth, creating a diverse range of pressure and temperature conditions suitable for CO<sub>2</sub> storage. The solubility of the injected CO<sub>2</sub> in the formation brine depends on the temperature, pressure and fluid salinity (Fig. 6, Dubacq et al., 2013) and the competing effects of pressure with temperature and salinity lead to solubility maxima for CO<sub>2</sub> at depths of between 0.7 to 1 km for typical geothermal gradients, pore fluid pressures and basin scale pore salinity profiles (Fig. 7). The dissolution of supercritical CO<sub>2</sub>, and its subsequent speciation, occurs via a series of pressure and temperature sensitive, linked reversible reactions:



Some fraction of the dissolved CO<sub>2</sub> (~0.3%; Drever, 1982) will hydrate to produce carbonic acid, with a maximum acid dissociation constant at ~55°C which increases with pressure, and this acidity will promote fluid-rock reaction, leading to the production of bicarbonate ions. The fluid-rock interactions in CO<sub>2</sub> injection sites can be divided into three categories: CO<sub>2</sub>-wellbore interactions, CO<sub>2</sub>-rock interactions and CO<sub>2</sub>-fluid-rock reactions

### 2.2.2 CO<sub>2</sub>-Wellbore Interactions

During injection of supercritical CO<sub>2</sub>, interactions will occur between the dry CO<sub>2</sub> and materials comprising the wellbore casing and cement, and the rock volume within the near wellbore region. The injected CO<sub>2</sub> will be at surface temperatures and thus cool relative to the surrounding rock volume. Thermal and dehydration effects are predicted to lead to the

precipitation of salt from formation brine, within the local pore volume (Ott et al., 2011; Zeidouni et al., 2009), with impacts for formation permeability (Peysson et al., 2011) and pressure build-up (Kim et al., 2012a; Okwen et al., 2011; Pruess and Müller, 2009). Joule-Thomson expansion of the CO<sub>2</sub> phase as it migrates from the site of injection to shallower depths will lead to cooling of the surrounding fluid and rock volume, which may influence mineral reactivity (André et al., 2010; Han et al., 2012; Oldenburg, 2007). The solubility of water in supercritical CO<sub>2</sub> is relatively limited (between 0.1 to 0.5 wt%; Dubacq et al., 2013; Spycher et al., 2003) and the zone dried by the CO<sub>2</sub> (which depends on the multiphase flow properties of the reservoir) will occupy only about 5% of the total volume filled by CO<sub>2</sub> and residual water (Spycher and Pruess, 2005). The diffusivity of H<sub>2</sub>O in supercritical CO<sub>2</sub> ( $2 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$  to  $2 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1}$ ; Espinoza and Santamarina, 2010) is one to two orders of magnitude faster than the diffusivity of CO<sub>2</sub> in water ( $\sim 2 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ ; Mutoru et al., 2010). Thus an initially dry CO<sub>2</sub> plume will hydrate, and the water content will homogenize relatively quickly.

Interaction of the CO<sub>2</sub> stream with wellbore cements is predicted to lead to mineral dissolution (Kutchko et al., 2007) and the development of carbonation fronts coupled to the penetration of CO<sub>2</sub> and porosity development (Corvisier et al., 2010; Gherardi et al., 2012; Huerta et al., 2012; Jacquemet et al., 2012; Rochelle and Milodowski, 2012). Such reaction fronts may lead to the development of fluid pathways that would allow CO<sub>2</sub> or CO<sub>2</sub>-charged fluid to escape into overlying formations or to the surface (Tao et al., 2011), but the development of armouring carbonate mineral coatings may limit the extent of reaction and these pathways may ultimately self-seal through mineral precipitation (Carroll et al., 2011; Huerta et al., 2012). Observations from field studies suggest the interfaces between cement, casing and the surround rock volume are likely to represent sites for focused fluid movement

and reaction (Carey et al., 2007), and critical sites for potential CO<sub>2</sub> leakage (Deremble et al., 2011; Dusseault et al., 2000).

### 2.2.3 Supercritical CO<sub>2</sub>-Rock Reactions

The reactions between supercritical CO<sub>2</sub> and minerals in the reservoir have not been studied extensively. Dry CO<sub>2</sub> may dehydrate hydrous minerals but as the solubility of water in CO<sub>2</sub> is limited, CO<sub>2</sub> penetrating reservoirs or caprocks will rapidly become water saturated. Laboratory experimental studies have documented the mobilisation of trace metals by dry supercritical CO<sub>2</sub> (Rempel et al., 2011), the relatively rapid carbonation of silicate minerals by water-bearing supercritical CO<sub>2</sub> (Loring et al., 2012; McGrail et al., 2009; Schaefer et al., 2013) and some carbonation by dry CO<sub>2</sub> (Regnault et al., 2009), but the mechanisms and rates of these reactions are not well known (e.g. Lin et al., 2008; Lea et al., 2011). The partitioning experiments of Rempel et al., (2011) demonstrate trace element solubility in supercritical CO<sub>2</sub> of up to 0.6 ppm for Fe and 39 ppm for Na, providing an initial evaluation of mineral solubility in supercritical CO<sub>2</sub>, although much more data is needed. Interaction of CO<sub>2</sub> with mineral surfaces may also cause de-wetting which will reduce capillary entry pressure, alter quantities of residually trapped CO<sub>2</sub> and relative permeability, and enhance CO<sub>2</sub> penetration into low permeability rock (Kim et al., 2012b).

Mineral-fluid reactions involving supercritical CO<sub>2</sub> are still poorly understood and should form a concerted focus of research. Much experimental work is still needed to evaluate the reactivity of hydrated supercritical CO<sub>2</sub>, and its impacts on the transport properties of reservoirs and caprocks. Specifically the long-term impacts of supercritical CO<sub>2</sub> on reservoir caprocks are of concern and scientific drilling of deep natural CO<sub>2</sub> reservoirs would provide invaluable information to test these impacts.

#### 2.2.4 CO<sub>2</sub>-Fluid-Rock Reactions

Most interest centres on the rates of CO<sub>2</sub> dissolution in formation brines and the nature and rates of reaction of the acid CO<sub>2</sub>-saturated brines with reservoir and caprock minerals. Acidity produced during the dissolution of CO<sub>2</sub> will promote mineral dissolution reactions and desorption of exchangeable or mineral surface bound ions that will modify the reservoir fluid chemistry.

Modelling (Knauss et al., 2005; Xu et al., 2007) and field observations (Kampman et al., 2009; Kharaka et al., 2006a) suggest that CO<sub>2</sub>-charged brines flowing through a reservoir rapidly dissolve and become saturated in carbonate and Fe-oxyhydroxide minerals near their source, followed by more sluggish reactions with silicate and phyllosilicate minerals that further raise the pH and cause precipitation of clays and carbonates in the more distal regions (Fig. 8). A similar set of chemical reactions is predicted for caprocks, that is initial dissolution of carbonate followed by precipitation of carbonate driven by the pH increase consequent on the more sluggish reactions with phyllosilicate minerals (Gaus et al., 2005) (Fig. 9). In general transport of CO<sub>2</sub> into caprocks will be by diffusion as rates of advective transport drop below diffusion rates at low permeabilities ( $<10^{-14}$  m<sup>2</sup>) even if the capillary entry pressures do not exclude the CO<sub>2</sub> phase.

Several aspects of modelling these fluid-mineral reactions are problematic. 1) The impact of injected CO<sub>2</sub> on the host rock may be moderated by mineral dissolution and/or precipitation. The reactions are kinetically limited and experimental data on mineral dissolution rate constants for crucial endmember mineral phases, and in complex solid-solutions, over a wide range of pressures, temperatures and fluid compositions are generally lacking. 2) The equilibrium thermodynamics of the mineral-fluid reactions may be uncertain, especially in high ionic strength brines and where experimental equilibrium constants are lacking. 3) The reaction paths may involve metastable reaction products which are not

accounted for by equilibrium thermodynamic models. 4) The controls on fluid-mineral reaction kinetics are complex, with rates measured in field sites frequently orders-of-magnitude slower than far-from-equilibrium laboratory-derived rates (White and Brantley, 2003) and the rate limiting steps may be either mineral surface dissolution, secondary mineral precipitation, CO<sub>2</sub> dissolution and diffusion or fluid transport. 5) The relative flows of CO<sub>2</sub> and brine are governed by the complexities arising from two-phase flow and the intrinsic heterogeneities in geological reservoirs. The nature of these flows governs the dissolution of CO<sub>2</sub> into the brines, and the subsequent geochemical evolution of the brines is controlled by the coupling of CO<sub>2</sub> diffusion and fluid-rock reactions. Most reactive-flow modelling experiments have modelled flow of an initially CO<sub>2</sub>-saturated brine in one or two dimension with grid sizes that are typically larger than the length-scales of geological heterogeneities, and have simplified or ignored two-phase flow phenomena and the potential for additional inputs of CO<sub>2</sub> along the flow path (Audigane et al., 2007; Knauss et al., 2005; Xu et al., 2005). Modelling the kinetics of fluid-mineral reactions in the context of CO<sub>2</sub> storage is reviewed in Hellevang et al., (2013). Such simplifications of the modelling efforts are necessary for the treatment of these computationally intensive processes but without capturing the underlying physics of flow, geochemical model predictions are undermined.

#### 2.2.4.1 Laboratory versus Field-Scale Reaction Rates

In natural CO<sub>2</sub> reservoirs, the rates of the silicate dissolution reactions (e.g. feldspars), that may ultimately promote CO<sub>2</sub> trapping or leakage, have been shown to differ by several orders of magnitude ( $10^2$  to  $10^5$ ) from those rates determined experimentally (Kampman et al., 2009). Growing evidence suggests that the apparent rate discrepancy between laboratory and field-scale rates may be due to the decrease in mineral dissolution rates near equilibrium (Kampman et al., 2009; Maher et al., 2009), with consequent transport-control of reaction rates (Maher, 2010; White et al., 2009).

Laboratory studies on quartz (Berger et al., 1994), feldspars (e.g. Beig and Lüttge, 2006; Burch et al., 1993; Hellmann and Tisserand, 2006; Schott and Oelkers, 1995; Taylor et al., 2000) and phyllosilicate minerals (Cama et al., 2000; Nagy et al., 1991) confirm theoretical predictions (e.g. Lasaga, 1984) that dissolution rates are independent of saturation state far from equilibrium (but see Oelkers et al., 1994) and decrease in a transition region as equilibrium is approached, with a critical step in the dependence close to equilibrium as the mechanism of dissolution changes (see Arvidson and Luttge, 2010; Hellmann and Tisserand, 2006). In addition, the dissolution rates of many important rock forming silicate minerals (e.g. feldspars) are highly sensitive to processes occurring at or close to the dissolving mineral surface including; the rate of secondary mineral precipitation (Maher et al., 2009; Moore et al., 2012); interfacial dissolution-reprecipitation phenomena (see Hellmann et al., 2012 and references therein), such as the development of silica surface layers (Amrhein and Suarez, 1992; Hellmann et al., 2003; Hellmann et al., 2012) and the carbonation of mineral surfaces (Béarat et al., 2006; Daval et al., 2009), which may be passivating (e.g. Daval et al., 2011; Daval et al., 2013); and the slow transport of insoluble metal species e.g.  $\text{Al}^{3+}$  (e.g. Muir and Nesbitt, 1991). Silicate mineral dissolution rates are further influenced by properties of the bulk solution including concentrations of carbonate ions (e.g. Berg and Banwart, 2000), organic acids (e.g. Drever and Stillings, 1997) and ligands (e.g. Blake and Walter, 1999). In addition the  $\text{CO}_2(\text{aq})$  ion itself may have an impact on the rates and mechanism of dissolution, not least through its impacts on surface charge and complexation, although such processes are not yet well understood (Carroll and Knauss, 2005; Hänchen et al., 2006; Hellmann et al., 2010). The role of mineral-surface processes during mineral dissolution are reviewed in Brown and Calas (2012). This myriad of complications is generally not treated in most reactive transport models, and further attempts to integrate such processes into modelling studies are needed.

In CO<sub>2</sub> reservoirs the nature of silicate mineral-fluid reactions is likely to range from surface-reaction controlled where brines are far-from-equilibrium with minerals and not limited by the supply of acidity, to transport-controlled where rates depend on the input of acidity close-to-equilibrium. Indeed where reactions take place close-to-equilibrium, reaction rates will adjust to balance the surface reaction-rate against transport controls. Conversely, the dissolution of carbonate, oxide and oxyhydroxide minerals with rapid kinetics is likely to be transport controlled by propagation of the dissolved CO<sub>2</sub> and acidity front moving ahead of the injected CO<sub>2</sub> plume.

This variability in the controls on natural reaction rates creates substantial complexities for the modelling of brine-mineral reactions during CO<sub>2</sub> injection. Kinetically slow silicate and phyllosilicate mineral dissolution reactions are likely to preside over the long-term fate of the CO<sub>2</sub> and the rate of these reactions will depend on the state of fluid-mineral thermodynamic disequilibrium, itself controlled by reaction progress, diffusion of CO<sub>2</sub> into the brine phase and transport of the brine (Wigley et al., 2013a). In the far-from-equilibrium conditions of dilute acidic CO<sub>2</sub>-rich solutions, feldspar dissolution rates are rapid enough to cause significant porosity increases over short time-scales (see for example Sorai et al., 2005), with consequent impacts for permeability in sandstones, which have extreme porosity-permeability relationships (e.g. Nelson, 1994). However, as reaction progress drives changes in solution composition and equilibrium is approached, pores may become clogged by clay and carbonate deposition (e.g. Bertier et al., 2006), most extremely illustrated by experiments on peridotite (e.g. Hövelmann et al., 2012). In natural systems the approach to equilibrium is complicated by the presence of multiple mineral phases which react and buffer solution chemistry at different rates, most notably soluble carbonates, sulphates, sulphides and oxides which rapidly consume acidity and the much slower reaction rates of most silicate minerals. On the short-term, the dissolution of soluble minerals may be transport-controlled

following complete consumption of the reactant, or attainment of fluid-mineral equilibrium, over the length scale under consideration, such that aqueous transport is the rate-limiting factor. If the system is transport-controlled, kinetic rate constants and mineral surface areas determine the geometry of the reaction front, but these parameters do not have a substantial influence on the propagation of the reaction front or the net transformation rate. However, factors that affect thermodynamic departure from equilibrium of the dissolving phase(s), such as the rates of CO<sub>2</sub> dissolution, pH buffering, secondary mineral precipitation reactions, and the evolution of porosity/permeability and fluid flow rate will determine the rate at which reaction fronts propagate.

#### 2.2.4.2 Secondary Mineral Precipitation

The subsequent growth of clay and carbonate phases within the reservoir will be controlled by these reactive fluid transport processes, buffering of fluid pH and the availability of metal cations from the slow dissolution of silicate minerals which, in the long-term, is likely to form a rate limiting step. Several authors have emphasized that clay mineral precipitation rates can also be important in controlling silicate mineral dissolution rates (e.g., Maher et al. 2009; Zhu and Lu 2013). Growth of clay and carbonate minerals may be linked to the availability of nucleation sites and precursor seed phases, which may exert a control on the stable growing phase, its growth rate and mechanism (e.g. Fernandez-Martinez et al., 2013; Fritz et al., 2013).

The acid hydrolysis of silicate minerals in natural fluids is largely incongruent being balanced by the precipitation of clay minerals, typified by kaolinite (Maher et al., 2009). The low solubilities of Al<sup>3+</sup> and SiO<sub>2</sub>(aq) at the temperatures and pressure conditions relevant to CO<sub>2</sub> storage preclude significant mass transport of these constituents from the surface of the dissolving silicate mineral. Since Al solubility is very small, clay mineral precipitation rates must essentially balance feldspar dissolution rates. Observations from natural CO<sub>2</sub> reservoirs

(Kampman et al., 2009) suggest the thermodynamic undersaturation of the silicate minerals is balanced by the thermodynamic overstep in clay mineral saturation and that clay mineral precipitation rates vary with, and as consequence of, silicate mineral dissolution rates (Bickle et al., 2013).

The chemistry and mineralogy of the clay mineral precipitates is highly sensitive to temperature, fluid pH and solute activities. Experimental and model predictions include the growth of illite, illite-smectite, smectite, kaolinite and Al-hydroxide minerals (e.g. Credoz et al., 2009; Kohler et al., 2009; Munz et al., 2012). Neutral  $\text{SiO}_2(\text{aq})$  concentrations are likely to be dependent on the supply from feldspar dissolution only on short times-scales as silica mineral solubilities are independent of pH, and natural fluids already contain (equilibrium) concentrations of dissolved silica. Observations from natural  $\text{CO}_2$  reservoirs (Kampman et al., 2009) and produced fluids from oil-fields (Houston et al., 2007) suggest that silica concentrations can be rapidly buffered by reaction with silica phases such as quartz and chalcedony, with the equilibrium concentrations being highly dependent on temperature and the time taken to return to equilibrium concentrations being dependent on the kinetics of the buffering reactions.

The growth of carbonate minerals in  $\text{CO}_2$ -brine-rock systems has been observed in a large number of experiments, including the carbonation of silicate mineral surfaces at high temperature (e.g. Munz et al., 2012). The stable growing phase(s) vary widely, being governed by the thermodynamic considerations of pressure, temperature and solute chemistry and by the activities of constituent species in the fluid phase. The mineralogy of carbonate cements formed in natural  $\text{CO}_2$  reservoirs provides an indication of the phases that may be stable in  $\text{CO}_2$  storage sites (see the review in section 5.2) and this varies from the relatively soluble pure calcite end-member to more insoluble Fe-Mg-Ca carbonate minerals, including dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), ankerite ( $\text{Ca}(\text{Fe},\text{Mg},\text{Mn})(\text{CO}_3)_2$ ) and siderite ( $\text{FeCO}_3$ ). Calcite

cements typically precipitate in natural CO<sub>2</sub>-reservoir sandstones poor in detrital Fe- and Mn-bearing minerals, or from fluids with high oxygen fugacities. In Fe-rich sediments, such as in red-bed aeolian sandstones, in contact with reducing formation fluids, the high activities of Fe<sup>2+</sup> and Mn<sup>2+</sup> in solution can lead to the formation of siderite and in the presence of Mg<sup>2+</sup> rich fluids, ankerite and/or Fe-bearing dolomite. Predicting the stable carbonate phase in CO<sub>2</sub> reservoirs is frustrated by the limited experimental data on the thermodynamic stability, nucleation, growth and kinetics of the more complex Ca-Mg-Fe carbonate minerals, and such data is necessary for accurate model predictions. Recent modelling studies predict the growth of dolomite, in CO<sub>2</sub> reservoirs at low temperature (37°C), which would not be predicated from classic nucleation theory (Hellevang and Aagaard, 2013). Such predictions are supported by observations from natural CO<sub>2</sub> reservoirs where dolomite is often the stable carbonate phase. Clearly an improved understanding of carbonate nucleation and growth is required to predict the long-term mineralization of CO<sub>2</sub> in storage reservoirs.

Ultimately a significant source of uncertainty in interpreting or predicting the various fluid-mineral reactions in injection experiments or natural systems is accurate assessment of the evolution of dissolved CO<sub>2</sub> and in-situ pH, crucial in determining the thermodynamic state of fluid-mineral disequilibrium, secondary mineral saturation and the rates of the controlling fluid-mineral reactions.

### **3 CO<sub>2</sub>-Fluid-Rock Interactions in CO<sub>2</sub> Injection Experiments**

#### **3.1 CO<sub>2</sub> Injection Experiments and CO<sub>2</sub>-EOR Projects**

Given the complex reservoir structures, flow paths and controls on reactive-transport processes involved, the progress of CO<sub>2</sub> dissolution in brines and fluid-rock reactions can be best studied by direct sampling of anthropogenic CO<sub>2</sub> injection projects or natural CO<sub>2</sub> accumulations. Anthropogenic CO<sub>2</sub> injection experiments which have attempted this are

listed in Table 1. Fluid sampling in these projects was conducted over a period of a few days to several months, typically from single observation wells, using in-situ sampling methods (see below). The Frio-I (Hovorka et al., 2006; Kharaka et al., 2006a) and Frio-II (Daley et al., 2007a; Daley et al., 2007b) Brine Pilot injection experiments are notable for the high temporal resolution of the sampling and quality of the resulting analyses. However the lack of spatially distributed sample points, the proximity of the injection and sampling well, and the averaging of fluid samples over significant vertical intervals in the reservoirs complicates the analysis of geochemical processes, given the expected decimetric-scale variability of flows of the CO<sub>2</sub> and brine.

CO<sub>2</sub> injection for enhanced oil recovery (CO<sub>2</sub>-EOR) projects provides an additional source of fluid samples relevant to subsurface CO<sub>2</sub> injection (Table 2). These projects are reviewed in Alvarado and Manrique, (2010). These CO<sub>2</sub>-EOR projects provide a high spatial density of sampling due to the presence of multiple production and monitoring wells and allow mapping spatial changes in solute chemistry related to flow and dissolution of the CO<sub>2</sub> and the CO<sub>2</sub>-induced fluid-rock reactions over periods of months to years. However, interpreting the results from CO<sub>2</sub>-EOR projects is complicated by the complex fluid injection history of old oil fields, the complex dynamic pressure and flow fields resulting from the interactions of numerous injection and production wells and the presence of an oil phase.

Geochemical sampling of the injection experiments has the potential to provide key information that supplements, or is not available from, other monitoring techniques:

- The amount of CO<sub>2</sub> dissolved in sampled brine;
- The time CO<sub>2</sub> arrives at the sample well;
- The progress of fluid-mineral dissolution or precipitation reactions;
- A constraint on the heterogeneity of flow paths;
- The CO<sub>2</sub> saturation in the reservoir interval sampled;

- The amount of CO<sub>2</sub> retained by capillary trapping.

Remote and downhole geophysical monitoring may be able to map the location of the supercritical CO<sub>2</sub> plume and measure CO<sub>2</sub> saturation but has neither the resolution to map heterogeneities of CO<sub>2</sub> and brine flow on the ~ 30 cm scale critical to CO<sub>2</sub>-brine interactions, nor the ability to measure the amount of CO<sub>2</sub> dissolved in the brine.

The magnitude of CO<sub>2</sub> dissolution in brine may be monitored from analysis of dissolved CO<sub>2</sub> concentrations at in-situ pressures and temperatures or estimated from analyses of oxygen isotopic compositions that reflect isotope exchange between the injected CO<sub>2</sub> and formation water. These measurements will also reveal the timing of CO<sub>2</sub> arrival at the sample well. The changes in brine chemistry and isotopic compositions provide a monitor of the progress of the mineral dissolution and precipitation reactions. Injection and analysis of inert (e.g. SF<sub>6</sub>), reactive (e.g. esters), and noble gas isotopic (e.g. <sup>3</sup>He/<sup>4</sup>He, <sup>129</sup>Xe) tracers can provide important additional information on CO<sub>2</sub>-brine interactions including estimates of field-scale capillary trapping (Myers et al., 2012; Zhang et al., 2011; Zhou et al., 2011). Perhaps the most critical information from geochemical sampling is the magnitude and impact of the small-scale heterogeneities that control the flow paths of CO<sub>2</sub> and brine and dissolution of CO<sub>2</sub> in brine. Pore-space CO<sub>2</sub> saturation may be estimated by direct measurement of CO<sub>2</sub> and brine volumes at surface or from the density of the brine-CO<sub>2</sub> mixture measured in-situ. However, measurements of the relative volumes of CO<sub>2</sub> and brine which flow into the sampling well may over-estimate the CO<sub>2</sub> fraction due to the contrast in viscosity and flow rate of the two phases.

Measurements of in-situ dissolved CO<sub>2</sub> concentrations and pH are crucial to quantify the progress of these trapping mechanisms. However, such measurements are not easily achieved because of the rapid degassing of CO<sub>2</sub>-rich fluids at surface pressures. Accurate

determination of dissolved CO<sub>2</sub> concentrations and pH requires specialist downhole equipment that allows either in-situ determination or the recovery and containment of fluid samples at reservoir pressure, on which measurements can be made at surface.

### **3.2 Sampling CO<sub>2</sub> Injection Experiments**

A range of specialist downhole sampling tools have been devised to sample reservoir fluids, including commercially available wireline samplers (Kuster Flow Through Sampler<sup>®</sup>, Leuter Bottom Hole Positive Displacement Sampler<sup>®</sup> and Cased Hole Dynamics Tester<sup>®</sup>), experimental piston samplers (Alfredsson et al., 2011), the U-tube in-situ sampling lines for wellbore fluids (Freifeld et al., 2005) and passive samplers of dissolved gases (Zimmer et al., 2011).

The U-tube in-situ multiphase fluid samplers comprise a stainless steel sampling U-tube, with check valve fluid entry ports, and two stainless steel lines that run to surface, through which pressurised nitrogen can be pumped to drive the sample to the surface at pressure. The U-tube sampling line can also be combined with inline pH sensors for determination of downhole fluid pH (Daley et al., 2007a), from which dissolved CO<sub>2</sub> concentrations can be estimated, where measurements of fluid alkalinity are available. A newly developed variant of the U-tube sampler has been developed and trialled at the Ketzin injection experiment (Zimmer et al., 2011). This Gas Membrane Sensor utilises phase separating membranes mounted in a perforated protective stainless steel housing to passively separate dissolved gas from the contacting reservoir fluid, which is then driven to surface by pressurised argon pumped through stainless steel capillaries (Zimmer et al., 2011).

U-tube sampling lines are frequently integrated with other monitoring tools including geophones and distributed temperature, pressure and fluid density sensors (Freifeld et al., 2008; Freifeld et al., 2005; Giese et al., 2009) and connected to portable quadrupole mass spectrometers for real time gas composition analysis (Freifeld and Trautz, 2006; Zimmer et

al., 2011). Such in-situ sampling lines provide a convenient and low cost method for repeatedly sampling two-phase formation fluid in on-going injection experiments. However, the sampling methods and surface sample processing employed to-date do not allow direct determination of dissolved CO<sub>2</sub> concentrations. Such in-situ sampling methods are also prone to corrosion of the sampling lines and housing by reactive CO<sub>2</sub>-rich fluids (Daley et al., 2007a; Zimmer et al., 2011).

To date there are no published analyses of dissolved CO<sub>2</sub> concentrations in CO<sub>2</sub> reservoirs sampled using wireline, although they have been widely used by the oil and gas industries to sample hydrocarbon reservoirs. **Kampman et al., this issue** show how reservoir pH and dissolved CO<sub>2</sub> concentrations can be determined at surface on pressurized fluids sampled by wireline, using high pressure pH probes and by the addition of an excess of base to convert dissolved CO<sub>2</sub> to CO<sub>3</sub><sup>2-</sup>, whose concentration can then be measured by titration.

### **3.3 Monitoring of CO<sub>2</sub> Dissolution and CO<sub>2</sub> Saturation**

Dissolved CO<sub>2</sub> concentrations in brines may be measured directly in samples recovered at formation conditions as discussed above or estimated from partition of conservative tracer concentrations or isotopic ratios. CO<sub>2</sub> saturation may be measured directly in the vicinity of observation wells by several geophysical techniques; neutron capture, resistivity and distributed thermal perturbation sensors (Freifeld et al., 2009). Attempts have also been made to infer CO<sub>2</sub> saturation and residual trapping from geochemical measurements but interpretation of these is complex as discussed below.

#### **3.3.1 Direct Measurements of Dissolved CO<sub>2</sub> and CO<sub>2</sub> Saturation**

Direct observations of the progress of CO<sub>2</sub> dissolution during CO<sub>2</sub> injection are limited because of the complexities associated with in-situ measurements or the recovery of reservoir fluids with high dissolved gas loads. The U-tube sampler is capable of returning

fluids to surface without decompression. In the Frio II experiment, combined measurements of pH at formation pressure and alkalinity allowed brine CO<sub>2</sub> concentrations to be reconstructed (Daley et al., 2007a). In the Ketzin CO<sub>2</sub> injection experiment, Zimmer et al. (2011) obtained in-situ dissolved CO<sub>2</sub> concentrations from measurements made using downhole gas membrane sensors installed at ~150m within two ~750m deep observation wells, sited ~50 and ~100m up-dip from the injection well. CO<sub>2</sub> breakthrough at the proximal observation well was observed after sixteen days and the breakthrough of the CO<sub>2</sub> phase was accompanied by reservoir fluids with measured dissolved CO<sub>2</sub> concentrations at saturation (0.63 mole/L using the gas membrane sensors and 0.65 mole/L using a wireline downhole fluid sampler, slightly above the expected CO<sub>2</sub> solubility of ~0.52 mole/L at reservoir temperature, pressure and salinity) suggesting that reservoir fluids in contact with the propagating CO<sub>2</sub> plume quickly saturate.

### 3.3.2 Indirect Estimation of Dissolved CO<sub>2</sub> Concentrations and CO<sub>2</sub>-gas Saturation

The degree of CO<sub>2</sub>-saturation in under-saturated brines has been estimated by using the concentrations or isotopic compositions of conservative tracers for which the relative exchange rates between CO<sub>2</sub> and brine are known. Once the supercritical CO<sub>2</sub> plume extends to the sample well, both CO<sub>2</sub> and CO<sub>2</sub> saturated brine are sampled. The relative fractions of CO<sub>2</sub> and brine can be estimated from the partition of tracer concentrations or isotopic ratios between the CO<sub>2</sub> and brine.

The most effective conservative tracers of CO<sub>2</sub>-brine interactions are likely to be the 5 stable noble gasses which have 22 isotopes between them (Holland and Gilfillan, 2012; Nimz and Hudson, 2005; Zhang et al., 2011). To date most indirect estimates of CO<sub>2</sub> saturation have exploited the marked difference between the oxygen isotopic composition of the injected CO<sub>2</sub> and formation brines in for example the Frio-I and Pembina injection experiments (Johnson et al., 2011a; Kharaka et al., 2006a).

For the Frio-I experiment (Fig. 10) Kharaka et al. (2006a) used a simple mass-balance calculation, constrained by measurements of the oxygen-isotope exchange between the injected CO<sub>2</sub> and formation brine, to calculate residual CO<sub>2</sub> saturation in the reservoir interval contacting the fluids sampled by the U-tube sampler. This implied CO<sub>2</sub> saturations rising rapidly to plateau at  $\sim 10 \pm 3\%$  over the 30 days after CO<sub>2</sub> breakthrough and  $\sim 50\%$  when sampled 5 months later. In comparison direct measurement of CO<sub>2</sub> saturation by downhole geophysical measurements using a Schlumberger wire-line pulsed neutron capture reservoir saturation tool (RST) imply that CO<sub>2</sub> has an average saturation of  $\sim 18\%$  on day 4 and  $\sim 34\%$  on day 10 although reaching  $>80\%$  in the centre of the plume (Hovorka et al., 2006, see Fig. 10b). Saturation calculated from the arrival time of the CO<sub>2</sub> and injected tracers using mass balance in a simple radial flow model (Frieffeld et al., 2005) gives an average value of  $\sim 16\%$  over the few days after CO<sub>2</sub> first broke through. Given that the Frio-I reservoir has significant dip (Fig. 10a), the radial flow model probably overestimates the volume occupied by CO<sub>2</sub> and therefore underestimates the calculated CO<sub>2</sub> saturations. Analytical modeling based on the arrival time of CO<sub>2</sub> and the retardation of injected tracers (Kr, SF<sub>6</sub>) suggests residual water saturations in the CO<sub>2</sub> plume at CO<sub>2</sub> breakthrough of  $\sim 40\%$ ,  $\pm 12\%$ , although the solutions are non-unique (Pruess et al., 2005).

Estimations of CO<sub>2</sub> saturation based on oxygen-isotopic mass balance is based on the following assumptions, 1) that CO<sub>2</sub> and brine reached oxygen-isotopic equilibrium in the pore space, 2) that neither the original (injection) oxygen isotopic composition of the CO<sub>2</sub> or the pre-injection composition of the brine were modified before CO<sub>2</sub> saturated the pore space adjacent to the sample well and 3) that either CO<sub>2</sub> and brine were sampled by the U-tube in the same proportions as in the pore space or that CO<sub>2</sub> and brine did not exchange oxygen isotopes during sample recovery in the U-tube.

Diffusive exchange on a  $\sim 0.1$  mm scale takes place in minutes so that the  $\text{CO}_2$  and brine would be expected to be in equilibrium in the pore space (Fig. 11). If  $\text{CO}_2$  and brine separate in the borehole during sampling as Frie field et al. (2005) infer, these compositions might be preserved. Whether the oxygen-isotopic compositions of either the brine or  $\text{CO}_2$  are modified by exchange before the  $\text{CO}_2$  enters the sampled pore space will depend on the time-scales and flow paths. The samples taken at Frio-I within a few days of injection had limited time for exchange and it is likely that the  $\text{CO}_2$  was little modified in composition. Monitoring of arrival times of  $\text{CO}_2$  and injected tracer gasses (PFT's,  $\text{SF}_6$ , Xe and Kr) over the few days of  $\text{CO}_2$  injection showed that the more soluble Kr was retarded compared with the other tracers (Freifeld et al., 2005) but given the likely solubility of Kr (inferred from the air-water Henry's law constant; Wilhelm et al., 1977), average Kr concentrations were only  $\sim 3\%$  of saturation implying limited  $\text{CO}_2$ -brine diffusive exchange. The samples taken 5 months later may have had a more complex history.

Measurements of the sampled fluid density in the U-tube give a ratio of  $\text{CO}_2$  to brine  $>80\%$  after  $\text{CO}_2$  breakthrough which Frie field et al. (2005) and Hovorka et al. (2006) ascribe to the higher mobility (lower viscosity) of  $\text{CO}_2$  than brine. The similarly high values of  $\text{CO}_2$  saturation calculated from the oxygen-isotope shifts (Fig. 12) are probably the result of diffusive exchange before or during sampling and not accounted for in the modelling.

Johnson et al. (2011a) calculate  $\text{CO}_2$  dissolution and  $\text{CO}_2$  saturation in the Pembina EOR injection experiment from shifts in the oxygen isotopic compositions of the produced brines. They model the shift in the oxygen isotopic composition of brine with a mass balance equation that assumes that the  $\delta^{18}\text{O}$  of the  $\text{CO}_2$  remains constant and that oxygen isotopic shifts of the brine result from addition of dissolved  $\text{CO}_2$  to the brine. The mass balance equation which relates the final oxygen isotopic composition of the brine ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{f}}$ ) to the initial oxygen isotopic composition of the brine ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{i}}$ ), the oxygen isotopic composition

of the CO<sub>2</sub> ( $\delta^{18}\text{O}_{\text{CO}_2}$ ), and the fraction of O in the system sourced from CO<sub>2</sub> ( $X_{\text{CO}_2}^0$ ), (Johnson et al., 2011a, equation 4) is

$$\delta^{18}\text{O}_{\text{H}_2\text{O}}^f = \delta^{18}\text{O}_{\text{H}_2\text{O}}^i (1 - X_{\text{CO}_2}^0) + X_{\text{CO}_2}^0 (\delta^{18}\text{O}_{\text{CO}_2} - \varepsilon) \quad (2)$$

where  $\varepsilon$  is the CO<sub>2</sub>(g)-H<sub>2</sub>O fractionation factor (Bottinga and Craig, (1968); 35‰ at Pembina reservoir conditions). The Pembina brine saturates with 1.3 mol/L CO<sub>2</sub> that would shift the  $\delta^{18}\text{O}$  of the brine only 0.4 ‰. The observed isotopic shifts at Pembina (up to 4 ‰) are much in excess of the expected shift due to oxygen transported by the CO<sub>2</sub> needed to saturate the brine and this must reflect diffusional exchange between the brine and CO<sub>2</sub>. Equation 1 does not model this and also doesn't allow for the corresponding changes in the  $\delta^{18}\text{O}_{\text{CO}_2}$ . Figure 11 illustrates the more complex reality where exchange of oxygen isotopes is controlled primarily by diffusion in the brine phase of the oxygen isotope signal carried by H<sub>2</sub>O that has exchanged with CO<sub>2</sub> with or at the plume interface.

The Frio and Pembina experiments demonstrate the fundamental problems of estimating CO<sub>2</sub> saturation. The large mobility difference between CO<sub>2</sub> and brine biases direct sampling, and geochemical measurements average over a range of saturations and are influenced by CO<sub>2</sub>-brine interactions along the flow path to the sample site and at the sample site.

### 3.3.3 Fluid-Rock Interactions inferred from CO<sub>2</sub> Injection Experiments

Injection experiments provide real-time constraints on the rate of fluid-mineral reactions. Perhaps the most important observation from all the injection experiments is the rapidity with which the brines saturate with CO<sub>2</sub> and then with exchangeable ions and carbonate and Fe-oxyhydroxide minerals. The Frio brine pilot injection experiments employed the most detailed fluid sampling programs published to-date (Hovorka et al., 2006; Kharaka et al., 2006a; Kharaka et al., 2006b; Kharaka et al., 2009) (Figs. 10, 13).

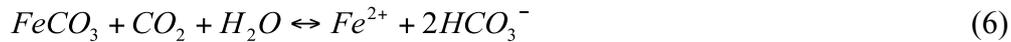
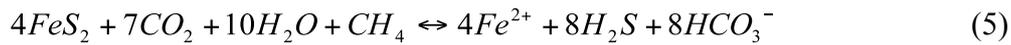
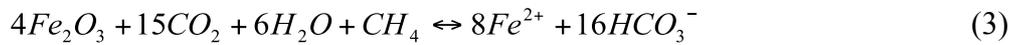
At Frio-I the arrival of the supercritical CO<sub>2</sub> plume at the observation well at 52 hours is tracked primarily by the step change in fluid composition in the U-tube samples (Fig. 13A) as well as injected PFT tracers (Freifeld et al., 2005). Small changes in fluid density and gas phase composition ~31 hours after the start of injection accompanied by shifts in the O-isotopic composition of the produced fluid are interpreted to reflect arrival of thin CO<sub>2</sub> fingers ahead of the main CO<sub>2</sub> plume at 52 hours. pH measured at surface starts dropping 30 hours after injection starts and continues dropping, with a reversal when the pumps were serviced, until CO<sub>2</sub> breakthrough. Alkalinity and the concentrations of divalent metal cations (Ca, Sr, Fe, Mn), Si and some trace metals (Zn, Pb, Cr) increase rapidly at CO<sub>2</sub> breakthrough (Fig. 13B-F).

The pH measurements at surface pressures will be increased by CO<sub>2</sub>-degassing as the fluids were decompressed. If the fluids are saturated in CO<sub>2</sub> at reservoir conditions just prior to the arrival of the CO<sub>2</sub> plume the pH would drop to 3.5 (calculated using PHREEQC, Parkhurst and Appelo, 1999), c.f. Xu et al., 2010). The subsequent rise in alkalinity of ~50 mmol corresponds to an increase in Ca of 10 mmol/L and Fe of 20 mmol/L, and if the brine remains CO<sub>2</sub> saturated, raises the calculated pH to ~4.6 at 3 days since CO<sub>2</sub> injection (Fig. 13 G, c.f. Xu et al., 2010).

The lag between the drop in pH and increase in alkalinity reflects the time taken for reactions to increase alkalinity, and is therefore controlled by the kinetics of those reactions. Ca and Sr concentrations increase concurrently (Fig. 13D) and the constant Sr/Ca molar ratio are consistent with carbonate mineral dissolution. Concentrations of Fe, Mn and Si increase more slowly reflecting the more sluggish dissolution of Fe-oxide, Fe-oxyhydroxide and/or Fe-sulphide, and silicate or phyllosilicate minerals.

The pulse of increased concentrations of Zn, Pb and Cr most likely reflect pH-driven desorption from mineral grain surfaces (Xu et al., 2010), see section 3.3.4). Increases in

alkalinity are mainly balanced by increases in Ca and Fe. Xu et al., (2010) model the increase in Fe from an unknown Fe-bearing mineral or minerals, or surface adsorption. The Fe:alkalinity ratio of 1:2, after subtraction for alkalinity sourced from calcite dissolution, is consistent with dissolution of Fe-oxide or Fe-oxyhydroxide, with a methane reductant (Eq. 3 & 4; c.f. Wigley et al., 2012). The important role of CO<sub>2</sub> in this acid-reduction is reflected in the reaction stoichiometry. Potential iron dissolution reactions from haematite, iron oxyhydroxides, pyrite, siderite and steel drill pipe are:



Several lines of evidence indicate derivation of the Fe from Fe-oxides, Fe-oxyhydroxides or pyrite; 1) Kharaka et al., (2006a) noted Fe-rich grain coatings on clays in the core, 2) pyrite is the dominant diagenetic Fe-bearing phase (McGuire, 2009) reflecting the reducing nature of the methane-rich groundwater (Kharaka et al., 2006a), 3) no siderite was observed in the core (McGuire, 2009), 4) the fluid Fe and Mn concentrations which exhibit a Mn/Fe molar ratio of 0.016 are similar to the Mn/Fe ratio of 0.015 measured in pyrite grains in core from the injection interval in the Frio C sandstone (McGuire, 2009), and 5) the initial rapid release of Fe is coincident with the small increase in fluid SO<sub>4</sub><sup>2-</sup>, which may reflect oxidization of H<sub>2</sub>S released during the acid dissolution of pyrite, although HS<sup>-</sup> and H<sub>2</sub>S concentrations in the fluid were not measured. Determining the origin of the released Fe is

complicated by multiple potential sources; use of trace element or isotopic tracers measured in the source minerals, equipment or casing would enable a more definitive assessment.

Calculations of mineral saturation indices during the Frio-I experiment, based on the measured fluid chemistry and at CO<sub>2</sub> saturation, show that release of Ca, Fe and HCO<sub>3</sub><sup>-</sup> to solution and neutralisation of pH buffers the fluid to equilibrium with siderite and ankerite over 1.5 to 2 days, although calcite and Fe-oxyhydroxides remain undersaturated (Fig. 13G). The continued increase in fluid Fe concentrations whilst maintaining equilibrium with siderite requires coprecipitation of a Fe-carbonate phase over short timescales.

Similar results have been obtained for the Frio-II Brine Pilot injection experiment (Fig. 14), where 360 tonnes of CO<sub>2</sub> were injected at 1650m into the Blue Sands unit of the Lower Frio Formation (Daley et al., 2007a; Daley et al., 2007b). The arrival of the CO<sub>2</sub> plume at the observation well, 32m up dip, ~62 hours after injection was accompanied by a sharp drop in fluid pH to ~3.5, and by a sharp increases in the concentration of Zn, Pb, Cr and Si at CO<sub>2</sub> breakthrough, followed by two pulses of alkalinity and Fe, Mn, and Co enriched fluids over a ~2 day period (Fig. 14). Recalculation of dissolved CO<sub>2</sub> concentrations using measured alkalinity and in-line pH indicate that the fluids reach CO<sub>2</sub> saturation with CO<sub>2</sub> after 75 hours but that this is followed by sampling of undersaturated brines.

Rapid release of Zn, Pb and Cr coincide with a sharp drop in fluid pH and their release is potentially the result of pH driven desorption from metal oxide grain surfaces (see section 3.3.4). The subsequent double pulse of alkalinity and metal enriched fluid may correspond to the arrival of distinct macroscopic CO<sub>2</sub> fingers at the observation well. The large changes in Fe and HCO<sub>3</sub><sup>-</sup> concentrations in these alkalinity pulses are highly correlated, with an approximate 1:3 molar ratio, suggesting the production of Fe, Mn and Co may originate from the dissolution of Fe-oxide or Fe-oxyhydroxide by acid-reductive dissolution involving reduced sulphur, or from the steel equipment or casing. Changes in Fe and Mn

concentrations are highly correlated ( $R^2=0.96$ ) and the low Mn/Fe ratio ( $\sim 0.007$ ) of the fluids is consistent with the dissolution of sedimentary Fe-oxides with low wt% Mn (Drever, 1982). As Fe concentrations increase the fluids evolve towards Fe-isotope ratios of  $\sim -0.5\text{‰}$  (Kharaka and Cole, 2011), which is compatible with either the dissolution of sedimentary Fe-oxides or borehole casing steel that typically have coincident Fe-isotope ratios of  $\sim -1\text{‰}$  to  $0\text{‰}$  (Johnson and Beard, 2006).

The reservoir fluids initially present in both the Frio-I and Frio-II contain high concentrations of dissolved methane. Reducing conditions promoted by high concentrations of methane, hydrocarbons, sulphide species and low dissolved oxygen concentrations are a ubiquitous feature of many subsurface reservoirs. The large amount of acidity produced by  $\text{CO}_2$  dissolution, in conjunction with the presence of such reducing conditions, allows the acid-reductive dissolution of minerals such as  $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$  and the conversion of relatively insoluble  $\text{Fe}^{3+}$  to soluble  $\text{Fe}^{2+}$ . The observations from Frio and natural analogues (Wigley et al., 2012 - see below) suggest this may be ubiquitous in carbon storage sites in impure sandstones. Similar dissolution of carbonates, Fe-oxides and oxyhydroxides has been observed at the Nagaoka  $\text{CO}_2$  injection site in Japan (Mito et al., 2008), where fluids sampled from the observation wells one year after completion of injection exhibit high bicarbonate concentrations and increased Ca, Mg, Fe, Mn and Si concentrations (see also Bowker and Shuler, 1991). In contrast, little change was observed in fluid chemistry at the Cranfield  $\text{CO}_2$  injection site due to the unreactive nature of the quartzite host reservoir (Lu et al., 2012). This highlights the importance of local factors, such as reservoir mineralogy, in determining the likely fluid-rock reactions in  $\text{CO}_2$  injection sites.

#### 3.3.4 Trace Metal Mobilisation

pH driven desorption of trace metals from metal oxide grain surfaces during  $\text{CO}_2$  injection is predicted from modelling studies (Apps et al., 2010; Karamalidis et al., 2013;

Navarre-Sitchler et al., 2012; Siirila et al., 2012), experiments (Frye et al., 2012; Little and Jackson, 2010; Lu et al., 2011; Payán et al., 2012) and recent field tests (Trautz et al., 2012). Experimental studies have shown that CO<sub>2</sub> can mobilise trace metals at concentrations above US Environmental Protection Agency (EPA) concentration limits (Little and Jackson, 2010); however field experiments have not shown hazardous levels of contamination (Keating et al., 2010; Kharaka et al., 2010; Trautz et al., 2012).

At the Plant Daniel pumped shallow release experiment, injection of CO<sub>2</sub> saturated water at ~50m depth into the Graham Ferry Formation resulted in the rapid release of divalent metals from the sediment (Trautz et al., 2012). A sharp drop in pH and increase in metal cations (Ca, Mg, Sr, Ba, Fe, Mn and Cr) and alkalinity was observed at the observation well ~5m from the injection well after 8 to 10 days. Concentrations peaked after 23 to 24 days and gradually returned to or near background concentrations. This pulse release behaviour is attributed to the rapid pH-driven desorption of trace metal from grain surfaces and complete dissolution of finite amounts of Fe-sulphide and dolomite at the low pH plume head, followed by a plume tail that encounters sediment that has been depleted by continuous mobilisation at the plume front (Trautz et al., 2012). Throughout this field experiment the concentrations of potentially hazardous trace metals (e.g. As, Pb, Hg) remained below EPA concentration limits.

The rate of trace metal release by pH-driven desorption will reflect trace metal absorption site density and mineral surface areas, the rate of carbonate and metal oxide dissolution reactions that buffer pH, the coupling of desorption to the dissolution of trace metal bearing mineral phases (Bearup et al., 2012) and the pre-existing redox state of the fluid. Trace metals may be subsequently removed from solution as pH rises across mineral-fluid reaction fronts (Wigley et al., 2013b; Wigley et al., 2012) or by re-adsorption in the presence of compatible mineral phases such as clays (Viswanathan et al., 2012). These

observations suggest, that in carbon storage sites, progressive fluid flow and fluid-rock reaction will act to immobilize trace metals previously mobilised by the CO<sub>2</sub>.

### **3.4 Organic Contaminants**

Subsurface reservoirs, especially depleted oil fields, contain a variety of organic compounds, many of which are toxic and carcinogenic (e.g., BTEX and PAH; Kharaka and Hanor, 2003) and the mobilisation of organic compounds has been observed during some CO<sub>2</sub> injection experiments (Daley et al., 2007a; Kharaka et al., 2009). Fluid samples collected ~20 days after the end of CO<sub>2</sub> injection at the Frio-I injection experiment had dissolved organic carbon (DOC) concentrations ~100 times those in samples collected prior to CO<sub>2</sub> injection, and were enriched in formate, acetate, and toluene, but showed no enrichment in organic acid anions and BTEX compounds (Kharaka et al., 2009). The Frio sandstone is not notably enriched in organic components (Kharaka et al., 2009) and such mobilisation highlights the efficacy of supercritical CO<sub>2</sub> as a solvent for organic compounds and hydrocarbons (Kolak and Burruss, 2006).

Burant et al., 2012 reviewed experimental data on the solubility of organic compounds in supercritical CO<sub>2</sub>, and the partitioning of organic compounds between water and CO<sub>2</sub>, and suggested that compounds with high volatility and low aqueous solubility will be preferentially mobilised into the CO<sub>2</sub> phase. The solubility of the organic compounds in CO<sub>2</sub> is strongly affected by cosolvency processes, the state of hydration of the CO<sub>2</sub> phase and the salinity of the contacting brine (Burant et al., 2012). The dearth of experimental data on the partitioning of organic compounds between supercritical CO<sub>2</sub> and brine makes assessment and modelling of the subsequent recontamination of the brine phase difficult. The routine measurement of such compounds during CO<sub>2</sub> injection experiments and further experimental studies would improve understanding of the relative partition and efficacy of CO<sub>2</sub> for mobilising organic molecules and contaminating groundwater.

## 4 Long Term Fluid-Rock Interactions in Injection Experiments and CO<sub>2</sub>-EOR Studies

### 4.1 Ionic Trapping

Long-term fluid-rock interactions that may stabilize the CO<sub>2</sub> in storage reservoirs include the ionic trapping of CO<sub>2</sub> as bicarbonate ions in solution and precipitation as carbonate minerals, which may impact flow. The results from Frio-I and Frio-II show that rapid dissolution of carbonate minerals and Fe-oxides, Fe-oxyhydroxides and Fe-sulphides lead to the production of ~50 mmol/L alkalinity after only a few days of reaction. Raistrick et al. (2006) and Myrntinen et al. (2010) examined long-term changes in the  $\delta^{13}\text{C}$  of HCO<sub>3</sub><sup>-</sup> from reservoir fluids at the Weyburn CO<sub>2</sub>-EOR project and Ketzin CO<sub>2</sub>-injection experiment, respectively. These studies used mass balance calculations, constrained by measurements of alkalinity and the  $\delta^{13}\text{C}_{\text{HCO}_3^-}$  in fluids sampled from observation wells to quantify the fraction of bicarbonate originating from the injected CO<sub>2</sub> as opposed to that produced from carbonate mineral dissolution or bacterial sulphate reduction. After 40 months of injection, bicarbonate concentrations at Weyburn and Ketzin respectively increased to between 12 to 24 mmol/L and 12 to 27 mmol/L, and between 65-81% and 69-95% of this newly formed bicarbonate was derived from the injected CO<sub>2</sub> (Equation 1 and by reaction with non-carbonate minerals), the remainder being derived from dissolved carbonate minerals.

Production of alkalinity above these concentrations will depend on the relative rates of insoluble silicate mineral dissolution and carbonate mineral precipitation and the time taken to reach carbonate and silicate mineral-fluid equilibrium. The total mass of carbon sequestered by ionic trapping will be limited by the rates of CO<sub>2</sub> flow and dissolution, and CO<sub>2</sub> diffusion and transport of CO<sub>2</sub> in formation brine. The efficacy of ionic trapping is highly dependent on the interaction of the CO<sub>2</sub> with large volumes of water; for example at 30°C and 100 bar, and a maximum concentration of bicarbonate of ~100mmol/L, each litre of

CO<sub>2</sub> must interact with 160 litres of water for the CO<sub>2</sub> to be completely trapped as bicarbonate ions.

## 4.2 Carbonate Mineral Precipitation

Post-injection fluid sampling at the Frio-I injection experiment revealed that Fe concentrations at the observation well had decreased to ~50% of their concentration maximum one month after CO<sub>2</sub> injection stopped (Kharaka et al., 2006a) and close to their initial values after ~6 months (Xu et al., 2010). Xu et al. (2010) reproduced the observed trends using reactive transport modelling and attributing the immobilisation of Fe to the precipitation of ankerite and siderite in the reservoir.

### 4.2.1 Pembina-Cardium EOR project

Observations from the Pembina-Cardium CO<sub>2</sub>-EOR project (Johnson et al., 2011a; Johnson et al., 2011b; Shevalier et al., 2009) provide a limited observational database on fluid-rock reactions over a 1.5 year period (Fig. 15). Arrival of CO<sub>2</sub> at the production wells surrounding the CO<sub>2</sub> injection well was accompanied by rapid shifts in oxygen isotopic composition of the brine due to exchange with the CO<sub>2</sub> (Fig. 15A-B; Johnson et al., 2011a) and increases in alkalinity (Fig. 15C-D; up to 40 to 70 mmol/L) and Ca, Sr, Fe and Mn concentrations (Fig. 15C-F) over a period of ~ 1 to 2 months (data from Penn West Energy Trust, 2007), which is attributed to the rapid dissolution of calcite, siderite and Fe-oxides present in the reservoir. Calculation of dissolved CO<sub>2</sub> concentrations and in-situ pH assuming CO<sub>2</sub> saturated conditions shows that the fluids rapidly become undersaturated in carbonate minerals due to CO<sub>2</sub> dissolution and calcite and siderite dissolves (Fig. 15G-H). The fluids remain undersaturated in calcite whilst moving rapidly to saturation with siderite and ankerite and remain at saturation throughout the 1.5 year sample period, whilst bicarbonate, Fe and Mn concentrations in the fluid decrease. This suggests that the fluid composition is modified

by calcite dissolution and reprecipitation of less soluble Fe-Mg-Ca carbonate phases, such as ankerite and siderite.

#### 4.2.2 Salt Creek EOR project

Observations from the large-scale CO<sub>2</sub>-EOR project at the Salt Creek Field, Wyoming provide important insights into the progress of fluid rock reactions during CO<sub>2</sub> injection (Fig. 16; Kampman et al., 2011). The 2<sup>nd</sup> Wall creek sandstone is a feldspathic litharenite and has a reactive mineralogy of abundant plagioclase (~20% An) and mica; it is heavily cemented with calcite at its top and base. The immature nature of the sediment preserves the detrital mica component, with only minor development of illite and kaolinite grain coatings.

Approximately 20 days after CO<sub>2</sub> injection the arrival of significant CO<sub>2</sub> at the up-dip production well was accompanied by a rapid increase in alkalinity corresponding to increases in the concentration of Ca, Sr, Na, K and Si. Changes in alkalinity over the first ~20 days are balanced mainly by changes in Ca in the fluid which, together with the covariance of Ca and Sr and the Ca/Sr ratio, is consistent with calcite dissolution. During this period Na, K and Si concentrations also start to rise, but more slowly, consistent with the sluggish dissolution of silicate minerals in the reservoir. Subsequently, CO<sub>2</sub>-rich fluid arrives at the production well and concentrations of K, Na and Si start to rise more rapidly due to the dissolution of biotite and plagioclase in the reservoir. The magnitude of the changes in Si and Al are significantly smaller than those of K and Na reflecting production of silica and clay minerals in the reservoir and possibly exchange of Ca for Na and K on clay minerals. Alkalinity increases from ~65 mmol/L to ~100 mmol/L after ~5 months of reaction which implies the fluids are close to saturation in CO<sub>2</sub>.

Simple mass balance calculations, accounting for changes in the evolving fluid composition due to calcite, plagioclase and biotite dissolution, reveal that initial calcite dissolution over 40 days moves to carbonate precipitation as the fluid saturates with

carbonate and Ca from plagioclase dissolution is redeposited as carbonate minerals. The role of ion exchange in this simple illustrative calculation was not assessed. The calculations show that ~1.5x the total mass of carbonate dissolved per litre of fluid is redeposited. The rate of Ca deposition and Na, and K production appears to decline over the 4 month period. This highlights the important role of silicate mineral dissolution as the rate limiting step for carbonate mineral precipitation. The results suggest that silicate mineral dissolution rates can initially be rapid in the mineral-undersaturated acidic conditions following injection.

## **5 Long Term Fluid-Rock Reactions - Observations from Natural Analogues**

Natural accumulations of CO<sub>2</sub> provide important insights into the long-term geochemical processes and trapping mechanism operating in CO<sub>2</sub> reservoirs. The study of natural CO<sub>2</sub> reservoirs and their implications for CO<sub>2</sub> storage are reviewed in Bickle et al., (2013). The important questions that may be answered by observations on natural analogues include the rates and significance of the stabilising mechanisms of CO<sub>2</sub> dissolution in brines and carbonate precipitation, the nature of the fluid-mineral reactions and the long-term consequences of interactions between CO<sub>2</sub> and CO<sub>2</sub>-saturated brines on caprocks and fault zones. The continued study of such sites is likely to provide important constraints on the coupling of advective-diffusive transport of CO<sub>2</sub> and CO<sub>2</sub>-charged brines with mineral dissolution and carbonate precipitation in low permeability rocks, with implications for the long-term integrity of reservoir seals.

There are numerous natural accumulations of CO<sub>2</sub> in geological reservoirs (Allis et al., 2001; Haszeldine et al., 2005; Pearce, 2004; Pearce, 2006). However in most of these, the reservoirs are inadequately sampled, fluid and gas samples maybe unavailable and details of the age and hydrology of the reservoirs are limited.

In the Colorado Plateau, USA, CO<sub>2</sub> produced by Cenozoic magmatic activity has been stored in a variety of geological reservoir for thousands to many millions of years (Fig. 17;

Allis et al., 2001; Gilfillan et al., 2008). CO<sub>2</sub> from several of these reservoirs is exploited for use in enhanced oil recovery (Allis et al., 2001) and therefore samples of CO<sub>2</sub> gas and some core are available. Analyses of travertine deposits (Burnside et al., 2013; Embid and Crossey, 2009; Kampman et al., 2012) and the noble gas isotopic composition of the CO<sub>2</sub> gas (Ballentine et al., 2001) have put important constraints on the age of the systems, CO<sub>2</sub> mobility (Gilfillan et al., 2011) and CO<sub>2</sub>-fluid interactions (Dubacq et al., 2012; Gilfillan et al., 2008; Gilfillan et al., 2009; Zhou et al., 2012). However samples of the reservoir, caprocks and waters are not generally available, the exception being the active leaking system at Green River, Utah, where natural CO<sub>2</sub>-driven cold water geysers allow sampling at surface (e.g. Kampman et al., 2009) and a 2012 scientific drilling campaign has sampled core and fluids from the active reservoir. The following sections discuss some of the constraints on long term fluid-fluid and fluid-rock reactions obtained from these natural reservoirs, focusing on the well-studied site at Green River.

### **5.1 Noble Gas Constraints on the Long Term Fate of Natural CO<sub>2</sub>**

Changes in the CO<sub>2</sub>/<sup>3</sup>He ratio and δ<sup>13</sup>C<sub>CO<sub>2</sub>(g)</sub> measured in reservoir gases from multiple wells across ten major CO<sub>2</sub> reservoirs from the Colorado Plateau and elsewhere reveal 40% to 90% of the CO<sub>2</sub> originally emplaced has been lost to solution over geological time-scales (Gilfillan et al., 2009; Zhou et al., 2012), highlighting the important role that dissolution into groundwater has on the long-term stabilisation of CO<sub>2</sub> reservoirs. For the young Bravo Dome accumulation, which may be undergoing contemporary CO<sub>2</sub> recharge (Baines and Worden, 2004), fractionation of the CO<sub>2</sub>/<sup>3</sup>He ratio and δ<sup>13</sup>C<sub>CO<sub>2</sub>(g)</sub> imply removal of gas from the fluid into solutions with high HCO<sub>3</sub><sup>-</sup> concentrations, implying that in this dynamic field fluid-rock reaction is an important source of alkalinity and ionic trapping of the CO<sub>2</sub> (Dubacq et al., 2012). The magnitude of the CO<sub>2</sub> loss in these reservoirs must be related to the hydrodynamics of groundwater flow and diffusive transport processes close to the gas

cap-formation water interface. Such transport processes likely produce compositional and isotopic disequilibrium between the gas cap and the contacting formation water. It is likely that only information about the dissolution of the CO<sub>2</sub> phase into the formation fluid is recorded in the composition of the gas cap, and processes related to subsequent mineralization of the CO<sub>2</sub> in solution are most likely not recorded, precluding the use of reservoir gases as a measure of subsequent mineral trapping mechanism in the formation fluid.

## **5.2 Fluid-mineral Reactions in Natural Reservoirs**

Petrological studies of natural CO<sub>2</sub> reservoirs reveal a range of degrees of fluid-mineral reaction from minor amounts of carbonate dissolution to complete dissolution of all reactive mineral phases and the deposition of relatively insoluble Fe-Mg-Ca carbonate minerals, including ankerite, siderite and dolomite (Franks and Forester, 1984; Heinemann et al., 2013; Watson et al., 2004; Wilkinson et al., 2009b), and dawsonite (Baker et al., 1995; Moore et al., 2005; Wilkinson et al., 2009b; Worden, 2006). The impact of CO<sub>2</sub>-promoted reactions will differ between sites depending on differences in; 1) pre-existing reservoir mineralogy; 2) CO<sub>2</sub> emplacement mechanism and rates; 3) CO<sub>2</sub> and mineral solubility across the wide range of pressure temperature conditions experienced by natural CO<sub>2</sub> reservoirs and; 4) variable reaction rates due to mineral surface and transport controlled reactions.

Some studies have observed trapping of CO<sub>2</sub> in carbonate minerals (Moore et al., 2005; Pauwels et al., 2007; Watson et al., 2004; Worden, 2006); however the volumes deposited are small as the rate limiting step for carbonate deposition within these reservoirs is alkalinity and divalent metal cation production from the slow weathering of silicate minerals. The formation of dawsonite is predicted from modelling studies (Hellevang et al., 2005; Xu et al., 2005) but its occurrence in natural CO<sub>2</sub> accumulations is rare (e.g. Moore et al., 2005). The scarcity of natural dawsonite is likely the result of its limited phase stability (Bénézech et

al., 2007) in carbon-rich alkaline fluids, and its subordinate stability to other alumino-silicate minerals (e.g. analcime; Kaszuba et al., 2005).

### 5.2.1 Implications for carbonate mineral deposition

The deposition of carbonate minerals is likely to be a significant process where CO<sub>2</sub> rich fluids diffuse into clay-rich caprocks containing reactive phyllosilicate minerals (Gherardi et al., 2007; Lu et al., 2009) or escape along faults and experience rapid CO<sub>2</sub> degassing (Gratier et al., 2012; Kampman et al., 2012; May, 2005). In both instances the deposition of carbonate is likely to have important long-term impacts on fluid flow and CO<sub>2</sub> leakage rates (McPherson and Heath, 2009). In addition, precipitation of carbonate minerals in faults and fractures may generate stresses due to the forces of crystallization sufficient to induce, sustain or enhance leakage (e.g. Gratier et al., 2012; Iyer et al., 2008; Jamtveit et al., 2009; Plümper et al., 2012).

Leaking natural CO<sub>2</sub> reservoirs at St Johns Dome, Arizona (Moore et al., 2003) and Green River, Utah (Burnside et al., 2013; Dockrill and Shipton, 2010; Kampman et al., 2012; Shipton et al., 2005; Shipton et al., 2004) both contain significant volumes of surface and fault-hosted carbonate deposits, where degassing of CO<sub>2</sub> during ascent of the fluid has driven carbonate deposition. Studying such deposits provides important insights into the long-term behaviour of fault hosted CO<sub>2</sub> leakage and the important role played by climate driven changes in groundwater hydrology and regional stresses in controlling fault hydraulic behaviour and CO<sub>2</sub> leakage rates over geological time-scales (Kampman et al., 2012).

## 5.3 Green River, Utah

The CO<sub>2</sub> accumulation at Green River, Utah (Fig. 18) provides important constraints on the nature and rates of the CO<sub>2</sub> promoted fluid-mineral reactions. Here the fluid-mineral reaction rates can be constrained both in flowing CO<sub>2</sub>-charged groundwaters where fluids

have been sampled along flow paths (Kampman et al., 2009), or in the exhumed CO<sub>2</sub>-reservoirs where mineralogical profiles across reaction fronts have been measured and fluid transport rates constrained or estimated from hydrological models (Wigley et al., 2013a).

### 5.3.1 Green River Active System

At Green River CO<sub>2</sub>-charged fluids flow through the Navajo Sandstone, escape to the surface through a number of abandoned petroleum exploration wells and the fault damage zones of the Little Grand Wash fault and Salt Wash Graben at the apex of the Green River anticline (Fig. 18; Dockrill and Shipton, 2010; Shipton et al., 2005; Shipton et al., 2004) where they form a series of natural CO<sub>2</sub> springs (Heath, 2004; Kampman et al., 2009), including the spectacular Crystal Geysers (Assayag et al., 2009; Gouveia and Friedmann, 2006; Gouveia et al., 2005; Han et al., 2013). The CO<sub>2</sub> and CO<sub>2</sub>-charged brines that migrate into the Navajo Sandstone originate from a supercritical reservoir of CO<sub>2</sub> in the White Rim sandstone at depth, and the system is a good analogue for processes occurring during CO<sub>2</sub> migration through the overburden and in shallow CO<sub>2</sub> gas reservoirs. Ancient travertine deposits along the faults attest to leakage of CO<sub>2</sub> from the site for at least the last 400,000 years (Burnside et al., 2013), characterised by successive pulses of CO<sub>2</sub>-leakage with a periodicity controlled by climate driven changes in the hydraulic behaviour of the faults (Kampman et al., 2012).

### 5.3.2 Scientific Drilling

Recent scientific drilling at Green River, near the intersection of the apex of the Green River anticline and the Little Grand Wash fault, has sampled core and CO<sub>2</sub>-rich fluids to a depth of 322m from a sequence of sandstone reservoirs (Fig. 19), (Kampman et al., 2013a). At the site of the CO<sub>2</sub>W55 drillhole, these CO<sub>2</sub>-charged reservoirs are juxtaposed against a fault damage zone that has previously hosted CO<sub>2</sub> leakage, being overlain by ancient

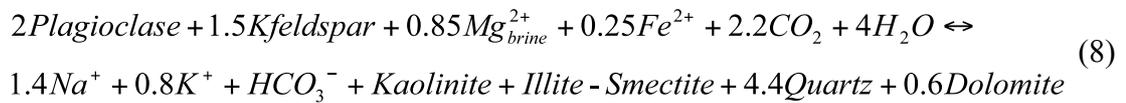
travertine deposits (Dockrill and Shipton, 2010). CO<sub>2</sub>-charged fluid was first encountered at a depth of 50m in the basal sandstones of the Entrada Sandstone, which is not overlain by a regional caprock in this region, indicating that the thin siltstone layers present in the upper portions of the formation act as a good seal to the CO<sub>2</sub>-charged fluids. A second larger reservoir of CO<sub>2</sub>-charge fluid was encountered in the Navajo Sandstone, capped by siltstone sequences of the Carmel Formation, and both the reservoir and lower portions of the caprock have been bleached by the CO<sub>2</sub>-rich fluids. The core revealed net carbonate precipitation in the reservoir rocks and in the siltstone caprocks around fractures, but mineral dissolution fronts of Fe-oxide grain coatings (c.f. Wigley et al., 2012) and dolomite cements at the caprock reservoir interface (Fig. 20; compare to Wigley et al., 2013a). Reaction of CO<sub>2</sub>(aq) as it diffuses into a caprock will retard the diffusion distance, and limit the extent to which CO<sub>2</sub> penetrates the caprock. Conversely these reactions may generate porosity, further enhancing the penetration depth of the CO<sub>2</sub> and weakening the overall integrity of the caprock. The preliminary observation that the mineral dissolution fronts have penetrated only tens of centimetres into the cored siltstone caprocks in the hundreds of thousands of years of exposure to CO<sub>2</sub> rich fluids suggests limited degradation by the CO<sub>2</sub>-charged fluids and attests to the efficiency of the sealing layers.

Downhole fluid sampling profiles (Kampman et al., 2013b this issue) reveal that the reservoir is being recharged by inflow of CO<sub>2</sub> and CO<sub>2</sub>-saturated brines through the fault damage zone, which then flow away from the fault and mix with meteorically derived fluid, and this has previously been inferred from the elemental and isotopic composition of the local CO<sub>2</sub>-springs (Kampman et al., 2009; Wilkinson et al., 2009a). Kampman et al. (2012), used U-Th ages calculated by Burnside (2010) combined with isotope ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) and trace element ratios (Sr/Ca and Ba/Ca) in carbonate veins to show that the reservoir has been periodically recharged over the last 135,000 years by inflow of these CO<sub>2</sub>-charged

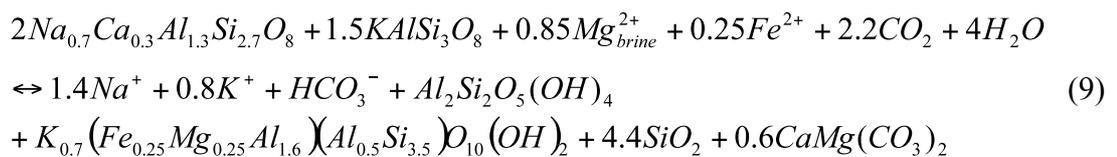
brines through the damage zones of the normal faults. The timing of these CO<sub>2</sub> pulses corresponds to periods of local climatic warming, during the transition from glacial to interglacial conditions. They hypothesize that changes in groundwater recharge rates, and in the continental stresses related to unloading of the continental ice sheet and associated draining of nearby pluvial Lake Bonneville, triggered changes in pore-fluid pressure and dilation of fractures in the fault damage zone, thus facilitating enhanced escape of CO<sub>2</sub>.

### 5.3.3 Fluid-rock Reaction

Kampman et al. (2009) examined fluid-rock reactions in the Navajo Sandstone that occur as these CO<sub>2</sub>-charge fluids flow away from the faults. Mass balance calculations on changes in fluid chemistry along flow paths, flow rates estimated from potentiometric maps, and mineral surface areas estimated from BET measurements were used to show that the dissolution of feldspars in the CO<sub>2</sub>-charged groundwater in the Navajo Sandstone are incongruent, being balanced by the deposition of carbonate and clays, and that the dissolution rates are close to, and highly dependent on proximity to thermodynamic equilibrium. CO<sub>2</sub> is introduced to the reservoir by inflow of CO<sub>2</sub>-charged brines along two major extensional faults (see below). Following introduction of the CO<sub>2</sub>, the release of Na<sup>+</sup> and K<sup>+</sup> to solution traces the dissolution of plagioclase and K-feldspar following the reaction;



With the stoichiometry;



The fluids are undersaturated in the feldspar reactants and oversaturated in dolomite, kaolinite, illite-smectite and silica reaction products. The breakdown of albite is likely the

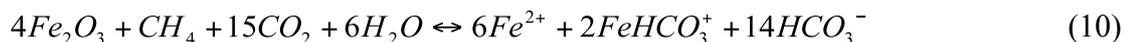
rate limiting step for feldspar dissolution given its insolubility relative to anorthite (c.f. Maher et al., 2009). The feldspar dissolution rates are initially two orders of magnitude slower than far-from equilibrium laboratory rates for feldspars at similar pH and temperature conditions (e.g. Taylor et al., 2000) and decrease over five orders of magnitude as equilibrium is approached. The precipitation rates of carbonate minerals, and thus the rate at which CO<sub>2</sub> is trapped from solution, are consequent on these slow silicate mineral dissolution rates, which are the source of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> ions.

The incongruent dissolution is reflected in the non-stoichiometric release of Al<sup>3+</sup> and SiO<sub>2</sub> to solution. Measured Al concentrations (~3-6 μmol/L) are several orders of magnitude below those thought to inhibit feldspar dissolution (e.g. Amrhein and Suarez, 1992). Measured silica concentrations (~0.1-1 mmol/L) decrease as fluid flows, shallows and cools towards the crest of the anticline and the concentration-temperature relationship is consistent with buffering of silica concentrations by a silica phase with a solubility close to that of chalcedony. Recent laboratory experiments have shown that the growth of silica surface layers during mineral (e.g. Hellmann et al., 2012 and references therein) and glass (see Gin et al., 2008 and references therein) dissolution through interfacial dissolution-reprecipitation can inhibit dissolution rates ( Béarat et al., 2006; Daval et al., 2013; Daval et al., 2011), such that the mineral dissolution rate may ultimately be controlled by the saturation state of the fluid with respect to the silica layer, its dissolution rate and passivating properties. Amorphous silica layers have been observed on naturally weathered feldspar surfaces from the Navajo Sandstone (Zhu et al., 2006), but the feldspar dissolution rates of Kampman et al., (2009) are independent of silica saturation state and most likely not determined by the presence of such a silica layer, or at least not in a simple way. This is consistent with the work of Jordan et al. (1999), which suggested that typical feldspar silica surface layers are not passivating (but see Berger et al., 2002) and only become passivating due to the

incorporation of trace metals such as  $Fe^{3+}$ , under fairly oxidizing conditions (Daval, pers. comm. 2013). These findings point to the important coupling of fluid-mineral reactions in geological reservoirs. The dependency of silicate mineral dissolution rate on the thermodynamic departure from equilibrium goes some way to explaining the long established discrepancy between fluid-mineral reaction rates measured in the laboratory and those measured in the field (e.g. White and Brantley, 2003), with important implications for the rates of potentially  $CO_2$  stabilising reactions in geological storage sites.

#### 5.3.4 Green River Exhumed Reservoir

The Entrada Sandstone is exhumed along the Salt Wash Graben at Green River where it exhibits spectacular large-scale bleaching (Fig. 21) which Wigley et al., (2012) interpret to result from the flow of  $CO_2$ -rich brines. The evidence for  $CO_2$ -rich fluids being involved includes the presence of  $CO_2$  with minor methane in fluid-inclusions, the oxygen and carbon isotopic compositions of secondary carbonates which are similar to those in the active system and markedly different from hydrocarbon related bleaching elsewhere in the Paradox Basin (Beitler et al., 2005; Chan et al., 2000; Eichhubl et al., 2009) and the restriction of the bleaching to the base of the formation consistent with denser  $CO_2$ -bearing brines. The flow of the  $CO_2$ -charged brines, containing small quantities of  $CH_4$ , dissolved haematite grain coatings by a reaction with the stoichiometry (Wigley et al., 2012),



The  $CO_2$  promoted reaction fronts are demarked by sharp mineralogical fronts where haematite and silicate minerals are dissolved from rock that has interacted with the  $CO_2$ -rich brine (Fig. 22). The km-scale lenticular topology of the bleached zone reflects propagation of the reaction front laterally by advection of the dense  $CO_2$ -saturated brine as a gravity current, driven in the direction of regional groundwater flow parallel to the fault, and propagation of

the upper boundary by a rate controlled by the upward diffusion of the CO<sub>2</sub>. Wigley et al. (2013a) have shown that haematite dissolution rates were inhibited by, and coupled to, the more sluggish silicate mineral dissolution rates close to thermodynamic equilibrium and at low rates of fluid transport. Wigley et al. (2013b) have shown that as pH was buffered across mineral reaction fronts, potentially harmful trace metals mobilised by the CO<sub>2</sub>-charged fluids were subsequently re-deposited in secondary Fe-oxide and Fe-rich dolomite that grow at the reaction front (Fig. 23-24). Such exhumed CO<sub>2</sub> reservoirs (see also Loope et al., 2010; Potter-McIntyre et al., 2013) provide invaluable insight into the coupled nature of fluid transport and mineral reaction and reveal reactive-transport processes not yet considered by modelling studies.

## **6 Conclusions and Future Work**

Remote imaging of large-scale commercial CO<sub>2</sub> projects attests to the complexities of macroscopic CO<sub>2</sub> flow during geological CO<sub>2</sub> storage but does not provide adequate constraints on the nature or rates of the fluid-fluid and fluid-mineral interactions, required to predict trapping of the injected CO<sub>2</sub>. Direct sampling of small-scale CO<sub>2</sub> injection experiments and CO<sub>2</sub>-EOR projects provide important constraints on the flow and dissolution of the CO<sub>2</sub>, and the subsequent CO<sub>2</sub>-fluid-mineral reactions. Measurements of in-situ dissolved CO<sub>2</sub> concentrations and elemental and isotopic tracers suggest that fluids in contact with the migrating CO<sub>2</sub> plume rapidly saturate with CO<sub>2</sub>(aq), and the total mass of CO<sub>2</sub> dissolved is likely enhanced by fingering of the CO<sub>2</sub> front on lengths scales controlled by the geological heterogeneity of the reservoir (i.e. bedding scales of ~10 to 100cm), and by convective mixing of dense CO<sub>2</sub> saturated brines. The rapid dissolution of carbonate and Fe-oxide minerals, in the initially low pH ~3.5 fluid, is observed in many experiments and in a variety of reservoir lithologies. Dissolution of soluble carbonate and oxide minerals buffers fluid to pH ~4.5 and accounts for the majority of early alkalinity production (up to ~50

mmol/L), quickly driving fluids to carbonate mineral saturation. Observations from the Salt Creek EOR project, where the reservoir is rich in feldspars and micas, suggest that dissolution of silicate minerals can generate further alkalinity with total alkalinity approaching ~100 mmol/L. Observations from CO<sub>2</sub>-EOR projects and natural CO<sub>2</sub> reservoirs suggest that the fluids remain buffered at carbonate mineral saturation by calcite, oxide and silicate mineral dissolution and the redeposition of less soluble Fe-Ca-Mg carbonates.

In the long-term carbonate mineral deposition may be rate limited by the balance between fluid transport and flow and dissolution of the CO<sub>2</sub>, and by sluggish surface-controlled silicate mineral dissolution close to thermodynamic equilibrium. More significant carbonate deposition is likely to occur where CO<sub>2</sub>-saturated fluids migrate vertically in faults and fractures, to lower pressures, degassing CO<sub>2</sub> driving carbonate mineral supersaturation and rapid deposition rates, which may ultimately self-seal such leakage pathways. Carbonation of reactive phyllosilicate rich caprocks has been observed during scientific drilling of a natural CO<sub>2</sub> accumulation, where penetration by diffusion of CO<sub>2</sub>-rich fluids has generated fluid-mineral reaction fronts which may impact on the long term integrity of the seal.

Laboratory experiments predict the mobilisation of harmful trace element and organic contaminants, which is observed during CO<sub>2</sub> injection experiments but typically not to harmful concentrations and observations from natural analogues suggest trace element contaminants may be immobilised as pH changes across mineral reaction fronts.

Further small-scale CO<sub>2</sub>-injection experiments are required to improve understanding of the coupled nature of CO<sub>2</sub> flow, dissolution and mineral-fluid reactions. The mobility of tracers and isotopes depends on two phase flow and fluid-fluid dissolution as well as on diffusive exchange. More detailed studies will enable inversion of such measurements to constrain the complexities of CO<sub>2</sub> flow and the efficacy of CO<sub>2</sub> dissolution and capillary trapping. The results of such studies could then be used to further refine numerical models of

two-phase flow processes at the length-scales over which the crucial physical processes, such as CO<sub>2</sub>-brine fingering, determine the efficacy of CO<sub>2</sub> trapping.

The measurement of in-situ pH and the recovery of samples at reservoir pressure on which pH and CO<sub>2</sub> saturation can be determined at surface, are crucial to successfully measure and interpret the progress of CO<sub>2</sub> dissolution and fluid-mineral reactions. The measurement of in-situ redox state will also be crucial to the successful interpretation and prediction of mineral stability and trace element contaminant mobilisation from mineral dissolution or surface desorption. The measurement of organic and trace element concentrations and partitioning between brine and CO<sub>2</sub> phases during injection experiments is also required to better predict future contaminant mobilisation and transport. Interpreting the results of future fluid sampling projects will be significantly enhanced by detailed studies of reservoir petrology and mineral surface properties (BET; silica coatings etc). Accurate modelling of CO<sub>2</sub>-fluid-mineral reactions and the progress of ionic and mineral trapping requires more laboratory measurements of mineral dissolution rate constants and mineral solubilities, especially for Fe-Mn oxides and oxyhydroxides and Fe-Ca-Mg carbonate minerals and their solid solutions. Ultimately, small-scale CO<sub>2</sub>-injection experiments and studies of natural CO<sub>2</sub> reservoirs provide the best constraints on the length-scales and the coupling of the crucial physical and geochemical processes that determine the long-term fate of CO<sub>2</sub> in anthropogenic storage sites.

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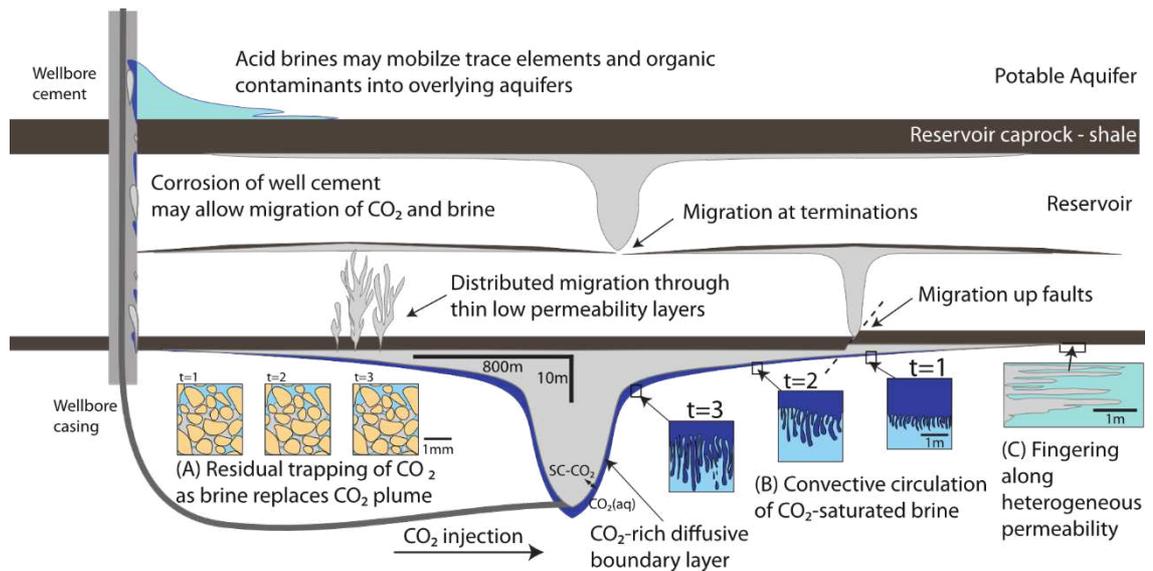
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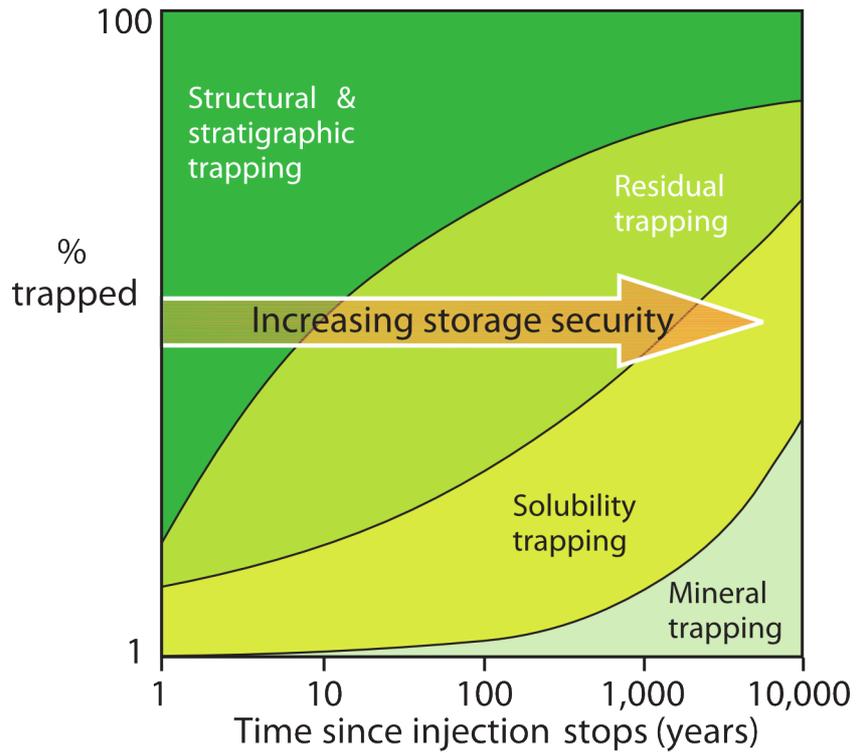
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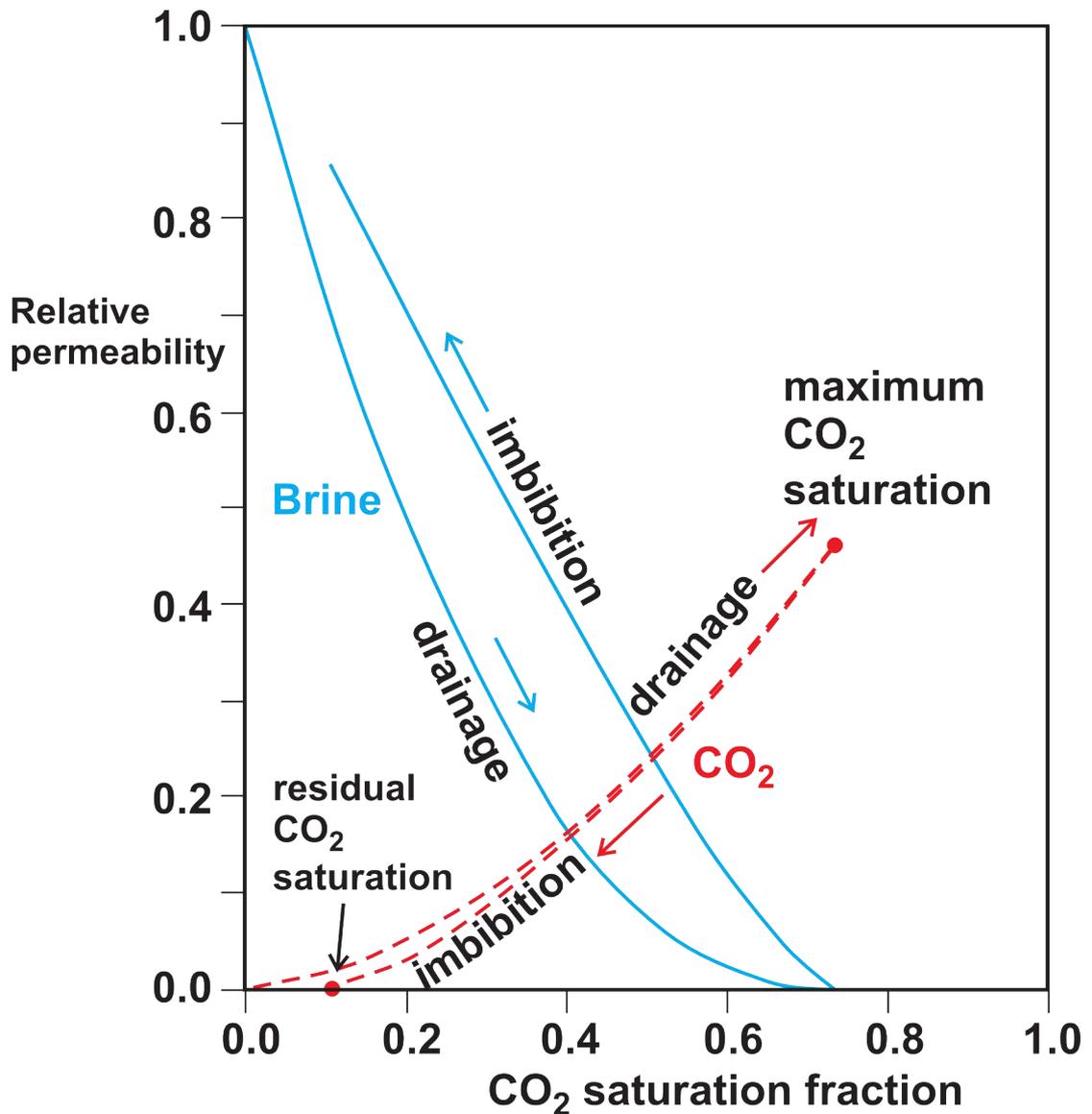
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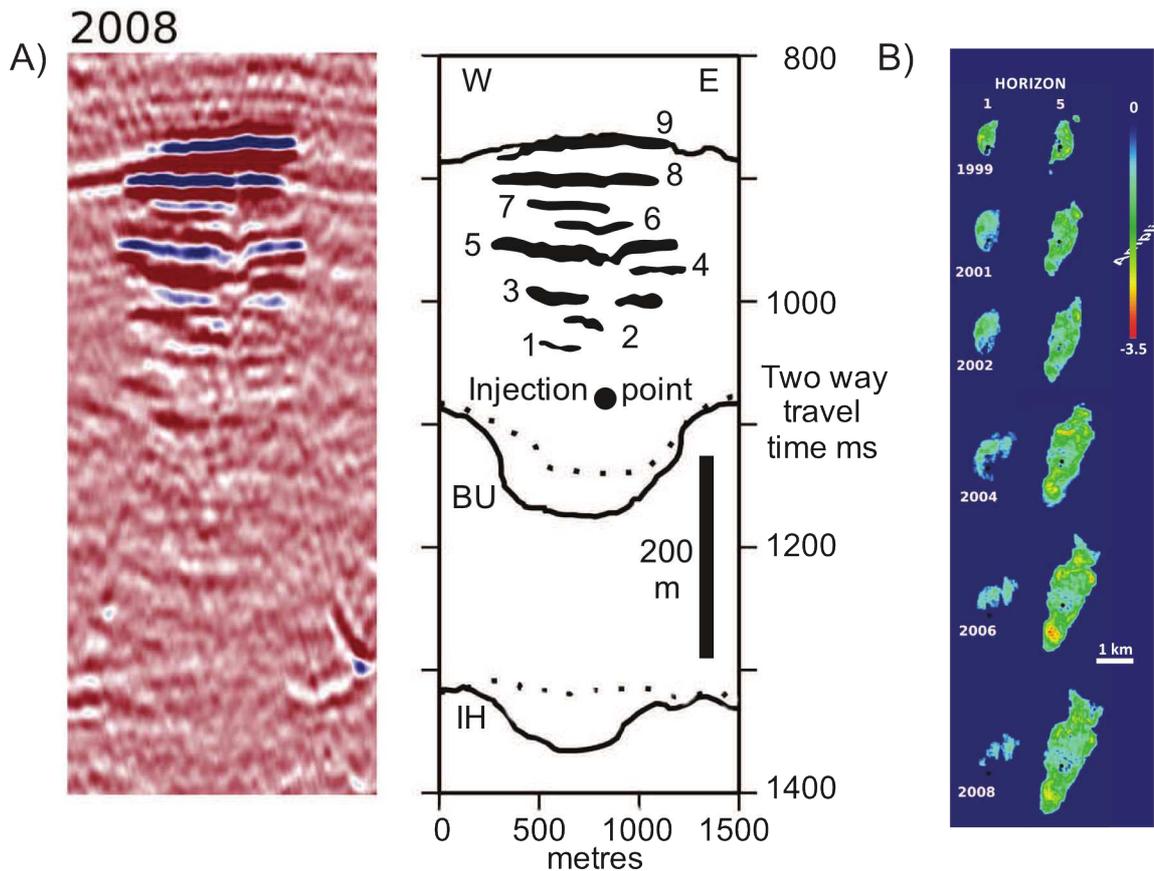
**Figure 1** Diagrammatic illustration of geological carbon storage. CO<sub>2</sub> from concentrated sources is separated from other gasses, compressed and injected into porous geological strata at depths > 800 m where it is in a dense or supercritical phase. The CO<sub>2</sub> is lighter than formation brines, rises and is trapped by impermeable strata. The risks are that the light CO<sub>2</sub> will exploit faults or other permeable pathways to escape upwards and acid CO<sub>2</sub>-charged brines might corrode the caprocks or fault zones. A variety of processes will tend to stabilise the CO<sub>2</sub> including 1) capillary trapping in bubbles of CO<sub>2</sub> after the CO<sub>2</sub> plume has passed (inset A), 2) dissolution in formation brines which forms a denser fluid which will sink (inset B), where fingering along bedding-related heterogeneities will enhance dissolution (inset C), and 3) precipitation of CO<sub>2</sub> in solid form as carbonate minerals as a result of reactions between CO<sub>2</sub>-charged brines and silicate minerals.



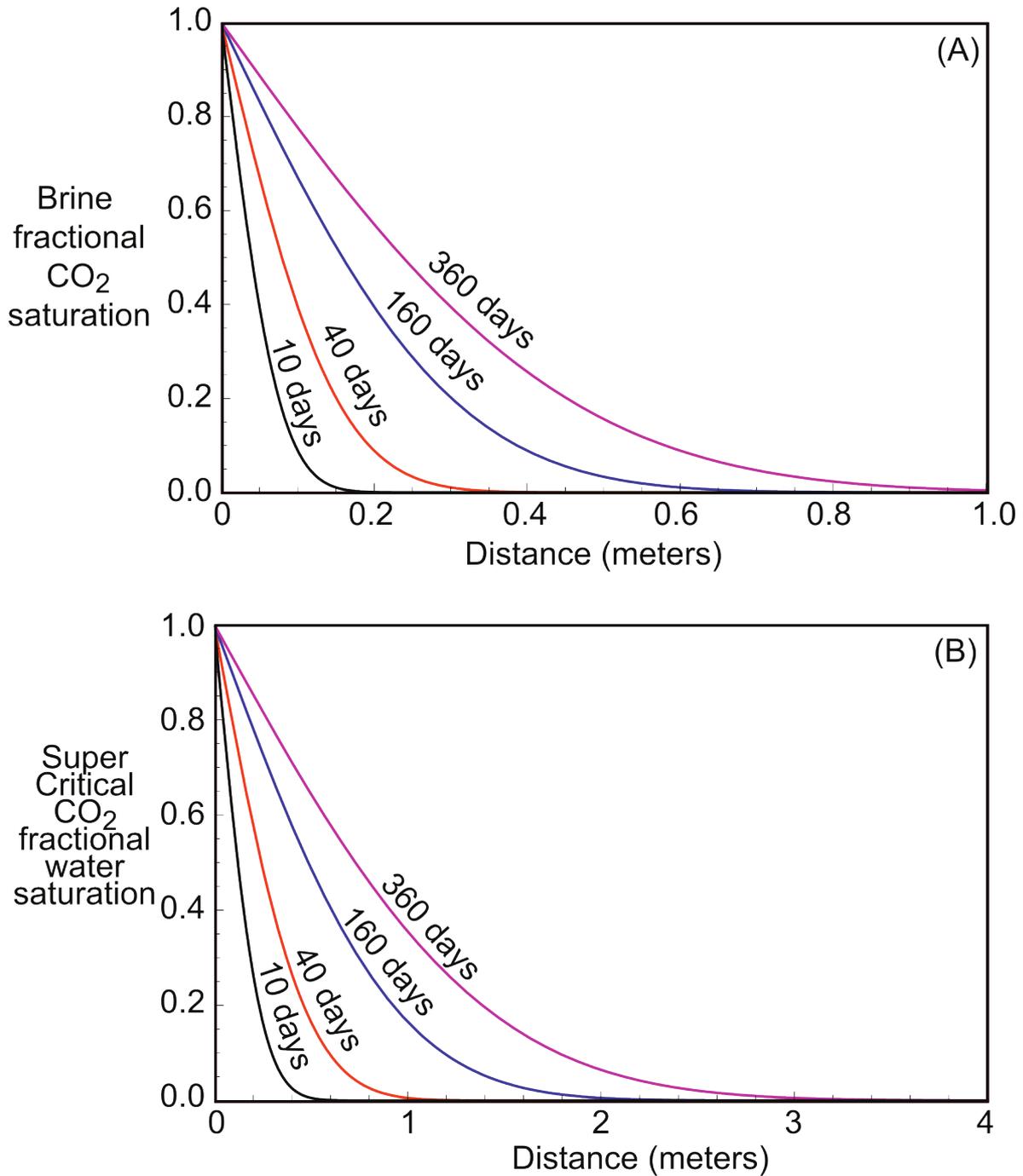
**Figure 2** Diagrammatic illustration of the proportions of a CO<sub>2</sub> plume trapped by residual, dissolution and mineral trapping as a function time (Metz et al., 2005). Note that the relative magnitudes of the three processes and their evolution with time are very poorly known and will depend on the physical state and mineralogy of the reservoir, and the complex coupling of fluid-flow and fluid-rock reaction.



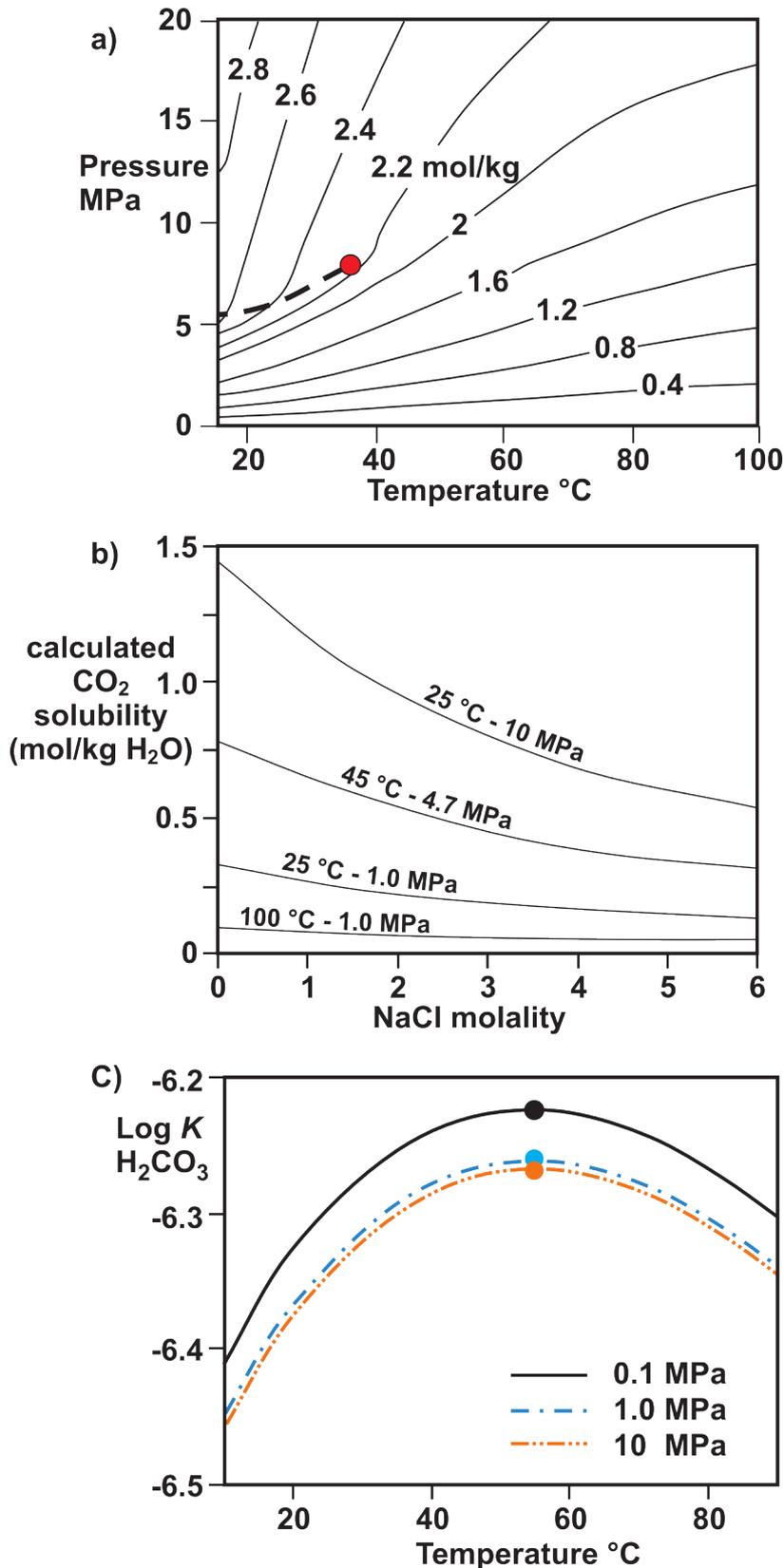
**Figure 3** Schematic brine-CO<sub>2</sub> relative permeability curves illustrating a) two phase flow in high and low permeability rocks and the strong dependence of CO<sub>2</sub> permeability on its relative saturation to brine and b) drainage and imbibition curves showing the relative permeability of brine and CO<sub>2</sub> during flow of CO<sub>2</sub> into the pore volume and then during return flow of brine as the CO<sub>2</sub> plume migrates. The return to a finite residual saturation of CO<sub>2</sub> reflects non-wetting CO<sub>2</sub> trapped in the pore space by capillary forces.



**Figure 4** A) Vertical seismic section from the 2008 Sleipner survey after Boait et al., (2012). Left shows seismic amplitudes with high amplitudes (blue) from CO<sub>2</sub> layers. Right is a line drawing with CO<sub>2</sub> accumulations numbered, CO<sub>2</sub> injection point labelled and solid lines denote formation contacts. The top of Utsira Sand coincides with the top of Layer 9, BU, base of Utsira Sand, and IH, intra Hordland formation. Dotted lines show location on pre-injection 1994 survey where the difference in 2008 reflects 'push down' due to low velocity CO<sub>2</sub> in the reservoir. B) Plan form seismic amplitude maps of the lower and middle CO<sub>2</sub> layers from the 1999-2008 seismic surveys showing i) initial growth and then shrinkage of the lower layer due to filling of the upper layers and ii) sustained growth of the middle layer with plan form moderated by asymmetric buoyant flow of the CO<sub>2</sub> and topographic filling. Redrawn after Boait et al., (2012)

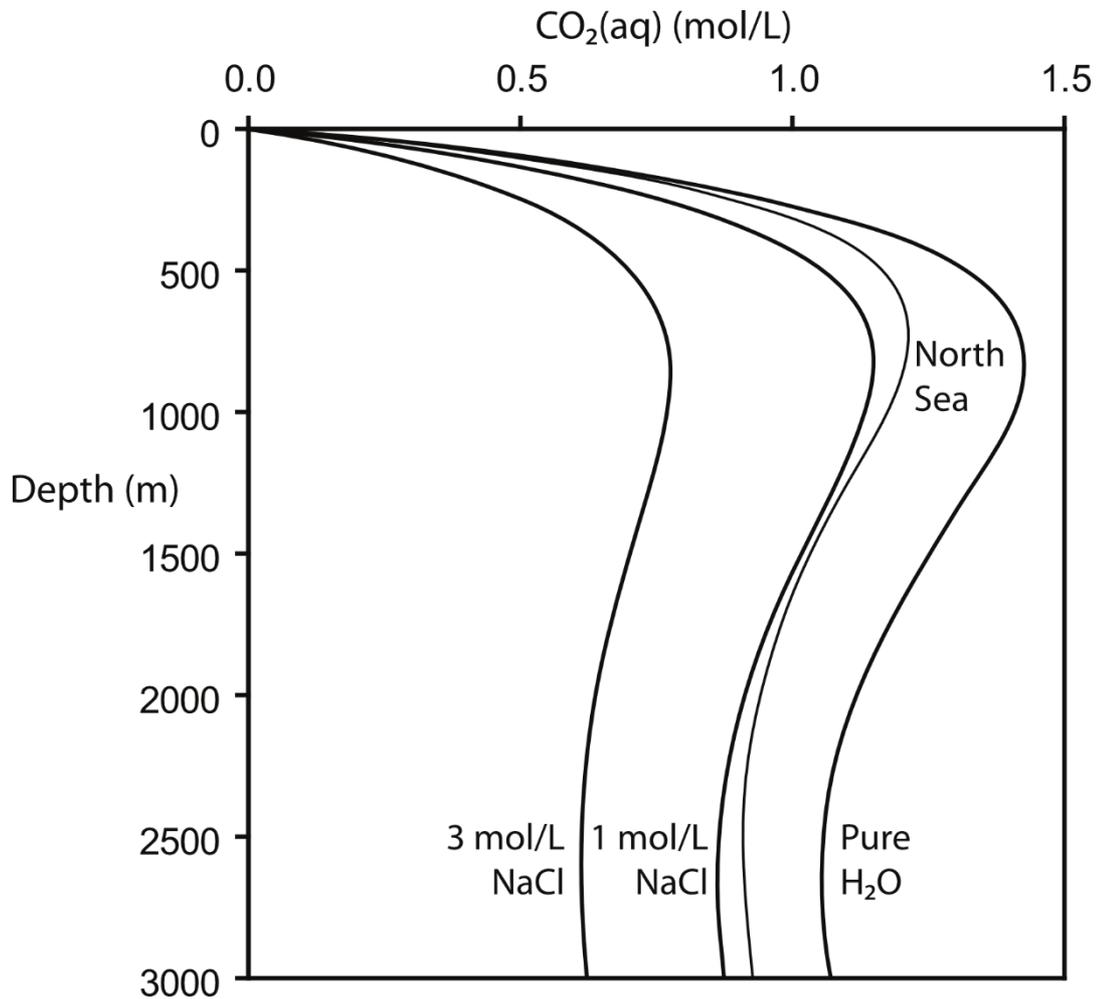


**Figure 5** Diffusion of a) CO<sub>2</sub> into brine and b) H<sub>2</sub>O into CO<sub>2</sub> calculated as a function of time for diffusivities of  $2 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$  and  $2 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$  given as fraction of CO<sub>2</sub> and H<sub>2</sub>O concentration at saturation. This calculation ignores the tortuosity of pore structure which might retard the diffusion distance by  $\sim 30\%$  of the linear calculation.

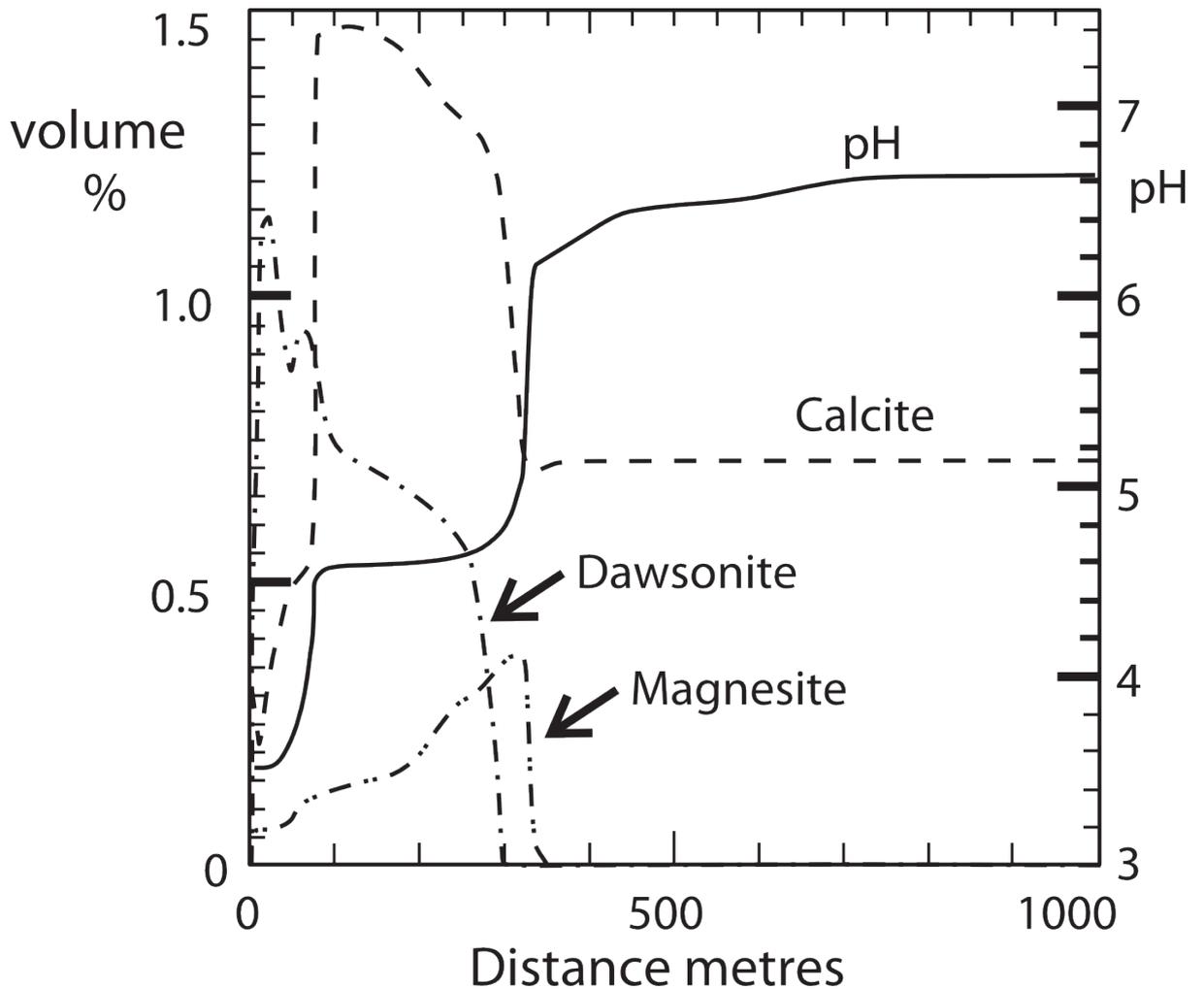


**Figure 6** a) CO<sub>2</sub> solubility in pure water as a function of pressure and temperature, redrawn from Dubacq et al., (2013); b) reduction in CO<sub>2</sub> solubility as a function of increasing fluid salinity, redrawn from Dubacq et al., (2013) and c) Temperature dependent dissociation constant for H<sub>2</sub>CO<sub>3</sub> showing maxima at ~55°C and weak dependence on pressure, calculated

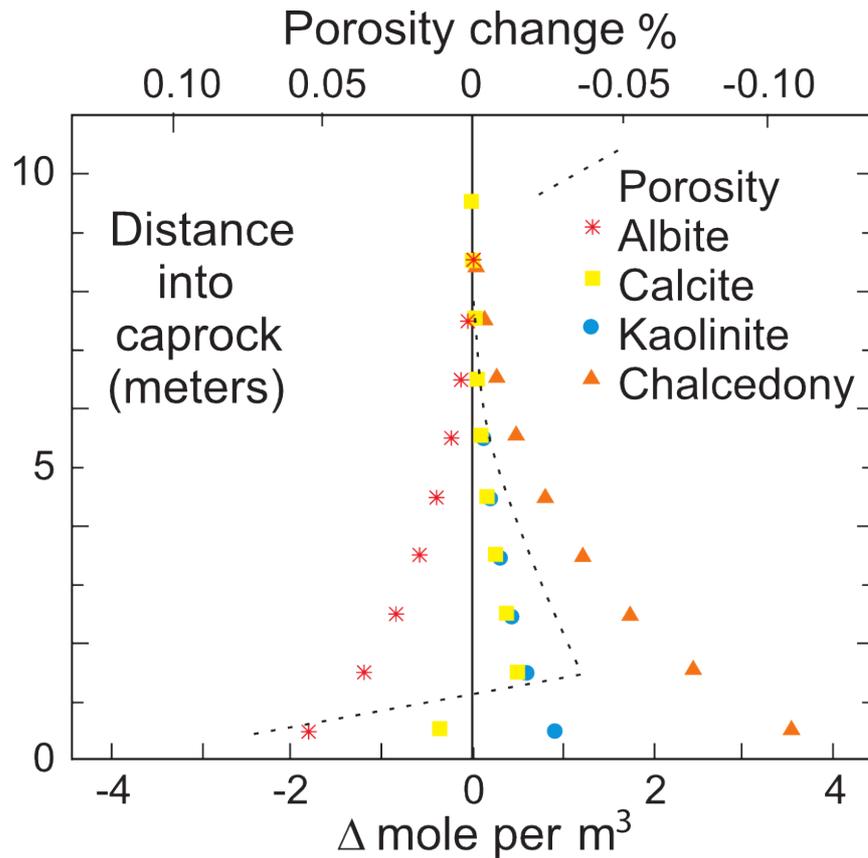
using SUPCRT92 (Johnson et al., 1992). Above and below  $\sim 55^\circ\text{C}$  the  $\log K$  decreases such that an initially weak acid becomes increasingly weaker.



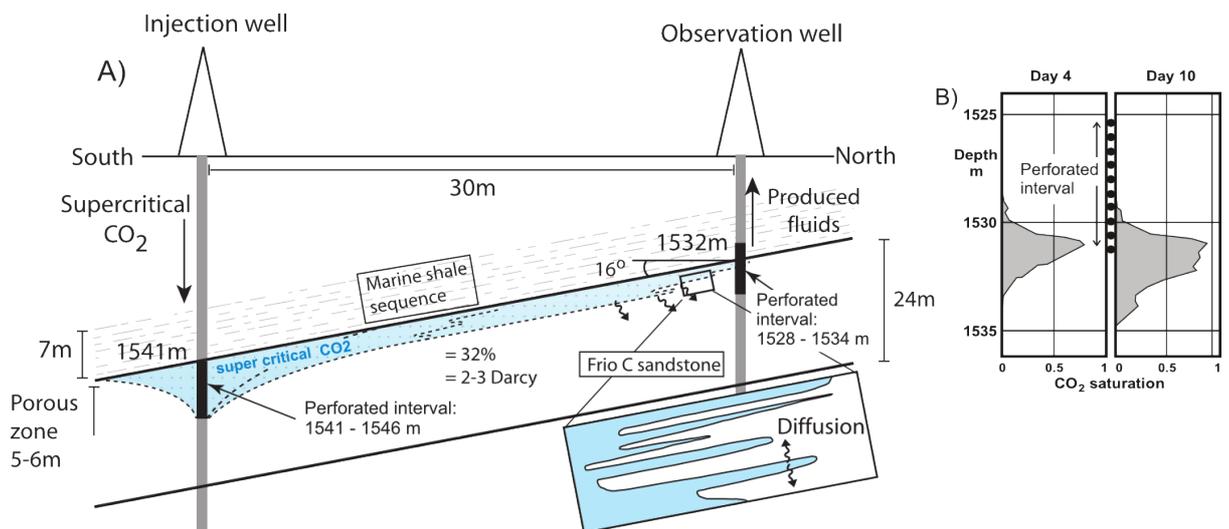
**Figure 7**  $\text{CO}_2$  solubility as a function of depth below surface. Solubility profiles calculated using equations from (Duan et al., 2006), considering typical geothermal gradients of  $25^\circ\text{C}/\text{km}$  and hydrostatic pressure gradients, in pure water and fluid salinities of 1 mol/L and 3 mol/L NaCl. An example for a typical North Sea geothermal gradient of  $25^\circ\text{C}/\text{km}$  and pore salinity profile of 25,000ppm/km (Bjørlykke and Gran, 1994) is also shown.



**Figure 8** Modelled mineral abundances as a function of distance along a radial flow path away from an injector of brine in equilibrium with 8.4 MPa CO<sub>2</sub> into an arkosic sandstone. Note that close to the injector the acid fluids (pH ~3.5) dissolve calcite but that further out more evolved fluids have reacted with silicate minerals which increases their pH to ~ 4.5 and causes precipitation of carbonate. Modelled precipitation of dawsonite, the carbonate NaAlCO<sub>3</sub>(OH)<sub>2</sub>, is uncertain because dawsonite is rare in nature and its equilibrium thermodynamics and precipitation rate constants are uncertain. Redrawn after Knaus et al., (2005).

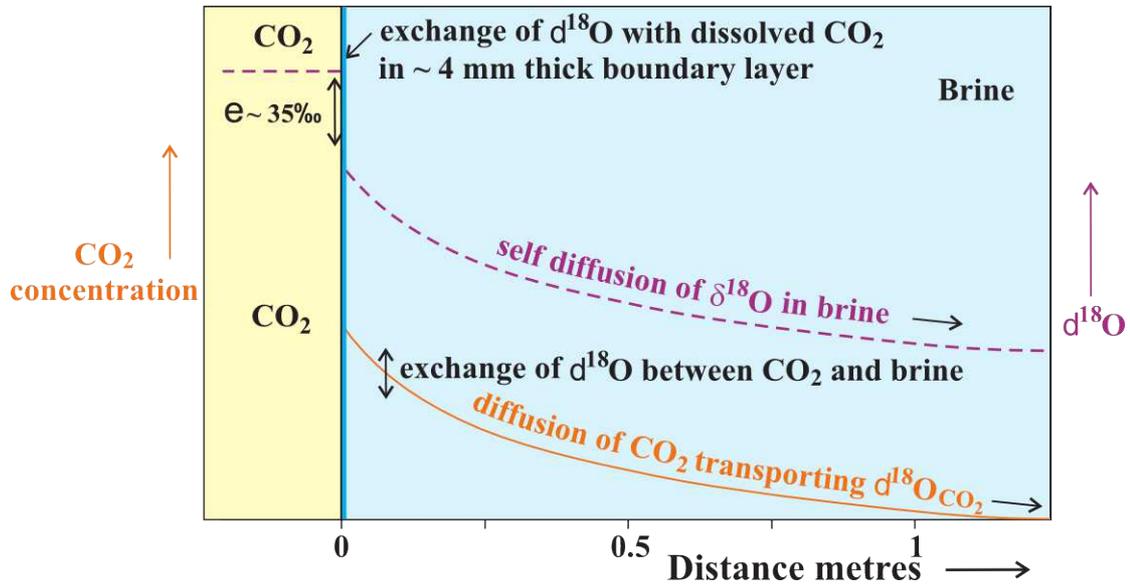


**Figure 9** Alteration at the base of caprock by supercritical  $\text{CO}_2$ , calculated from reactive transport modelling (redrawn after Gaus et al., 2005). Changes in mineral modes reflect dissolution of albite and precipitation of kaolinite and chalcedony throughout the profile, and dissolution of calcite at the base of the profile but precipitation greater than  $\sim 1$  m above the base. Note the net decrease in porosity except at the very base of the profile. Redrawn after Gaus et al., (2005).

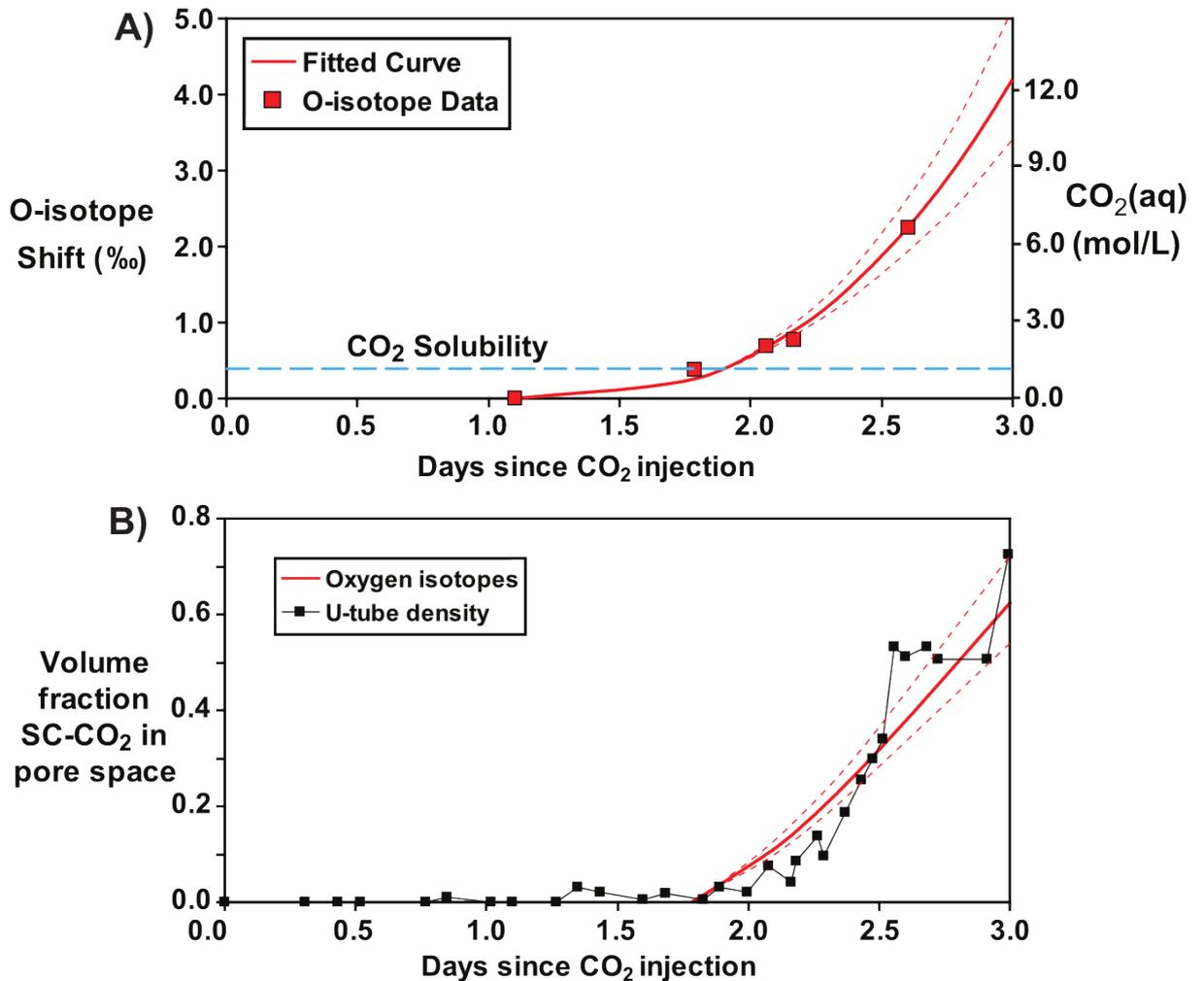


**Figure 10** The Frio-I injection experiments involved injection of 1600 tonnes of supercritical  $\text{CO}_2$  at a depth of 1500m into the Upper Frio Formation, over 11 days. The injection experiment utilised a U-tube sampling line in a single observation well sited 30m to the north and at  $\sim 9$ m higher elevation with a 6 m perforated interval. This was used to monitor changes in in-situ fluid density and gas phase compositions and to recover single and two-phase fluid samples for chemistry and stable isotope measurements. Fluid pH was

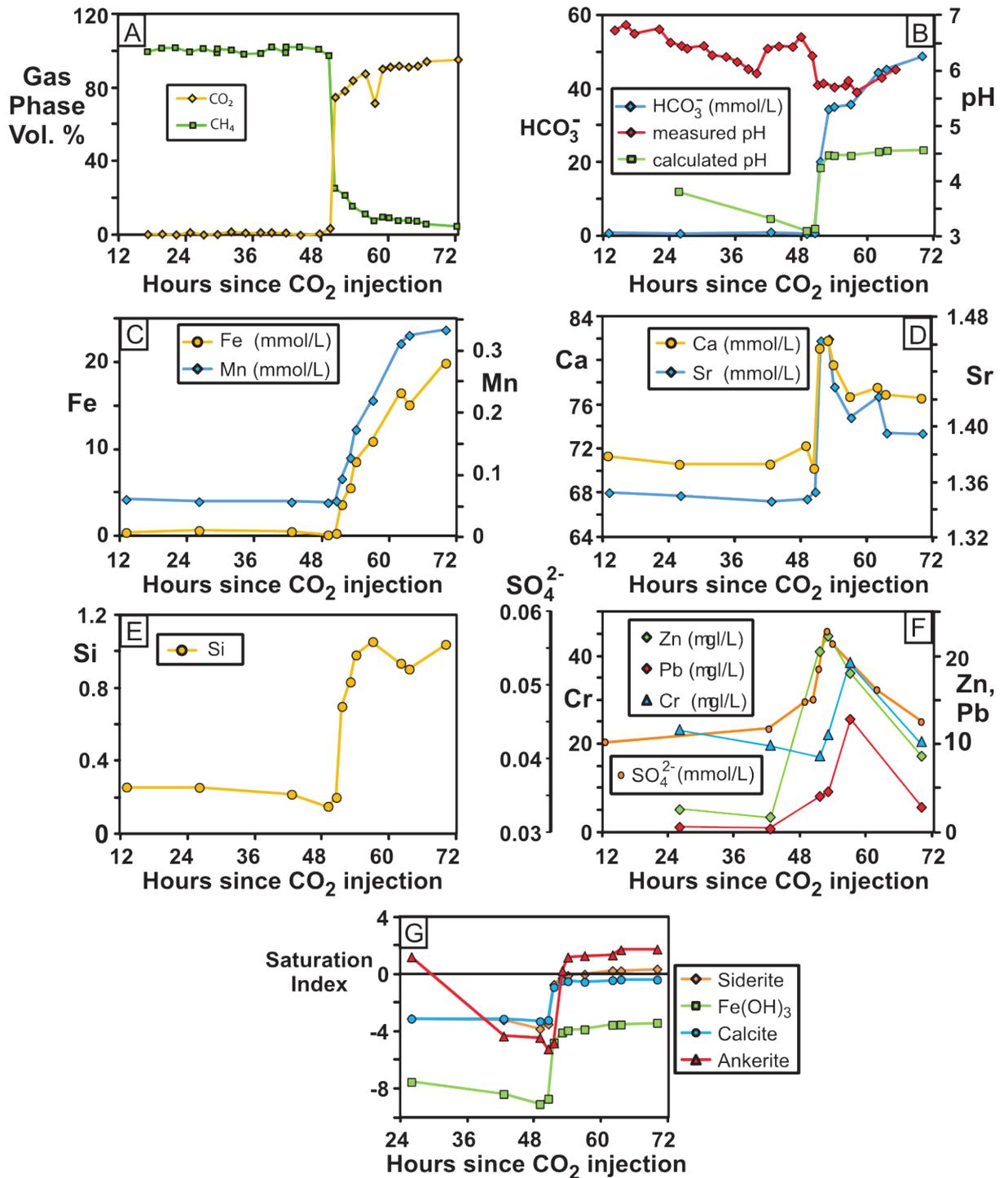
measured at the surface, soon after sample collection but at surface pressures and temperatures. The supercritical CO<sub>2</sub> plume is shown diagrammatically in blue at the time of CO<sub>2</sub> breakthrough 2 days after injection started. Inset shows the inferred complex flow patterns at the head of the CO<sub>2</sub> plume, with diffusion of CO<sub>2</sub> into the formation brine across the interface. Drawn from information in Friefield et al., (2005). Right: CO<sub>2</sub> saturation measured with a Schlumberger wire-line pulsed neutron capture reservoir saturation tool (RST) on day 4 and day 10 after initiation of injection. Redrawn after Hovorka et al., (2006).



**Figure 11** Mechanisms of oxygen-isotope exchange between CO<sub>2</sub> plume and brine for the case where flow of CO<sub>2</sub> maintains a fixed  $\delta^{18}\text{O}$  composition on the contact. CO<sub>2</sub> will diffuse into the brine setting up a boundary layer of decreasing CO<sub>2</sub> concentration illustrated for 1 year (see Fig. 5). Oxygen isotopes exchange rapidly between CO<sub>2</sub> and water (hours) and the diffusing CO<sub>2</sub> will therefore be in isotopic equilibrium with the adjacent water (i.e. brine  $\sim 31$  ‰ lower than the CO<sub>2</sub>) with transport of the  $\delta^{18}\text{O}$  signal at high Damköhler number beyond a  $\sim 4$  mm boundary layer. In this region the oxygen isotope profile will diffuse at a similar rate to the CO<sub>2</sub> but at a 3 order-of-magnitude higher  $\delta^{18}\text{O}$  flux reflecting the relative amounts of oxygen in H<sub>2</sub>O and CO<sub>2</sub> in the brine. Therefore, for CO<sub>2</sub> in contact with brine for more than the  $\sim 4$  hour time constant for CO<sub>2</sub>-H<sub>2</sub>O isotopic exchange, the  $\delta^{18}\text{O}$  flux will be predominantly carried by the brine.

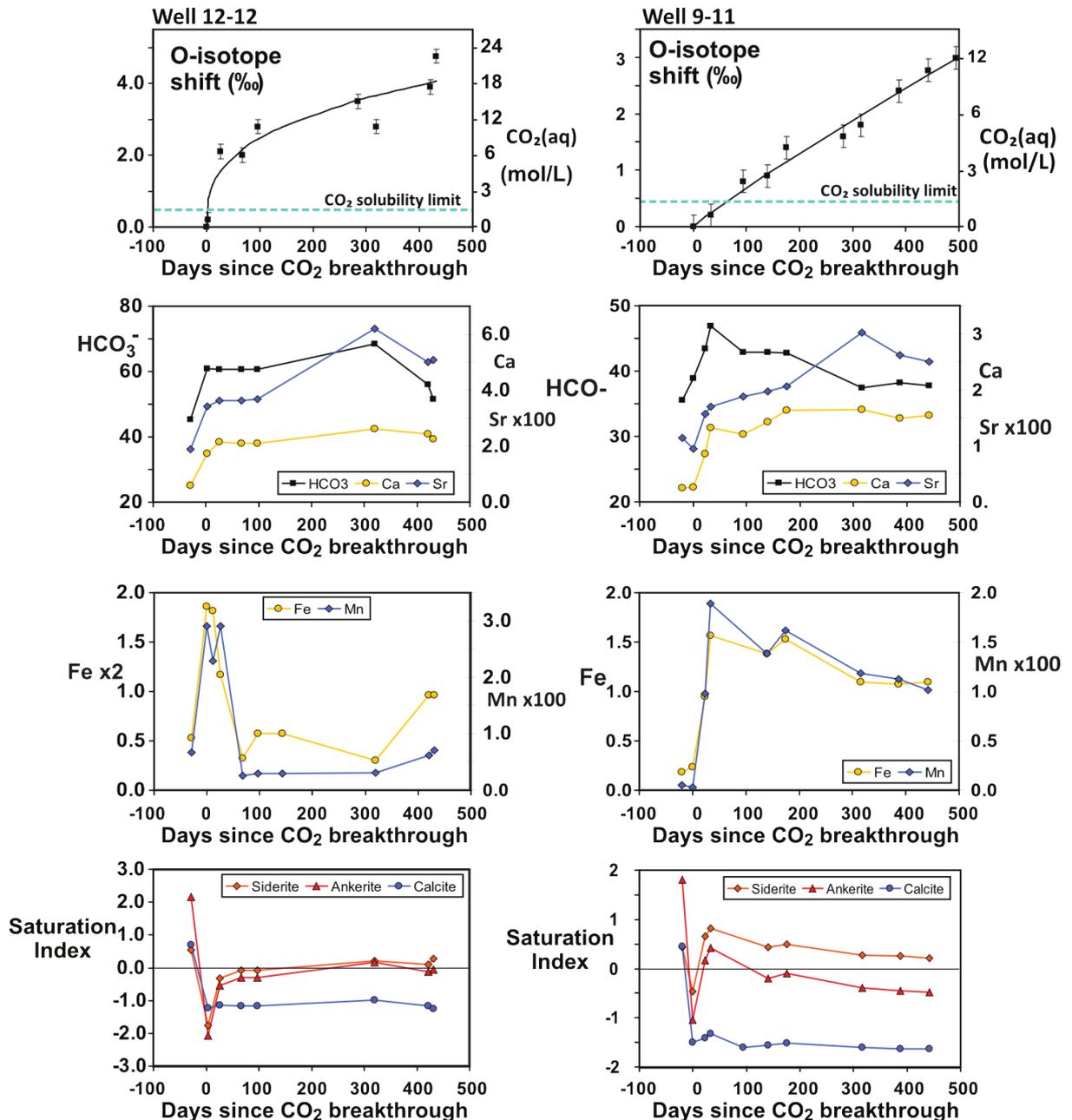


**Figure 12** O-isotope shifts in produced water from the Frio-I Brine Pilot injection experiment (Kharaka et al., 2006a). A) Best fit line to shifts in O-isotopic composition (left-hand axis) of sampled brine (red squares). O-isotopic exchange between  $\text{CO}_2$  and brine rapidly modifies the isotopic composition of the brine. In-situ dissolved  $\text{CO}_2$  concentrations (right-hand axis) were calculated from the O-isotopic composition of  $\text{H}_2\text{O}$  using equations of Johnson et al. (2011a). B) Fraction of  $\text{CO}_2$  occupying the total pore volume at the observation well as determined by fluid density changes sampled by the U-tube sampler, compared to estimates from the O-isotope shift in Fig. 11A (Hovorka et al., 2006). Note that the U-tube sampler preferentially samples  $\text{CO}_2$  (geophysical RST measurements indicate only 20 to 30% saturation and a flow model based on arrival times  $\sim 16\%$ ) and the correspondence between the estimates from oxygen isotopes and the U-tube densities probably reflects diffusive exchange in the reservoir or during sampling.



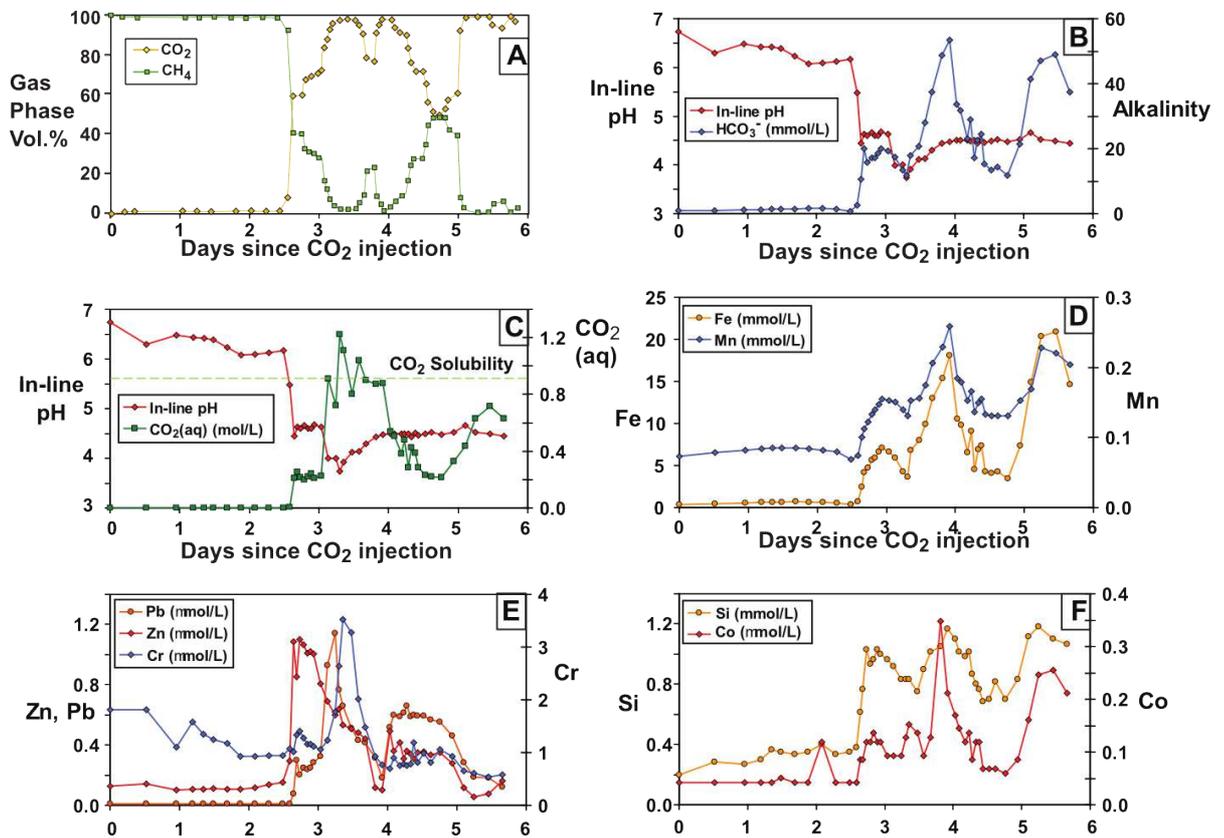
**Figure 13** Frio-I fluid chemistry redrawn after Kharaka et al., 2006 and analyses provided by Kharaka (pers. comm. 2012). A) Arrival of the CO<sub>2</sub> plume at the observation well is observed in the changes in the gas composition measured on gases produced from the U-tube sampler. B) Arrival of the CO<sub>2</sub> plume is preceded by a low pH front of fluid containing dissolved CO<sub>2</sub>. pH measured at surface is consistently two pH units higher than in-situ pH recalculated using O-isotope data suggesting degassing of samples brought to surface P,T. Arrival of the main CO<sub>2</sub> front is accompanied by a rapid increase in fluid alkalinity due to fluid-rock reaction, which rapidly buffers pH. C) Alkalinity is generated by the rapid dissolution of Fe-bearing minerals, D) and the dissolution of calcite, releasing Ca and Sr to solution. E) Increases in silica concentrations most likely reflect dissolution of phyllosilicate minerals. F) Changes in major element chemistry are accompanied by a spike

in trace metal concentrations most likely sourced from pH driven desorption and dissolution metal oxides. G) Mineral saturation index calculations using PHREEQC (Parkhurst and Apello, 1999) based on calculated pH and measured fluid compositions imply that the properties of the fluid are buffered by reaction with a Fe-carbonate phase. As CO<sub>2</sub> arrives at the observation well the fluid rapidly moves to equilibrium with siderite, whilst Fe-oxide phases remain undersaturated.

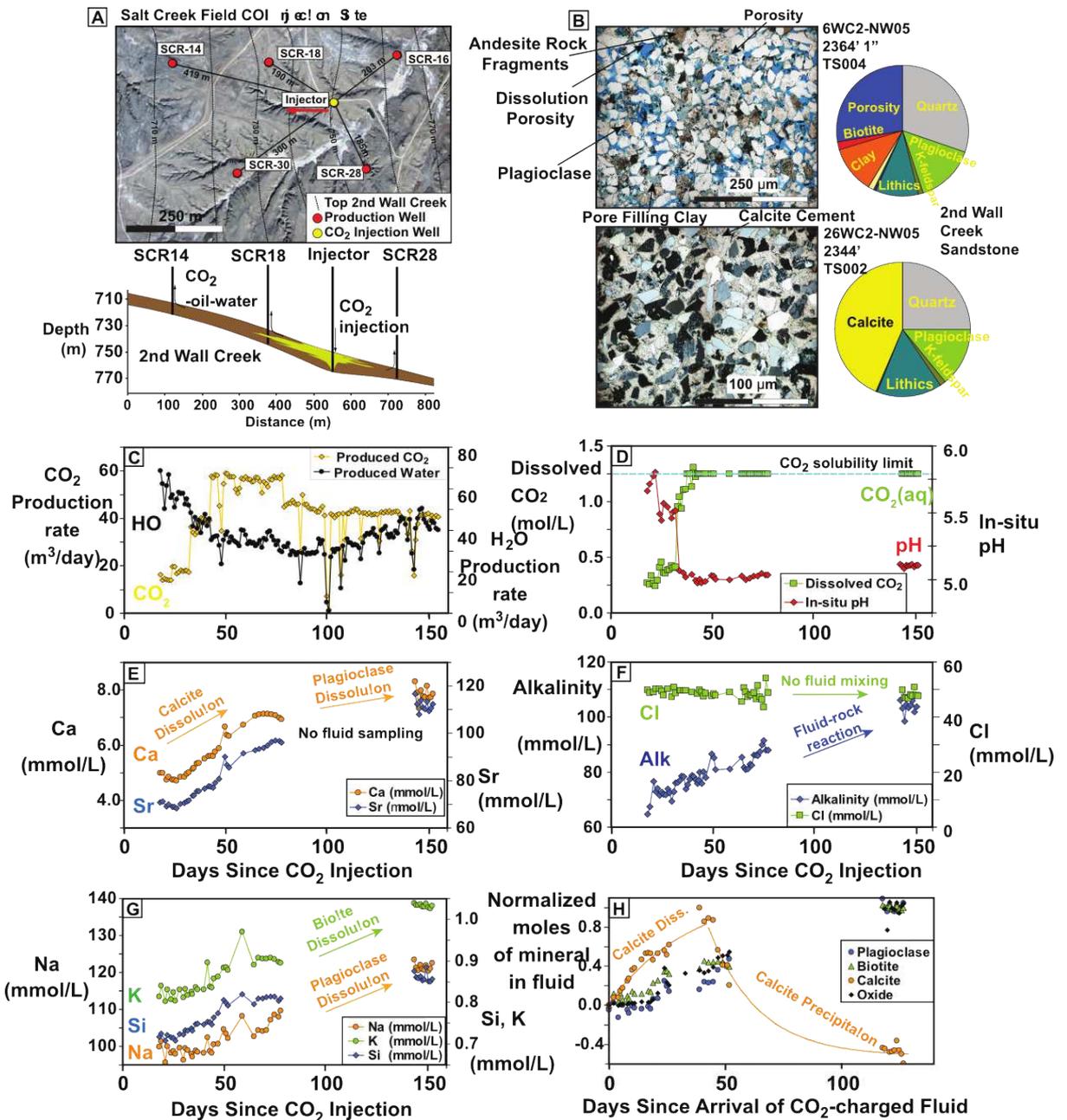


**Figure 14** Pembina-Cardium CO<sub>2</sub>-EOR project fluid chemistry, data from Penn West Energy Trust, (2007), excluding data with charge imbalance >5% and incomplete fluid chemical analyses (see also Shevalier et al., 2009). A) The O-isotope shift in water from production wells 12-12 and 9-11 since the first arrival of injected CO<sub>2</sub> (after Johnson et al., 2011). The magnitude of the shift implies that waters saturate with CO<sub>2</sub> within several days of the first arrival of CO<sub>2</sub> and continue to undergo diffusive exchange with a free CO<sub>2</sub> phase. B and C) Rapid saturation of the fluid with CO<sub>2</sub> is accompanied by rapid increases in the concentration of Ca and Sr, and Fe and Mn reflecting rapid dissolution of calcite, siderite and

Fe-oxides. D) Saturation indices for carbonate minerals present in the formation, calculated using dissolved  $\text{CO}_2$  concentrations determined from O-isotope shift and  $\text{CO}_2$  saturated concentrations determined using the models of Duan et al., 2006. The fluid is initially saturated in the major carbonate phases; however, dissolution and dissociation of the  $\text{CO}_2$  drive rapid undersaturation. Calcite and siderite subsequently dissolve driving fluid towards saturation of insoluble Fe-Mg-Ca carbonate. The fluid is then buffered at saturation by the continued dissolution of calcite and reprecipitation of insoluble Fe-Mg-Ca carbonate.

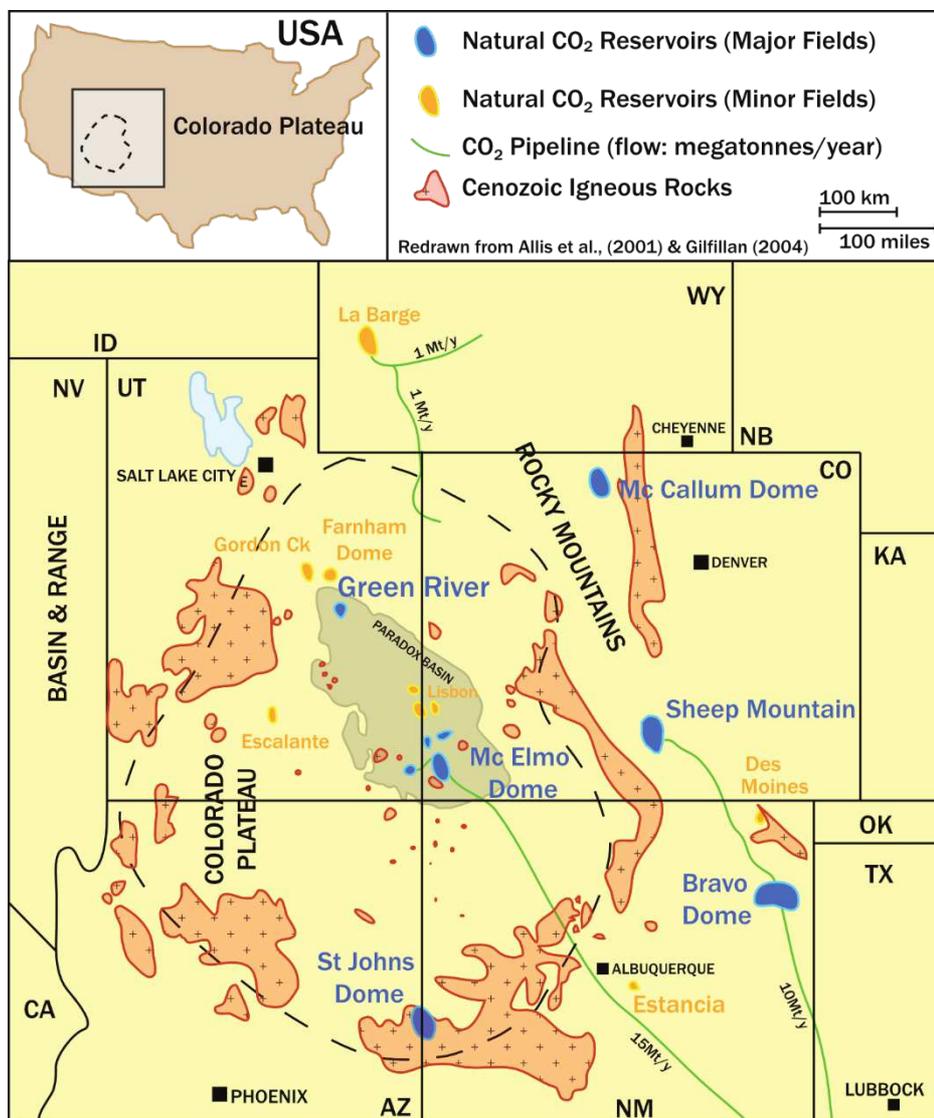


**Figure 15** Frio-II fluid chemistry from Daley et al., (2007a), with  $\text{CO}_2$  and  $\text{CH}_4$  concentrations changes redrawn after Daley et al., (2007a). A) Proportions of  $\text{CO}_2$  and  $\text{CH}_4$  in the gas phase at the observation well. B-C) In-line pH measured in U-tube sampler and alkalinity (B) and dissolved  $\text{CO}_2$ , recalculated in PHREEQC using in-situ pH and alkalinity (C). D) Fe, and Mn concentrations. Changes in these elements are strongly correlated to changes in alkalinity, and are sourced from the dissolution of Fe-oxides. E) Zn, Pb and Cr concentrations. Changes in these elements precede the alkalinity front and coincide with the sharp drop in fluid pH. They are sourced from pH driven desorption from mineral surfaces. F) Si and Co concentrations.



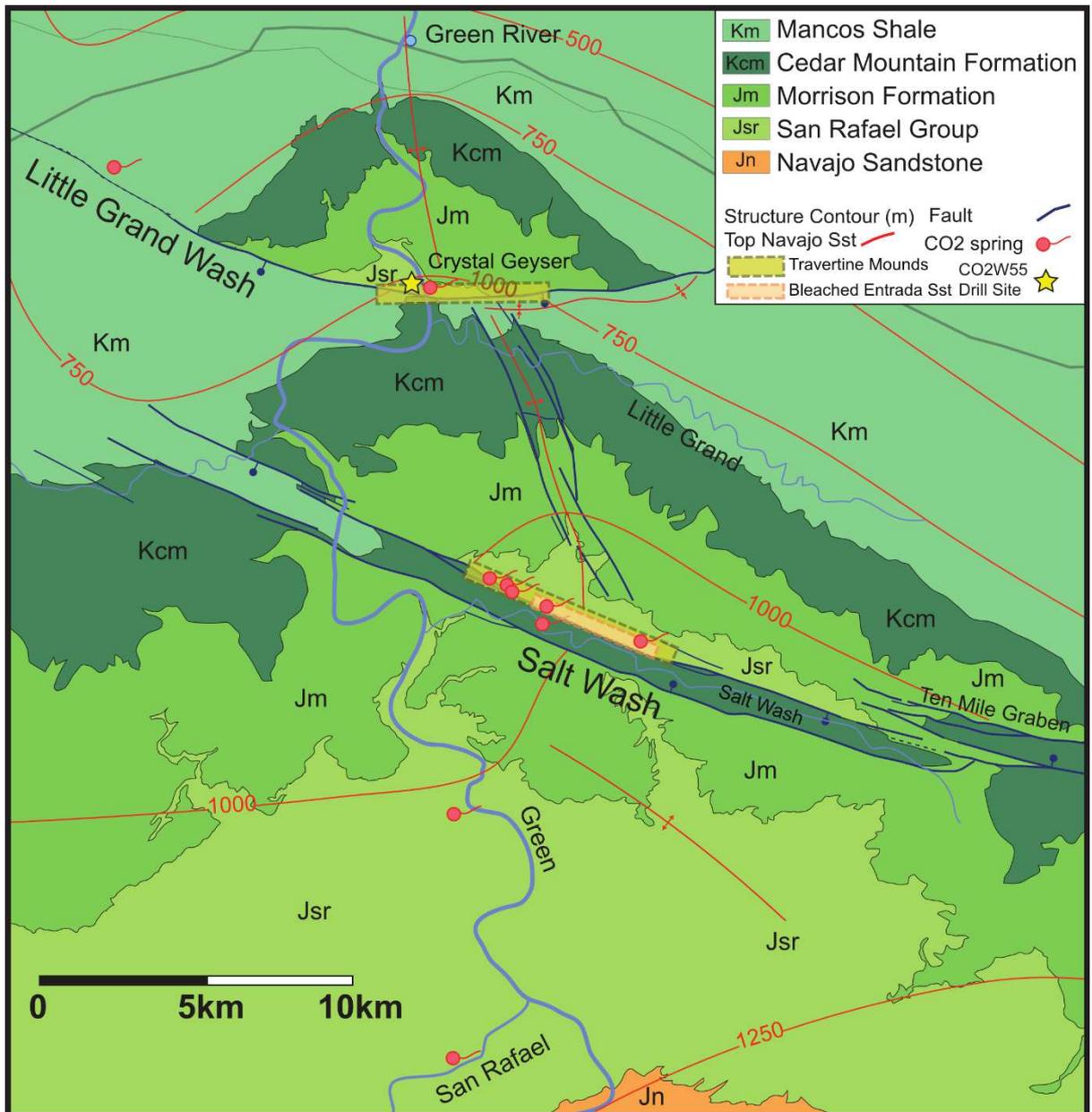
**Figure 16** (A) Surface map from the Salt Creek Field, CO<sub>2</sub>-EOR project showing the location of the CO<sub>2</sub>-injection well and surrounding production well pattern from which CO<sub>2</sub> and fluids were sampled over a 6 month period, during the noble gas spiked CO<sub>2</sub> injection. Structure contours are the top surface of the Second Wall Creek reservoir into which CO<sub>2</sub> is being injected for enhanced oil recovery. (B) Thin section photomicrographs and mineralogical point counting data for the Second Wall Creek Sandstone from cores from wells 6WC2-NW05 and 26WC2-NW05, drilled adjacent to the CO<sub>2</sub> injection site. These show the abundance of reactive feldspar and diagenetic calcite cements in the injection interval. (C) Water and CO<sub>2</sub> gas production data for Well SCR18 the up dip production well sampled during this project, and the first well to see arrival of the noble gas spiked CO<sub>2</sub>. (D) Dissolved CO<sub>2</sub> concentrations in the produced fluid calculated from fluid and gas production volumes using fluid densities calculated at reservoir pressure and temperature conditions. Fluid pH calculated using the calculated CO<sub>2</sub> concentrations and measured alkalinity. (E) Measured Ca and Sr concentrations in the produced fluid showing rapid increases due to the arrival of CO<sub>2</sub> and CO<sub>2</sub>-charged fluid at the production well and the dissolution of calcite.

Concentrations plateau at day 80 as the fluid saturates with carbonate and calcite dissolution moves to calcite precipitation. (F) Cl and alkalinity concentrations in the produced fluid showing that Cl concentrations are stable, precluding fluid mixing, whilst cation concentrations and alkalinity dramatically increase due to fluid-mineral reactions. (G) Measured Na, K and Si concentrations in the produced fluid reflecting the dissolution of silicate and phyllosilicate minerals in the host reservoir, predominantly plagioclase and biotite. (H) The moles of mineral dissolved in the fluid from mass balance calculations using changes in the measured fluid composition and mineral compositions from electron microprobe analyses. The mass balance modelling shows that the initially rapid dissolution of calcite is followed by the more sluggish dissolution of plagioclase and biotite. The fluid evolves to precipitate carbonate after ~45 days since the arrival of the first CO<sub>2</sub>-charged fluids as cation and alkalinity production from fluid-mineral reactions saturate the fluid with carbonate, whilst silicate dissolution reactions continue to produce cations and alkalinity, driving carbonate deposition.



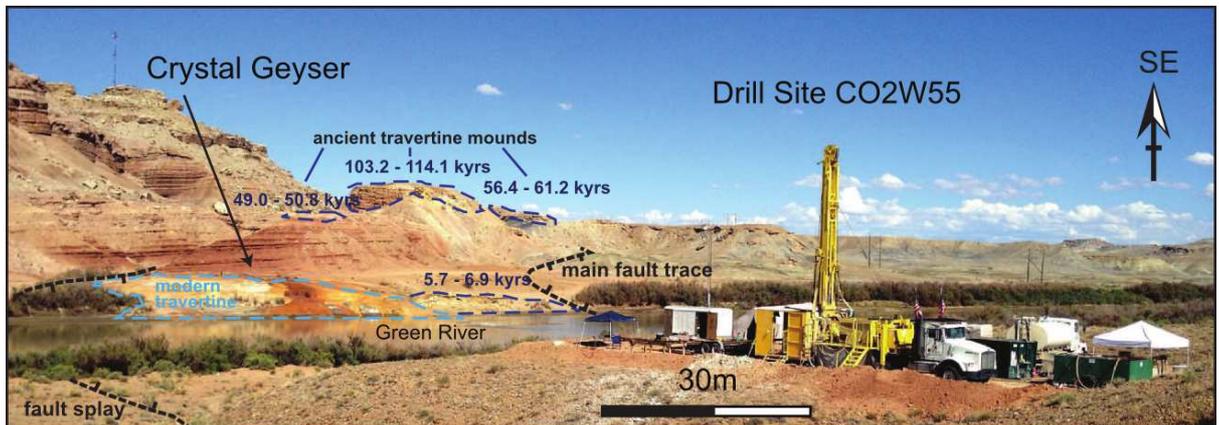
**Figure 17** The Colorado Plateau CO<sub>2</sub> Province, is an extensive uplifted region covering portions of Utah, Colorado, Arizona and New Mexico, that contains abundant natural accumulations of CO<sub>2</sub> (redrawn after Allis et al., 2001). Some CO<sub>2</sub> fields, notably Bravo Dome (NM), McElmo and Sheep Mountain (CO), Farnham Dome (UT), Springerville (AZ), and Big Piney-LaBarge (WY) have been exploited for commercial purposes, mainly

for enhanced oil recovery and dry ice production. The source of the CO<sub>2</sub> is considered to be dominantly volcanogenic, juvenile CO<sub>2</sub> generated from Cenezoic magmatic activity and mantle degassing (Gilfillan et al., 2008, 2009). The gas reservoirs, usually sandstone or dolomite, lie in four way dip closed or anticlinal structures with mudstone or anhydrite top seals. Fault seals are common along the margins of the reservoirs (Allis et al, 2001; Shipton et al., 2004). The gases from the fields can be > 98% CO<sub>2</sub> with trace quantities of N<sub>2</sub> (4%), He (0.1-1%), Ar, and CH<sub>4</sub> (Allis et al., 2001).

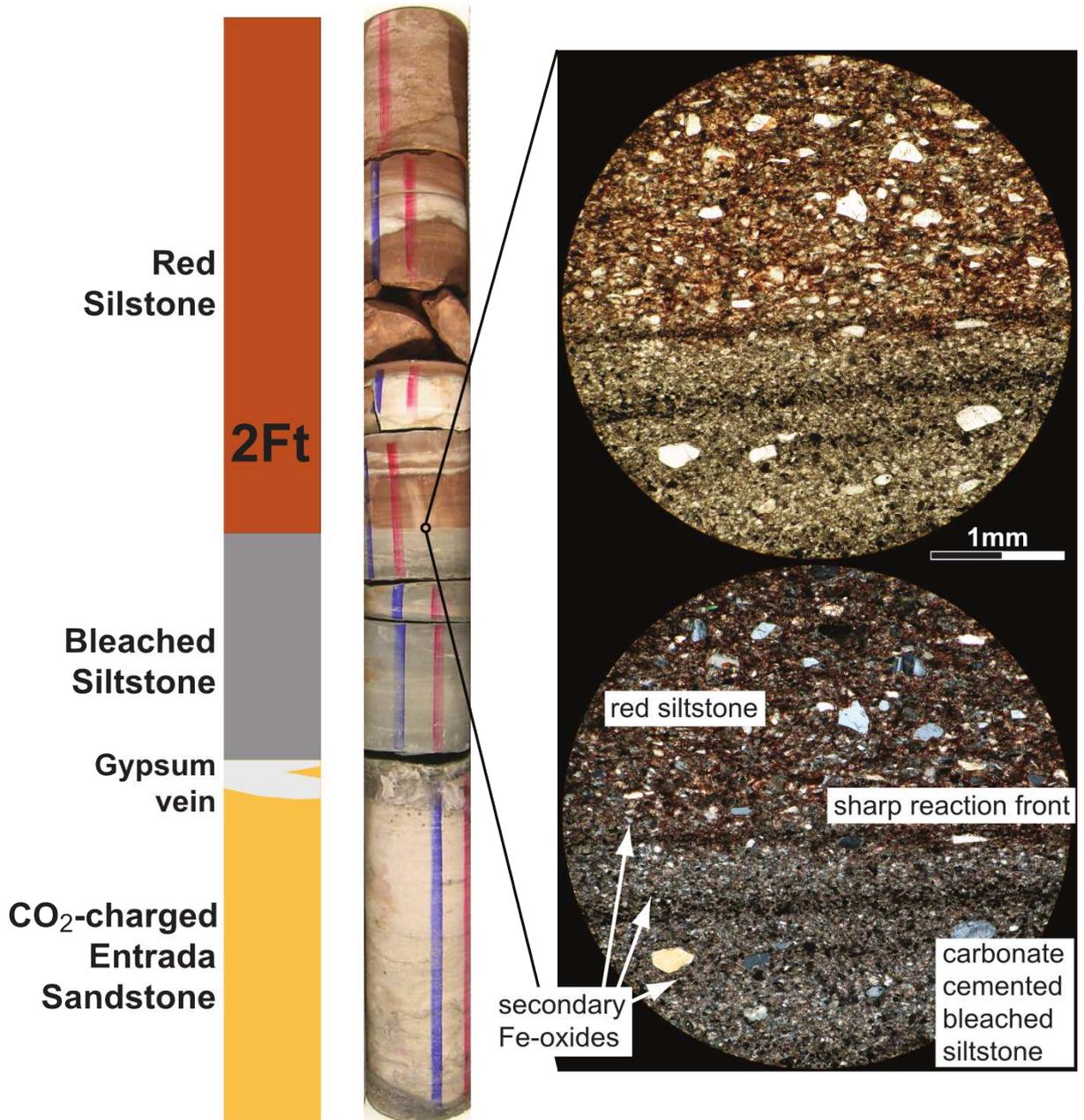


**Figure 18** Geological map of the Green River anticline showing locations of the Little Grand Wash and Salt Wash Graben normal fault systems, CO<sub>2</sub>-springs and location of drill hole CO<sub>2</sub>W55 (redrawn after Kampman et al., 2009). Supercritical CO<sub>2</sub> is buoyantly accumulated within the White Rim sandstone (>800m depth) at the anticline crest in traps formed by the faults, which are laterally sealing due to shale and clay gauge cores (Dockrill et al., 2010). The faults contain a damage zone of open fractures that allows CO<sub>2</sub> and CO<sub>2</sub>-charged brine to migrate vertically, filling a series of shallow sandstone reservoirs in the Wingate, Navajo and Entrada Sandstones. The CO<sub>2</sub> and CO<sub>2</sub>-charged brines mix with

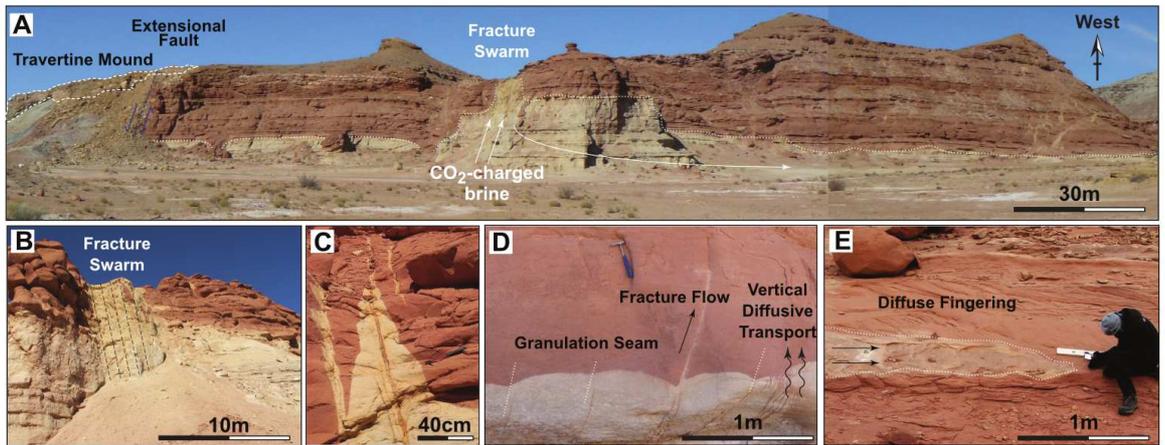
meteoric fluids in the sandstone reservoirs and flow parallel to the faults where they are sealing, and to the south where they are transmissive, being driven by the regional gradient in groundwater head (Hood and Patterson, 1984; Kampman et al., 2009). Also shown are the regions of travertine mounds discussed in Kampman et al., 2012 and Burnside et al., 2013, and the sandstone bleaching discussed in Wigley et al., 2012, 2013a and 2013b. Structure contours are for the top surface of the Navajo Sandstone, the major source of CO<sub>2</sub>-charged brine escaping at surface.



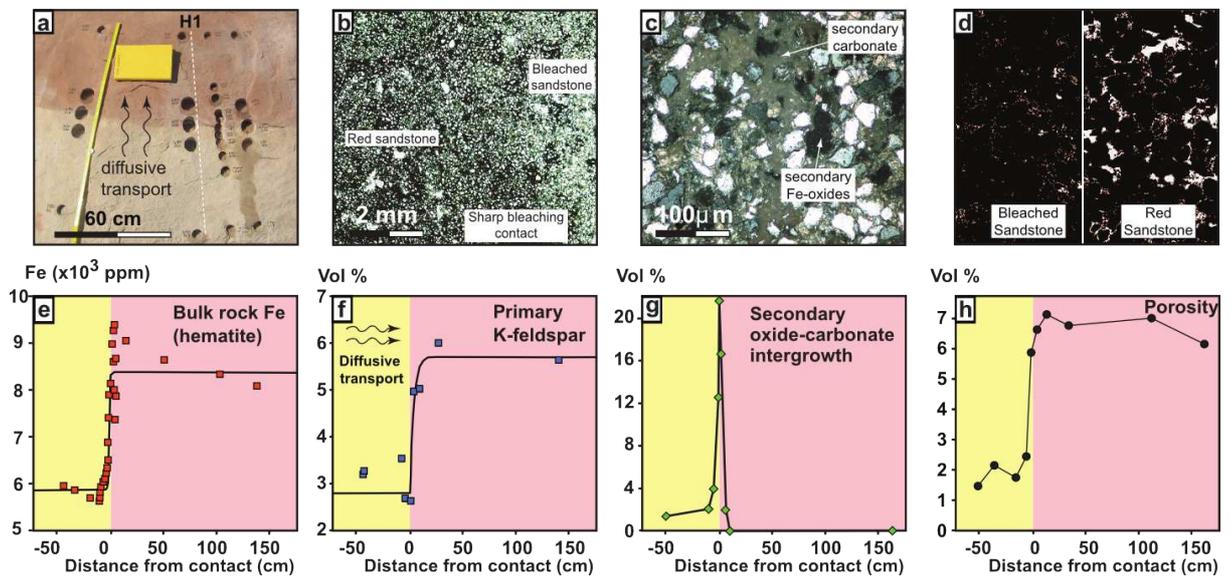
**Figure 19** Field photograph of the drill site of well CO2W55 showing the CS4002 Truck Mounted Core Drill in the foreground and the travertine mound formed by Crystal Geyser on the opposite bank of the Green River. Also shown are the main fault trace of the Little Grand Wash Fault, and the local fault splays. Ancient travertine mounds form away from the main fault trace, within the footwall block of the fault, above the main fault damage zone through which CO<sub>2</sub> and CO<sub>2</sub>-charged brine escape to surface. Travertine mound ages from Burnside *et al.*, 2013 are also shown.



**Figure 20** Core photograph from well CO<sub>2</sub>W55 showing the contact between CO<sub>2</sub>-bearing sandstone of the Entrada Sandstone and siltstone horizons that form internal seals to the CO<sub>2</sub>-charged fluids. The lower 10cm's of siltstone has been bleached by removal of Fe-oxide grain coatings by interaction with the CO<sub>2</sub> and micrographs from the bleached-unbleached contact show the mobilized Fe has been redeposited at the reaction front in bands of coarse Fe-oxides, along with abundant carbonate cement throughout the bleached interval. The short distance over which the siltstone has been bleached suggests that the CO<sub>2</sub> has penetrated the siltstone by diffusion and that reactions with the host rock have attenuated the reactivity of the CO<sub>2</sub> over this cm length scale. These observations suggest that fluid-mineral reactions help retard the diffusion distance of the CO<sub>2</sub>, potentially aided by the formation of carbonate cement that blocks pores, and that such siltstone layers can form impermeable barriers to the CO<sub>2</sub> and effective seals over 100,000 year time scales.

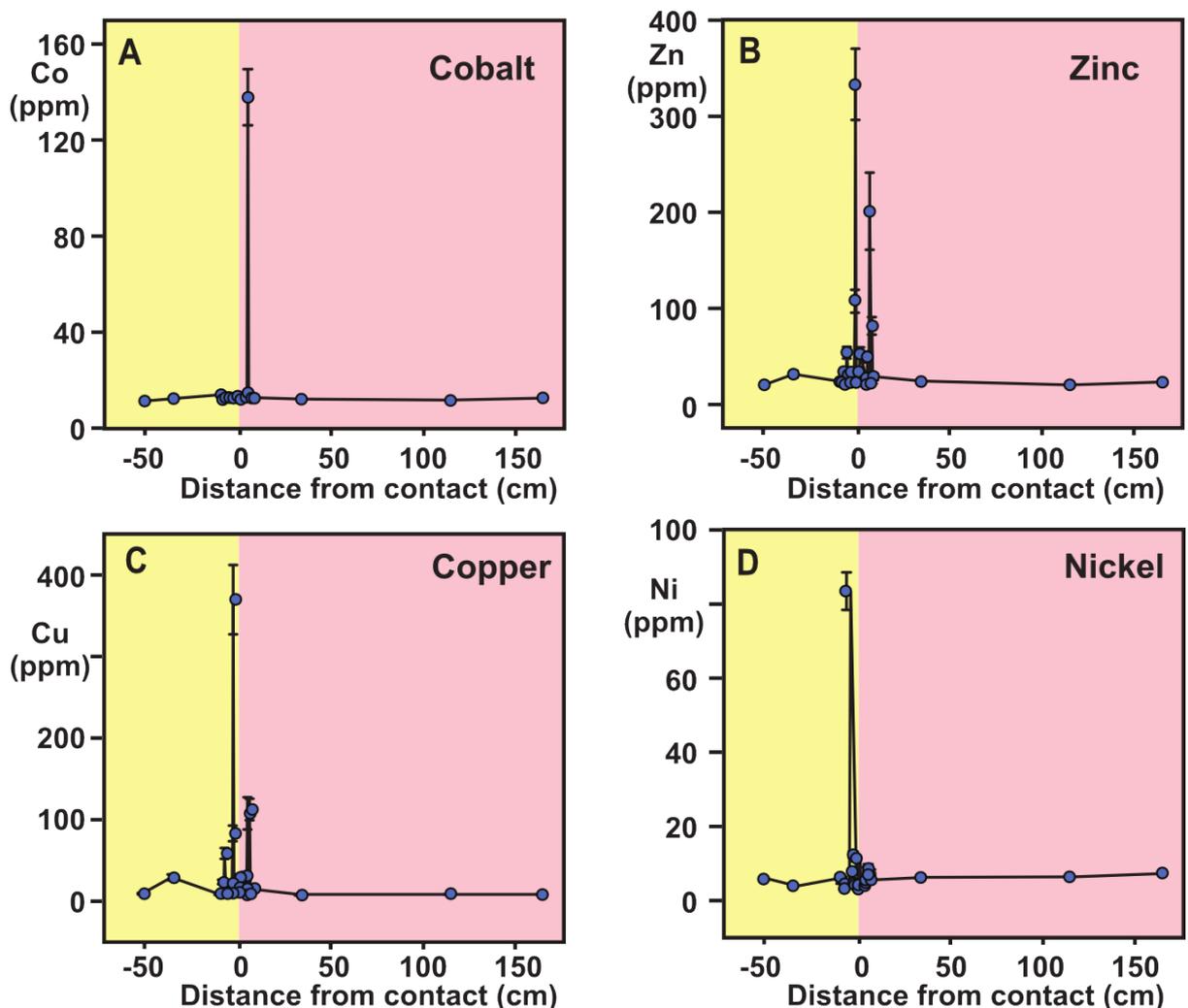


**Figure 21** Field photographs showing bleached portions of the Entrada Sandstone, Salt Wash Graben, Green River, Utah. (A) Shows the outcrop of the northerly major normal fault of the graben, dipping to the south (left of view) and the extensive zone of sandstone bleaching at the base of the Entrada Sandstone. The bleached contact dips steeply to the north and shallowly to the east forming a lenticular zone running parallel to the broadly east-west running fault. The bleached zone was fed by inflow of CO<sub>2</sub>-charged fluid through a fracture swall, close up pictured in (B). (C) The bleached contact is elevated where fluids flow up and along fractures, which frequently contain Fe-oxide remineralisation at their cores. (D) The bleached contact is sharp and the topology of the surface is sensitive to extreme changes in porosity and tortuosity such as those developed in granulation seams and in open fractures. (E) Towards the east the bleach zone dies out in a series of diffuse horizontal fingers of bleached sandstone.

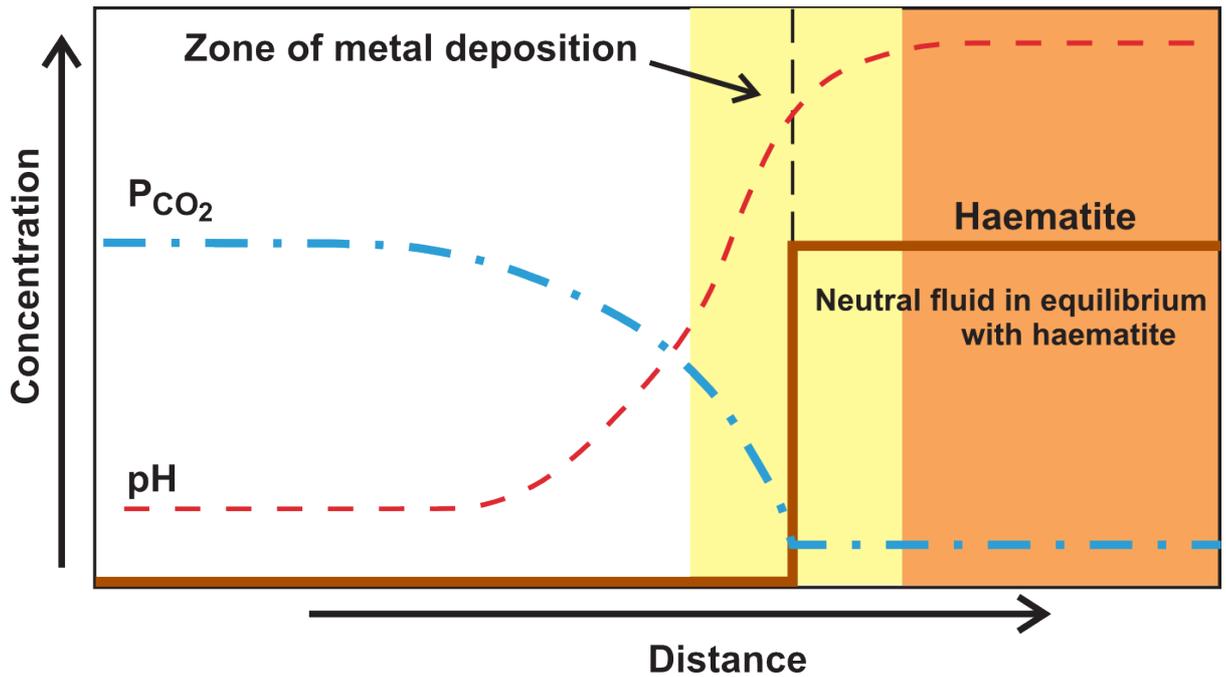


**Figure 22** (A) Field photograph showing sample transect H1 of core plugs drilled from outcrops of the bleached and red Entrada Sandstones, analysed for geochemical and mineralogical profiles. (B) Thin-section micrograph showing removal of haematite grain coatings from the bleached sandstone, and the sharp bleached-unbleached contact. (C) Close-up micrograph showing the precipitation of carbonate and Fe-oxide intergrowths at the bleached-unbleached contact. (D) rasterised BSE micrographs showing differences in porosity between the bleached and unaltered sediment. Geochemical and mineralogical profiles across

the bleached-unbleached sandstone contact showing (E) Mobilisation of  $\text{Fe}^{3+}$ , in the form of haematite grain coatings, from the bleached sandstones and the redeposition of Fe on the reaction, resulting in high Fe contents at the front, relative to the background concentrations in the sediment. (F) Acidity generated from the dissociation of the  $\text{CO}_2$  dissolved silicate grains in the sediment, predominantly K-feldspar, resulting in step changes in mineral concentrations across the reaction front. (G) Buffering of fluid pH across the front, and the generation of alkalinity and cations by mineral dissolution produced a spike in carbonate and Fe-oxide mineral saturation at the reaction front driving the precipitation of carbonate and Fe-oxide minerals at the front. (H) The precipitation of clay minerals (kaolinite and illite-smectite) from the incongruent dissolution of feldspars clogs pores and reduces porosity in the bleached sediment. (Redrawn from and using data in Wigley et al., 2013a).



**Figure 23** Geochemical profiles through the bleached-unbleached Entrada Sandstone showing trace element enrichment at the contact where elements mobilized by the  $\text{CO}_2$ -rich fluids are redeposited into and onto the surface of carbonate and Fe-oxides minerals that grow at the reaction front (Drawn using data in Wigley et al., 2013b). Fluid-mineral reactions buffer pH across the reaction front driving mineral precipitation and lowering the solubility of trace elements which are soluble at acidic pH's but become increasingly insoluble at circum-neutral pH's. The figure shows a selection of the elements (Co, Zn, Cu, Ni) analysed and similar enrichments are observed in other elements including As, Pb and Cd.



**Figure 24** Conceptual model of the evolution of fluid  $CO_2$  content, bicarbonate concentration and pH across the fluid-mineral reaction fronts and the correspondingly stabilization of carbonate and Fe-oxide minerals and trace metal redeposition at the reaction front. (Redrawn after Wigley et al., 2013a).

Table 1 CO<sub>2</sub>-injection experiments

Project Name	Frio-I Brine Pilot Experiment	Frio-II Brine Pilot Experiment	Ketzin CO <sub>2</sub> SINK Project	CO <sub>2</sub> CRC Otway Project	Nagaoka Injection Project
Location	Texas, USA	Texas, USA	Ketzin, Germany	Otway, Australia	Nagaoka, Japan
Start Date	Oct. 2004	Sept. 2006	June 2008	April 2008	July 2003
Injection Duration	11 days	4 days	2 years	17 months	18 months
CO <sub>2</sub> Injected (tonnes)	1,600	360	60,000	65,000 (CO <sub>2</sub> -CH <sub>4</sub> )	10,400
Reservoir Formation	Upper Frio Formation	Lower Frio Formation	Stuttgart Formation	Waarre C Sandstone	Haizume Formation
Facies	Fluvial	Fluvial	Fluvial	Shoreface	Shlw. Marine
Lithology	feldspathic litharenites	feldspathic litharenites	feldspathic litharenites	quartz arenite	argillaceous sandstones
Porosity (%)	32	34	23	15	22.5
Permeability (D)	2-3	3-4	0.5-1	0.01-1	0.01-0.03
Depth (m)	1500	1650	650	2000	1100
Temperature (°C)	50	55	36	85	48
Pressure (bar)	150	165	70-80	180-190	110
Fluid Type	Na-Ca-Cl	Na-Ca-Cl	Na-Ca-Cl	Na-Cl	Na-Br
Salinity (mol/L NaCl)	1.35	1.60	3.90	0.1	0.3
Hydrocarbons	CH <sub>4</sub> gas			CH <sub>4</sub> gas	
References	Doughty et al., 2008; Kharaka et al., 2006a	Daley et al., 2007a	Förster et al., 2006; Giese et al., 2009; Schilling et al., 2009	Boreham et al., 2011; Freifeld, 2009; Underschultz et al., 2009	Kikuta et al., 2005; Mito et al., 2008

Table 2 CO <sub>2</sub> -EOR projects				
Project Name	Pembina-Cardium CO <sub>2</sub> -EOR Pilot	Weyburn-Midale CO <sub>2</sub> -EOR Project	Salt Creek CO <sub>2</sub> -EOR Project	SECARB Cranfield Project
Location	Alberta, Canada	Saskatchewan, Canada	Wyoming, USA	Mississippi, USA
Start Date	March 2005	September 2000	January 2004	July 2008
Injection Duration	3-5 years	25-30 years	25-30 years	1.5 years
CO <sub>2</sub> Injected (tonnes)	79 tonnes/day	~5,000 tonnes/day	~7,500 tonnes/day	2,100,000
Reservoir Formation	Upper Cretaceous Cardium Formation	Mississippian Charles Formation.	Late Cretaceous Frontier Formation	Tuscaloosa Formation
Facies	Shallow Marine	Shallow Marine	Shoreface	Fluvial
Lithology	subarkose	carbonates and evaporites	arkose	quartzite
Porosity (%)	15	14	16	25
Permeability (Darcies)	0.01-0.03	0.1-1	0.01-0.2	0.1
Depth (m)	1650	1300-1500	750	3000
Temperature (°C)	50	62	35	125
Pressure (bar)	190	150	80	320
Fluid Type	Na-Cl	Na-K-Cl	Na-Cl	Na-Ca-Cl
Salinity (mol/L NaCl)	0.1	1.3	0.1	2.00
Hydrocarbons	oil	oil	oil	oil
References	Dashtgard et al., 2008; Lawton et al., 2009; Shevalier et al., 2009	Emberley et al., 2004; Emberley et al., 2005; Quattrocchi et al., 2006; White and Johnson, 2009; Whittaker et al., 2011	Kampman et al., 2011	Hovorka et al., 2011; Lu et al., 2012