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Experimental Perspectives of Mineral Dissolution and Precipitation due to Carbon Dioxide-Water-Rock Interactions

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INTRODUCTION

Interactions between CO_2 and H_2O fluids and the rocks that host them are of significance for Geological Carbon Storage (GCS) for several reasons. These interactions determine the amount of CO_2 that can be trapped in solution and in minerals. The petrophysical properties of reservoir and cap rocks, especially porosity and permeability, are also affected. Carbon storage in fluids and minerals, coupled with potential changes to the petrophysical properties of rocks, have a direct bearing on the long-term effectiveness of GCS.

Many potential reservoir rocks contain a range of minerals that may react at very different rates. In particular, carbonate minerals are widespread minor components of sedimentary rocks and react much more rapidly than silicates, while clay minerals are often much more reactive than minerals such as quartz or alkali feldspars. It follows that the evolution of pore fluid composition in a reservoir into which CO_2 is injected may be strongly influenced by kinetic factors. Dissolution of fast-reacting minerals may be limited by the transport of reactants to the mineral surface, while minerals whose surfaces react only slowly may persist out of equilibrium with pore fluid for extended periods. Some reactions, such as congruent dissolution, proceed until the reacting mineral is in equilibrium with the pore fluid, but other, incongruent reactions may involve unstable reactants which never attain equilibrium with the pore fluid, resulting in very extensive mineralogical transformations over time.

This chapter examines interactions between CO_2 and H_2O fluids and the rocks and minerals that comprise GCS reservoirs, as well as the caprocks that seal these reservoirs, from the perspective of laboratory experiments. Laboratory experiments determine thermodynamic and kinetic parameters and can identify fluid-rock reactions and processes that may have been previously unknown or unappreciated. Experimental studies of equilibrium and kinetic aspects of mineral dissolution and precipitation relevant to GCS are now quite mature, and there is a growing body of work investigating petrophysical consequences of CO_2 injection. This chapter examines fluid-mineral and fluid-rock interactions that take place in water at a range of scales, from the micro- to the core scale. Other chapters evaluate fluid-mineral interactions within supercritical CO_2 (Rosso et al. 2013), at the nano-scale (DeYoreo et al. 2013), the field scale (Kharaka et al. 2013), and in natural analogues (Bickle and Kampman 2013). In addition, this chapter focuses on abiotic CO_2-water-rock interactions; Cappuccio and Ajo-Franklin (2013) evaluate the role of biological processes relevant to GCS.

This chapter is divided into three major sections. In the first section we discuss relationships between hydrogeology (i.e. flow paths, heterogeneities, porosity-permeability, etc.) and fluid-rock interactions. We also discuss the influence that CO_2 exerts on reactions and processes in a water-rock system. Our discussion assumes that the reader possesses a basic understanding of the geochemistry and mineralogy of water-rock interactions and focuses on the changes that CO_2 brings to these interactions. The reader can consult any of a large number of books that provide the basic theory of mineral precipitation and dissolution, pH control of reactions, and other relevant subjects discussed in this chapter (e.g. Stumm and Morgan 1996; Drever 1997; Langmuir 1997). In addition, much of the kinetic rate data that we present has been recently tabulated (Palandri and Kharaka 2004; Brantley et al. 2008). The second section is a brief summary of the experimental equipment and techniques used to evaluate reactions between fluids and minerals. The third section evaluates fluid-mineral behavior in laboratory experiments. This section focuses on the important rock-forming minerals within reservoirs and cap rocks as well as accessory minerals that are pertinent to GCS. Olivine and pyroxene are discussed because storage as carbonate is likely to be most important in mafic and ultramafic rocks. The common silicate minerals, feldspars, phyllosilicates, and quartz, are then addressed. We subsequently consider carbonate minerals, followed by sulfates, sulfides, and Fe-oxyhydroxides. The section concludes with discussion of fluid-rock behavior in laboratory experiments assessing both reservoir rocks and caprocks as opposed to individual minerals. It is worth noting that the results of experimental studies focused on GCS also provide insights into other geologic environments, including engineered geothermal systems, enhanced oil and gas recovery, and unconventional hydrocarbon resources. The chapter concludes with a summary section and and a section that suggests directions for future work.

CARBON DIOXIDE IN A FLUID-ROCK SYSTEM

Under all likely conditions for CO_2 storage, H_2O and CO_2 are immiscible even in the absence of dissolved salts (Kaszuba et al. 2006). Carbon dioxide solubility in water decreases with increasing temperature and salinity at surface conditions, but increases with pressure (Todheide and Franck 1963; Takenouchi and Kennedy 1964, 1965). Over the range of conditions relevant for GCS, CO_2 solubility is almost independent of temperature, but does have a strong pressure dependency. It is also subject to "salting-out" effects (Takenouchi and Kennedy 1965). In a rock-dominated system typical of most natural reservoirs, CO_2 solubility is further influenced by mineral-fluid interactions.

Under conditions likely to prevail in a GCS site, the pH of unreacted CO_2-charged water is markedly acid (<4), and so the dominant carbonate species will be aqueous CO_2 and undissociated carbonic acid. The effect of fluid-mineral interactions is almost invariably to neutralize some of this carbonic acid acidity, resulting in a rise in pH. Provided the pH remains below the apparent first dissociation constant of carbonic acid (pKa = c. 6 according to temperature and salinity of the fluid (e.g. Bodnar et al. 2013)), the dominant aqueous carbonate species remain as $CO_2(aq)$ and $H_2CO_3^o$, and mineral dissolution has little effect on total dissolved inorganic carbon. If mineral reactions result in a rise in pH above pK_a, however, significant additional CO_2 may enter solution as bicarbonate, enabling additional carbon to be stored through solubility trapping.

Targets for modeling

In a storage environment, the starting condition involves rocks that contain formation water which is likely to be saline and already saturated with the minerals in the host rock. Injection of CO_2 leads to the creation of a plume of CO_2 which expands away from the point of injection along the most permeable horizons and whose ascent is prevented by a cap rock (Fig. 1). In the direction of advance of CO_2 along permeable beds, water ahead of the CO_2 front becomes acidified and reacts with the host rock (Kharaka et al. 2009), but is pushed ahead of the advancing plume. The thickness of the zone of acidified water ahead of the plume is controlled by transport processes within the water phase (Kampman et al. 2013). Although initially very reactive, this migrating slug of water will rapidly approach equilibrium with the more reactive minerals in the host rock, probably in a matter of days. Nevertheless, as the radius of the advancing plume increases, the volume of acidified water must also continuously increase. Consequently, there will always be reaction in the rocks at the front of the advancing plume (Fig. 1, location A). While injection continues to drive the plume front forward, reactivity ahead of it will inevitably be limited to rapid reactions.

Behind the advancing plume front, residually trapped water persists and can continue to react with host minerals. The capacity to directly dissolve minerals into this static, acidified water is strictly limited. However, this water can persist for an extended period of time until all the water has completely evaporated into the CO_2 or been consumed as a reactant in, for example, the formation of clays (Fig. 1, location B). In this situation, slow reactions may nevertheless have a significant impact on rock properties. Comparable reactions may be expected in reservoirs where alternating CO_2 and water injections have been used to stabilize CO_2 through residual trapping (Qi et al. 2009), except that salinity is unlikely to reach extreme values as in a zone of evaporation. The upper and lower surfaces of permeable layers into which CO_2 has preferentially migrated provide relatively stable sites for CO_2-water-mineral interactions (Fig. 1 locations C and D), and these may be particularly effective at the lower surface (location D) where the increase in density triggered by dissolution of CO_2 in water can set up convection cells and enhance mixing (Riaz et al. 2006; Xu et al. 2006). Reactions near persistent interfaces have the potential to continue for extended periods, and could result in changes to the local permeability structure. In addition to the different types of interaction between fluids and minerals that can take place in different settings, short term reactivity is also likely to be affected by temperature fluctuations caused by ongoing and very large scale injections of carbon dioxide.

The significance of these different settings of reactivity is that they involve different timescales and degrees of disequilibrium. It is important to ensure that kinetic experiments address the relevant rate-limiting step for the part of the injection system of interest. For example, it is unlikely that CO_2-water interactions will lead to significant dissolution of additional alumina and silica from aluminum silicates since the original formation water is already saturated with the host rock. Indeed these elements may even be precipitated as a result of dissolution of CO_2 causing a reduction in water activity. On the other hand, reactions involving cation leaching or exchange are likely to be triggered by acidification of formation waters and consequent dissolution of carbonates.

Fluid- and rock-dominated reaction systems

Injection of supercritical CO_2 into a fluid-rock system alters the balance between rock- and fluid-dominated reaction systems (Kaszuba and Janecky 2009). In general, rock-dominated systems such as deep brine formations are not affected by fluid infiltration such as recharge and mineral reactions control the aqueous geochemistry (Langmuir 1997). In contrast, fluids control the mineralogy and aqueous geochemistry in fluid-dominated systems. Examples include aquifers that are replenished by fresh water recharge as well as reservoirs and deep brine formations into which CO_2 is injected.

In experimental studies and in brine formations at GCS sites, injection of supercritical CO_2 initially shifts the pore fluid composition from being dominated by the rock towards one dominated by the injected fluid (Kaszuba et al. 2003, 2005); CO_2-H_2O interactions result in acid-dominated reactions and related mineral dissolution and/or precipitation (Kaszuba and Janecky 2009). This fundamental change from rock- to fluid- control triggers almost all emergent geochemical phenomena. Subsequent mineral-fluid interactions counter carbonic acid acidity as the rock begins to reassert its control.

Within the reservoir, the variability of flow properties due to structural heterogeneity can also lead to spatial variation of the type of reaction control: fluid-dominated reactions occur preferentially along main flow paths of higher permeability, while rock-dominated reactions are favored in more protected areas where flow is reduced. With time, dissolution and precipitation reactions progressively modify flow pathways and may locally shift the reaction control. This phenomenon induces chemical gradients at various scales that can affect the distribution of reactions, especially in multi-mineral reservoirs (e.g. Molins et al. 2012). Heterogeneity of reaction has even been noted at the micrometric to centimetric scale during the experimental percolation of CO_2-enriched brine within olivine-rich sinters (Andreani et al. 2009). Local variations of fluid flow induce variable chemical gradients at the silicate surface and create microenvironments of dissolution (high flow regions) close to microenvironments of precipitation (low flow regions) (Fig. 2). At the sample scale, dissolution reactions preferentially occur at the inlet of the core while carbonate precipitation is favored toward the core outlet until CO_2 is consumed; phyllosilicates precipitate at the core outlet.

It is evident that the departure from equilibrium of the solution can vary with space and time in massive rock samples. Many experimental studies investigate the reactivity and kinetics of water-rock interactions at conditions that are far from equilibrium (see section discussing olivine and pyroxene) whereas few experiments investigate water-rock reactions at saturation indices approaching equilibrium. The rate-free energy (r-ΔG_r) relationship may be inadequately modeled within the classic Transition-State-Theory framework (Daval et al. 2010; Hellmann et al. 2010). Indeed, experiments on diopside show a considerable departure from models that leads to an overestimation of the reaction rate in the case of CO_2 storage (Daval et al. 2010). Hence, the dependence of the reaction rate of silicates upon ΔG_r is fundamental for GCS. These processes have important implications for determining whether transport or reaction (kinetics) is the rate-limiting process at the macroscopic scale.

Role of co-contaminants

Geologic storage of CO_2 that contains impurities such as SO_x, NO_x, H_2S, Hg and potentially O_2 and other constituents is known as co-sequestration, a term first used with reference to co-injected CO_2 and H_2S (Williams 2002). While the body of literature regarding experimental evaluation of mineralogic and geochemical effects of CO_2-water-rock interactions is quite extensive, experimental studies of co-injected impurities have only recently received attention (see sections discussing sulfate and sulfide minerals). Chialvo et al. (2013) address the behavior of CO_2-rich environments containing H_2O, SO_x, H_2S, or NO_x. In this chapter we evaluate the limited data that is available for mineral precipitation and dissolution due to reaction with CO_2-H_2O fluids containing such impurities. In general, SO_x and other impurities provide new sources of acidity and dissolved solutes such as sulfate. Additional acidity is almost invariably neutralized by mineral reactions and additional solutes may lead to precipitation of new minerals and growth of preexisting minerals.

EXPERIMENTAL TECHNIQUES

The various parts of the injection system differ in their physico-chemical conditions due to the pCO_2 gradient created by the injection. Consequently, different CO_2-water-rock interactions take place in different parts of the system. Initial reactions close to the injection well are dominated by acidification of pore waters; either the migrating formation waters pushed ahead of the CO_2 plume or the residual water trapped behind the plume front and progressively evaporated as additional CO_2 is injected. Mineral dissolution includes both direct dissolution (mainly of carbonates, e.g. Kjøller et al. 2011; Canal et al. 2013; Jun et al. 2013) and hydrolysis of feldspars and phyllosilicates leading to precipitation of clays and other secondary silicate minerals (Lin et al. 2008; Hangx and Spiers 2009). Precipitation of secondary carbonates is likely to take place further away, after the initial acidification of formation waters has been neutralized and silicate reactions have disturbed the initial carbonate-fluid equilibrium (Bateman et al. 2010). Interpretations of experiments relevant for GCS have to address these two settings, even if most experiments have been designed to measure dissolution rates under far-from-equilibrium conditions, where reasonably consistent results can be obtained. Many differences in results between studies probably reflect different experimental approaches. No one approach can be said to provide a universal best analogue for what will happen during injection and subsequent storage because of the range of settings in which reactions are possible within even a simple storage site and the range of injection scenarios that might be implemented. Injection of CO_2 as a single continuous process disrupts the equilibria in an existing system in which formation waters are already at saturation with respect to aluminum silicates, whereas alternating injection of water and gas to enhance capillary trapping introduces water that is low in silica and aluminum.

Variations of two different types of apparatus, batch and flow through, are used to reproduce as much as possible these different conditions. Both are used in experiments for reactivity, thermodynamics, kinetics, and hydrodynamic investigations. Schematic drawings of the major types of experimental apparatus we discuss are presented in Figure 3.

Materials for experimental apparatus

Experimental apparatus must be designed to span a wide range of pressure, temperature, and pCO_2 conditions, up to and exceeding supercritical CO_2 pressures, and should be constructed of inert materials so as not to participate in the reactions of interest. The latter is particularly true for experiments conducted with high pCO_2 and high-salinity brines that are extremely corrosive. These conditions require the experimentalist to exercise caution on the nature of the reaction cell chosen for the experiments. Metal alloys, like Hastelloy, titanium, and gold, are usually favored compared to steel. Most laboratories rely on stainless steel or titanium pressure vessels that can be rated to several tens of MPa and used in an oven to several hundred degrees C. A liner is often used to contain the sample and solution, to minimize corrosion. For experiments with CO_2, rupture discs of Inconel alloy prove susceptible to corrosion and must be frequently replaced unless first coated with gold. However, at pressures of just a few atmospheres, PTFE vessels have been used because they are cheap, allowing many experiments to be run simultaneously. While these pressures are well below the critical pressure of CO_2, they are much greater than the partial pressure of CO_2 in the atmosphere, and so they provide useful pointers to likely behavior at higher pressures.

Specific surface area measurements

At the simplest level, in most of the apparatus, the samples investigated are in powder form, typically sieved to dimensions of 100-200 micrometers, and lie loose in the bottom of the reaction cell. Knowledge of the reactive surface area is essential to interpret the results of dissolution rate experiments. Reactive surface area is most commonly determined by BET measurements of inert gas adsorption or by geometrical estimates. Typically BET surface areas are greater than simple geometrical estimates. The magnitude of the difference varies greatly between different materials and is particularly sensitive to microporosity effects that may vary between samples of the same mineral species (Brantley and Mellott 2000). Brantley and Mellott (2000) reported BET surface areas between 10-40 times greater than geometrical surface areas based on a spherical approximation. Unfortunately, it cannot be assumed that BET surface areas provide an ideal measure of the reactive surface area available during hydrothermal reactions; access of dissolved species to surfaces of micropores beneath the surface may be transport-limited in a way that access to surface sites is not. At the core scale, not all available surface area necessarily reacts because of the variable connectivity of pores and because of localized reaction close to preferential flow paths. Additionally, it is clear from SEM images of grains that have undergone reaction that the surface area is not constant and commonly increases due to selective dissolution along cracks and cleavage planes as the experiment progresses. Dissolution-precipitation reactions may also modify the reactive surface area. To further complicate matters, some studies perform kinetic calculations using surface areas determined before the experiment begins whereas others use surface areas of minerals determined after the experiment is terminated.

A magnetic stirrer is generally used to ensure that the reactions taking place in the experiments are not inhibited by sluggish transport. Possible problems that can arise include changes in grain size due to vigorous stirring and clogging of the dip tube, especially by clay minerals. Some workers have used less vigorous forms of agitation, such as shaking tables, and the dip tube will normally be fitted with a filter. Clay-bearing samples may be retained in a membrane made from dialysis tubing to prevent clay clogging (e.g. Allan et al. 2011), although dialysis tubing material will disintegrate in the course of extended experiments, especially at elevated temperatures.

An alternative solution to the problem of accurately determining surface area is the use of discs of monomineralic rock or part of a mineral single crystal, embedded in resin and with a polished surface of accurately known area (Sjöberg 1983). The disc rotates in the vessel, and by comparing rates at different rotation speeds it is possible to evaluate the importance of transport for the dissolution process (Pokrovsky et al. 2005). For minerals which react rapidly with fluid, notably calcite, mineral dissolution rate experiments produce results that are strongly dependent on the configuration inside the vessel and resulting hydrodynamic effects (Sjöberg 1983). These factors emphasize the need for care before applying experimental reaction rates to GCS systems. The main lesson in the case of calcite is that it is not the surface reaction but the transport step that is rate controlling.

Batch reactors

Batch experiments at specific CO_2 pressures are carried out in closed vessels under elevated pressure, either for dissolution studies of single minerals, or to characterize reaction paths and equilibrium assemblages in more complex polymineralic assemblages in which dissolution and precipitation occur simultaneously (e.g. Hövelmann et al. 2012a). A typical configuration (Fig. 3a) involves a sealed vessel with at least two ports. Carbon dioxide is introduced at the top of the vessel and water is sampled via a dip tube, which may be fitted with a filter to prevent clogging. Some configurations use an additional port to allow the headspace gas to be changed or flushed. The advent of pH electrodes capable of withstanding pressure-temperature conditions appropriate to investigations of GCS permit in-situ measurement of pH (below). If the fluid is not repeatedly sampled during the experiment, repeated runs of increasing duration are required to characterize the rate of reaction advancement by removing fluids and solids at different times.

A major challenge for high-pressure experiments involving CO_2 is sampling the fluid during the course of the run. It is necessary to take samples with considerable care to prevent water from degassing CO_2 as it is sampled. For determinations of the dissolved CO_2 content, samples may be bled off into a syringe containing alkali hydroxide solution, either using delicate human control of the sampling valve or a syringe pump to control back pressure. Rosenqvist et al. (2012) reported that the pressure drop using manual sampling was measured to less than 0.001 MPa by instrumenting the assembly with pressure transducers. An alternative method for determining dissolved CO_2 content is accomplished by coulometric titration (Huffmann 1977; Kaszuba et al. 2005). In this method, samples are bled off into a glass gas-tight syringe. Carbon dioxide dissolved in brine and exsolved at ambient pressure and temperature are injected together into a carbon coulometer.

Another type of batch reactor, initially described by Dickson et al. (1963) and improved later by different authors (e.g. Seyfried et al. 1979; Seyfried et al. 1987; Rosenbauer et al. 1993), consists of a flexible reaction cell, made of titanium or gold, with a detachable titanium cap (Fig. 3b). This cell is placed in a steel vessel similar to the previously described batch reactor. Pressure and temperature are externally controlled and water ensures pressure transmission to the cell. The cell is plumbed with an exit capillary tube linked to a sampling valve block. This system allows the isobaric and isothermal sampling of reacted fluids during the course of the experiment and permits the injection of fluids such as CO_2 when required (e.g. Kaszuba et al. 2003). Samples are cooled and depressurized to ambient conditions in a few seconds to prevent retrograde reactions that may occur during a prolonged quench process. Measurements of mineral solubilities and determination of coupled dissolution-precipitation rates can then be estimated using measurements of cation and anion concentrations. A related type of batch reactor is known as the Barnes-type rocking autoclave (Barnes 1971). This is a fixed-volume hydrothermal system in which pressures are determined by the liquid-vapor curve for reactant solutions.

With exceedingly few exceptions, solid samples can only be recovered from batch apparatus after the experiments are terminated. Batch apparatus that permit time sampling of solids are custom-made apparatus not available commercially, such as stacked-vessel autoclaves (Cole et al. 1992). Availability of solid samples only after termination of the experiment may affect the study of reaction mechanisms since some intermediate phases or processes may be missed. In addition, fluid sampling does not always manage to correctly record the reaction in polymineralic assemblages because of assumptions made for mineral compositions and proportions for mass balance. These limitations have motivated the development of 'microreactors' capable of in-situ monitoring of fluid-rock interactions (Fig. 3c) (Béarat et al. 2006; Schaef et al. 2011; Schaef et al. 2012). Microreactors are a few microliters in size and contain transparent windows constructed of diamond or moissanite (SiC). In-situ monitoring of reactions is performed using methods such as X-Ray diffraction of solid products, X-ray fluorescence for solid and fluid composition, or Infrared or Raman for solids and some dissolved species (e.g. carbonate, bicarbonate ions). This type of approach has been limited so far to mineral physics for high-pressure experiments using diamond-anvil cells (DAC). Development of low-pressure DAC or low-pressure reactors with an external control on the fluid opens new perspectives for the study of CO_2-water-rock interactions using a wider range of characterization tools (e.g. Wolf et al. 2004; Daval et al. 2010). The main constraint of this type of experiment is that the size of the window may require the use of synchrotron radiation in order to get the required spatial resolution and beam intensity for analyzing small volumes of minerals and fluids.

Mixed flow-through reactors

Batch experiments provide measurements of dissolution rates in fluid-dominated settings in which the reaction affinity changes as equilibrium is approached. Progressive sampling of solution in the course of the experiment changes the proportion of mineral to fluid so that the amount of mineral dissolution needed to produce a given change in fluid composition gradually decreases as the experiment proceeds. An alternative approach is to carry out experiments in which fluid flows at a steady rate through the experimental vessel and is sampled at the exit point (Fig. 3d). The composition of the exit fluid is considered representative of that inside the vessel. Mixing ensures fluid homogeneity and stirring rate is fixed in order to avoid mass transport limitations on the reaction rate. In flow-through reactors, the composition of the introduced fluid remains constant, so that the reaction affinity reaches a steady state. As a result, conditions are likely to be further from equilibrium than is the case for batch experiments, but affinity remains constant. Dove and Crerar (1990) developed a hydrothermal mixed flow-through reactor capable of working over the range of pressure-temperature conditions appropriate to GCS. This approach was further developed by Carroll and Knauss (2005) for experiments with CO_2-bearing fluids. Water (or brine) is first saturated with CO_2 at the required pressure in a separate pressure vessel and is then injected into the stirred reactor vessel containing the mineral charge. Since a single fluid phase passes though the reaction vessel and a backpressure is maintained to prevent the dissolved gas from separating, issues with two-phase flow do not arise. Hydrothermal mixed flow-through reactors arguably offer the best-constrained environment for determining far-from equilibrium mineral dissolution rates in CO_2-bearing water. However, depending on the stage of the GCS process that is being investigated, these may not be the key reaction rates for the problem of interest.

Plug-flow/flow-through reactors

Batch reactors and mixed flow-through reactors monitor the dissolution of small mineral volumes in large fluid volumes. In order to predict the consequences of injection of CO_2 into rock-dominated reservoir rocks, there is clearly a case for carrying out experiments where fluid flows through a rock or sediment plug, reacting as it moves. However, it is not normally possible to back out absolute rate information from the results. This type of approach also better emulates the dynamics of CO_2 injection in a natural reservoir where a coupling between chemical reactions and hydrodynamic properties is expected. Moreover, a rock is a chemically and physically heterogeneous media in which fluid flow and reaction may vary with space, even at the micrometric scale. Most flow-through reactor experiments investigate the characteristics of specific rocks from prospective reservoirs or their caps, but it is also possible to carry out experiments on packed columns containing solids that are well-characterized (Bateman et al. 2010).

An example of a plug-flow reactor, also known as a flow-through or core-flood reactor, is shown schematically in Figure 3e. The fluid to be injected is prepared in a separate vessel and pumped into a cm-scale rock core held in a core holder. The confining pressure around the jacket containing the core is substantially greater than the fluid pressure at the point of injection to prevent leakage. Reservoir conditions (greater than 200°C and 20 MPa) can be achieved within the core (e.g. Luquot and Gouze 2009). Fluid pressure at the outlet is adjusted to give a pre-determined constant flow rate, and the measured difference of pressure across the core provides a continuous record of permeability (as calculated using Darcy's law). Both dissolution and precipitation reactions can be investigated depending on the inlet fluid composition. Initial porosity measurements correlated to mass balance calculations during the course of the experiment provide the porosity evolution and hence the determinant permeability-porosity (k-φ) relationship for reactive transport modeling as a function of fluid reactivity and fluid flow. Some apparatus are ported such that pH is continuously monitored on the outflow line and fluid samples may be collected during the run. Some apparatus are constructed such that the entire assembly is set up in a CT scanner so that changes in the distribution of porosity can be monitored periodically as the run proceeds. NMR can also be used to monitor changes in porosity and pore size distribution. Further measurements can be made at the end of the run, including off-line measurements of permeability and seismic velocities (V_p, V_s). Noiriel et al. (2009) carried out experiments close to atmospheric pressure, which allowed the core to be removed periodically to be scanned in a micro-CT scanner. This approach yielded high-resolution spatial images of the evolution of reactive surface area, porosity and tortuosity while reaction progressed. Experiments of this type do not readily yield fundamental kinetic data, but they do provide a test for the available theoretical models.

pH measurements under GCS conditions

A major consequence of CO_2 injection is acidification of formation waters, but only recently have electrodes been developed to allow pH determinations at elevated pressure and temperature in experimental systems. Many studies with CO_2 still measure pH as quickly as possible after reducing pressure to ambient, and rely on geochemical models to calculate pH at in-situ conditions.

Solid state pH and reference electrodes that can be inserted into a pressure vessel using additional ports in the lid were used by Pokrovsky et al. (2005), who combined a commercial pH electrode with a home made reference electrode. Comparable electrodes are currently available commercially from Corr Instruments. Because these electrodes remain in place for the entire duration of an experiment they must be both robust and stable, but if they meet this requirement they permit monitoring of pH throughout an experiment. An alternative approach employed by Rosenqvist et al. (2012) is to use small volume solid-state electrodes in-line on the dip tube, between the vessel and sampling syringe (Fig. 3f). This configuration allows measurements to be made whenever a sample is taken, and the same electrode assembly can be used during sampling from a number of vessels rather than being dedicated to just one. Rosenqvist et al. (2012) used Unisense micro pH electrodes, rated to 1 MPa, and so were unable to work at full GCS pressures. The same assembly can be used for plug flow experiments as well as for batch experiments.

A growing number of studies do report high pressure pH measurements. It appears that they are comparable to those obtained by careful thermodynamic modeling, although oversimplistic application of modeling codes can produce misleading results depending on the treatment of CO_2 fugacity (Allen et al. 2005; Rosenqvist 2012). Until the release of PHREEQC v.3 in 2012 (http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html), modeling codes did not allow for the non-ideal behavior of CO_2. To get meaningful results it was necessary to calculate CO_2 fugacity off-line (e.g. Duan et al. 2006) and then input the resulting value as a pressure into the model. PHREEQC now incorporates a fugacity correction.

Both pH and fluid composition have been widely investigated as variables controlling mineral dissolution rates, with or without the presence of CO_2. Studies that specifically address mineral dissolution in the presence of CO_2 report that it is the role of dissolved CO_2 in determining pH that influences dissolution rate, rather than the presence of dissolved carbonate *per se* (e.g. Carroll and Knauss 2005; Pokrovsky et al. 2005). In effect, mineral dissolution experiments relevant to GCS represent a subset of the available data performed over a relatively narrow range of moderately acid conditions.

CARBON DIOXIDE-WATER-ROCK INTERACTIONS IN RESERVOIR ROCKS AND CAPROCKS: EXPERIMENTAL PERSPECTIVES

Olivine and pyroxene

Olivine and pyroxene are the predominant minerals in mafic and ultramafic rocks forming the oceanic lithosphere and the upper mantle. These rocks represent the greatest potential for CO_2 storage capacity by mineral trapping, i.e. ~2 tons and 1.3-1.4 tons of CO_2 per m^3 of rock, respectively (Xu et al. 2004). This capacity is a consequence of 1) the strong disequilibrium of olivine and pyroxene in the presence of aqueous fluids under shallow crustal conditions and 2) the high ratio of divalent cations to silica that provides abundant Mg^{2+}, Fe^{2+} and Ca^{2+} to form carbonates when olivine and pyroxene dissolve in a CO_2-rich aqueous fluid. Hence, in addition to possible oceanic disposal, fragments of ancient oceanic lithosphere and major flood basalts exposed on land constitute large and accessible reservoirs for CO_2 storage (McGrail et al. 2006; Kelemen and Matter 2008). Iceland already hosts the first pilot holes where in situ injection of CO_2 into basalt is currently tested as part of the CARBFIX project (Gislason et al. 2010; Matter et al. 2011). Kelemen and Matter (2008) estimated that present-day, natural weathering of exposed mantle rocks in the Oman ophiolite stores 10^4 to 10^5 tons of CO_2 per year, under atmospheric pCO_2 and temperature < 100°C (compared to sequestration targets of c. 10^9 tons per year). This natural phenomenon motivated experimental work to identify optimum conditions for accelerating the carbonation reaction (Dipple et al. 2013).

As silicate dissolution is assumed to be the rate limited step of the overall carbonation process, several experimental studies evaluated the kinetics of olivine and pyroxene dissolution in the presence of CO_2. This type of experiment has been performed very far from equilibrium in stirred-batch or mixed flow-through reactors. Final solution compositions were undersaturated with respect to expected secondary products (e.g. carbonates, Mg-Fe-hydroxydes or phyllosilicates) such that secondary mineral formation cannot affect dissolution rates. The effect of fluid composition on reactions has sometimes been taken into account. At least two types of effects have been evaluated: the effect of ΔG and the effect of aqueous complexes or formation of secondary minerals that may retard or accelerate the reaction.

With such reactors, numerous studies have been devoted to the dissolution kinetics of forsteritic olivine with Mg > 1.8 atoms per formula unit (see Rimstidt et al. 2012 for a review). Experimental conditions range in temperature from 25 to 120°C, pCO_2 from 0 to 18 MPa, pH from 2 to 12, and NaCl concentration from 0 to 50 g/L. The pH values were either directly related to the pCO_2 or to $NaHCO_3$ content, or fixed using acid or basic salts such as HCl and LiOH, in order to compare the effect pH to the effect of carbonate ions in solution. All of these experiments show that the rate of olivine dissolution increases with increasing pCO_2, temperature and NaCl concentration and with decreasing pH. Incongruent dissolution is observed at the initiation of the reaction when fresh olivine is introduced into low pH or high pH solutions. At low pH, magnesium is released faster than silica while the opposite is observed at high pH; dissolution is stoichiometric only near pH 6. Nevertheless, once a steady-state dissolution rate is achieved, it appears to be stoichiometric across the entire pH range. This justifies the use of either magnesium or silica release rate for calculations (Rimstidt et al. 2012). When compiling data for a given temperature of 120°C, Prigiobbe et al. (2009) show that the rate of olivine dissolution mainly depends on pH for pH values greater than 8 (Fig. 4); pCO_2 and NaCl concentration affect the rate through their effect on pH. This relationship suggests that carbonate ions neither inhibit nor enhance olivine dissolution and that kinetics as a function of pH can be used directly (Fig. 4). However, the importance of the effect of carbonate ions is still debated regarding CO_2 mineralization at high pH and pCO_2 greater than atmospheric levels. Under these conditions, an inhibiting effect of CO_3^{2-} has been observed (Fig. 4) at 25°C for pH greater than 7 (Wogelius and Walther 1991; Pokrovsky and Schott 2000), and at 120°C for pH greater than 5 (Hänchen et al. 2006). These authors attribute this behavior to the adsorption of carbonate ions on $>MgOH_2^+$ groups present on the dissolving olivine surface under alkaline conditions. Comparison of predicted rates using regression models for experiments with and without dissolved carbonates indicates that the inhibiting effect of carbonate is the highest around pH 5 for temperature less than 40°C (0.7 difference in log rate value, Rimstidt et al. 2012). This observation is inconsistent with previous experiments and the authors conclude that the current dataset is too incomplete to correctly estimate this effect.

Some compounds have also been recognized as enhancing olivine dissolution. Organic additives, like citric or oxalic acids that can be important ligands in soils, increase the rate of olivine dissolution around neutral pH at low T (25°C) (Wogelius and Walther 1991; Olsen and Rimstidt 2008). Prigiobbe and Mazzotti (2011) extended this study for high temperature and pCO_2 relevant for CO_2 sequestration. They show that for a pH range of 1 to 7 at temperatures of 90 and 120°C, sodium oxalate and sodium citrate increases the rate of olivine dissolution; this effect increases with pH. Chen and Brantley (2000) added aluminum to solution at 25°C in olivine dissolution experiments but did not notice any effect on the reaction rate. Using a closed microreactor (low-pressure DAC) at higher pressure and temperature conditions (200 MPa, 200°C and 300°C), Andreani et al. (2013) observed a significant increase of the hydrothermal alteration rate of olivine. They attributed the rate increase to an enhanced olivine solubility due to alumina-silica complexation, as previously observed for aluminosilicates for pH values greater than 4 (Salvi et al. 1998). No experiments have been performed between these extreme conditions; further investigations under conditions relevant for GCS are warranted since aluminum is present in mafic and ultramafic reservoirs, notably in feldspars.

Very few studies investigate the dissolution rate of fayalite, the pure iron end-member of olivine, but these studies cover a wide range of conditions. Available data provide kinetic rates for $25°C \leq T \leq 100$ °C, without CO_2, at pressures up to 30 MPa for pH 1-3, and variable pH at low pressure and temperature (Wogelius and Walther 1992; Daval et al. 2010). Under far from equilibrium conditions, fayalite dissolves faster than forsterite, especially at 25°C where the rate is about one order of magnitude higher; however, the stoichiometry of dissolution is not yet determined. Similar to forsterite, the dissolution rate of fayalite increases with increasing temperature and acetate concentrations or decreasing pH.

Dissolution of pyroxene has been less well studied than that of olivine, especially in CO_2-bearing fluids. Ca-clinopyroxenes diopside and augite were the most studied, in comparison to the FeMg-orthopyroxene enstatite. Chen and Brantley (1998) provide dissolution rates of diopside at 25 ($\sim10^{-9}$ mol/m^2/s for pH <4) and 90°C ($\sim10^{-7}$ to 10^{-8} mol/m^2/s) under acidic conditions (pH 1 to 4), these values are about an order of magnitude lower than the values of Golubev et al. (2005) for the same pH range. At these conditions and up to pH values of ~10, at which the dissolution rate is $\sim10^{-9}$ mol/m^2/s (Knauss et al. 1993; Golubev et al. 2005), diopside dissolves non-stoichiometrically at early stages of reaction and until it reaches a stoichiometric steady state. In more basic solutions a preferential release of silica suggests the formation of a Ca-Mg-rich layer on mineral surfaces (Golubev et al. 2005). Diopside dissolution rates are much slower than other silicates, notably olivine (Fig. 4), with rates 3 orders of magnitude slower at 25°C and approximately 2 to 3 orders of magnitude slower at 70 and 90°C, respectively. This is in accordance with common petrographic observations of alteration in mafic rocks. It is worth noting that the values of Chen and Brantley (1998) at 25°C and acidic pH are slightly lower than those published by other authors (e.g. Schott et al. 1982; Knauss et al. 1993; Golubev et al. 2005), although all of the studies agree that dissolution kinetics are very slow. Augite dissolves more rapidly at 25°C under very acidic pH of 1 to 3 (approximately 10^{-7} to 10^{-9} mol/m^2/s) but the reaction rate decreases with pH greater than 4. The reported pH-dependence of dissolution for pyroxene also varies from author to author. Variations are possibly the result of the reactive surface area chosen for calculations, since both initial and final surface areas have been used. This effect may be more important for pyroxenes because of preferential dissolution along cleavage planes. However, the reaction rate generally tends to decrease with increasing pH and decreasing temperature. As with olivine, the presence of CO_2 up to 0.1 MPa and of carbonate ions has no direct effect on diopside dissolution (Golubev et al. 2005).

Enstatite dissolution was studied by Oelkers and Schott (2001) at 28 to 168°C and pH 1 to 11 in CO_2-free solutions containing variable amounts of magnesium and silica. Enstatite dissolution rate follows the same trend as other pyroxenes with very similar values as diopside at 70°C (10^{-7} to 10^{-9} mol/m^2/s from pH 1 to 12), but the rate decreases with increasing aqueous Mg^{2+} concentration (0 to $4x10^{-4}$ mol/kg) while aqueous silica (up to $5x10^{-4}$ mol/kg) has no effect. This observation is interpreted to stem from a peculiar dissolution mechanism controlled by a Mg/H^+ exchange reaction within Mg octahedra that link silica tetrahedral chains. This mechanism, which depends on aqueous Mg activity and pH, is also expected to occur for other pyroxenes and pyroxenoids in general. This suggests that the role of magnesium has to be taken into account for CO_2 storage in such reservoirs since the concomitant dissolution of neighboring olivine releases abundant magnesium into solution. Experiments performed at 25°C and higher pH (8 to 13), both with and without atmospheric CO_2, demonstrate an inhibiting effect of CO_3^{2-} on enstatite dissolution at pH greater than 10, attributed to the same mechanism as the one proposed for olivine (Halder and Walther 2011). Wollastonite, a pyroxenoid rarely found in natural systems, has also been studied under ambient and GCS conditions to investigate the behavior of Ca-silicates (Rimstidt and Dove 1986; Weissbart and Rimstidt 2000). While its structure is very close to pyroxene, wollastonite displays much faster dissolution rates than pyroxene (about 3 orders of magnitude higher than diopside at 25°C); these rates are close to olivine dissolution rates. An explanation for differences between wollastonite and pyroxene dissolution rates has yet to be determined. The pH dependence varies from one author to another but the rate tends to decrease with increasing pH. For example, at 25°C for a pH ranging from 1 to 6, the dissolution rate is either nearly constant at 10^{-6} mol/m^2/s (Rimstidt and Dove 1986) or decreases to approximately 10^{-7} mol/m^2/s when pH increases (Xie and Walther 1994). The presence of CO_2 has no effect on the dissolution rate of wollastonite, but its dissolution rate increases with HCO_3^- in solution (0.01 to 0.1 molar) at pH 7 to 8 and slightly decreases with CO_2^{3-} in solution (10^{-4} molar) at pH 12 (Golubev et al. 2005).

Batch experiments have been used to investigate the entire process of mineral carbonation, both dissolution and precipitation, under conditions relevant for GCS since mineralization is the main reaction expected in basaltic and ultramafic reservoirs. Batch experiments are able to test the effect of precipitation of secondary minerals on the dissolution rate of primary silicates as well as the rate of carbonation in the reservoir in order to identify optimum conditions for CO_2 storage. In general, the carbonation reaction is much faster than the dissolution reaction of olivine and pyroxene. Olivine and wollastonite are fully transformed to carbonate in few hours to few days, respectively, under favorable conditions (Gerdemann et al. 2007; Daval et al. 2010). In some cases, the solution reaches supersaturated conditions with respect to magnesite, but magnesite does not precipitate. In this case, precipitation is limited by the nucleation process that requires a critical saturation index (Giammar et al. 2005). Surprisingly, olivine carbonation is the highest under alkaline conditions where CO_3^{2-} is dominant, whereas olivine dissolution is inhibited under such conditions (Hänchen et al. 2006). Optimum carbonation conditions identified for olivine are 15 MPa pCO_2, 185°C, 0.64 molar $NaHCO_3$, and 1 molar NaCl (Gerdemann et al. 2007). The reaction rate increases with temperature and $p\text{CO}_2$ up to these optimum values (see Kelemen and Matter 2008). The exothermic nature of olivine carbonation is also proposed to “self enhance” reaction rates by increasing temperature; energy costs required to heat fluids utilized for *ex-situ* CO_2 mineralization (see Dipple et al. 2013) are consequently reduced, provided this effect is not overwhelmed by influx of cold fluid.

The role of secondary phase precipitation on the carbonation rate is a matter of debate and depends on the product mineralogy and permeability, and on the primary silicate. The formation of a silica passivation layer on silicate surfaces limits olivine carbonation (Béarat et al. 2006) while it only has a minor effect on diopside and wollastonite carbonation (Daval et al. 2009a; Daval et al. 2009b; Daval et al. 2010). Some studies noticed an inhibition or decrease in the reaction rate when carbonate forms on silicate surfaces (Stockmann et al. 2008; Daval et al. 2009a) while fast precipitation also shifts the composition of the aqueous solution at negative free energy values, promoting the reaction (Daval et al. 2009a). In plug-flow experiments, carbonate, iron oxides and phyllosilicates can precipitate simultaneously near olivine surfaces in areas of reduced permeability, preventing the formation of the passive silica layer (Andreani et al. 2009) (Fig. 2B and 2C).

Feldspars

The feldspars are one of the most widespread groups of potentially reactive minerals in reservoir rocks, and have been the subject of considerable attention from both a theoretical and experimental viewpoint. Classically, studies of feldspar dissolution kinetics have mainly focused on albite, but Ca-bearing plagioclases have been seen as particularly important for GCS because of their potential to promote mineral storage through calcite growth consequent on calcium release (Gunter et al. 1997). Labradorite in particular has been the subject of a number of solubility studies (Stillings and Brantley 1995; Carroll and Knauss 2005; Allan et al. 2011) and is the subject of the GaMin11 interlaboratory comparison study. The application of conventional dissolution rate data on feldspars to GCS sites is particularly fraught because of the strong dependence on aluminum concentrations in solution (Amrhein and Suarez 1992; Schott et al. 2009). Oelkers et al. (1994) developed a treatment to account for the effect of aluminum concentration in solution on feldspar dissolution, linking dissolution to the degree of undersaturation and the formation of silica complexes on mineral surfaces. This is particularly significant for GCS applications because the initial pore fluid is already near feldspar saturation before the introduction of CO_2, so that conventional kinetic experiments starting without dissolved alumina and silica are likely to indicate much faster dissolution than occurs in real systems. An additional factor which has been highlighted in a series of papers by Zhu and co-workers (Lu et al. 2013 and references therein) is that, in a reservoir setting, feldspar dissolution is coupled to precipitation of secondary minerals such as phyllosilicates. Owing to sluggish precipitation of secondary minerals, the pore fluid remains supersaturated with them, and this in turn can significantly inhibit the feldspar dissolution step of the process. Most rate determinations have been made under far-from-equilibrium conditions, whereas rates are greatly reduced as equilibrium is approached (Burch et al. 1993).

Albite dissolution under far from equilibrium conditions has been studied over a wide range of pH values and at temperatures from 25 to greater than 100°C (Chou and Wollast 1984; Knauss and Wolery 1986; Hellmann 1994) with additional data at pH 3 from Stillings and Brantley (1995) and Allan et al. (2011). There is generally good agreement between these studies despite different experimental approaches. For example, Chou and Wollast (1984) used a fluidized bed reactor, Stillings and Brantley (1995) employed a mixed through-flow reactor, making allowance for increase in surface area in the course of the experiment, while Allan et al. (2011) employed a batch reactor with long run times and minimal stirring to avoid physical damage to mineral powders as the run proceeded. It is clear from all the results (Fig. 5) that dissolution rates range from around 10^{-11} mol/m^2/s at 25^{o}C to around 10^{-9} mol/m^2/s at 100^{o}C. Allan et al. (2011) found that an increase in NaCl from 0.01 to 1 molar resulted in a decrease in dissolution rate by around 1 order of magnitude. Albite reaction with CO_2 under more extreme hydrothermal conditions (200 to 300°C) were studied by Hangx and Spiers (2009), and although no kinetic data were obtained they did show the development of secondary aluminosilicates from albite breakdown, as discussed further by Lu et al. 2013.

Results from studies on labradorite show much less agreement. Dissolution rates based on increases in silica in low salinity fluids at pH 3 and near room temperature range from 10^{-10} mol/m^2/s (Carroll and Knauss 2005) to 10^{-12} mol/m^2/s (Allan et al. 2011). Possible reasons for these discrepancies include the possible effects of increasing surface area noted by Stillings and Brantley (1995) and the very mild agitation used in the work of Allan et al. (2011), coupled with the approach towards equilibrium in these batch experiments. It is also worth noting that there can be considerable variation in the compositions of different natural labradorites. Carroll and Knauss (2005) noted that labradorite dissolution becomes congruent with increasing temperature above 60^{o}C, but they confirmed the role of aluminum in inhibiting dissolution.

K-feldspar occurs in a wide range of reservoirs, although since detrital grains are often perthitic it usually coexists with albite. Fu et al. (2009) investigated dissolution of perthitic K-feldspar in batch experiments at relatively high temperatures and pressures for GCS (200^{o}C and 30 MPa) and an initial pH of 3.1. The metastable coexistence of K-feldspar with kaolinite and sometimes also illite is well known in sandstone diagenesis, suggesting that K-feldspar dissolution can be accompanied by the growth of secondary phases. Fu et al. (2009) were able to document this in their experiments. Contrasting runs of 5 days and 78 days duration, they found evidence for continued dissolution of the albite component of the perthite. After around 400 hours the fluid became supersaturated with K-feldspar, muscovite, boehmite and kaolinite, and secondary precipitates of boehmite and kaolinite began to develop on feldspar surfaces. Further work by Lu et al. (2013) has extended our understanding of secondary mineral formation from alkali feldspar and the effect this has on overall reaction rates. Secondary clay minerals are very significant for reducing sandstone permeability, and these results indicate that extended exposure to acidified formation waters will lead to progressive alteration of K-feldspar to clay.

Phyllosilicates

Phyllosilicates are hydrous minerals that classically form during the aqueous alteration of silicates, such as those forming CO_2 storage reservoirs (e.g. feldspars, olivine). Phyllosilicates can be present in the reservoir before CO_2 is injected or form during CO_2-water-silicate interactions. They are also important components of argillaceous caprocks (mudstone, clays, and shale) where an understanding of their interaction with CO_2-bearing fluids is important for evaluating caprock integrity after injection.

As with most minerals, phyllosilicate dissolution is sensitive to pH and temperature, two determinant parameters for GCS. Dissolution experiments of illite at 5 to 50°C and pH 1 to 12 in mixed flow-through reactors show the same rate behavior at all temperatures: a decrease of dissolution rate with increasing pH at acid condition, a minimum rate near neutral conditions ($5x10^{-14}$ to 10^{-15} mol/m^2/s), and an increase of dissolution rate with increasing pH at basic conditions (Köhler et al. 2003). The rate also slightly increases with increasing temperature and is a maximum (10^{-12} to 10^{-13} mol/m^2/s) at low pH. Comparison with available data on other aluminous clay minerals at 25°C shows similar trends with pH, and very close rate values suggesting similar dissolution behavior despite their chemical variability (Nagy 1995; Huertas et al. 1999) (Fig. 6). A slowing of clay dissolution rate with elapsed time during experiments is generally observed but not yet explained.

Micas can be important phyllosilicates in GCS reservoirs and cap rocks (e.g. Sleipner, Gaus et al. 2005). The reactivity of micas in CO_2-rich brines at conditions relevant to GCS has been investigated using batch reactors. Phlogopite served as a first model for dissolution rates of clays in experiments performed at 95°C, 10.2 MPa pCO_2, and 1 molar NaCl (Shao et al. 2010). Incongruent dissolution with an enhanced release of the interlayer potassium through ion-exchange is observed, similar to behavior at ambient pressure conditions, while Mg, Si and Al dissolve congruently. The dissolution of phlogopite is more important in CO_2–bearing aqueous solution than in acidic solutions without CO_2, suggesting a role for CO_2 on the dissolution mechanism. Complementary experiments at 75 and 95°C, 7.6 MPa, with supercritical CO_2 in 1 molar NaCl brines describe the precipitation of illite and amorphous silica on phlogopite surfaces (Garcia et al. 2012a). Similar experiments performed with biotite at 35 to 95°C and 7.5 to 12 MPa pCO_2 in 1 molar NaCl solutions also suggest a role for CO_2, expressed as a pH decrease, bicarbonate complexation, and an interlayer CO_2 intercalation (Hu and Jun 2012). Interlayer CO_2 intercalation promotes swelling and creation of new surface area that enhances dissolution and, in turn, increases permeability in natural settings. On the other hand, biotite alteration results in the precipitation of fibrous illite grains that become detached and mobilized, altering flow pathways. Experiments on powdered clay-rich shale containing aluminous phyllosilicates like illite show little reactivity in 1 molar NaCl, CO_2-rich solution at 11 MPa pCO_2 between 80 and 150°C, suggesting little porosity/permeability alteration (Alemu et al. 2011). However, plug-flow experiments on core or fractured core samples reveals processes that may affect caprock integrity. For example, experimental and theoretical studies demonstrate that the formation of small quantities of clay can significantly change the porosity and permeability of reservoirs or caprocks (Gaus et al. 2005; Gaus 2010; Luquot et al. 2012) (Fig. 7 and 8). When clays form along main flow paths, the increased tortuosity can lead to strong a permeability decrease without significant porosity change (Godard et al. 2013).

Phyllosilicates are distinctive minerals because they have high specific surface areas due to their sheeted structure and present a wide range of chemical compositions. These characteristics lead to specific properties of phyllosilicate-bearing rocks, such as high tortuosity, but also give rise to high sorption capacity, ion exchange capacity, or swelling ability that can influence macroscopic properties of the rocks. CO_2 sorption experiments on clay minerals in shales performed at 50°C and total pressure less than 20 MPa (Busch et al. 2008; Wollenweber et al. 2010) demonstrated a maximum sorption capacity of 1mmol/g for pCO_2 of 7 to 12 MPa. This phenomenon could expand the CO_2 storage capacity of caprocks in case of leakage. However, swelling sorption can decrease permeability and result in microcracks, with an increased risk of leakage. Implications of sorption on caprock integrity are not fully understood and require further research.

To simulate a CO_2 leak through fractured caprocks, CO_2-rich brines and CO_2-gas were alternately flowed through a fractured claystone in a plug flow apparatus (Andreani et al. 2008). An abrupt increase of the fracture aperture occurred after each gas flow. The aperture increase is controlled by the decohesion of the clay framework induced by acidification from the CO_2 gas. Numerical simulation of kaolinite/CO_2-brine/kaolinite interaction at crystal scales suggest repulsion between kaolinite aggregates in acidic solutions (Pèpe et al. 2010). This process is expected to produce a progressive decrease of the capacity of the caprock to maintain its seal. In contrast, an opposing process may be induced in clays with a high swelling capacity, like Na- or Ca-saturated montmorillonite, after exposure to supercritical CO_2, suggesting again that CO_2 may be trapped by intercalating the interlayer region (Schaef et al. 2012; Romanov 2013; Tokunaga and Wan 2013). However, other studies observed that supercritical CO_2 partially saturated with H_2O can still dehydrate clays (Ilton et al. 2012). Hence, if the supercritical CO_2 flux is significant, the potential increase of permeability may lead to caprock failure.

Few phyllosilicates react directly to produce carbonate minerals, instead phyllosilicates serve as a source of divalent cations for formation of carbonates. The only layered phases proposed for direct carbonation reactions are serpentines (phyllosilicate group) and brucite (hydroxide group); both have been tested experimentally under conditions relevant to GCS using batch reactors or microreactors. As with olivine or pyroxene, the reaction kinetics must be accelerated in order to develop an economically feasible GCS process. Exploitation of brucite from mine tailings has been proposed for *ex-situ* CO_2 storage via processing in industrial reactors (e.g. Lin et al. 2008; Zhao et al. 2010; Dipple et al. 2013). Its dissolution rate increases with decreasing pH and increasing $NaHCO_3$ concentration (Hövelmann et al. 2012b). The rate of the carbonation process increases with pCO_2 and HCO_3^- in solution, similar to olivine. At high pCO_2, the CO_2 uptake is the limiting process (Harrison et al. 2013). Surprisingly, hydrated carbonates like nesquehonite ($MgCO_3{\cdot}3H_2O$) are the predominant product, whereas magnesite is predicted. Magnesite may form after brucite at greater than 50°C and but definitely at 75°C (Schaef et al. 2011). These authors also show that brucite carbonation is not effective in anhydrous supercritical CO_2 and that the conversion of brucite to carbonate increases rapidly with increased water content of the fluid. Like brucite, serpentine can be harvested from asbestos mines, but it is also very abundant in ultramafic reservoirs. Hence its behavior with CO_2-rich fluid is of interest for both *ex-situ* and *in-situ* solutions. As with brucite and olivine, carbonation is optimized by adding NaCl and $NaCO_3$ to the heated solution. The dissolution of serpentine during carbonation first produces an amorphous silica-rich layer before magnesite precipitates. This layer is the limiting step for cation diffusion and reduces reaction progress (Schulze et al. 2004). Pre-heating (up to 630°C) and grinding have been proposed to optimize *ex-situ* CO_2 processing by causing dehydroxylation and increasing reactive surface area, respectively.

Quartz

Relatively little attention has been paid to the solubility of quartz in the context of GCS, primarily because quartz solubility is not enhanced by reduction in pH (Knauss and Wolery 1988). Indeed, significant dissolution of CO_2 in water lowers quartz solubility (Walther and Orville 1983). Furthermore, detrital quartz grains possess relatively small effective surface areas compared to many other silicates, such as clays or partially weathered feldspars (Sardini et al. 1995). Rates of quartz dissolution are likewise independent of pH below values around 6 (Knauss and Wolery 1988). Under near neutral conditions, rates of quartz dissolution are enhanced by the presence of cations in solution, with sodium and calcium giving rise to a greater enhancement than magnesium (Dove 1999 and references therein, Fig. 9). Interestingly, further investigation of this effect indicates that the mechanism may also enhance release of silica from other silicate minerals (Wallace et al 2010). Most data are for far from equilibrium conditions, but Davis et al. (2011) have reported results for near-equilibrium dissolution in mildly alkaline solutions. At relatively low temperatures appropriate for GCS (up to about $125^{o}C$), quartz dissolution rates agree well with the predictions of Bickmore et al. (2008), but they are slower than expected at higher temperatures (greater than $200^{o}C$) (Davis et al. 2011).

While quartz dissolution rates should be rather slow, Houston et al. (2007) reported evidence for silica dissolution into injected seawater during a seawater enhanced oil recovery operation in the Miller Field, UK North Sea, but suggested that it was released from feldspars or other silicate minerals, rather than directly from quartz dissolution. Carroll et al. (2013), in a study of reactivity of reservoir and caprocks with CO_2, even reported amorphous silica precipitation from silica released during clay transformations. Overall, injection of CO_2 into existing formation waters is unlikely to have a significant effect on the amount of silica in solution, although it may lead to silica being redistributed from feldspars to clays. Where water is also injected and is undersaturated with silica under reservoir conditions, net dissolution of silica can be expected, but this may not be released directly from quartz if other silicates are present. Under relatively high-temperature conditions ($200^{o}C$) Kaszuba et al. (2003) did however report the development of etch pits on quartz grain surfaces.

Carbonates

Carbonate behavior in aqueous solutions is often quite distinctive from that of silicates; for example, carbonates exhibit retrograde solubility under conditions relevant to GCS. It has long been appreciated that many carbonates react more quickly than silicates with acidified pore fluids, and they probably play a key role in controlling fluid pH and composition in the rapidly-moving fluid packet ahead of an advancing CO_2 plume (Fig. 1). There are many studies of calcite and dolomite dissolution rates in the literature and more limited data for magnesite, siderite and other carbonates (e.g. Morse and Arvidson 2002; Golubev et al. 2009; Pokrovsky et al. 2009a; Pokrovsky et al. 2009b; Schott et al. 2009).

In addition to classical reaction rate studies on carbonate minerals, some recent studies have used high-resolution imaging to document the movement of specific surface steps on cleavage planes. Xu et al. (2013) used hydrothermal atomic force microscopy to monitor dolomite dissolution in solutions of varying ionic strength. They were able to document increased dissolution rates in more concentrated solutions, although bulk experiments of Pokrovsky et al. (2005) found little influence of ionic strength in solutions up to 1 molar.

Much early work on carbonate mineral solubility was aimed at weathering studies and so used CO_2 pressures less than 0.1 MPa. This work provided an overview of carbonate dissolution rates and allowed the development of models for carbonate dissolution (Pokrovsky et al. 1999b, a; Morse and Arvidson 2002) but could not evaluate whether $p\mathrm{CO}_2$ influenced dissolution rates other than through the effect on pH. Pokrovsky et al. (2005) carried out rotating disc batch experiments to determine calcite and dolomite dissolution rates at $p\mathrm{CO}_2$ greater than 5.5 MPa and 25°C, with pH measured directly, and also measured dissolution of these minerals as powders in a mixed-flow reactor. Magnesite dissolution rates were also measured at elevated $p\mathrm{CO}_2$ on powders using a batch reactor. Overall, the results of this work showed that carbonate dissolution rates are not strongly dependent on $p\mathrm{CO}_2$ except through the influence that it exerts on pH, and only weakly dependent on ionic strength up to 1 molar NaCl. In particular, the effect of $p\mathrm{CO}_2$ was not significant at pressures greater than about 1 MPa. For magnesite and dolomite, dissolution rates can be predicted at $p\mathrm{CO}_2$ values up to 5 MPa by the Surface Complexation Models of Pokrovsky et al. (1999a, b).

Subsequently, Pokrovsky et al. (2009b) presented experimental results for calcite, magnesite and dolomite in 0.1 molar NaCl at temperatures to 150°C, and presented an empirical fit to the experimental data for a range of pH values. This work showed only a small dependence of dissolution rate on temperature, with the highest rates at around 100°C. Figure 10 shows the dissolution rates of these three carbonates at 60, 100 and 150°C as a function of $p\mathrm{CO}_2$ and demonstrates the order of magnitude differences between them. The calculations were performed for pH of about 4 and a rather dilute (0.1 molar NaCl) matrix. On the basis of these results it appears that carbonate dissolution rates are not strongly dependent on either temperature or $p\mathrm{CO}_2$ over the range of conditions likely to be encountered in GCS sites.

Surface reaction rates of calcite are so fast in acid to neutral fluids that in practice reactivity in a calcite-bearing geological reservoir will always be transport controlled (Sjöberg 1983; Morse and Arvidson 2002). Surface reaction rates of calcite are therefore not in general relevant to GCS problems and it is the rate of dissolution and transport of CO_2 that dictates how fast calcite dissolves. Dolomite is slower to react than calcite but its dissolution may also be transport controlled in many situations (Pokrovsky et al. 2005). Magnesite is, however, even slower to react than dolomite under conditions relevant to GCS, and for magnesite the dissolution rate may well be controlled by surface reaction.

Sulfates

Sulfate minerals, predominantly anhydrite but also gypsum, are common accessory minerals in sedimentary rocks that comprise GCS reservoirs and caprocks. Anhydrite can also be a major mineral in an evaporate caprock. In addition, anhydrite may serve as a mineral trap for sulfur in CO_2-SO_2 co-sequestration (Knauss et al. 2005; Xu et al. 2007; Kaszuba et al. 2011; Chopping and Kaszuba 2012). The predominant reaction involving SO_2 in geologic carbon sequestration, and in water-rock systems in general, is the disproportionation reaction

$$4SO_2 + 4H_2O = 3H_2SO_4 + H_2S \qquad (1)$$

(Holland 1965; Getahun et al. 1996; Palandri and Kharaka 2005; Palandri et al. 2005; Kaszuba et al. 2011; Chopping and Kaszuba 2012). Anhydrite may precipitate in response to the subsequent increase in dissolved sulfate.

As with carbonate minerals, sulfates exhibit retrograde solubility under conditions relevant to GCS. Reaction kinetics for sulfate minerals are also orders of magnitude faster than many of the silicate minerals (Palandri and Kharaka 2004 and references therein), thus anhydrite readily precipitates and dissolves at laboratory time scales. The most important control on the precipitation and dissolution of anhydrite is the concentration of dissolved sulfate. Experiments have been conducted with a wide range of aqueous sulfate concentrations. Some experiments contain no aqueous sulfate in the initial brine, others contain sufficient sulfate to saturate or supersaturate brine with respect to anhydrite. Interpretation of anhydrite behavior in experiments must take into account the parameters at which the experiments are performed, including brine chemistry (ionic strength) and temperature.

Anhydrite dissolves in batch experiments evaluating reactions among rocks containing anhydrite, brine containing no aqueous sulfate, and supercritical CO_2. Such is the case for experiments evaluating the Eau Claire Formation, the shale caprock for the Mount Simon sandstone in the Midwestern United States (Liu et al. 2012), and the Stuttgart Formation, the sandstone reservoir for the pilot storage site at Ketzin, Brandenburg, Germany (Fischer et al. 2010). It is conceivable that gypsum may replace anhydrite at the temperatures of these experiments (56°C and 40°C, respectively), but no gypsum was reported in either study.

Anhydrite does not react in a core-flood experiment evaluating reactions in the Three Fingers evaporite unit, the lower part of the caprock at the Weyburn-Midale reservoir, Saskatchewan, Canada (Smith et al. 2013). The brine used in this study was formulated to emulate a typical in-situ brine that is near equilibrium with anhydrite, slightly saturated with respect to calcite and dolomite, and equilibrated with CO_2 at a pressure of 3 MPa. Dolomite dissolved during the experiment in response to the acidity of the brine. Anhydrite, however, did not react because anhydrite stability is not sensitive to pH and because the brine injected into the rock was already close to equilibrium with anhydrite. Dissolution of the dolomite matrix physically mobilized anhydrite crystals, a finding with potential implications for redistributing permeability and porosity in the rock.

Anhydrite precipitates in a series of hydrothermal batch experiments using Dickson cells that were performed to evaluate CO_2-water-rock interactions in carbonate rocks from the Leadville Limestone Formation, Paradox Valley, Colorado, United States (Rosenbauer et al. 2005). Injection of supercritical CO_2 dissolves calcite in these experiments. Dolomite precipitates in experiments containing high-sulfate brine but dissolves in experiments containing low-sulfate brine. This study reported similar results for carbonate rocks reacted with high-sulfate brine but no CO_2. Anhydrite also precipitated in a series of batch experiments evaluating CO_2-water-rock interactions in the Madison Limestone of the Moxa Arch, Southwest Wyoming, United States (Chopping and Kaszuba 2012). Following injection of supercritical CO_2, dolomite and calcite dissolve due to increased acidity whereas anhydrite precipitates (Fig. 11). Reaction-path calculations suggest that dolomite will become stable and precipitate once acidity in the brine is fully buffered by the rock (Fig. 12).

Similar behavior is observed in experiments that evaluate co-injection of SO_2 with CO_2 into Madison Limestone (Chopping 2011) and into arkose (Mandalaparty et al. 2011). Carbonate minerals dissolve in response to the increased acidity whereas anhydrite precipitates in response to the increase in dissolved sulfate (equation 1). Pronounced calcite dissolution is attributed to increased acidity due to SO_2 co-injection (Chopping 2011). Carbonate dissolution buffers the acidity such that pH values are similar to values observed for CO_2 injection (approximately pH 5); increased acidity predicted by computer models (e.g., Knauss et al. 2005) is not observed.

Collectively, these experiments demonstrate that co-injected SO_2 and CO_2 increases aqueous sulfate concentrations, precipitates anhydrite, acidifies the water and dissolves carbonate minerals. All of these reactions will take place in the acidified water ahead of the CO_2 front (Fig. 1, Location A). These experiments also demonstrate that injection of CO_2 (without SO_2) will lead to anhydrite precipitation if sufficient aqueous sulfate is present. Mineral-fluid interactions will neutralize some of this carbonic acidity, resulting in a rise in pH and reprecipitation of carbonate minerals.

Sulfides

Sulfide minerals, most commonly pyrite, are common accessory minerals in sedimentary rocks that comprise the reservoirs and caprocks targeted for geologic carbon sequestration. Dissolution of pyrite can augment mineral storage by providing Fe^{2+} for siderite and ankerite. Pyrite can also be important in CO_2-SO_2 co-sequestration due to the increase in dissolved sulfide (equation 1). On the other hand, oxidized impurities in the CO_2 will oxidize pyrite, generate sulphuric acid, and potentially decrease pH to values lower than injection of CO_2 without impurities. However, SO_2-CO_2 injection in batch reactions with Madison Limestone showed no significant pH decrease. Much would depend on the rate at which oxidized impurities are supplied; even feldspars will neutralize additional acid as it is generated if oxidants are not delivered too quickly.

Very few experimental studies report results for pyrite precipitation or dissolution. Pyrite precipitates due to alteration of basaltic glass beginning at temperatures of 150-250°C (Gysi and Stefansson 2012). Siderite precipitates near pyrite in response to CO_2 injection (Liu et al. 2012). In the CO_2-water-Madison Limestone experiments of Chopping and Kaszuba (2012), pyrite exhibits minor dissolution textures that developed in response to injection of CO_2. Finally, pyrite forms in experiments that evaluate hematite and goethite dissolution (section on iron oxyhydroxides, below).

Iron oxyhydroxides

Although not as abundant as silicate minerals, Fe^{3+}-bearing oxyhydroxide minerals occur in sedimentary rocks, especially redbeds, which are generally thick and widely distributed. Fe^{3+}-bearing oxyhydroxide minerals can promote mineral storage via reactions forming siderite and ankerite, if the minerals can be dissolved and aqueous Fe^{3+} reduced to Fe^{2+}. Hematite and goethite in particular have been the subject of studies coupling mineral dissolution and iron reduction. Hematite has also been proposed as an important mineral for geologic co-sequestration of SO_2

$$Fe_2O_3 \text{ (hematite)} + 2CO_2 + SO_2 + H_2O = 2FeCO_3 \text{ (siderite)} + H_2SO_4 \qquad (2)$$

(Palandri and Kharaka 2005; Palandri et al. 2005).

Hydrothermal batch experiments using Dickson cells and performed at 150°C and 30 MPa in 1.0 molal NaCl solution demonstrate that hematite and goethite dissolve, aqueous Fe^{3+} reduces to Fe^{2+}, and siderite precipitates in response to co-injection of supercritical CO_2 and SO_2 (Palandri et al. 2005; Garcia et al. 2012b). Roughly 0.05 to 0.1 vol% of the hematite and 2.4 vol% of the goethite reacted to siderite in these experiments. Other minerals that precipitated in the hematite-bearing experiment are pyrite (and or amorphous iron sulfide), dawsonite ($NaAlCO_3(OH)_2$), and native sulfur. Dawsonite probably precipitated in response to injection of NaOH immediately before the experiment was terminated (Palandri et al. 2005). As may be expected, goethite reacted to form siderite quicker than hematite (576 vs 611 hours). Kinetic dissolution rates for goethite have not been determined at low pH. At neutral pH, goethite dissolution rates (~10^{-8} mol/m^2/s) are indeed much faster than hematite dissolution rates (~10^{-15} mol/m^2/s) (Palandri and Kharaka 2004 and references therein). At low pH, hematite dissolution rates are around 10^{-9} mol/m^2/s. Rapid dissolution of Fe^{3+}-bearing oxyhydroxide minerals will be important in continental redbed sandstones (Palandri and Kharaka 2005).

Iron oxyhydroxide minerals also reacted rapidly to form siderite and native sulfur or pyrite in a sequence of experiments performed at lower temperature (70 and 100°C) and pressure (8.2 to 8.3 MPa) (Murphy et al. 2010; Lammers et al. 2011; Murphy et al. 2011). These studies employed two different types of apparatus, a micoreactor configured to perform in-situ infrared spectroscopy and a standard batch reactor. Mineral dissolution, reduction of iron, and subsequent precipitation of siderite occurred on exceedingly short time scales (< 1 hour). Nanocrystals of several iron oxyhydroxide minerals were evaluated, including hematite, ferrihydrite, and iron hydroxide polymorphs (goethite, lepidocrocite, or akaganeite). The NaCl solutions injected with supercritical CO_2 in these experiments contained aqueous hydrogen sulfide as a proxy for co-injected SO_2. Finally, hematite nanocrystals precipitated in batch hydrothermal experiments performed at 150°C and 20 MPa in CO_2-saturated 0.5 molar NaCl solution in a batch reactor (Montes-Hernandez and Pironon 2009). Iron-bearing montmorillinite (plus iron from the reactor walls) reacted to form hematite in 15 days and hematite + siderite in 60 days.

Reservoir and cap rocks

A number of studies have investigated the effect of CO_2-saturated fluids on rocks, most commonly in plug flow reactors. The overwhelming conclusion from such studies is that reactions with natural rocks are dominated by carbonate dissolution, in accordance with results of field trials (Lu et al. 2012). Kjøller et al (2011) found that even after 13 months at 70°C and 20 MPa, carbonate dissolution was the predominant process with calcite, dolomite and siderite dissolving in different rock types. By comparison, clay minerals and feldspars did not react, possibly because the carbonate reactions prevented low pH conditions from being attained. In contrast, experiments by Carroll et al. (2013) on sandstone and shale at 51°C and 19.5 MPa found that Fe-rich clays appear to have dominated the reactions, dissolving incongruently to secondary clays and amorphous silica.

The effects of reactivity on petrophysical properties of reservoir rocks have been investigated in several studies. Canal et al. (2013) measured changes in porosity due to calcite dissolution and found a marked increase in permeability and changes to seismic velocities. Bachaud et al. (2011) measured increased porosity in limestone caprock; in contrast, permeability remained low in these experiments. Hangx et al. (2010) carried out creep tests on sandstones partially cemented by calcite and found that reaction of the calcite did not affect rock strength. Busch et al. (2008) evaluated diffusive loss of CO_2 through a 100 m thick clay-rich, carbonate poor caprock. They determined that diffusive gas breakthrough occurs at the top of the caprock after approximately 0.3 Ma. Their experimental results also suggest that shale caprocks provide additional CO_2 storage capacity, predominantly through sorption (see discussion on phyllosilicates), but the related geochemical and mineralogic processes were not well constrained.

Experiments on natural rock cores provide a test for computer models (Canal et al. 2013) and have been used to investigate trapping mechanisms (Iglauer et al. 2011) and the effect of reactivity on the physical properties of reservoir rocks (Hangx et al. 2010). In the event that GCS is implemented commercially, it seems likely that such measurements will be an important part of site characterisation and evaluation. An obvious limitation is the complexity of natural rocks which can make it difficult to extract fundamental data. Some workers have carried out column experiments using packed mineral grains of known composition and abundance instead of natural rock cores to try to address this issue. Bateman et al. (2010) carried out an extended (3.5 month) experiment flowing a synthetic brine pre-saturated with CO_2 through a 1m column packed with a mix of calcite, labradorite and quartz. In addition to monitoring the outflow fluid, the changes to the solid constituents were investigated along the length of the column. Over much of its length, calcite was completely dissolved and labradorite showed some evidence of pitting. Near the outflow however, there was evidence for new precipitation of calcite cement, apparently the result of neutralising of acidity by silicate reactions.

SUMMARY AND CONCLUSIONS

This brief review has demonstrated the considerable breadth of experimental data that is available for mineral dissolution and precipitation due to CO_2-water-rock interactions as well as the diversity of laboratory techniques used to acquire these data. In particular, a sizeable dataset quantifying the dissolution rates of minerals likely to be of significance for Geological Carbon Storage has been assembled. We hope this review has also demonstrated that further laboratory experiments, particularly kinetic measurements, are needed for conditions close to those likely to be encountered in CO_2 reservoirs. Here, pore fluids are likely to be already close to equilibrium with their host rocks prior to CO_2 injection, and will respond primarily to the lowering of pH which results as CO_2 dissolves into pore waters.

Despite limitations in our understanding, a number of important conclusions can be drawn about CO_2-water-rock interactions, particularly with respect to relative rates, that may be of value for the design of sequestration schemes. The fastest minerals to respond to the changes in fluid chemistry induced by CO_2 injection are calcite, anhydrite and dolomite. When present in the reservoir, these minerals serve to raise pH on a timescale of days in response to dissolution of CO_2 in formation waters, and as a result may further inhibit the slower response of silicate minerals to injection. Nevertheless, silicate reactions may take place within the lifetime of an injection site. Conversion of feldspars to secondary clay minerals is likely to be an important reservoir reaction, but at present the rates of such reactions are difficult to predict because they may be more dependent on the rate of precipitation of the secondary phases than on feldspar dissolution. This is important, because the secondary minerals may reduce permeability significantly and if this happens on the timescale of the original injection, it could reduce reservoir capacity. Impurities co-injected with CO_2 may provide new sources of acidity as well as dissolved solutes that may promote precipitation of new minerals and additional growth of preexisting minerals. Along main flow paths exhibiting high permeability, fluid composition will likely be dominated by the injected fluid; more protected areas exhibiting reduced flow may instead retain rock-dominated fluids. Over time, mineral dissolution and precipitation may progressively modify flow pathways and shift the types of reaction taking place. These processes will collectively determine the interplay between reaction kinetics and mass transport processes in CO_2 reservoirs.

DIRECTIONS FOR FUTURE WORK

Upscaling experimental laboratory data to reservoir scale is one of the most challenging issues to predicting the long-term fate of CO_2 in reservoirs that display an evolving reactivity. Reactive-transport modeling uses kinetic data determined from laboratory experiments to predict larger scale behavior, but two main issues need to be addressed to achieve better predictions. First, the interplay between chemical reactions, changing rock geometry, and hydrodynamic properties is crucial but not well constrained. This interplay notably controls fluid accessibility to reaction sites and the evolution of reactive surface areas. The latter may vary significantly in natural systems compared to those estimated for powders used in experiment because preferential flow paths can be created depending on the local flow rate. All these parameters vary from one rock to another and are strongly dependent on the departure from equilibrium (ΔG) of the fluid-rock reaction. Experiments at intermediate ΔG, below values expected for the injection site, are rare but very useful to constrain the evolution of reaction rate, porosity and permeability as a function of pCO_2. The experimental measurement of characteristic non-dimensional numbers that describe the timescale of reaction versus the one of transport (Damkholer number) under various conditions may also help to upscale the laboratory-scale processes. Second, reaction-transport modeling usually follows a macroscopic approach, using chemical properties averaged at the scale of a representative elementary volume (REV) that depends on rock structure. This approach fails to describe the complex spatial arrangement of rock-forming minerals, especially in polymineralic rocks, the connectivity of pores as it relates to accessible reactive surface area (Landrot et al. 2012), or the resulting heterogeneities in geochemical reactions. This has been emphasized in experiments in which dissolution and precipitation can both occur during fluid flow through the rock. From an experimental point of view, it is necessary to combine batch and dynamic approaches to discriminate between the intrinsic properties of minerals and the effect of rock structure on macroscopic reaction rates. Identifying the processes that control the overall behavior of the reservoir will inform decisions and assumptions needed to simplify computer models of reservoir and caprock behavior.

Taking the large-scale view to try to understand reservoir injection and storage, we can identify several areas where more work is needed. Experimental studies performed to date underline difficulties in predicting the behavior of caprocks and clay-rich lithologies in presence of a CO_2-rich fluid. Batch experiments on powders allow characterization of numerous properties of phyllosilicates; however, they fail to predict the macroscopic behavior of a real rock. Many opposing processes, such as CO_2 sorption, swelling, and sheet repulsions in an acidic media can occur simultaneously in nature. The extent to which these processes will occur depends on the fluid composition and the mineralogy and structure of the rock. The resulting macroscopic implications on caprock integrity are not fully understood and require further research.

An important target for GCS is the creation of enhanced residual or capillary trapping of CO_2 as isolated bubbles surrounded by water, and therefore physically captured by capillary forces (Qi et al. 2009; Tokunaga and Wan 2013). Although capillary trapping has been achieved in the laboratory on a short time scale (Iglauer et al. 2011), the experiments were only of short duration. Experiments evaluating the long-term stability of capillary trapping are needed because this trapping mechanism will depend on chemical processes since CO_2 is relatively soluble in water. Long-term experiments are also needed to evaluate whether the chemical connectivity between apparently isolated bubbles, through their solubility in the enclosing medium, has any effect on the stability of this trapping mechanism.

Most carbonation experiments conducted under GCS conditions have focused on the conversion of CO_2 into carbonate minerals. However, companion redox reactions may occur. Luquot et al (2012) showed that CO_2 may be converted into reduced carbon when injected in a ferrous iron-bearing sandstone reservoir, resulting in the precipitation of poorly-crystallized graphite. In mafic and ultramafic reservoirs, the oxidation by H_2O of the ferrous iron component of olivine or pyroxene can result in H_2 production (Stevens and McKinley 2000; Marcaillou et al. 2011). In CO_2-poor experiments, a part of the CO_2 is reduced to methane and possibly more complex carbon compounds (McCollom 2013). If magnesite precipitation after olivine is faster than iron oxidation under high pCO_2 (Jones et al. 2010), pCO_2 gradients in natural reservoirs may produce regions where hydration, carbonation and redox reaction compete, inducing a risk of CH_4 production that could alter storage integrity. In addition, the fraction of CO_2 possibly converted abiotically into heavier organic compounds is totally unknown, whatever the type of reservoir and the pressure, temperature, and pCO_2 conditions. The stability of such an organic fraction is also of interest for long-term safety. Redox reactions associated with CO_2 may strongly influence the fate of CO_2 and need to be experimentally investigated. The effect of CO_2 on the redox potential of the system also requires examination. It will be worth considering both problems under abiotic and biotic conditions since H_2 and CH_4 can be associated with autotrophic microbial activity.

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Figure Captions

Figure 1. Schematic representation of CO_2 injection into an aquifer sandstone beneath a caprock. The CO_2 fingers ahead down more permeable sandstone beds. A: sites in the most permeable beds where the advancing CO_2 front pushes acidified water ahead of it; B: region behind the CO_2 front containing interconnected CO_2 and residually trapped brine; C: upper surfaces of CO_2 fingers where CO_2 interacts by diffusion with overlying formation brines in less permeable beds; D: lower surfaces of CO_2 fingers where CO_2 interacts with underlying formation brines by diffusion and in some circumstances convection.

Figure 2. TEM images of main reaction textures observed in samples of sintered olivine and diopside reacted with CO_2-enriched water in a percolation experiment, a type of flow-through experiment. These textures illustrate the variability of transport-reaction resulting from the structural heterogeneity of the sample. Along main flow paths (A), olivine dissolution prevails because of an efficient advective removal of elements due to strong chemical gradients between the fluid and the mineral. A silica-passivation layer is created on olivine surfaces where magnetite precipitates. In reduced flow zones (B), chemical gradients and removal of elements are both reduced. Mg-Si phyllosilicates can precipitate instead of the silica layer. In dead-end-zones (C), chemical gradients are reduced and carbonate supersaturation can be achieved to form magnesite and siderite on olivine surfaces, in addition to an Mg-Si-rich phyllosilicate [Used by permission of the American Chemical Society, from Andreani M, Luquot L, Gouze P, Godard M, Hoisé E, Gibert B (2009), Environmental Science & Technology, Vol. 43, Fig. 4, p. 1228.].

Figure 3. Schematic drawings of the major types of experimental apparatus. A) Typical configuration for a batch reactor [Used by permission of Elsevier, from Hövelmann, J., Austrheim, H., Jamtveit, B. (2012a), Chemical Geology, Vol. 334, Fig. 2, p. 258.]. B) Batch reactor containing flexible reaction cell [Used by permission of the American Chemical Society, from McCollom and Seewald (2007), Chemical Reviews, Vol. 107, Fig. 6, p. 388.]. C) Microreactor [Used by permission of the American Chemical Society, from Wolf, G.H., Chizmeshya, A.V.G., Diefenbacher, J., McKelvy, M.J. (2004), Environmental Science & Technology, Vol. 38, Fig. 1, p. 933.]. D) Mixed flow-through batch reactor [Used by permission of Elsevier, from Pokrovsky, O.S., Schott, J. (2000), Geochimica et Cosmochimica Acta, Vol. 64, Fig. 1, p. 3314.]. E) Plug-flow reactor, also known as a flow-through and core-flood reactor [Used by permission of the American Chemical Society, from Andreani M, Luquot L, Gouze P, Godard M, Hoisé E, Gibert B (2009), Environmental Science & Technology, Vol. 43, Fig. 2, p. 1227.]. F) Batch reactor including a micro-pH electrode assembly in the sampling line (Rosenqvist 2012). [Used by permission of Elsevier, from Rosenqvist, J., Kilpatrick, A.D. Yardley, B.W.D. (2012), Applied Geochemistry, Vol. 27, Fig. 1, p. 1611.].

Figure 4. Experimental dissolution rates of olivine as a function of pH at 25°C (dotted line: data from Blum and Lasaga 1988; Wogelius and Walther 1991; line and grey area: data from Pokrovsky and Schott 2000), at 45°C (data from Rosso and Rimstidt 2000), at 50°C (dots: data from Wang and Giammar 2013), at 65°C (data from Wogelius and Walther 1991; Chen and Brantley 2000), at 90°C (data from Hänchen et al. 2006), at 120°C (data from Hänchen et al. 2006: without CO_2 (dotted line and dots), with CO_2 (open circles); line: data from Prigiobbe et al. 2009), and at 150°C (data from Hänchen et al. 2006).

Figure 5. Comparison of a range of experimental dissolution rates for albite (C&W,'84 data from Chou and Wollast 1984; S&B,'95 data from Stillings and Brantley 1995; B&C,'76 data from Busenberg and Clemency 1976; K&W,'86 data from Knauss and Wolery 1986; H,'94 data from Hellmann 1994). [Used by permission of Elsevier, from Allan et al. (2011), Applied Geochemistry, Vol. 26, Fig. 6, p. 1295.].

Figure 6. Comparison of apparent dissolution rates for illite and other clay minerals. Dissolution rates are normalized to 10 oxygen atoms. Closed system experiments in excess of 1 month are denoted by open symbols; those of shorter duration are denoted by open symbols [Used by permission of Elsevier, from Köhler, S.J., Dufaud, F., Oelkers, E.H. (2003), Geochimica et Cosmochimica Acta, Vol. 67, Fig. 7, p. 3592.].

Figure 7. SEM images of laumontite dissolution features and kaolinite precipitation in CO_2 percolation experiments through chlorite/zeolite-rich sandstone samples from the Pretty Hill Formation (Otway Basin, Australia). Dissolution of laumontite and chamosite are the potential sources of calcium, iron and magnesium required for carbonate precipitation. The experiment emulates in situ temperature and pressure conditions (95°C and 10 MPa) [Used by permission of Elsevier, from Luquot L, Andreani M, Gouze P, Camps P (2012), Chemical Geology, Vol. 294-295, Fig. 7, p. 82.].

Figure 8. Sketch illustration of laumontite, chamosite and feldspars dissolution and kaolinite precipitation in Figure 7, explaining reactive surface and permeability decrease with time. Permeability decreases of about one order of magnitude due to the localization of the kaolinite precipitation in the main flow paths, while porosity increases. [Used by permission of Elsevier, from Luquot L, Andreani M, Gouze P, Camps P (2012), Chemical Geology, Vol. 294-295, Fig. 14, p. 86.].

Figure 9. Effect of chloride salts on quartz solubility under conditions relevant to GCS [Used by permission of Publishing Company, from Dove (1999), Geochimica et Cosmochimica Acta, Vol. 63, Fig. 3, p. 3722.].

Figure 10. Dissolution rates of carbonate minerals as a function of $p\mathrm{CO}_2$, calculated from the equations of Pokrovsky et al. (2009b) for a 0.1molar NaCl solution with pH = 4. a) calcite, b) dolomite, c) magnesite. Solid lines are calculated for 60°C, long dashed lines for 100°C and short dashed lines for 150°C.

Figure 11. FE-SEM micrographs of anhydrite. Scale bars vary among the images. A) Unreacted anhydrite used in experiments conducted in flexible cell batch reactors at 110°C and 25 MPa. B) Anhydrite recovered from experiment reacting brine with dolomite, calcite, anhydrite, and pyrite. The brine is approximately saturated with respect to anhydrite. Dissolution textures are evident. C) and D) Euhedral anhydrite crystals that precipitated in experiments containing brine, dolomite, calcite, pyrite, ± anhydrite (C and D, respectively). Anhydrite precipitated in response to injection of supercritical CO_2. The brine is slightly undersaturated with respect to anhydrite at the time the CO_2 was injected [Used by permission of Elsevier, from Chopping and Kaszuba (2012), Chemical Geology, Vol. 322–323, Fig. 5, p. 231.].

Figure 12. Geochemical evolution of $scCO_2$-brine-rock experiments in the CaO-CO_2-SO_4^{2-}-H_2O system at 110°C. Stability fields for dolomite, anhydrite, and aqueous fluid at in-situ conditions prior to (solid lines) and after (long dashed lines) injection of $scCO_2$ are depicted. Stability fields predicted for equilibrium conditions in the $scCO_2$-brine-rock experiments (short dashed lines, filled square) are also depicted. A) Diagram plotting log a_{HCO3-} versus log a_{SO42-} for ±$scCO_2$-brine-Do-Cc-Anh-Py experiments. Aqueous samples are plotted for brine-Do-Cc-Anh-Py experiment (open circles) and $scCO_2$-brine-Do-Cc-Anh-Py experiment (open squares). The temporal sequence of samples in the $scCO_2$ experiment defines a reaction path trajectory (bold dashed arrows) towards the dolomite saturation boundary. B) Diagram plotting log a_{HCO3-} versus log a_{SO42-} for ±$scCO_2$-brine-Do-Cc-Py experiments. Aqueous samples are plotted for brine-Do-Cc-Py experiment (open circles) and $scCO_2$-brine-Do-Cc-Py experiment (open squares). The temporal sequence of samples in the $scCO_2$ experiment defines a reaction path trajectory (bold dashed arrows) towards the aqueous stability field. Anhydrite field appears after injection of supercritical CO_2 [Used by permission of Elsevier, from Chopping and Kaszuba (2012), Chemical Geology, Vol. 322–323, Fig. 7, p. 233.].