**Mineralization of carbon dioxide sequestered in volcanogenic sandstone reservoir rocks**

**Shuo Zhang1,2, Donald J. DePaolo1,2, Tianfu Xu2 and Liange Zheng2**

1Earth and Planetary Science Department, University of California, Berkeley, CA 94720-4767, USA

2Earth Sciences Division, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720, USA

**Abstract**

Geological storage of carbon dioxide in deep saline formations can decrease the accumulation of CO2 in the atmosphere, and thus slow down global warming. Most CO2 injected into subsurface rock formations is expected to remain for a long time as either a separate supercritical phase or in solution in brine; both forms present the possibility of leakage back to the surface or other environmental impacts. Mineralogical trapping of injected CO2 is more secure but usually thought to be too slow to add significantly to sequestration security. For quartz-rich sandstones (quartzarenite and arkose), only ca. 5 percent CO2 mineralization is achieved over 1000 to 10,000 years ([Audigane et al., 2007](#_ENREF_3)). However, if volcanogenic and other sandstones that have larger amounts of reactive minerals were used for storage, there could be a larger fraction of CO2 mineralized in a shorter time. The limitation is that porosity and permeability tend to decrease with increase of volcanic rock fragments (VRF), which limits the rate at which CO2 can be injected. We evaluate these tradeoffs to assess the feasibility of using volcanogenic sandstone to achieve secure CO2 storage. Using relationships between VRF percent, porosity and permeability from available geological data, the reactive transport code TOUGHREACT was used to model the flow, transport, mineral reactions, changes in fluid chemistry, and the rate and extent of CO2 mineralization over 1000 years during and after CO2 injection into a sandstone reservoir. We use the models specifically to evaluate the expected trade-off between higher reactivity and lower porosity and permeability. A model volcanic fragment mineralogy is used (pyroxene and feldspar mainly for which kinetic data are available) along with conservative estimates for silicate and oxide mineral dissolution kinetics and reactive surface area. Substitution of other more common reactive minerals such as chlorite and amphibole would not significantly change the results. The simulations show that in rocks with 10 to 20% reactive minerals, as much as 80% CO2 mineralization could occur in 1000 years and still allow sufficient injectivity so that 1 megaton of CO2 could be injected per year per well. The calculated mineralized fraction depends on several factors, most notably the kinetics and reactive surface area of dissolving silicates and the detailed relationship of reactive mineral content to effective permeability and injectivity.

**Keywords**

CO2 sequestration; CO2 mineralization; volcanogenic sandstones; reactive transport modeling

## Introduction

The accumulation of CO2 in the atmosphere increases greenhouse forcing and contributes to global warming. Because it is likely that fossil fuels will continue to be a vital component of energy resources in the next several decades, the emitted CO2 has to be dealt with in some way. Geological carbon storage is one of the primary options to reduce CO2 emission during the extended transition to carbon neutral energy sources. Geological formations, especially deep saline aquifers are promising for carbon storage due to their large potential storage capacity and geographic extent. The success of this option will be measured by the storage duration and the risk for leakage. Effective CO2 storage requires that ≥99% of injected CO2 be retained in the subsurface for >1000 years ([Intergovernmental Panel on Climate Change, 2005](#_ENREF_14)).

There are four so-called trapping mechanisms that contribute to retention of CO2 in the subsurface during geological carbon sequestration ([Intergovernmental Panel on Climate Change, 2005](#_ENREF_14)): (1) structural trapping, in which CO2 is trapped as a single supercritical phase according to the structural lithology of the storage zone, (2) capillary trapping, where CO2 is retained as small (≤1mm) bubbles in pore space due to the fact that CO2 generally does not wet mineral surfaces whereas saline brine does, (3) dissolution trapping, which refers to CO2 that becomes dissolved in the ambient liquid phase (brine), and (4) mineral trapping, which is CO2 that has been incorporated into minerals due to chemical precipitation. Mineral trapping is considered to be the most secure form of CO2 storage, but is also slow to develop because it follows the slow release of cations like Fe, Mg and Ca by dissolution of silicate and oxide minerals in the rocks. The most likely candidate storage formations for CO2 sequestration are sedimentary rocks with relatively high porosity and permeability, such as sandstones. The lithologies with the highest porosity and permeability usually are rich in quartz (SiO2) with some feldspar, and do not contain an abundance of silicate minerals that contain divalent cations that can combine with CO2 to form carbonate minerals (CaCO3, MgCO3, FeCO3). For sequestration in these types of rocks, modeling studies have shown that only a few percent of injected CO2 is trapped in minerals even after 1000 to 10000 years has elapsed from the time of injection ([Audigane et al., 2007](#_ENREF_3)).

Dissolution of CO2 into the brine and subsequent formation of carbonic acid is the first step in the mineral trapping mechanism. Carbon dioxide dissolves slightly in water to form carbonic acid, which in turn can slowly dissolve silicate minerals. Under appropriate conditions, the divalent cations released by silicate mineral dissolution can combine with dissolved carbonate ions to form stable carbonate minerals. This mechanism, however, requires host rocks with a high acid neutralization potential ([Baines and Worden, 2004](#_ENREF_5)). Rocks rich in calcium, magnesium, and iron silicate minerals can neutralize acids by providing Ca2+, Mg2+, Fe2+ that can form stable carbonate phases in the presence of CO2 ([Gunter et al., 2000](#_ENREF_11)).

Igneous rocks, especially mafic and ultramafic rocks, are rich in magnesium, iron, and calcium silicate minerals, and could theoretically provide a high potential of mineral trapping by mineral carbonation ([Kelemen and Matter, 2008](#_ENREF_15)). However, plutonic igneous (and metamorphic) rocks have negligible matrix permeability and porosity. The permeability in such rocks is determined primarily by the presence, type and orientation of fractures. Thus intrusive igneous and metamorphic rock bodies are normally unpromising hosts for subsurface disposal or sequestration of CO2, despite the apparently favorable rates of chemical reactions.

Most extrusive igneous rocks are subject to similar limitations for the disposal of CO2. The most extensive are flood basalts, found covering large areas of the earth’s surface in certain parts of the world. Basalts are commonly heavily fractured, and also possess rubble zones and vesicle porosity. Both microcrystalline groundmass and residual glass contain significant Ca, Mg and Fe. Therefore basalts could be candidate host rocks for CO2 sequestration ([Matter et al., 2007](#_ENREF_20); [McGrail et al., 2006](#_ENREF_21)). If the basalt flows are buried and overlain by impermeable sedimentary cap rocks, they could be favorable potential repositories of supercritical CO2, particularly if tectonic deformation were to create structural traps. However, the generally low permeability and porosity of the matrix would suggest that CO2 injection rates would be limited, even if injectivity could be enhanced by hydraulic fracturing. Furthermore, because crystalline rocks do not contain a significant amount of indigenous brine, reaction can only be achieved by injection of CO2-saturated water ([Matter et al., 2007](#_ENREF_19" \o "Matter, 2007 #96)). Since CO2 is sparingly soluble in H2O, roughly 200 times the volume of fluid would need to be injected into the rocks to store the same amount of CO2 that would be accomplished with injection of pure supercritical CO2. This large volume of fluid translates to the need for 200 times more injection wells, water, and pore space. There are cases where ophiolite complexes are subjected to severe hydrothermal alteration to serpentinites. Large amount of CO2 mineralization can be expected in these serpentinite-hosted aquifers and serpentinized peridotites due to high reactivity of these rocks. The upscaling of existing technologies that accelerate serpentinite carbonation may prove sufficient for offsetting local industrial emissions, however, global-scale implementation will require considerable incentives and further research and development ([Power et al., 2013](#_ENREF_26)){Power, 2013 #1549}.

Volcanogenic sandstones with a relatively high percentage of volcanic rock fragments (VRF) could be a promising target for CO2 sequestration in that they have a sufficient percentage of reactive minerals to allow substantial mineralization of injected CO2, but can also be porous and permeable enough to allow injection at acceptable rates. The potential shortcoming is that sediments with high VRF fractions tend to be more heavily modified during burial diagenesis, including more compaction and secondary mineral precipitation in pore space, and hence tend to have decreased porosity and permeability ([Remy, 1994](#_ENREF_29)). However, volcanogenic sandstones are potential or actual petroleum reservoirs in a number of locations ([Summer and Verosub, 1992](#_ENREF_36)), which indicates that there are instances where porosity and permeability are high enough for oil recovery. Several porosity-enhancing natural mechanisms such as framework-grain dissolution, devitrification of glass at shallow depths, precipitation of early cements that retard compaction, and fracturing have been identified in volcanogenic sandstones ([Hawlader, 1990](#_ENREF_12)). These processes can produce volcanogenic sandstone formations that are deeply buried but still relatively porous and permeable. Questions remain concerning how common these porosity-enhancing processes are, and our understanding of the major controls on the diagenesis of volcanogenic sandstones is incomplete.

In this study, we evaluate, using model rock compositions and measured hydrological properties of sandstones taken from the literature, how volcanic rock fragment abundance will affect the amount of CO2 that can be injected from a single well and mineralized in a flat-lying 40 meter-thick sandstone reservoir. The reactive transport code TOUGHREACT is used to calculate the amount of CO2 that can be injected and trapped in minerals, the timescale over which such mineralogical trapping would occur, and how the total amount of mineralized CO2 varies as a function of rock porosity, permeability and mineralogy. Key uncertain parameters are reactive surface area and residual gas saturation, so sensitivity tests are conducted with varying values for these parameters.

# Problem Setup

## Mineralogy of sandstone

To mineralize injected CO2, the requirement is that there be sufficient Ca, Mg and Fe available to combine with CO2 to form carbonate minerals, and also that these divalent cations be held in minerals that dissolve relatively rapidly so that the cations are released into solution on a time scale of hundreds of years. In general, those minerals that contain Ca, Mg and Fe in large proportions are also the minerals that dissolve fastest in the presence of acidic aqueous solutions, so there is a correlation between the amount of available cations and the rapidity with which the cations will become available.

Our approach is to evaluate model sedimentary rock compositions that involve mixtures of quartz, alkali feldspar, and basaltic minerals such as plagioclase feldspar and pyroxene, plus iron-titanium oxides. The anorthite component of plagioclase is a source of Ca ions, and the “diopside” and orthopyroxene are sources of Mg, Fe, and additional Ca. Oxide minerals are mainly a source of Fe. This specific mineralogy we use for the simulations is not typical of most volcanogenic sandstones, but we use for illustrative purposes because the dissolution kinetics of these minerals is relatively well studied. In most volcanogenic sands, the divalent cation-bearing minerals are more likely to be chlorite, zeolites, smectite, amphibole, and devitrified lithic fragments that may still contain some of the original igneous minerals such as those we are using for our model composition. The simulations using typical igneous minerals provide us with generalizable results that we can apply in a qualitative way to other sandstone mineralogies.

For our modeling purposes we use an idealized basaltic rock composition for the mineralogy of VRF based on the mineralogy of the Palisades Sill, which is holocrystalline and consequently the mineralogy can be specified better than for volcanic rocks that contain devitrified glass and poorly crystalline groundmass. Matter et al. ([2007](#_ENREF_20)) presented a dolerite analysis from the contact zone between the Palisades Sill and the underlying Newark Basin sediments. The dolerite is rich in Ca-bearing plagioclase and pyroxenes (augite and orthopyroxene) and free of olivine. The whole rock chemistry and observed mineralogy based on thin section analysis of the dolerite are summarized in Table 1. The mineralogy used in the model is determined from normative calculation as shown in Table 2 from the elemental chemistry, because for the purposes of the model we need to separate out the (Mg,Fe) and (Na,Ca) endmembers as separate minerals, although we use the same dissolution kinetics for the solid solution endmembers. The value of Fe3+/ (total iron) is assumed to be 0.2. Apatite and chromite are ignored since they are present in very small amounts. The diopside in our model is different from the “diopside” of normative calculation in that the diopside in our model only has Mg and Ca, and has no Fe as in the diopside from the normative calculation. This will cause some differences in results but they should not change the conclusions because Mg and Fe are playing similar roles.

Our strategy is to use the Palisades sill mineralogy as our “volcanic rock fragment” composition, and then to use natural sandstone samples that contain mafic volcanic rock fragments to evaluate the relationships between VRF content and hydrological parameters. Sandstone samples from the Tangbe formation of north central Nepal ([Durr and Gibling, 1994](#_ENREF_9)) are used as models for sandstone mineralogy (Table 3). Volcaniclastic grains are characteristic of Tangbe sandstones, which classify as lithic arenites. The lithic volcaniclastic grains (Lv) are separated into two major groups on the basis of their mineral composition and texture. Mafic grains Lv(M) represent basaltic fragments according to their chemistry. Felsic grains Lv(F), on the other hand, are mainly composed of quartz, plagioclase and K-feldspar (with the ratio of 0.52:0.35:0.13). From their modal composition, felsic grains represent rhyolite and dacite. A small number of volcanic grains Lv(Ch) fits neither group. These grains are made up of material with a chert-like appearance but a characteristic dark brown stain. Feldspar laths in these lithic grains enable classification as volcanogenic grains. For the purposes of calculation of silicate dissolution rates, the Lv(M) component of the sandstones is assumed to have a modal mineralogy the same as the normative mineralogy of the Palisades Sill basalt.

## Relationships between volcanic rock fragment percent, porosity and permeability

Several processes can affect porosity during diagenesis of volcanogenic sandstones, including early diagenesis (early leaching by fresh meteoric water, compaction, authigenic mineral precipitation, cementation of first-generation clays and burial dissolution) and late diagenesis (late-stage cements, dissolution of framework grains or cement during structural deformation). The diagenetic processes are controlled by a number of factors, such as depositional environment, detrital mineralogy, grain size, pore-water chemistry, temperature, pressure, and burial history ([Remy, 1994](#_ENREF_29)). Porosity is strongly influenced by detrital mineralogy. Remy ([1994](#_ENREF_29)) showed that rocks with abundant VRF experienced the most compaction, hence had decreased post-compaction porosity (which equals current macroporosity plus cement and can be considered as the remaining porosity after early compaction but before cementation). Cements vary in mineralogy. First-generation chloritic mixed-layer clays are most abundant in volcaniclastic petrofacies, whereas first-generation illite-smectite and calcite are most abundant in nonvolcaniclastic petrofacies, so the relationship between the extent of cementation and VRF is not easy to generalize. Also uncertain is the production of secondary porosity due to dissolution as a function of VRF. In rocks rich in VRF and with very low initial porosities, pore-water circulation is severely restricted, thereby preventing significant dissolution of framework grains. In rocks rich in VRF and with relatively high porosity, the presence of chemically-unstable lithic fragments promotes the formation of secondary porosity. The complexities of diagenesis make it difficult to predict permeability based on original sandstone mineralogy or any other single compositional or textural parameter. Ultimately, because it is impossible to specify permeability accurately even if porosity is known, we vary permeability over a small range to evaluate its importance in determining the outcome of the simulations.

As one approach to representing the effect of VRF abundance on rock porosity, we used the empirical relationships Eq. 1 and Eq. 2 from Bloch ([1991](#_ENREF_6)) to calculate porosity and permeability from mineralogy.

*Porosity = -6.1+9.8(1/sorting) +0.17rigid grain content* (1)

*Log10Perm =-4.67+1.34grain size+4.08(1/sorting) +0.0342rigid grain content* (2)

Here “sorting” is the Trask sorting coefficient ([Trask et al., 1932](#_ENREF_37)), “perm” is permeability in millidarcys, and “grain size” is grain diameter in millimeters. The two equations were obtained by fitting the data from Yacheng field, South China Sea. The model has a large amount of independent information, and a high coefficient of determination (R2=0.75 for porosity and 0.86 for permeability). All of the fitted sample data lie within a 95% confidence interval of predicted values as shown in Bloch ([1991](#_ENREF_6" \o "Bloch, 1991 #761)) (figure 14 and figure 15), although these limits are large enough to significantly affect the performance of potential reservoirs in a CO2 sequestration scenario.

The empirical equations from Bloch (1991) imply that porosity and permeability are affected by mineralogical variables (rigid grain content) and textural variables (grain size and sorting). Since the objective is to evaluate the effect of mineralogy on rock porosity and permeability, we assigned typical values to textural variables. The Trask sorting coefficient is given a value of 1.5 for well to moderately sorted sandstone, and grain size is assigned as 0.8 mm. Since the calibration data set is based on wells with similar temperature and pressure histories, post-depositional parameters (temperature, pressure, time) are not incorporated in these models. So all the uncertainties in textural variables (sorting and grain size) and post-depositional parameters (temperature, pressure, time) are gathered in the constants calculated with sorting coefficient =1.5 and grain size =0.8. Below we see that these values lead to slightly smaller permeabilities than expected from field data, and this is compensated by generating another permeability set that covers slightly larger permeability values.

Another approach to evaluating mineralogy-permeability relations is to use natural sandstones where there are sufficient characterization data to evaluate the variability as well as the overall trends. Gibson-Poole et al. ([2008](#_ENREF_10)) presented porosity and permeability data from Gippsland Basin in southeast Australia. The data for the Kingfish Formation sediments are reprinted here in Fig. 1. The porosities are mostly in the range 10% to 30% and the permeabilities vary from about 0.1 to 10,000 mD. The majority of the points lie in the 15-30% porosity and 10-10,000 mD permeability ranges. The empirical formula generated by determining a best fit to these data is:

(3)



where *k* is permeability in mD and ** is porosity. According to this equation, at least 8.6% porosity is needed to provide a minimum permeability (i.e. 1md) for injection. Clearly this relationship has limited applicability because the permeability can vary by a factor of over 100 for the same porosity. Nevertheless, we use this relationship as a reference, and use equations 1 and 2 and the mineralogy of the Tangbe sedimentary rocks to calculate porosity and permeability. These calculated values all lie close to but below the best-fit line of the Kingfish Formation porosity-permeability data.

Our conclusion is that equations 1 and 2 give a reasonable estimate of porosity-permeability relations in arenites, but that the large spread in permeability at all porosities means that no one porosity-permeability curve can adequately represent the likely range in natural reservoirs. To account for this range, and to evaluate the effect of permeability, we use two sets of permeability values. Those calculated directly from Equations 1 and 2 are noted as “low permeability,” and another set of porosity-permeability data (“high permeability”) is also used in our model where all permeabilities are increased by 5 times. This additional set of permeability data is beneficial in that the relationship between VRF and permeability is key to this study and the two data sets allow us to illustrate the large effect of the permeability-porosity relationship. Our selected range of values is nevertheless small in comparison to the likely natural range as illustrated in Fig. 1. Further discussion of permeability and its effects is provided in the Results section.

## Hydrogeological setting and model

The mafic volcanic rock fragment percent of the Nepal samples ranges from 1.6% to 32.3%. Reservoir porosities and permeabilities are calculated for each sample and then listed in Table 4. Brine compositions are obtained by pre-equilibrating 1.0 mol/L NaCl saline water with the respective corresponding mineral assemblage for 10 years. All simulations are run initially with a 1-D model with radial symmetry. The model is therefore in some sense a 2-D model, but we refer to it as 1-D because the fluids are not allowed to segregate vertically due to buoyancy forces. We have run 2-D radial models as well, and the differences between 1-D and 2-D models are relatively small and discussed further below. Initial reservoir pressure is set at constant 200 bar with a formation temperature of 75 oC. This temperature is calculated for a depth of 2 km, given a land surface temperature of 15 oC and a geothermal gradient of 30 oC/km. Formation thickness is set to 40m. Continuous injection is assumed to take place over a period of 100 years at a constant injection rate of 1 megaton CO2 per year. For the lower reservoir permeabilities that are associated with our model rocks with higher VRF, injection pressure needs to be increased to achieve the same injection rate of 1 Mt/yr. We set a maximum injection pressure of 390 bar (39 MPa). In cases where the reservoir permeability is too low to allow injection of 1 Mt/y CO2 at this injection pressure, the injection pressure is set at 39 MPa and the rate is decreased to be consistent with the permeability. Geochemical transport simulations are continued until 1000 years; an arbitrary cutoff chosen to limit the computational time for the models and to allow us to compare the amount of CO2 mineralized in a specified amount of time.

# Modeling Approach

## Simulation method

Simulations are conducted using the nonisothermal reactive transport code TOUGHREACT V2 ([Xu and Pruess, 2001](#_ENREF_41)). This code introduces reactive chemistry into the existing multiphase fluid and heat flow code TOUGH2 ([Pruess, 1991](#_ENREF_27)). A new fluid property module, ECO2N, is used based on the work by Spycher and Pruess ([2005](#_ENREF_34)). ECO2N provides an accurate description of the thermophysical properties of water and CO2 mixtures under conditions typically encountered in saline aquifers for CO2 disposal (10 oC ≤ T ≤110 oC; P ≤ 600 bars).

Fluid and heat flow processes considered in this code are: (1) fluid flow of liquid and gas phases under pressure and gravity forces, (2) capillary pressure effects for liquid phases, and (3) heat flow by conduction, convection and diffusion. Transport processes that affect aqueous and gaseous species are advection, molecular diffusion and hydrodynamic dispersion. For our simulations, chemical reactions between dissolved aqueous species and gas (i.e. supercritical CO2) are assumed to be locally at equilibrium (although TOUGHREACT V2 can consider aqueous species kinetics). Mineral dissolution and precipitation are subject to kinetic limitations.

The space discretization in our modeling is based on the integral finite difference (IFD) method ([Narasimhan and Witherspoon, 1976](#_ENREF_24)). This method allows the use of unstructured grids, which is well suited for simulation of flow, transport, and fluid-rock interactions in heterogeneous and fractured rock systems with varying petrology, and hence provides flexible discretization of geologic media. For regular grids, the IFD method is equivalent to the conventional finite difference method.

TOUGHREACT uses a sequential iteration approach for calculations of flow, transport, and kinetic geochemical reactions (but noniterative between transport and chemistry). After solving flow equations, velocities and saturations of the aqueous phase are used for aqueous chemical transport calculations. Chemical transport is solved on a component basis. Resulting concentrations obtained from the transport and CO2 gas pressures from multiphase flow calculation are then substituted into a chemical reaction model. The system of chemical reaction equations is solved on a grid-block basis by Newton-Raphson iteration.

An automatic time step control is used for the flow calculation. Time step size is doubled if convergence occurs within 4 Newton-Raphson iterations. The starting time step is 1 second and the upper limit for time step size is set to be 5 days. For transport equations, a stabilized bi-conjugate gradient solver is used. No limit of the time step size for chemical reactions is included.

## Flow and transport model setup

The specific model we used for our calculation is a 1-D model with distance *d* ranging from 0 m to 100 km, which can be considered as infinitely long. For boundary conditions, there is no flow at both *d*=0m and *d*=105m. For fixed injection pressure condition, the first grid is assigned an infinitely large volume (1050m3) and a gas saturation of 100% so that it serves as a CO­­2 source and its properties don’t change during the simulation. For the fixed injection rate condition, the injection well is also located in the first grid. Since the distance is large enough to be considered infinite in the model, the right end boundary condition is equal to an open end although there is no flow at d=105m. For initial conditions, the temperature is set to be 75 oC and the pressure is 200 bar. Initial gas saturation is zero and the formation is filled with all brine. Initial brine compositions are obtained by pre-equilibrating 1.0mol/L NaCl saline water in a batch model for 10 years with minerals that are used later for reactive transport modeling. Water chemistry is not changing after 10 years, which indicates that a steady state fluid composition has been reached under pre-injection conditions.

The equations for calculating relative permeability and capillary pressure and corresponding parameters are listed in Table 5. They are all from Van Genuchten([1980](#_ENREF_38)). Changes in porosity and permeability due to mineral dissolution and precipitation are taken into account in our model. Changes in porosity during the simulation are monitored by tracking changes in mineral volume fractions. We chose a simple grain model of Kozeny-Carman to calculate changes in permeability due to changes in porosity, although the actual porosity-permeability correlation in geologic media depends on a complex interplay of many factors such as pore size distribution, pore shapes, and connectivity. The Kozeny-Carman equation relates permeability *k* (in m2) to porosity () by

 (4)

where R0 is the initial local spherical close-pack radius. Hence, the ratio of permeability *k* to initial permeability *k*0 can be expressed as

 (5)

where ­0 is the initial porosity. Since porosity decreases are of order 10% of initial porosities during the course of the simulations, and the initial porosities average about 16.8%, the typical permeability change over 1000 years is *k/k*o ≈ 0.68. Using the fitted porosity-permeability relationship from Gibson-Poole et at. ([2008](#_ENREF_10)) presented earlier, the ratio of final permeability and initial permeability *k/k*o is 0.52 (initial porosity= 16.8%, final porosity= 15.0%), which is in the same order with the result from the Kozeny-Carman model used in the simulation. Considering the several orders of magnitude of permeability range and the deviation in determining the porosity-permeability relation from geological data, the error caused from using the Kozeny-Carman equation is negligible.

For species transport, the diffusion coefficient for aqueous species is set to be 10-9 m2/s. The diffusion coefficient is then multiplied by the tortuosity and liquid saturation. The diffusion coefficient of the medium for gaseous species is 10-5m2/s. Tortuosity is calculated internally from the Millington and Quirk ([1961](#_ENREF_22)) model, which is listed in Table 6.

## Geochemical data

The reaction rate expression used in this paper is based on the transition state theory (TST) ([Steefel and Lasaga, 1994](#_ENREF_35)):

 (6)

where *r* is the kinetic rate (positive values indicate dissolution, and negative values indicate precipitation), *k* is the rate constant (moles per unit mineral surface area and unit time) which is temperature dependent, *A* is the specific reactive surface area per gram of mineral, *Q* is the reaction quotient, and *K* is the equilibrium constant for the mineral-water reaction written for the destruction of one mole of mineral, whose values originated from the EQ3/6 V7.2b database ([wolery, 1992](#_ENREF_40)). The parameters ** and ** must be determined by experiment, but are commonly set to unity when experimental quantification is not available. Precipitation of secondary minerals is represented using the same kinetic expression, although as noted below this is a simplification for which there is little justification other than lack of more detailed information.

The kinetic rate constant *kT* (where *T* is the temperature in Celsius) can be summed from three mechanisms ([Palandri, 2004](#_ENREF_25)):

(7)



where subscripts *nu*, *H*, and *OH* indicate neutral, acid, and base mechanisms respectively, *E* is the activation energy, *k*25 is the rate constant at 25°C, *R* is gas constant, *T* is absolute temperature, *a* is the activity of species, and n is a constant power term.

Mineral dissolution and precipitation rates are a product of the kinetic-rate constant, the reactive surface area and the affinity term (1-*Q/*K), which describes how far the system is from equilibrium, as represented by Eq. 6. The parameters used for the kinetic rate expression are given in Table 6. We included separate rate constants (*k25*), activation energies (*E*), and reaction orders (*n*) for processes catalyzed by H+ and OH-. At any pH, the total rate is the sum of the rates from all mechanisms. However, catalysis by H+ or OH- is only considered for mineral dissolution, not for precipitation. Parameter values for the rate law were taken from Palandri ([2004](#_ENREF_25)), who compiled and fitted experimental data reported by many investigators. Solid solution effects are not considered in this study. To make up for this deficiency, the kinetic parameters of end members of each solid solution are set equal to the *slowest* one, e.g. anorthite is set to albite; ferrosilite is set to enstatite; and smectite-Na is set to smectite-Ca. These simplifications are conservative but all potentially significant. We have not attempted to evaluate each one independently because that would result in an unwieldy number of simulations and would affect the results in reasonably predictable ways (e.g. faster dissolution kinetics will allow for more dissolution per unit time and hence more mineralization).

If the aqueous phase supersaturates with respect to a potential secondary mineral, a small volume fraction of 1×10-6 is used for calculating seed surface area for the new phase to grow. Possible secondary minerals that are considered in this model are listed in Table 7. Precipitation of secondary minerals is represented using the same kinetic expression as that for dissolution. However, several aspects of precipitation are different from dissolution, such as nucleation and crystal growth. Some authors have argued that dissolution and precipitation are fundamentally identical but opposite in sign ([Dove et al., 2008](#_ENREF_8)), whereas others provide evidence that there are pronounced differences. The kinetics of dissolution are more likely to be important for the results presented here, and it is clear that all reactive transport models are simple representations of what are likely to be complex relationships that depend on solution composition in ways that are not reflected by just the degree of saturation of the particular mineral under consideration. The complications relating to mineral precipitation are not considered in the current model. Since precipitation rate data for most minerals are unavailable, only parameters for neutral pH rates were employed to describe precipitation. Multiple kinetic precipitation mechanisms can be specified in an input file of the TOUGHREACT program, should such information become available.

Mineral reactive surface areas (RSA) are based on the work of Sonnenthal et al. ([2005](#_ENREF_33)), and are calculated assuming a cubic array of truncated spheres constituting the rock framework. In conformity to White and Peterson ([1990](#_ENREF_39)) and Zerai et al. ([2006](#_ENREF_43)), a surface roughness factor of 10 is incorporated and defined as the ratio of true surface area to equivalent geometric surface area. Interaction with minerals is generally expected to occur only at selected sites of the mineral surface, and the actual RSA could be one to three orders of magnitude less than the surface roughness-based surface area due to coating or armoring ([Zerai et al., 2006](#_ENREF_43)). To account for these effects, the actual RSA are decreased by 100 times from the surface roughness-based surface areas. The RSA used here (9.8 cm2/g) for most minerals are similar to those used by Zerai et al. (2006). Clay minerals are assigned much larger RSAs (151.6 cm2/g) due to small particle size.

To provide the reactive surface area in the unsaturated system corrected by rock/water ratio, the surface area of each mineral (in units of m2mineral/kgwater), which is internally calculated, is given by:



Where Ar is the reactive surface area in units of m2/m3fracture medium, fm is volume fraction of the mineral, w is the density of water (in kg/m3), f is porosity of the medium, Sw­ is water saturation, Sm­ is the minimum liquid saturation for which water-rock reactions are considered. Sm was set to a small saturation (e.g. 1x10-4) in our model, to ensure that reactions take place until virtually no water is left since water is the wetting phase during CO2 sequestration.

Typically in reactive transport modeling a representative element volume is a well-mixed homogenous block. So here we don’t treat the volcanic rock fragments and the rest of the sandstone as two spatially separate materials in one grid block. Instead the effects of volcanic fragments on the properties of the grid blocks are taken into account in two ways. First, the percentages of volcanic rock fragments are used to calculate porosity and permeability of the whole sandstone. Second, the rock fragment percentages are used to calculate the percentages of reactive minerals; these reactive minerals are then embedded in the rock homogenously with RSA=9.8 cm2/g which is the same as the other minerals in the sandstone. In this approach, we are assuming that the rock fragments have the same porosity, permeability and RSA as the rest of the rock. These assumptions represent the simplest possible approach, but may be justified for our purposes. For example, we have examined volcanic sandstone samples from the Echegoin Formation near Coalinga, California (thin section picture shown in Figure 2). The volcanic fragments of this sandstone have similar sizes as the other mineral grains, which should give similar RSAs for reactions. Also the volcanic fragments are mostly equally distributed in the sandstone, which is reasonable support for our assumption of homogeneous porosity and permeability.

# Results

As described in section 2, we selected 5 volcanogenic sandstone samples from Central Nepal that have chemical and mineralogical data available. Porosities and permeabilities were calculated for each sample using empirical equations generated from the Yacheng field. Another set of permeability data was generated by multiplying the original ones by 5 to cover a larger range of permeability values, but a range that is still small in comparison to the full range of possible permeabilities as represented by the Gibson-Poole et al. ([2008](#_ENREF_10)) data (Figure 1). Injection rate is fixed at 1 megaton per year for samples with a large permeability that requires no larger than 390 bar injection pressure, whereas samples with low permeabilities that would need more than 390 bar were set at constant injection pressure of this maximum value and thus had less than 1 Mt/yr of CO2 injected. All samples were run with the reactive transport code TOUGHREACT using a 1-dimensional (radial) model. The simulations generated results for the distance that the CO2-bearing fluid would flow, how much CO2 is mineralized, and how system properties such as gas saturation and pH are distributed along the flow path.

## Relationships between VRF and CO2 mineralization amount

The relationships between the amount of mineralized CO2 and %VRF are presented in Fig. 3 and Fig. 4. For the Low Permeability case, sample 1 and sample 2 have injection rates of 1 Mt/yr while samples 3-5 (progressively higher VRF) are fixed at constant injection pressure of 390 bar since they would need a pressure higher than 390 bar to achieve 1 Mt/yr and we assume that standard injection equipment can achieve an injection pressure only as high as 390 bar. As permeability decreases from sample 2 to sample 5, the amount of injected CO2 decreases. However, since the amount of reactive VRF increases from sample 1 to sample 5, a larger percent of injected CO2 is mineralized. The trade-off between increasing reactivity and decreasing permeability generates an optimal case at VRF ≈ 6% where the amount of mineralized CO2 has the largest value. For the High Permeability case, the amount of injected CO2 and mineralized percent show similar patterns as those in the Low Permeability set, but the optimal case shifts from 6% to somewhere between 10% and 21% VRF. Thus it can be seen that the amount of mineralized CO2 depends on how we determine permeabilities from mineralogy, or more generally the relationships between mineralogy, porosity and permeability. Nevertheless, the results suggest that if formations can be identified that have relatively high VRF and modest permeability, mineralization of injected CO2 can be almost quantitative over a timescale of 1000 years.

Fig. 5 shows the evolution of total sequestered CO2 in the mineralized phase, aqueous phase and supercritical phase for the entire reservoir in the case of 21% VRF in the High Permeability case. CO2 injection is conducted for 100 years and then stopped. Supercritical CO2 phase dominates at first and then decreases rapidly after injection ceases, first due to dissolution into the aqueous phase, and then due to mineralization. The amount of aqueous CO2 increases first until it reaches saturation in water; its value stays roughly stable until about 700 years. Overall, supercritical CO2 first dissolves in the aqueous phase, and then reacts with cations in the aqueous phase released by mineral dissolution and produces carbonate precipitation. About 78% of injected CO2 is mineralized, 6% remains in the aqueous phase, and 16% remains as the supercritical phase at time = 1000 years.

## Radial distribution of system properties for the optimal case

The radial distribution of reservoir pressure, gas saturation, pH, porosity, and CO2 sequestration amount per medium volume are presented in Fig. 6a – 6e. The CO2 - affected region is limited within a radial distance of 4500m-6000m except for pressure. In our 2-fluid phase 1-D model, the primary variables are pressure, temperature, gas phase saturation and salt mass fraction. The pressure near injection well as shown in Fig. 6a is 390 bar from the beginning to 100 years, when CO2 is injected into the formation. Pressure decreases further way from the injection well, and the affected distance reaches 60 km, where the hydrostatic pressure is 200 bar. The high pressure decays after injection ceases at 100 years and already returns to hydrostatic pressure at 200 years. Gas saturation is close to 100% within 200 meters from the CO2 injection well at the time of 100 years, which means that water is almost completely replaced by supercritical CO2. Further away from the injection well, supercritical CO2 phase and water phase coexist, where the gas saturation decreases from 1 to 0 as shown in Figure 6b. Mutual dissolution of CO2 and water is also considered and calculated in the model. Subsequently supercritical CO2 dissolves into the brine and is consumed by mineralization, so the gas saturation line moves down after 100 years, which indicates a decrease of gas saturation in the system. At the same time, water gradually flows back spontaneously due to the suction of water by the rock (capillary pressure). This process of spontaneous flow of the wetting phase into porous media is called imbibition. Gas saturation and water saturation add up to 1 at any time and at all places.

The pH decreases from 8.0 to 5.0 close to the injection well due to CO2 injection. The low pH induces accelerated mineral dissolution due to the increase in dissolution rate at low pH. The track along which the pH line moves is similar with that in the gas saturation graph. The line moves forward during the first 100 years, and gradually moves backward during the next 900 years, which indicates that a large amount of CO2 is mineralized subsequent to 100 years when water flows back. Porosity decreases from the original value of 0.168 to 0.150 at 1000 years. This decrease happens because CO2 mass is added to the solid matrix by rock alteration. The change in porosity reduces permeability to 77% of its original value according to Eq. 5. The total mineralized CO2 reservoir per unit volume keeps increasing monotonically during the whole time period. After 1000 years, the value reaches about 37 kg/m3. This value would keep increasing if the simulation were not stopped.

## Mineral alteration and aqueous phase composition of the optimal case

Minerals and aqueous species with significant changes of abundance are presented in Fig. 7a, 7b and 8. The minerals of the model volcanic rock fragment (pyroxene mainly) all dissolve significantly. As these minerals dissolve, the concentrations of Mg, Fe, and Ca are all increased in the aqueous fluid, and pH is also increased, eventually leading to precipitation of secondary phases. Some of the injected CO2 is immobilized by precipitation of three carbonate minerals: magnesite, ankerite and calcite. Precipitation of ankerite is due to ferrosilite dissolution to provide Fe2+. Magnesite and calcite precipitation is due to the dissolution of anorthite, enstatite and diopside components to provide Ca2+ and Mg2+. Some Ca2+ and Mg2+ remain in the aqueous phase. There is also significant precipitation of quartz, and significant dissolution of anorthite and precipitation of albite. Minor precipitation of K-feldspar, siderite and dawsonite with abundance changes in the order of 10-5 also occur but are not plotted due to their small values. The decrease in pore volume is attributable largely to the fixation of CO2  into mineral phases and secondarily to the fact that the replacement minerals have lower average density than the primary minerals used for the calculation.

# Discussion and implications

Our simulations suggest that volcanogenic sandstones may be attractive reservoir rocks for geologic carbon sequestration. Volcanogenic sandstones have the advantage of high reactivity as in basalt and peridotite, but are in other respects typical porous sandstones that would allow for deep injection of supercritical CO2 rather than shallow injection of carbonated water as in Kelemen and Matter ([2008](#_ENREF_15)). The results of our simulation study, which is based on a combination of observed properties of impure sandstones and a model mineralogy including up to 30% by volume of reactive, divalent cation-bearing minerals, a 40m-thick homogeneous formation with a radius of 5000 m could accommodate injection of 85 megatons of supercritical CO2 through a single well in 100 years, with 77 percent of the injected CO2 being converted to carbonate minerals within 1000 years. Because CO2 storage will only be justifiable if injected CO2 stays immobilized in the subsurface for thousands of years, this high percentage of mineralization would be attractive.

Typical volcanogenic sandstones are mixtures of mineral grains and volcanic and sub-volcanic rock fragments ([Ingersoll, 1983](#_ENREF_13); [Linn et al., 1992](#_ENREF_19)). To simulate the reactive behavior of volcanic rock fragments we have used a combination of minerals, mainly pyroxenes and feldspar, for which laboratory dissolution rate data are available. In general we have used conservative values for dissolution rate constants and reactive surface area. Nevertheless, the critical control on the percentage of mineralization that can be achieved is the relationship between the volume fraction of reactive minerals (or the fraction of volcanic rock fragments) and permeability. The models suggest that >50% mineralization could be achieved within 1000 years in formations containing at least 10% VRF and a permeability of about 60 mD. We assume, and there are some data in the literature to bear this out, that permeability declines as VRF increases. With this assumption, there is a trade-off between higher reactivity and lower permeability with increasing VRF. But for any reactive mineral content, there is a range of permeabilities that are likely as a result of variable diagenetic histories and proportions of cements. For our low permeability cases, permeability drops off quickly at high VRF, which means that the total amount of CO2 that can be injected per well is small, and hence the optimum condition for mineralization occurs at low %VRF. For our high permeability cases, the optimum condition shifts to about 15 to 20% VRF, and much more CO2 can be both injected and mineralized.

## Reactive surface area

The evaluation of reactive surface area (RSA) in natural geologic media is complex, especially for multi-mineral systems, and has not yet been described in a manner that would allow accurate estimation for a given mineralogy and porosity. RSA calculated from grain size is often a poor estimate of the hydrologically accessible mineral surface area. The specific RSA may vary over several orders of magnitude depending on grain size, mineralogy, surface roughness, coatings, weathering, and biological effects.

Sensitivity tests with respect to RSA are based on the optimal case with 21% VRF in the high permeability set. Two additional simulations were performed by respectively increasing and decreasing all RSAs uniformly by a factor of 5, which is arbitrarily chosen. The RSAs for secondary minerals are changed by the same factor. Results in Fig. 9 show that RSA has a direct effect on the rate of CO2 mineralization. The amount of injected CO2 also changes, but very slightly, so only the original injection line is plotted. Varying RSA between 2cm2/g and 50cm2/g changes the mineralized fraction from 29% to 95% at 1000 years. In the RSA= 50 cm2/g case, reaction is very fast and the CO2 mineralization reaches its maximum at about 400 years and stops increasing afterwards.

## Residual gas saturation

Residual gas saturation (RGS) was shown to play an important role in storing CO2 by Kumar et al.([2004](#_ENREF_2); [2004](#_ENREF_17)). In our baseline model a value of 0.10 was assigned to RGS, which is consistent with experimental measurements by Kitamura et al. ([2006](#_ENREF_16)). In the sensitivity tests a smaller value of 0.05 and a larger value of 0.2 are arbitrarily chosen for comparison. However, such values are both possible from core scale measurements or previous models ([Andre et al., 2006](#_ENREF_1); [Bachu and Bennion, 2008](#_ENREF_4)). Fig. 10 shows that small values of RGS lead to increased mineralization of CO2. This increase comes about because a greater amount of gas remains mobile, which leads to increased contact between CO2 and brine. In terms of relative permeability, a smaller value of residual gas saturation gives larger values of the relative permeability of supercritical CO2 phase, especially in low gas saturation zones. The exact equation that describes the relationship between gas relative permeability and residual gas saturation used in this study can be found in Table 5. Thus more CO2 can be injected into the formation for smaller residual gas saturation due to larger gas permeability. About 95 Mton of CO2 is injected into the formation in 100 years with an injection pressure of 390 bar for RGS=0.05, while only 85 Mton of CO2 can be injected at the same pressure with RGS = 0.2. Also, CO2 flows farther for smaller residual gas saturations and occupies a larger volume of the domain. For example, the pH front for RGS=0.1 is at 6000 meters at 100 years as shown in Figure 6c, while the pH front of RGS=0.05 is around 9000 meters. So, the volume of rocks that are exposed to CO2 is larger for smaller RGS values. For our model, the rate-controlling step of mineralization is the dissolution of mafic minerals, which is measured in moles of minerals per unit time per unit volume of rock. With similar dissolution rates, the amount of mineralized CO2 is thus proportional to the volume of rock that is involved in reactions with CO2, and increases with smaller values of RGS.

## Mineralogy and trapping efficiency

Minerals that are sources of divalent cations and common in impure sandstones are biotite, chlorite, glauconite, amphibole, epidote, and montmorillonite. Chlorite and montmorillonite are common alteration products of volcanic glass, and VRF are commonly composed of combinations of such minerals as well as devitrified glass that is effectively amorphous. Available data suggest that the dissolution rates of these minerals are not much different from those used for our simulations. However, they may critically affect the types of secondary minerals formed and the ability for CO2 to be sequestered by carbonates due to the different types of secondary minerals, and their effect on permeability. Nevertheless, to first order it appears that the specific mineralogy is less important than the amount of reactive minerals. It is also noteworthy that minerals such as chlorite and montmorillonite could have significantly higher reactive surface areas than the values we are using ([Landrot et al., 2012](#_ENREF_18)).

As shown in Table 6, typical dissolution rate constants for divalent cation-bearing silicates are near 10-10 mol/m2/sec at temperature of 75 oC, which translates to about 0.003 mol/m2/y. This number has also included the acceleration by the acid mechanism as indicated by Equation 7, and will approximate the actual dissolution rate if the solutions are moderately far from equilibrium. If a rock contains 10 volume percent of a mineral with density of 2800 kg/m3 and specific surface area of 1 m2/kg, 1m3 of such rock would contain 280 m2 of reactive surface area. With these numbers, the predicted timescale of mineral dissolution would be about 1000 years; or in other words roughly 2/3 (actually 1 – e-1) of the reactive mineral inventory would dissolve in 1000 years. Assuming a molecular weight similar to feldspar (about 280 g/mol), about 600 moles of reactive mineral would be dissolved in 1000 years. For comparison, if 5 to 10% of the rock volume is initially filled with CO2 at a density of 600 kg/m3, then the 1m3 volume contains about 30 to 60 kg of CO2 or about 680 to 1360 moles of CO2. Hence the release of cations from mineral dissolution over 1000 years is approximately enough to mineralize 40 to 90 percent of the capillary-trapped CO2.

The above calculation is significant because it implies that the reaction rate and reactive mineral fraction of reservoir rocks are the critical parameters for assessing mineralization of injected CO2. It also shows that slight changes in the rates can have a large effect on the result. If dissolution rates are retarded by 10x, there will likely be 10x less mineralization over 1000 years. And if the rates could be enhanced, there would be significant benefit in terms of increasing the amount of mineralized CO2.

Audigane et al (2007) used a reactive transport model to estimate the relative fractions of capillary trapped, dissolved, and mineralized CO2 in the Utsira Formation, a quartz-rich sandstone that is being used as a reservoir formation for the Sleipner CO2 sequestration project. In their simulation, they calculate that only 1-2% of the CO2 is mineralized after 1000 years. This small amount of calculated mineralization is consistent with the fact that they had only 1.3% by volume of reactive mineral (Fe-rich chlorite), and that the conversion of CO2 to FeCO3 (about 20 mol/m3 by 1000 years) was offset by a similar amount of CO2 release by dissolution of calcite.

Our simulations suggest that the mineralogical trapping efficiency of impure sandstones can be reduced to a relatively simple parameter that involves permeability, reactive mineral percentage and residual CO2 saturation:



where Xrm is the volume fraction of reactive minerals containing divalent cations, and sg is the residual gas saturation for CO2 in brine. The approximate sign applies because the ratio of densities and molecular weights is close to unity for typical minerals and supercritical CO2. This ratio is effectively a ratio of the number of divalent cations available per unit volume of reservoir rock to the number of CO2 molecules present as capillary-trapped bubbles. If Xrm / sg ≥ 1, then a large fraction of injected CO2 can be expected to be mineralized. For our simulations that produce high mineralization fractions in 1000 years this ratio is in the range 1 to 2. If reaction rates are higher or lower than assumed in our models, it will not greatly affect the fraction of CO2 mineralized, but it will affect the timescale over which the mineralization happens. The remaining significant parameter is the injectivity, which scales roughly with permeability. Hence, in economic terms, the figure of merit would be:



If this number is high, it will maximize the amount of CO2 that can be injected and expected to mineralize in 1000 years *per injection well*. Based on our simulations, more than half of injected CO2 could be mineralized with an injection rate of 1 MT CO2/yr for formations where this number is ≥50 mD.

**5.4 Fractures, heterogeneity, and 2-D effects**

A critical component of our analysis is the formation injectivity for CO2. Our models assume that injectivity is directly determined by the core-scale permeability, which may be an overly conservative assumption. In most cases, the effective permeability at the scale of injection (10’s of meters) can be 1 or even 2 orders of magnitude higher than the core-scale permeability ([Raghavan, 2006](#_ENREF_28)). This difference is usually attributed to larger scale heterogeneity, including the presence of fractures, and tends to be more significant in rocks with lower permeability. If this scale dependence effect were taken into account, it would greatly enhance the potential for mineralization. In terms of our figure of merit, sandstones with much lower permeability could still be effective storage targets. One additional factor that will be important, however, is how mineralization and dissolution will affect the fracture permeability ([Sausse et al., 2001](#_ENREF_32)).

Formation heterogeneity can also affect both hydrology and geochemical evolution during sequestration. If, for example, a formation has mineralogical heterogeneity, and if permeability decreases as reactive minerals increase as we assumed in our model, then during injection, flow will be concentrated in the regions of high permeability (low %VRF). This would mean that during injection, much of the CO2 will be separated from the reactive minerals, with the separation distances being similar to the length scales that characterize the permeability heterogeneity. This effect might increase mineralization. The high permeability zones will enhance the injectivity and allow more CO2 to be injected into the formation per unit time per well. In the early stages of system evolution there is some separation of CO2 from reactive minerals, but on longer time scales, the CO2 (and or H+) will be able to diffuse into the reactive zones. Assuming that the effective diffusivity of CO2 D ≈ 0.23 m2/yr at 100°C([Zeebe, 2011](#_ENREF_42)), the diffusion lengthscale in 100 years Ld ≈ (4Dt)0.5= 3 meters, and in 1000 years is about 10 meters. Thus, the low pH conditions in the high-permeability zones will penetrate the low permeability zones if the scale of the heterogeneity (mostly vertical heterogeneity), is of order a few meters or less. The overall effect may be positive as injectivity will be increased but reactivity on a 1000-year time scale will remain similar. As noted by Bryant et al. ([2006](#_ENREF_7)), permeability heterogeneity may also enhance structural and capillary trapping of CO2.

Although the calculations we present are 1-dimensional (quasi 2-dimensional because they are radially symmetric), the results do not change much when the extra (vertical) dimension is added. Simulations done using a 2-D (quasi 3-D) allow for buoyancy effects, which allow the CO2 to rise upward toward the caprock and spread somewhat farther. It also results in more contact area between CO2 and brine, and hence somewhat faster dissolution of CO2 into brine and slightly more extensive mineral-rock interaction. The overall effect is to allow somewhat more CO2 (ca. 18% more) to be mineralized as shown in Figure 11.

# Conclusions

As a potential target lithology for CO2 sequestration, volcanogenic sandstone has both the advantage of high reactivity as in basalts and peridotite, reasonable injection rates as in standard sandstones, and contains native brine so that pure supercritical CO2 can be injected. According to this simulation study, a 40 m thick homogeneous formation with a radius of 5000 m is able to achieve an injection of 85 megatons CO2 in 100 years and mineralization of about 80% injected CO2 at 1000 years.

There is a trade-off for geochemical trapping of CO2 between higher reactivity and lower permeability with increasing volcanic rock fragment fractions. The key relationship is between mineralogy and permeability. For Low Permeability, the peak of mineralized CO2 amount lies at less than 10% VRF, while for slightly higher Permeability, it shifts to around 10-20%. Reactive surface area and residual gas saturation affect the rate of CO2 sequestration significantly. Sensitivity tests are conducted for these parameters.

Further work is necessary to better constrain the critical parameters that control the rate and extent of carbon mineralization; a direct means to this end would be to conduct experiments with volcanic sandstone samples in supercritical CO2 saturated brine to measure CO2 mineralization rates. It would also be beneficial to identify volcanogenic sandstone formations that are suitable for CO2 sequestration projects and evaluate the sequestration potential of such formation by field characterization. .Two such formations that are worthy of study are the Haizume and Tomokomai formations of onshore and offshore Japan, which are being used for CO2 injection experiments (cf. Mito et al., ([2008](#_ENREF_23)) ; .Sato et al.,([2011](#_ENREF_31)))

**Acknowledgement**

This manuscript has benefited from discussions with Eric Sonnenthal, Jenny Druhan and the comments of two anonymous reviewers. The work was supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy as part of an Energy Frontier Research Center under Contract No. DE-AC02-CH11231.

**References**

Andre, L., AUDIGANE, P., AZAROUAL, M., MENJOZ, A., 2006. Numerical modeling of fluid-rock chemical interactions at the supercritical CO2-liquid interface during CO2 injection into a carbonate reservoir, the Dogger aquifer (Paris Basin, France). Energ Convers Manage 48, 1782-1797.

Armstrong-Altrin, J.S., Lee, Y.I., Verma, S.P., Ramasamy, S., 2004. Geochemistry of sandstones from the upper Miocene Kudankulam Formation, southern India: Implications for provenance, weathering, and tectonic setting. J Sediment Res 74, 285-297.

Audigane, P., Gaus, I., Czernichowski-Lauriol, I., Pruess, K., Xu, T.F., 2007. Two-dimensional reactive transport modeling of CO2 injection in a saline Aquifer at the Sleipner site, North Sea. Am J Sci 307, 974-1008.

Bachu, S., Bennion, B., 2008. Effects of in-situ conditions on relative permeability characteristics of CO2-brine systems. Environ Geol 54, 1707-1722.

Baines, S.J., Worden, R.H., 2004. The long-term fate of CO2 in the subsurface: natural analogues for CO2 storage. Geological Society, London, Special Publications 233, 59-85.

Bloch, S., 1991. Empirical prediction of porosity and permeability in sandstones.

Bryant, S.L., Lakshminarasimhan, S., Pope, G.A., 2006. Buoyancy-Dominated Multiphase Flow and Its Effect on Geological Sequestration of CO2. Spe J 13, 447-454.

Dove, P.M., Han, N., Wallace, A.F., De Yoreo, J.J., 2008. Kinetics of amorphous silica dissolution and the paradox of the silica polymorphs. Proceedings of the National Academy of Sciences.

Durr, S.B., Gibling, M.R., 1994. Early Cretaceous Volcaniclastic and Quartzose Sandstones from North Central Nepal - Composition, Sedimentology and Geotectonic Significance. Geol Rundsch 83, 62-75.

Gibson-Poole, C.M., Svendsen, L., Underschultz, J., Watson, M.N., Ennis-King, J., van Ruth, P.J., Nelson, E.J., Daniel, R.F., Cinar, Y., 2008. Site characterisation of a basin-scale CO2 geological storage system: Gippsland Basin, southeast Australia. Environ Geol 54, 1583-1606.

Gunter, W.D., Perkins, E.H., Hutcheon, I., 2000. Aquifer disposal of acid gases: modelling of water-rock reactions for trapping of acid wastes. Appl Geochem 15, 1085-1095.

Hawlader, H.M., 1990. Diagenesis and reservoir potential of volcanogenic sandstones--Cretaceous of the Surat Basin, Australia. Sediment Geol 66, 181-195.

Ingersoll, R.V., 1983. Petrofacies and provenance of late Mesozoic forearc basin, Northern and Central California. Aapg Bull 67, 1125-1142.

Intergovernmental Panel on Climate Change, 2005. IPCC special report on carbon dioxide capture and storage : summary for policymakers. IPCC, S.l.

Kelemen, P.B., Matter, J., 2008. In situ carbonation of peridotite for CO2 storage. P Natl Acad Sci USA 105, 17295-17300.

Kitamura, K.X., Z., 2006. An experimental study of Residual Gas Saturation of Carbon Dioxide in water-saturated porous sandstone by using multi-channel seismic wave imaging method. American Geophysical Union, Fall Meeting 2006, abstract #H51E-0531.

Kumar, M. Noh, G.A. Pope, K. Sepehrnoori, S. Bryant, L.W. Lake, 2004. Reservoir Simulation of CO2 Storage in Deep Saline Aquifers. SPE/DOE Symposium on Improved Oil Recovery, 22-26 April 2006, Tulsa, Oklahoma, USA.

Landrot, G., Ajo-Franklin, J.B., Cabrini, S., Steefel, C.I., 2012. Measurement of the reactive surface area relevant to CO2 mineralization in a reservoir sandstone. Chem Geol 318-319, 113-125.

Linn, A.M., Depaolo, D.J., Ingersoll, R.V., 1992. Nd-Sr Isotopic, Geochemical, and Petrographic Stratigraphy and Paleotectonic Analysis - Mesozoic Great Valley Fore-Arc Sedimentary-Rocks of California. Geol Soc Am Bull 104, 1264-1279.

Matter, J.M., Takahashi, T., Goldberg, D., 2007. Experimental evaluation of in situ CO2-water-rock reactions during CO2 injection in basaltic rocks: Implications for geological CO2 sequestration. Geochem Geophy Geosy 8, Q02001.

McGrail, B.P., Schaef, H.T., Ho, A.M., Chien, Y.J., Dooley, J.J., Davidson, C.L., 2006. Potential for carbon dioxide sequestration in flood basalts. J Geophys Res-Sol Ea 111.

Millington, R.J., Quirk, J.P., 1961. Permeability of porous solids. Transactions of the Faraday Society 57, 1200-1207.

Mito, S., Xue, Z., Ohsumi, T., 2008. Case study of geochemical reactions at the Nagaoka CO2 injection site, Japan. Int J Greenh Gas Con 2, 309-318.

Narasimhan, T.N., Witherspoon, P.A., 1976. An integrated finite difference method for analyzing fluid flow in porous media. Water Resour. Res. 12, 57-64.

Palandri, J.K., Y.K., 2004. A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling. US Geol. Surv. Open File Report2004-1068, 64pp.

Power, I.M., Wilson, S.A., Dipple, G.M., 2013. Serpentinite Carbonation for CO2 Sequestration. Elements 9, 115-121.

Pruess, K., 1991. TOUGH2: A general-purpose numerical simulator for multiphase fluid and heat flow, p. Medium: ED; Size: Pages: (102 p).

Raghavan, R., 2006. Some observations on the scale dependence of permeability by pumping tests. Water Resour. Res. 42, W07402.

Remy, R.R., 1994. Porosity Reduction and Major Controls on Diagenesis of Cretaceous-Paleocene Volcaniclastic and Arkosic Sandstone, Middle Park Basin, Colorado. J Sediment Res A 64, 797-806.

Rutqvist, J., Tsang, C.-F., Stephansson, O., 2000. Uncertainty in the maximum principal stress estimated from hydraulic fracturing measurements due to the presence of the induced fracture. Int J Rock Mech Min 37, 107-120.

Sato, K., Mito, S., Horie, T., Ohkuma, H., Saito, H., Watanabe, J., Yoshimura, T., 2011. Monitoring and simulation studies for assessing macro- and meso-scale migration of CO2 sequestered in an onshore aquifer: Experiences from the Nagaoka pilot site, Japan. Int J Greenh Gas Con 5, 125-137.

Sausse, J., Jacquot, E., Fritz, B., Leroy, J., Lespinasse, M., 2001. Evolution of crack permeability during fluid‚rock interaction. Example of the Brzouard granite (Vosges, France). Tectonophysics 336, 199-214.

Sonnenthal, E., Ito, A., Spycher, N., Yui, M., Apps, J., Sugita, Y., Conrad, M., Kawakami, S., 2005. Approaches to modeling coupled thermal, hydrological, and chemical processes in the Drift Scale Heater Test at Yucca Mountain. Int J Rock Mech Min 42, 698-719.

Spycher, N., Pruess, K., 2005. CO2-H2O mixtures in the geological sequestration of CO2. II. Partitioning in chloride brines at 12-100°C and up to 600 bar. Geochim Cosmochim Ac 69, 3309-3320.

Steefel, C.I., Lasaga, A.C., 1994. A Coupled Model for Transport of Multiple Chemical-Species and Kinetic Precipitation Dissolution Reactions with Application to Reactive Flow in Single-Phase Hydrothermal Systems. Am J Sci 294, 529-592.

Summer, N.S., Verosub, K.L., 1992. Diagenesis and organic maturation of sedimentary rocks under volcanic strata, Oregon. Aapg Bull 76, 1190-1199.

Trask, P.D., Hammar, H.E., Wu, C.-c.e., American Petroleum, I., 1932. Origin and environment of source sediments of petroleum. American Petroleum Institute, Houston.

Van Genuchten, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal 44, 892-898.

White Art, F., Peterson Maria, L., 1990. Role of Reactive-Surface-Area Characterization in Geochemical Kinetic Models, Chemical Modeling of Aqueous Systems II. American Chemical Society, pp. 461-475.

wolery, T.J., 1992. EO3/6:Software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 7.0). Lawrence Livermore Natioinal Laboratory Report UCRL-MA-210662 PT I.

Xu, T., Pruess, K., 2001. Modeling Multiphase Non-isothermal Fluid Flow and Reactive Geochemical Transport in Variably Saturated Fractured Rocks: 1. Methodology. Am J Sci 301, 16-33.

Zeebe, R.E., 2011. On the molecular diffusion coefficients of dissolved CO2 and their dependence on isotopic mass. Geochim Cosmochim Ac 75, 2483-2498.

Zerai, B., Saylor, B.Z., Matisoff, G., 2006. Computer simulation of CO2 trapped through mineral precipitation in the Rose Run Sandstone, Ohio. Appl Geochem 21, 223-240.