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# Reactive Transport Modeling to Study Fluid-Rock Interactions in Enhanced Geothermal Systems (EGS) with $CO_2$ as Working Fluid

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## ABSTRACT

There is a growing interest in the novel concept of operating Enhanced Geothermal Systems (EGS) with $CO_2$ instead of water as heat transmission fluid. Initial studies have suggested that $CO_2$ will achieve larger rates of heat extraction, and can offer geologic storage of carbon as an ancillary benefit. A fully developed EGS with $CO_2$ would consist of three distinct zones, (1) a central zone or "core" in which all aqueous phase has been removed by dissolution into the flowing $CO_2$ stream, so that the reservoir fluid is a single supercritical $CO_2$ phase; (2) a surrounding intermediate zone, in which the reservoir fluid consists of a two-phase water-$CO_2$ mixture; and (3) an outer or peripheral zone, in which the reservoir fluid is a single aqueous phase with dissolved $CO_2$. Fluid-rock interactions in EGS operated with $CO_2$ are expected to be vastly different in zones with an aqueous phase present, as compared to the central reservoir zone with anhydrous supercritical $CO_2$. We have performed chemically reactive transport modeling to investigate fluid-rock interactions in the peripheral zone of an EGS operated with $CO_2$.

## 1. INTRODUCTION

The U.S. Department of Energy has broadly defined Enhanced (or Engineered) Geothermal Systems (EGS) as engineered reservoirs that have been created to extract economical amounts of heat from geothermal resources of low permeability and/or porosity (MIT, 2006). The MIT report indicated that EGS could become a major supplier of primary energy for U.S. base-load generation capacity by 2050. Here we consider a novel EGS concept that would use carbon dioxide ($CO_2$) instead of water as heat transmission fluid, and would achieve geologic sequestration of $CO_2$ as an ancillary benefit (Brown, 2000).

Numerical simulations of fluid dynamics and heat transfer indicate that $CO_2$ is superior to water in its ability to mine heat from hot fractured rock (Pruess, 2006). Carbon dioxide also offers advantages with respect to wellbore hydraulics, in that its larger compressibility and expansivity as compared to water would increase buoyancy forces and reduce the parasitic power consumption of the fluid circulation system. While the thermal and hydraulic aspects of a $CO_2$-EGS system look promising, major uncertainties remain with regard to chemical interactions between fluids and rocks. As shown in Figure 1, a fully developed EGS with $CO_2$ would consist of three distinct zones (Fouillac et al., 2004; Ueda et al., 2005), (1) a central zone or "core" (Zone 1) in which all aqueous phase has been removed by dissolution into the flowing $CO_2$ stream, so that the reservoir fluid is a single supercritical $CO_2$ phase; (2) a surrounding intermediate zone (Zone 2), in which the reservoir fluid consists of a two-phase water-$CO_2$ mixture; and (3) an outer or peripheral zone (Zone 3), in which the reservoir fluid is a single aqueous phase with dissolved $CO_2$.

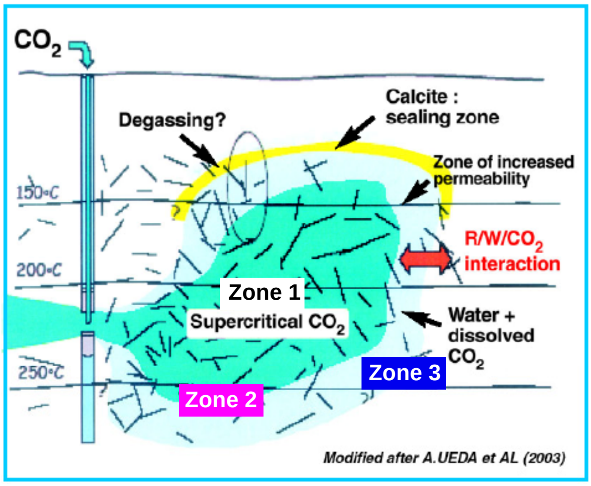

**Figure 1: Schematic of the three zones created by injection of $CO_2$ into hot fractured rock (after Fouillac et al., 2004).**

Geochemical processes are expected to be quite different in the three zones. The absence of water in the inner (core) zone poses unique questions, as little is presently known about the geochemistry of non-aqueous systems. The aqueous fluids initially present in an EGS reservoir would be quickly removed by immiscible displacement by the $CO_2$, and by dissolution (evaporation) into the flowing $CO_2$ stream. Continuous operation of a $CO_2$-EGS may produce a rather dry $CO_2$ stream. Research on reactions between supercritical $CO_2$ and rocks in the absence of an aqueous phase has started only recently (Regnault et al., 2005; Jacquemet, 2006; McGrail et al., 2009). Carbon dioxide is not an ionic solvent, which would reduce the potential for dissolution and subsequent re-precipitation of minerals, and avoid problems of scaling and formation plugging (Brown, 2000). However, CO2 can dissolve water, which can be chemically active (McGrail et al., 2009). It appears likely that prolonged exposure to supercritical $CO_2$ with small concentration of dissolved water will cause dehydration reactions that would remove loosely bound water from rock minerals. Such reactions may reduce the molar volume of the minerals involved, which would increase porosity and permeability of the formations, and might promote reservoir growth (Pruess and Azaroual, 2006). Anhydrous supercritical $CO_2$ could be quite reactive with some minerals. Regnault et al. (2005) performed lab experiments on batch reactions between pure minerals and $CO_2$(sc) at 200°C and 105/160 bar. Portlandite ($Ca(OH)_2$) was totally carbonated to form calcite and aragonite; anorthite also displayed surface alteration patterns with secondary precipitation of fibrous calcite. The strong reactivity of portlandite suggests a potential for reactions with cement structures around the borehole, and a possible creation of short-cuts or increased porosity. The properties of the cap-rock might be altered: due to its lower density, the $CO_2$(sc) is bound to flow upwards to the cap-rock. Its lower viscosity might then enable it to migrate through the cap-rock; eventually, local reactions could occur, which could alter the sealing properties of the cap-rock.

The peripheral zone (Zone 3) of an EGS operated with $CO_2$ may experience a combination of mineral dissolution and precipitation effects that could impact reservoir growth and longevity. The long-term behavior of this outermost zone will be crucial for sustaining energy recovery, for estimating $CO_2$ loss rates, and for figuring tradeoffs between power generation and geologic storage of $CO_2$. We have performed reactive geochemical transport simulations to study $CO_2$ induced mineral alteration in the outer zone, associated changes in reservoir porosity, and sequestration of $CO_2$ by secondary carbonate precipitation.

## 2. PROBLEM SETUP

### 2.1 Geometric and Flow Conditions

Before moving into site-specific investigations, general features and issues should be explored. This can be done by abstracting site-specific features and thereby attempting to represent characteristics that may be common to many $CO_2$-EGS systems. Basic issues in such systems are the physical and chemical changes induced by dissolved $CO_2$, including dissolution of primary minerals, formation of secondary minerals, $CO_2$ mineral trapping, and changes in reservoir porosity and permeability.

As pointed out by Gherardi et al. (2007), when interactions between $CO_2$-rich fluid and rock occur under fully liquid-saturated conditions and a diffusion-controlled regime, pH will be buffered at higher values, favoring carbonate precipitation that leads to further sealing of the caprock of the $CO_2$ storage reservoir. Even though their simulations were performed for a low temperature of 45°C, the peripheral zone in a higher temperature $CO_2$-EGS reservoir may show similar trends. For the simulations presented here, we used a one-dimensional model (Figure 2). At the left boundary, water chemical composition was specified by equilibrating with a high $CO_2$ pressure and primary mineral assemblage (see below), to represent the single-aqueous-phase peripheral zone of a $CO_2$-EGS reservoir. The right boundary is closed for water flow and chemical transport. The chief benefit of the 1-D flow model is its conceptual and calculational simplicity, which allows to identify the geochemical parameters and controls that have the most sensitive influence on reservoir behavior. The geometric and hydrogeologic specifications of the 1-D flow problem are given in Table 1. An initial tortuosity ($\tau$) of 0.46 was calculated from $\tau = \phi^{1/3}$ (Millington and Quirk, 1961), where $\phi$ is porosity. All simulations were performed under an isothermal condition of 200°C. For most simulation cases, temperature and pressure at the left and right boundaries were set constants throughout the simulation time and equal to their initial values, or 200°C and 500 bar. Therefore, advection would occur only in response to pressure changes from dissolution and precipitation reactions.

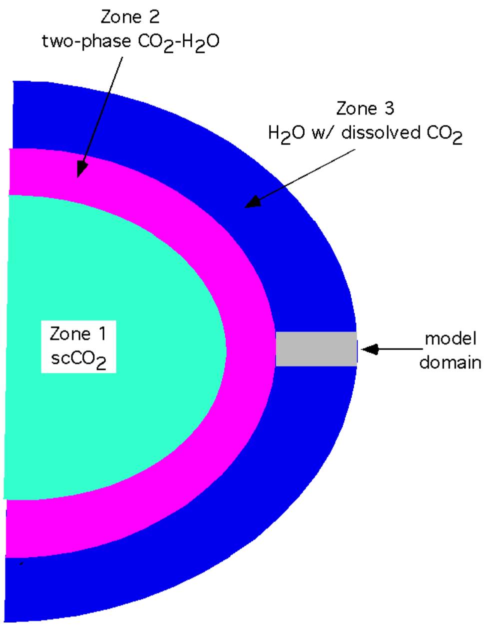

**Figure 2: The model domain studied in this paper, which is in the single-phase Zone 3, extending from the two-phase Zone 2 on the left to the outer boundary of the EGS on the right."sc" stands for supercritical $CO_2$.**

**Table 1: Geometric and hydrogeologic specifications for 1-D flow problem**

| Geometric variables: | |
|---|---|
| Length of the column | 12 m |
| Gridding | 60 x 0.2 m |
| Cross-sectional area | 1 $m^2$ |
| Reservoir properties: | |
| Permeability | $1 \times 10^{-13}$ $m^2$ |
| Porosity | 10 % |
| Rock grain density | 2600 $kg/m^3$ |
| Rock specific heat | 920 J/kg/°C |
| Thermal conductivity | 2.51 W/m/°C |
| Initial and boundary conditions: | |
| Pressure | 500 bar |
| Temperature | 200 °C |
| Aqueous transport: | |
| Tortuosity | 0.46 |
| Aqueous diffusion coefficient | $1 \times 10^{-9}$ $m^2/s$ |

### 2.2 Mineralogical Composition and Reaction Kinetics

Data for temperature and pressure conditions, and mineralogical composition were taken from the European Hot Dry Rock research site (HDR, Soultz project), which is situated at Soultz-sous-Forêts, Alsace, France (Jacquot, 2000; Durst, 2002; Bächler, 2003; André et al., 2006). The Soultz reservoir is composed of altered granite blocks partly cemented by alteration products that consist essentially of clay minerals and carbonates (see Table 2). As the primary minerals initially present in the rock matrix dissolve due to $CO_2$ intrusion, some secondary carbonate minerals (siderite, ankerite and dawsonite) may be formed; all these minerals were included in the simulation. Mineral dissolution and precipitation are considered under kinetic constraints. A general kinetic rate expression is considered, which is based on transition state theory (Lasaga et al., 1994). The parameters are taken from Xu et al. (2006).

**Table 2: Initial mineral volume fractions in altered granite from Soultz (Jacquot, 2000; Durst, 2002; Bächler, 2003) and potential secondary mineral phases (with zero volume fractions)**

| *Mineral* | *Volume fraction in term of solid* | *Specific surface area A* *($cm^2/g$)* |
|---|---|---|
| Primary**:** | | |
| Quartz | 0.0409 | 9.8 |
| Calcite | 0.033 | 9.8 |
| K-feldspar | 0.139 | 9.8 |
| Chlorite | 0.048 | 108.7 |
| Dolomite | 0.008 | 9.8 |
| Na-smectite | 0.07469 | 108.7 |
| Ca-smectite | 0.02231 | 108.7 |
| Pyrite | 0.007 | 12.9 |
| Illite | 0.246 | 108.7 |
| Non-reactive | 0.3681 | |
| Secondary**:** | | |
| Amorphous silica (precipitation) | 0.0 | 9.8 |
| Siderite | 0.0 | 9.8 |
| Ankerite | 0.0 | 9.8 |
| Dawsonite | 0.0 | 9.8 |

### 2.3 Water Chemistry

We started with a 165°C water sample taken from Soultz Well CPK1 at 3500 m depth. Initial water chemistry in the porous medium column was obtained by equilibrating the measured water composition with their corresponding primary mineral assemblage (Table 2) at a temperature of 200 °C. The resulting initial water composition is shown in Table 3. The important boundary parameter controlling rock-fluid interactions is the aqueous concentration of $CO_2$. At the left boundary, we applied a water that was obtained by equilibrating the initial water with a $CO_2$ partial pressure of 500 bar. The resulting chemical composition of the boundary water is also given in Table 3.

**Table 3: Chemical composition (units are mol/kg $H_2O$ except for pH) of initial and boundary waters used in the simulation, which were derived from a Soultz Well GPK1 sample (Durst, 2002)**

| Water type | Initial water | Boundary water |
|---|---|---|
| Chemical components | Equilibrium with the minerals (200°C) | Equilibrium with the minerals at 500 bar |
| Ca | $1.705\times10^{-1}$ | $2.137\times10^{-1}$ |
| Mg | $5.536\times10^{-3}$ | $6.887\times10^{-3}$ |
| Na | 1.211 | 1.137 |
| K | $9.432\times10^{-2}$ | $2.942\times10^{-2}$ |
| Fe | $1.981\times10^{-7}$ | $8.456\times10^{-3}$ |
| Cl | 1.719 | 1.673 |
| $SiO_2$(aq) | $4.131\times10^{-3}$ | $7.594\times10^{-3}$ |
| **Total $CO_2$(aq)** | **$1.724\times10^{-3}$** | **1.528** |
| $SO_4$ | $2.391\times10^{-3}$ | $1.975\times10^{-3}$ |
| Al | $1.519\times10^{-6}$ | $1.674\times10^{-7}$ |
| **pH** | **5.7** | **4.1** |

### 2.4 Simulation Tool

The simulations employed the reactive geochemical transport code TOUGHREACT (Xu et al., 2006); which introduces reactive chemistry into the multiphase fluid and heat flow code TOUGH2 (Pruess, 2004). More information on TOUGHREACT can be found at http://www-esd.lbl.gov/TOUGHREACT/.

Temporal changes in reservoir rock porosity and permeability due to mineral dissolution and precipitation can modify fluid flow path characteristics. This feedback between flow and chemistry is considered in our model. Changes in porosity are calculated from variations in mineral volume fractions. A simple cubic Kozeny-Carman grain model was used to derive changes in permeability k as function of porosity

$$\frac{k}{k_0} = \left(\frac{\phi}{\phi_0}\right)^3 \left(\frac{1-\phi_0}{1-\phi}\right)^2 \qquad (1)$$

Here, subscripts 0 denote initial variable values.

### 3. RESULTS AND DISCUSSION

pH profiles along the column at different times are presented in Figure 3. The initial value throughout the column is close to 6. The pH close to the left boundary has a value of 4.5, higher than at the boundary (4.2; see Table 3), which is buffered by mineral assemblage. The pH evolution is caused by both transport and reactions. Distribution of conservative tracer concentrations is presented in Figure 4, to illustrate transport effects.

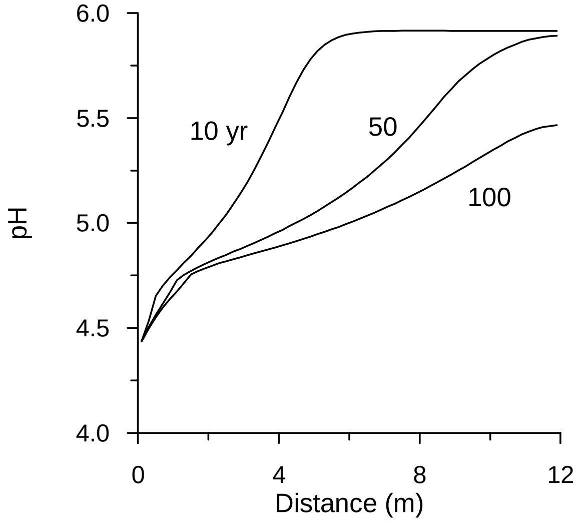

**Figure 3: pH distribution at different times obtained from the 1-D problem using a Soultz mineralogy. The left boundary of the model domain has $CO_2$-saturated aqueous phase (Table 3).**

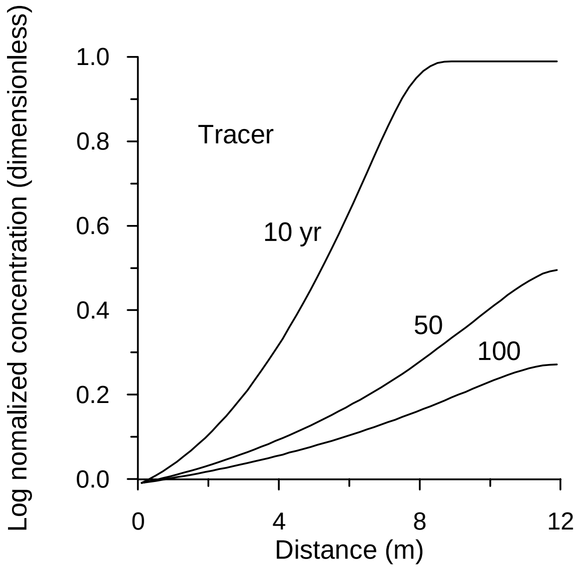

**Figure 4: Concentrations of a conservative solute tracer at different times.**

The total dissolved $CO_2$ concentrations, including $CO_2$(aq) and associated aqueous species such as $HCO_3^-$, $CO_3^{2-}$, $CaHCO3^+$, $MgHCO_3^+$, and $FeHCO_3^+$, are presented in Figure 5. The total $CO_2$ concentration close to the left boundary has a value of 1.7 mol/kg, which is somewhat larger than in the boundary water (in Table 3, boundary value is 1.53 mol/kg $H_2O$). This is because precipitation of the secondary clay minerals smectite and illite consumes $H_2O$ (hydration) which was considered in our geochemistry model.

The lowered pH due to the intrusion of $CO_2$-rich water induces dissolution of primary minerals such as calcite, K-feldspar, and chlorite, and precipitation of secondary carbonate and clay minerals such as siderite, dolomite, smectite and illite. Consequently, porosity decreases significantly close to the left boundary (Figure 6), because (1) $CO_2$-rich water adds solute mass to the rock matrix and (2) molar volumes of secondary clays are larger than those of the primary minerals. The extent of porosity change is consistent with the mineral alteration mentioned above. The porosity was reduced down to 0.087, from the initial value of 0.1.

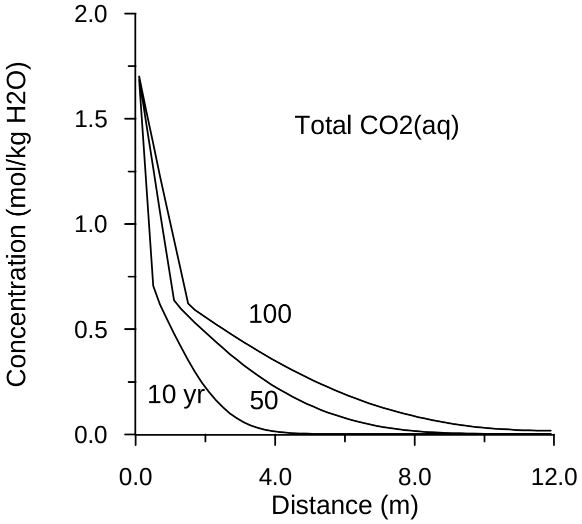

**Figure 5: Distribution of total $CO_2$(aq) concentrations at different times.**

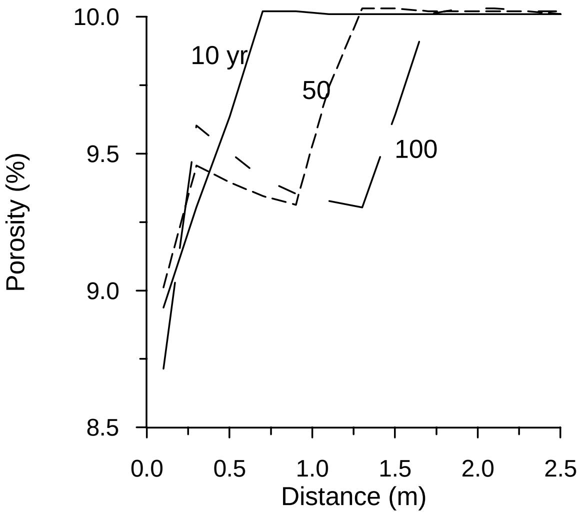

**Figure 6: Profiles of porosity at different times.**

Although calcite was initially present in the rocks, it generally dissolves due to the low pH. The calcite dissolution front moves with time (Figure 7). K-feldspar dissolution occurs close to the $CO_2$ source and gradually decreases away from it (Figure 8). As primary minerals dissolve, secondary carbonate and clay minerals are formed. Chlorite (Figure 9) dissolves and supplies Mg and Fe to induce dolomite (Figure 10) and siderite (Figure 11) precipitation.

The precipitation fronts of dolomite and siderite move with time, coinciding with the fronts of dissolution of calcite (Figure 7) and chlorite (Figure 9). Precipitation of clay minerals (smectite-Na, smectite-Ca, and illite) was observed in the simulation; only that of smectite-Na is presented in Figure 12. Precipitation of dolomite and siderite sequesters a significant amount of $CO_2$ (Figure 13). A maximum of about 50 kg $CO_2$ per $m^3$ of medium was trapped by carbonate precipitation.

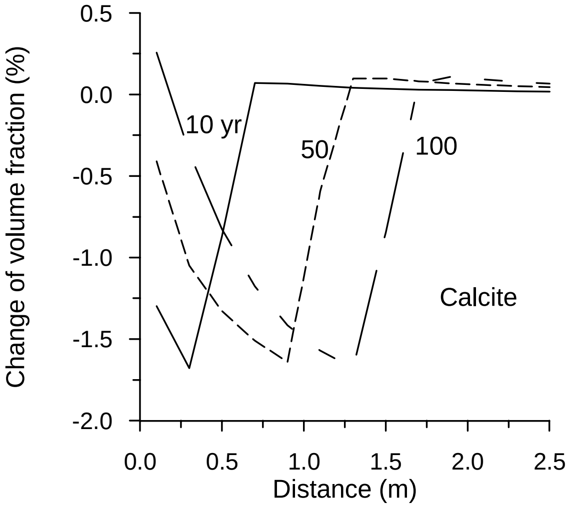

**Figure 7: Changes of calcite abundance (in volume fraction in terms of porous medium; positive values indicate precipitation and negative dissolution) along the distance at different times.**

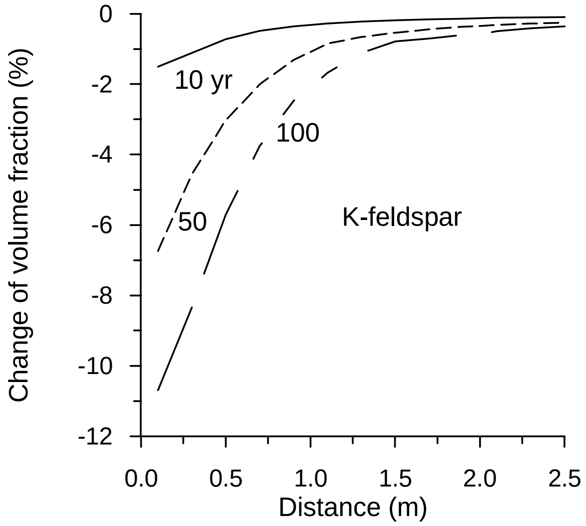

**Figure 8: Changes of K-feldspar abundance along the column at different times.**

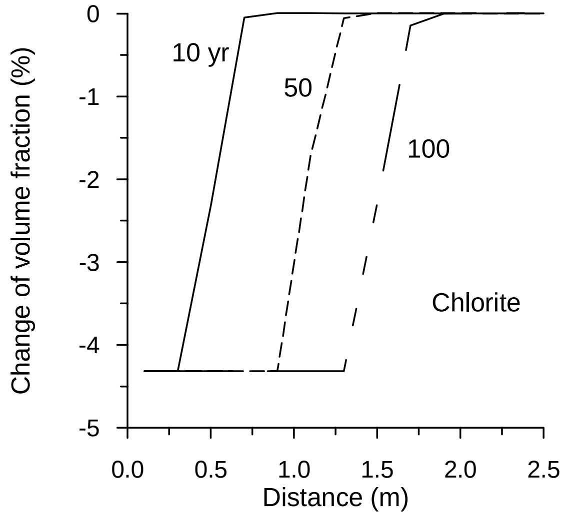

**Figure 9: Changes of chlorite abundance along the column at different times.**

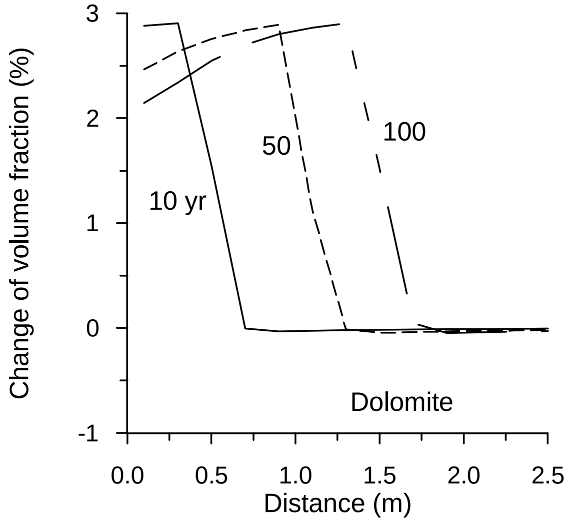

**Figure 10: Changes of dolomite abundance along the column at different times.**

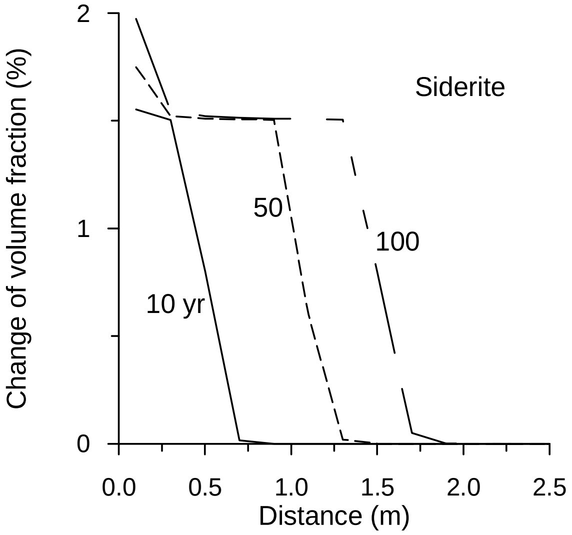

**Figure 11: Changes of siderite abundance along the column at different times.**

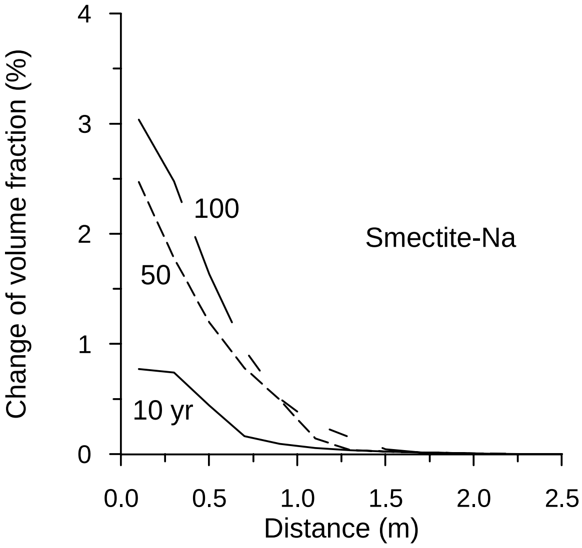

**Figure 12: Changes of smectite-Na abundance along the column at different times.**

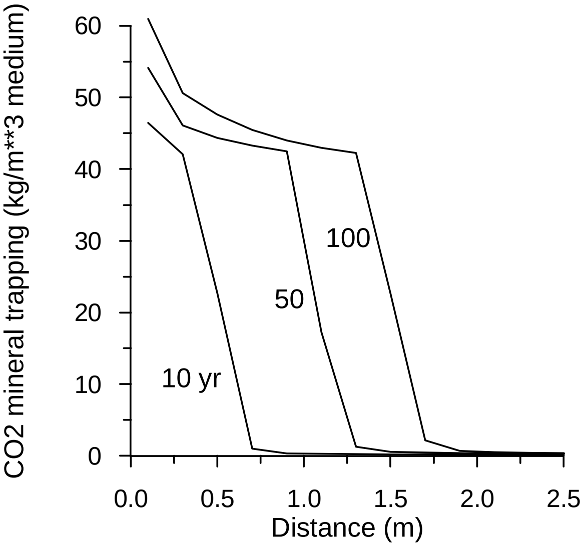

**Figure 13: Cumulative amounts of $CO_2$ sequestered by secondary carbonate precipitation along the column at different times.**

## 4. CONCLUSIONS AND RECOMMENDATIONS

We have developed a one-dimensional model for the peripheral zone of a $CO_2$-EGS system using temperature and pressure conditions, mineralogical composition and water chemistry from the Soultz EGS site. Major findings from our simulation are:

- Dissolved $CO_2$ may diffuse to the peripheral zone of the EGS and induce dissolution of primary minerals and precipitation of secondary carbonate and clay minerals. For mineralogy of altered granite at Soultz, the main dissolving minerals are calcite, K-feldspar, and chlorite. Major precipitating secondary carbonates are dolomite, siderite and ankerite, and clay minerals are Na-smectite, Ca-smectite and illite.
- The transport of dissolved $CO_2$ and associated mineral alteration generally decreases porosity, which could result in the formation of a lower permeable barrier that may impede reservoir growth and longevity. Significant $CO_2$ could be fixed through precipitation of carbonate minerals, which can offer geologic storage of carbon as an ancillary benefit.

The time frame to form a lower permeable barrier and the fixation of $CO_2$ is a function of reaction kinetics of mineral dissolution and precipitation, which requires further study. The extent of porosity decrease and amount of $CO_2$ mineral trapping depends on the primary mineral composition. Sensitivity studies on different rock mineralogies should be performed in the future. Using natural analogues of high-pressure $CO_2$ reservoirs, refinements on thermodynamic, kinetic and physical data should be useful. Reactivity between supercritical $CO_2$ and rock is not well understood. Experimental studies are required to quantitatively describe the reaction kinetics. Investigations on chemical changes for the entire reservoir domain should be addressed in the future.

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