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Francesco Parisio and Victor Vilarrasa contributed equally.

### Key Points:

- We propose a novel geologic carbon storage concept that reduces the buoyancy-driven CO<sub>2</sub> leakage risk
- By injecting CO<sub>2</sub> in reservoirs where the resident water stays in supercritical conditions, CO<sub>2</sub> sinks because it is denser than pore water
- Supercritical reservoirs are found at relatively shallow depths between 3 and 5 km in deep volcanic areas

### Supporting Information:

- Supporting Information S1
- Figure S1
- Movie S1

### Correspondence to:

V. Vilarrasa,  
victor.vilarrasa@idaea.csic.es

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### Author Contributions:

**Formal analysis:** Francesco Parisio, Victor Vilarrasa

**Methodology:** Francesco Parisio, Victor Vilarrasa

**Writing - original draft:** Francesco Parisio, Victor Vilarrasa

**Writing - review & editing:**

Francesco Parisio, Victor Vilarrasa

## Sinking CO<sub>2</sub> in Supercritical Reservoirs

Francesco Parisio<sup>1</sup> and Victor Vilarrasa<sup>2,3,4</sup>

<sup>1</sup>Chair of Soil Mechanics and Foundation Engineering, Institute of Geotechnics, Technische Universität Bergakademie Freiberg, Freiberg, Germany, <sup>2</sup>Institute of Environmental Assessment and Water Research (IDAEA), Spanish National Research Council (CSIC), Barcelona, Spain, <sup>3</sup>Mediterranean Institute for Advanced Studies (IMEDEA), Spanish National Research Council (CSIC), Esporles, Spain, <sup>4</sup>Associated Unit: Hydrogeology Group UPC-CSIC, Barcelona, Spain

**Abstract** Geologic carbon storage is required for achieving negative CO<sub>2</sub> emissions to deal with the climate crisis. The classical concept of CO<sub>2</sub> storage consists in injecting CO<sub>2</sub> in geological formations at depths greater than 800 m, where CO<sub>2</sub> becomes a dense fluid, minimizing storage volume. Yet CO<sub>2</sub> has a density lower than the resident brine and tends to float, challenging the widespread deployment of geologic carbon storage. Here, we propose for the first time to store CO<sub>2</sub> in supercritical reservoirs to reduce the buoyancy-driven leakage risk. Supercritical reservoirs are found at drilling-reachable depth in volcanic areas, where high pressure ( $p > 21.8$  MPa) and temperature ( $T > 374^{\circ}\text{C}$ ) imply CO<sub>2</sub> is denser than water. We estimate that a CO<sub>2</sub> storage capacity in the range of 50–500 Mt yr<sup>-1</sup> could be achieved for every 100 injection wells. Carbon storage in supercritical reservoirs is an appealing alternative to the traditional approach.

**Plain Language Summary** Geologic carbon storage, which consists in returning carbon deep underground, should be part of the solution to effectively reach carbon neutrality by the middle of the century to mitigate climate change. CO<sub>2</sub> has been traditionally proposed to be stored in sedimentary rock at depths below 800 m, where CO<sub>2</sub> becomes a dense fluid, minimizing the required storage volume. Nevertheless, CO<sub>2</sub> is lighter than brine in the traditional concept, so a rock with sufficient sealing capacity should be present above the storage formation to prevent leakage. Indeed, one of the main hurdles to deploy geologic carbon storage is the risk of CO<sub>2</sub> leakage. To reduce this risk, we propose a novel storage concept that consists in injecting CO<sub>2</sub> in reservoirs where the pore water stays in supercritical conditions (pressure and temperature higher than 21.8 MPa and 374°C, respectively) because at these conditions, CO<sub>2</sub> becomes denser than water. Consequently, CO<sub>2</sub> sinks, leading to a safe long-term storage. This concept, which could store a significant portion of the total requirements to decarbonize the economy, should start being implemented in deep volcanic areas, given that supercritical reservoirs are found at relatively shallow depths between 3 and 5 km.

## 1. Introduction

Carbon Capture and Storage (CCS) is envisioned as a key technology to accomplish net negative carbon dioxide (CO<sub>2</sub>) emissions during the second half of the century and meet the COP21 Paris Agreement targets on climate change (Bui et al., 2018; Intergovernmental Panel on Climate Change [IPCC], 2018). However, CCS should overcome two main hurdles, namely, the risks of induced seismicity (Vilarrasa & Carrera, 2015; Zoback & Gorelick, 2012) and CO<sub>2</sub> leakage (Lewicki et al., 2007; Nordbotten et al., 2008; Romanak et al., 2012), before its widespread deployment takes place. Proper site characterization, monitoring, and pressure management should allow minimizing the risk of perceivable induced seismicity in Gt-scale CO<sub>2</sub> injection (Celia, 2017; Rutqvist et al., 2016; Vilarrasa et al., 2019). The considered storage formations to date include deep saline aquifers, depleted oil and gas fields, and unmineable coal seams in which CO<sub>2</sub> stays in supercritical conditions with a relatively high density but lower than the one of the resident brines (Hitchon et al., 1999). Thus, the risk of CO<sub>2</sub> leakage, although low (Alcalde et al., 2018), may be present for up to millions of years until all CO<sub>2</sub> becomes dissolved into the resident brine or mineralized (Benson & Cole, 2008).

A few concepts have been proposed to date to reduce the risk of CO<sub>2</sub> leakage. These concepts consist either in promoting fast mineralization or storing CO<sub>2</sub> already dissolved in the resident brine. Regarding rapid CO<sub>2</sub> mineralization, injecting CO<sub>2</sub> in shallow basaltic rock allows a quick mineralization thanks to the

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favorable chemical composition of the host rock, although leakage through buoyancy remains a major concern in the absence of low-permeable caprocks or whenever the caprock integrity is compromised (Gislason & Oelkers, 2014). Another storage rock for mineralization could be peridotite, in which carbonation occurs naturally when exposed to atmospheric CO<sub>2</sub> (Kelemen & Matter, 2008). Peridotite is rare at shallow depths, and its total capacity for CO<sub>2</sub> storage is in the order of Gt, provided that the rock is massively hydraulically fractured to reach all the available mineral. Regarding dissolved CO<sub>2</sub> storage, the leakage risk is mitigated because brine is heavier when it is CO<sub>2</sub> saturated (Burton & Bryant, 2009; Sigfusson et al., 2015). CO<sub>2</sub> dissolution can be performed either on surface (Burton & Bryant, 2009) or at the reservoir depth (Pool et al., 2013). To balance the injection and pumping energetic cost, geothermal heat can be recovered and even electricity could be produced if the temperature is high enough (Pool et al., 2013). However, this storage concept has the drawback that CO<sub>2</sub> injection capacity is limited by CO<sub>2</sub> solubility into the brine, which is around 4% at 60°C. Such solubility leads to a storage of roughly 0.1 Mt of CO<sub>2</sub> per year and per doublet for a circulating brine flow rate of 80 L s<sup>-1</sup>, that is, 2.5 Mt yr<sup>-1</sup> of water being pumped and reinjected. Thus, very large volumes of brine would need to be circulated—a scenario that makes injection of dissolved CO<sub>2</sub> only feasible for small-scale decentralized CO<sub>2</sub> storage. Overall, the alternatives that have been proposed to reduce the risk of CO<sub>2</sub> leakage entail a limited storage capacity per well with respect to conventional CO<sub>2</sub> injection in free phase, which diminishes their attractiveness.

To overcome this limitation, we propose an innovative CO<sub>2</sub> storage concept that reduces the CO<sub>2</sub> leakage risk, does not require the presence and integrity of a caprock, and maintains a high storage capacity per well. This concept consists in storing CO<sub>2</sub> in free phase into supercritical reservoirs, that is, reservoirs where water is in supercritical state. Supercritical reservoirs are found in the deeper part of volcanic areas (depth >3 km), where pressure,  $p$ , and temperature,  $T$ , of the pore water are likely to exceed its critical point ( $p > 21.8$  MPa and  $T > 374^\circ\text{C}$  for pure water). At water's supercritical conditions, an interesting situation occurs: CO<sub>2</sub> density is higher than the one of water and thus, sinks. Consequently, a low-permeable caprock is not needed in deep volcanic areas. Injecting CO<sub>2</sub> into deeper and hotter reservoirs is a new concept that we propose and we deem possible in the light of the recent achievements in deep drilling in volcanic areas demonstrated at the IDDP-2 project, in which a 4.5-km-deep well has been drilled in the Reykjanes volcanic area, Iceland, reaching supercritical water conditions (Friðleifsson et al., 2017).

We examine the potential of storing CO<sub>2</sub> in deep volcanic areas where resident water is in supercritical state. First, we analyze the plausible injection conditions at the wellhead that permit injecting CO<sub>2</sub> with a reasonable compression cost. Next, we explore the CO<sub>2</sub> sinking potential and quantify the CO<sub>2</sub> plume shape and injectivity. Finally, we estimate the injection rates that could be achieved and discuss the worldwide CO<sub>2</sub> storage potential in deep volcanic areas.

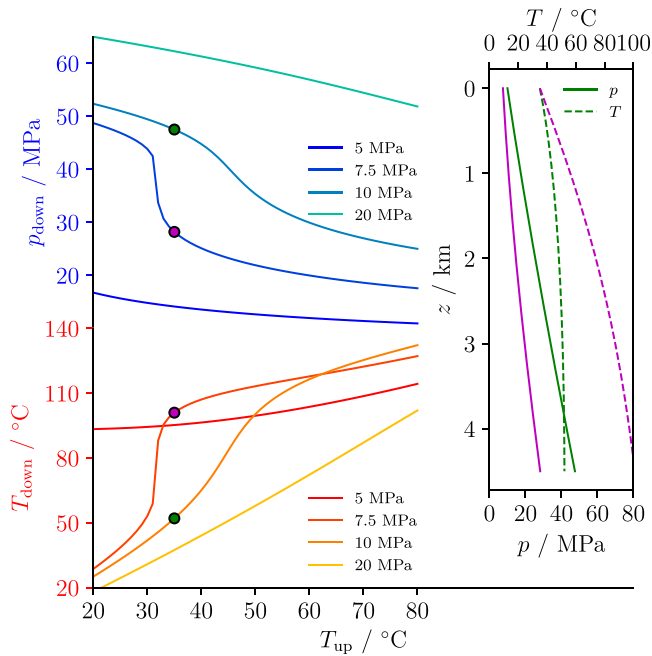
## 2. Materials and Methods

### 2.1. Water and CO<sub>2</sub> Equation of State

The equation of state (EOS) of water and CO<sub>2</sub> is computed via the C++ library CoolProp (Bell et al., 2014), available at CoolProp (<http://www.coolprop.org/>). CoolProp employs the Span and Wagner (1996) EOS of CO<sub>2</sub>, which is valid up to 800-MPa pressure and 1100-K temperature, and the Scalabrin et al. (2006) viscosity model. The EOS of water is valid up to 1 GPa of pressure and 2000-K temperature and is taken after Wagner and Pruß (2002), which is based on the IAPWS Formulation 1995. The viscosity of water is taken after Huber et al. (2009).

### 2.2. Temperature, Pressure, and Density Profiles Along the Wellbore

We have implemented an explicit scheme to compute the fluid properties variation with depth along the wellbore. During CO<sub>2</sub> injection, the cold fluid quenches the well in a relatively short time (days to months), so that at equilibrium a colder annulus forms around the well, hindering heat transfer from the surrounding rock, and the injection process becomes adiabatic (Pruess, 2006). The enthalpy is fixed at corresponding wellhead conditions of pressure and temperature  $h(z_0) = f(p(z_0), T(z_0))$ , and CO<sub>2</sub> density is evaluated with CoolProp functions along the discretized ( $n = 1,000$  intervals) wellbore depth as a function of temperature and pressure  $\rho(z_i) = f(p(z_i), T(z_i))$ . At each depth increment  $i + 1$ , the pressure increase is given



**Figure 1.** CO<sub>2</sub> injection conditions at the wellhead and downhole. Each curve shows the pressure,  $p_{down}$ , and temperature,  $T_{down}$ , conditions at depth of injection (4.5 km) for several wellhead pressures and as a function of wellhead temperature,  $T_{up}$ . Injecting CO<sub>2</sub> at a higher wellhead temperature implies that it reaches the reservoir depth with a lower pressure: In order to ensure injectivity into the rock formation, a minimum downhole pressure threshold should be guaranteed and can therefore be achieved by increasing the wellhead pressure. The sharp transition in the curves corresponding to a wellhead pressure of 7.5 MPa is connected to the phase transition from liquid to supercritical close to the critical point, around which abrupt changes in density take place. The inset displays the evolution of CO<sub>2</sub> pressure and temperature along the wellbore depth for two different cases, indicated by points in the main figure (color corresponding to two different wellhead conditions). Because of the adiabatic hypothesis, the heating of CO<sub>2</sub> is a consequence of pressure increase along the wellbore.

by  $p(z_{i+1}) = p(z_i) + g\rho(z_i)(z_{i+1} - z_i)$ , where  $g$  is gravity acceleration and  $T(z_{i+1} - z_i)$  is calculated assuming constant enthalpy  $h(z_i) = h(z_0)$ .

To compute the initial reservoir in situ conditions of the resident water, the weight of the water column to the corresponding depth is calculated assuming thermal equilibrium with the geothermal gradient, hence the only difference with the described procedure is that  $T(z_i)$  is known a priori.

### 2.3. CO<sub>2</sub> Plume Calculations

We use both analytical and numerical solutions to compute CO<sub>2</sub> injectivity (ratio between flow rate and wellhead pressure) and the plume geometry (see supporting information [SI] for more details). For the analytical solution, we use the Dentz and Tartakovsky (2009) solution with the correction to incorporate CO<sub>2</sub> compressibility effects of Villarasa et al. (2010). The CO<sub>2</sub> plume evolution is computed for a specific injection scenario of temperature and pressure that is deemed to be representative of the application. We assume initial pore fluid pressure of 34 MPa and temperature of 500°C and a pressure buildup at the wellhead of 10 MPa in isothermal conditions. The analytical solution is valid for a confined aquifer scenario, which we have assumed to be 500 or 1,000 m thick. The hypothesis of a confined aquifer represents a lower bound case in terms of injection rate: the structural geology features at depth in volcanic areas are quite uncertain and the presence of low-permeability structures could be represented by faults, chemically altered layers or magmatic intrusions, but could not be present as well.

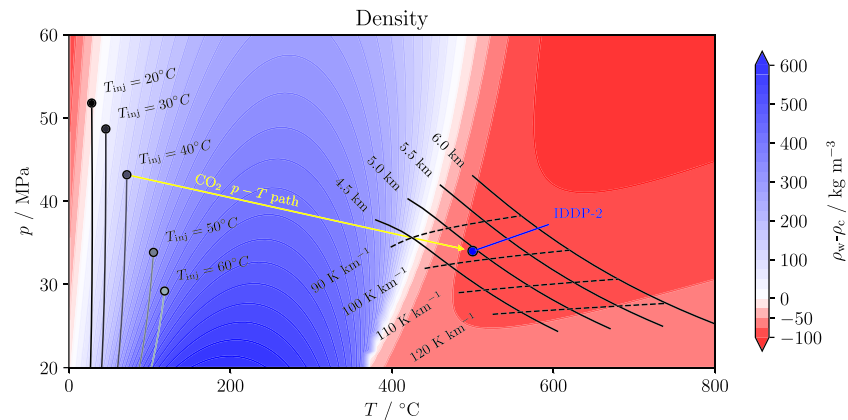
## 3. Results

### 3.1. Injection Conditions in the Wellbore

CO<sub>2</sub> downhole pressure and temperature conditions are constrained by limiting reservoir cooling and by ensuring an adequate flow rate through sufficient pressure buildup. Assuming wellbore quenching during continuous injection, the injection temperature and pressure at depth depend on the CO<sub>2</sub> wellhead temperature and pressure (Figures 1 and S1). According to the EOS of CO<sub>2</sub>, its density is a function of both temperature and pressure and the adiabatic compression generates an increase in CO<sub>2</sub> tempera-

ture with depth (inset in Figure 1). The density profile, in turn, is responsible for the weight of the fluid column, which translates into a pressure increase with depth (Figure S1). At 5 MPa of wellhead pressure, the downhole conditions mildly depend on the wellhead temperature. CO<sub>2</sub> is strongly heated up by compression along the wellbore because of its high compressibility as it transitions from gas to supercritical fluid (the critical point of CO<sub>2</sub> is  $T = 31.04^\circ\text{C}$  and  $p = 7.39$  MPa) and reaches the reservoir at approximately 100°C and 15–17 MPa, a pressure lower than the one of the reservoirs that prevents CO<sub>2</sub> flow into the rock. At a wellhead pressure slightly above the critical pressure (see 7.5 MPa in Figure 1), the downhole conditions strongly depend upon the wellhead temperature because of phase transition phenomena. While CO<sub>2</sub> is in its supercritical phase when injected warmer than its critical temperature, CO<sub>2</sub> is in liquid phase for cooler injection temperature and reaches the reservoir with higher pressure and lower temperature because of the higher density of the liquid than its gas or supercritical phases. A similar situation occurs when the wellhead pressure equals 10 MPa. At 20 MPa of wellhead pressure, the downhole conditions exhibit small changes between wellhead and downhole temperature because CO<sub>2</sub> density changes are small at such high pressure.

Downhole overpressure is necessary to ensure that CO<sub>2</sub> enters into and flows within the reservoir and, if we assume a reservoir pore fluid pressure as in IDDP-2 of 34 MPa (Friðleifsson et al., 2017), the downhole pressure should not fall below approximately 40 MPa. For example, to achieve such downhole pressure, the wellhead temperature should not exceed 30°C for a wellhead pressure of 7.5 MPa. We can limit reservoir cooling only by injecting at high wellhead pressure and temperature, which implies a high energetic cost.



**Figure 2.** Density difference map between water and CO<sub>2</sub>. The figure shows the density difference between water and CO<sub>2</sub> as a function of pressure (up to 60 MPa) and temperature (up to 800°C). Positive (in blue) values indicate that CO<sub>2</sub> has a lower density than water, which leads to CO<sub>2</sub> buoyancy, and negative (in red) values indicate that CO<sub>2</sub> has a higher density than water, leading to sinking potential in the reservoir. The downhole conditions of IDDP-2 are temperature of 500°C and pressure of 34 MPa, which would lead to CO<sub>2</sub> sinking potential. The dotted black lines indicate the  $p$ - $T$  conditions of a hydrostatic water column for a variety of geothermal gradients and the solid black lines are isodepth for the same case. The trajectories on the left-hand side indicate CO<sub>2</sub> injection conditions at the reservoir for several wellhead temperatures and for a wellhead pressure of 10 MPa. The yellow line connects the downhole conditions (buoyant) of a hypothetical injection at IDDP2 with the CO<sub>2</sub> conditions (sinking) within the reservoir far from the injection well.

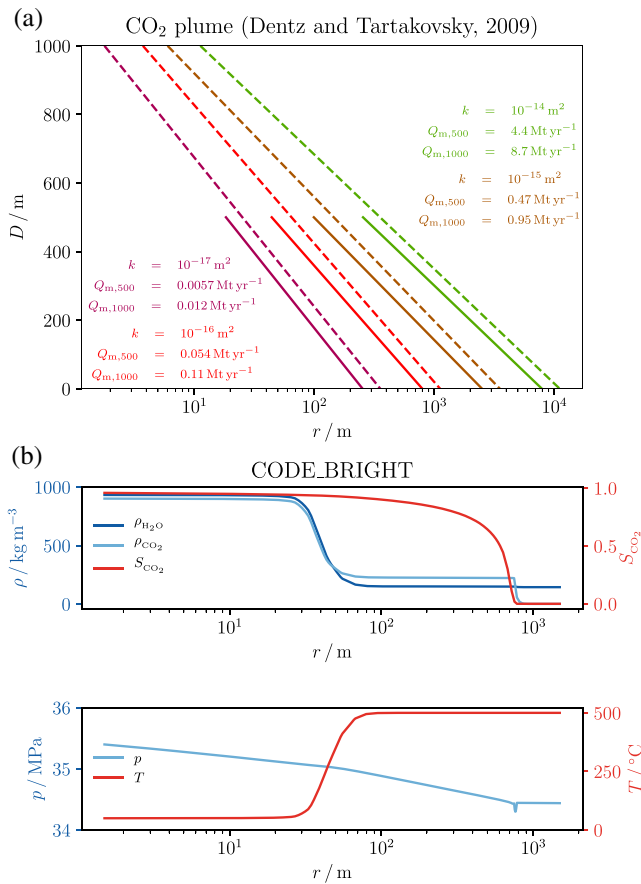
### 3.2. CO<sub>2</sub> Sinking Potential

Above the critical point of water, both fluids are in supercritical phase and CO<sub>2</sub> becomes denser than water at increasingly higher pressure as temperature increases (Figure 2). The black solid lines in Figure 2 indicate the pressure and temperature conditions reached by a hydrostatic water column at several depths by taking into account a range of geothermal gradients typical of volcanic areas, indicated with dotted lines. Figure 2 also shows the CO<sub>2</sub> injection conditions for a wellhead pressure of 10 MPa and several wellhead temperatures along with the estimated in situ conditions of IDDP-2 of 34 MPa and 500°C (Friðleifsson et al., 2017). For a wellhead pressure of 10 MPa, the maximum wellhead temperature to enable CO<sub>2</sub> injection is approximately 40°C. At higher wellhead temperature, the CO<sub>2</sub> density along the wellbore is too small to yield a downhole pressure higher than the one of the reservoirs. Thermal exchange heats up CO<sub>2</sub> as it flows through the reservoir and CO<sub>2</sub> temperature and pressure equilibrate to the ones of the reservoir at a given distance from the injection point. The starting and end points of the path (yellow line in Figure 2) in the phase diagram depend upon the reservoir initial conditions and the wellhead injection pressure and temperature. Following our assumptions, the optimum in terms of CO<sub>2</sub> sinking potential corresponds to gradients between 90 and 120 K km<sup>-1</sup> and at depths >5 km.

### 3.3. CO<sub>2</sub> Plume and Injectivity

The analytical solution of Dentz and Tartakovsky (2009), with the correction of Vilarrasa et al. (2010) applied to consider CO<sub>2</sub> compressibility effects for accurately computing CO<sub>2</sub> density within the plume, estimates a downward CO<sub>2</sub> plume (Figure 3a). We consider a 10-year injection of CO<sub>2</sub> over 500- and 1,000-m-thick reservoirs, assuming a pressure buildup of 10 MPa in a water-saturated reservoir initially at  $p = 34$  MPa and  $T = 500$ °C. The extension and shape of the plume are a function of the reservoir permeability and thickness, with its maximum located in the lower part of the reservoir. The maximum extension of the downward plume spans over almost 2 orders of magnitude for a range of permeability of 3 orders of magnitude, ranging from approximately  $2.5 \times 10^2$  m for the least permeable case to approximately  $1.0 \times 10^4$  m for the most permeable one. The achievable mass flow rate is also proportional to the reservoir permeability and thickness and ranges from 0.0057 to 4.4 Mt yr<sup>-1</sup> for a 500-m-thick reservoir and from 0.012 to 8.7 Mt yr<sup>-1</sup> for a 1,000-m-thick reservoir.





**Figure 3.** CO<sub>2</sub> plume. (a) Analytical solutions (Dentz & Tartakovsky, 2009; Vilarrasa et al., 2010) of the CO<sub>2</sub> plume position for a 10-year injection into a 500-m-thick (solid lines) and 1,000-m-thick (dotted lines) reservoirs. We assume a fixed overpressure of 10 MPa at injection, isothermal injection, an initial reservoir temperature and pressure of 500°C and 34 MPa, respectively, and a range of reservoir permeability,  $k$ , that spans 3 orders of magnitude. The mass flow rate,  $Q_m$ , is a function of the reservoir permeability and thickness. The analytical solution predicts a sinking profile due to the density difference between water and CO<sub>2</sub>. (b) Simulation results after 10 years of injecting 1.0 Mt yr<sup>-1</sup> of CO<sub>2</sub> at 50°C through 500 m of open well centered into a 2,000-m-thick reservoir. The extent of the cooled region has a limited size compared to the CO<sub>2</sub> plume and does not affect its sinking tendency.

The gravity number  $N$  (Equation S5), which is the ratio between gravity to viscous forces, is computed for the near field ( $T = 50^\circ\text{C}$  and  $p = 44$  MPa), that is, close to the injection point, and for the far field ( $T = 500^\circ\text{C}$  and  $p = 34$  MPa), that is, the initial reservoir conditions. At the near field, water is liquid with  $\rho_w = 1,006.3$  kg m<sup>-3</sup> and CO<sub>2</sub> is supercritical with  $\rho_c = 940.2$  kg m<sup>-3</sup>, which yields a  $|\Delta\rho| = 66.2$  kg m<sup>-3</sup> that favors CO<sub>2</sub> buoyancy. At the far field, both fluids are supercritical, with  $\rho_w = 138.1$  kg m<sup>-3</sup> and  $\rho_c = 219.2$  kg m<sup>-3</sup>, which yields a  $|\Delta\rho| = 81.0$  kg m<sup>-3</sup> that favors CO<sub>2</sub> sinking. For a 500-m-thick reservoir, the gravity number is for the near field and for the far field and for a 1,000-m-thick reservoir for the near field and for the far-field conditions. According to the gravity number values, at the near wellbore range, viscous forces dominate or are in the range of gravity forces and far enough from the injection point, buoyant forces become predominant. Although the near-field conditions would favor CO<sub>2</sub> buoyancy, viscous forces are in the same range of buoyant ones, and thus, CO<sub>2</sub> buoyancy does not take place or is limited in very thick reservoirs. Far from the injection well, buoyant forces dominate over viscous forces, and since CO<sub>2</sub> has a higher density than water, CO<sub>2</sub> tends to sink (Figure 4). Finite element analyses of CO<sub>2</sub> injection further confirm that an uprising CO<sub>2</sub> plume does not develop near the injection well and that CO<sub>2</sub> sinks once it reaches thermal equilibrium with the rock (Figures 3b and 4). The cooled region concentrates around the injection well (Figure 3b) and even though CO<sub>2</sub> is lighter than water within this cold region, no upward flow occurs due to buoyancy. Thus, CO<sub>2</sub> sinks, leading to a safe storage despite cooling around the injection well.

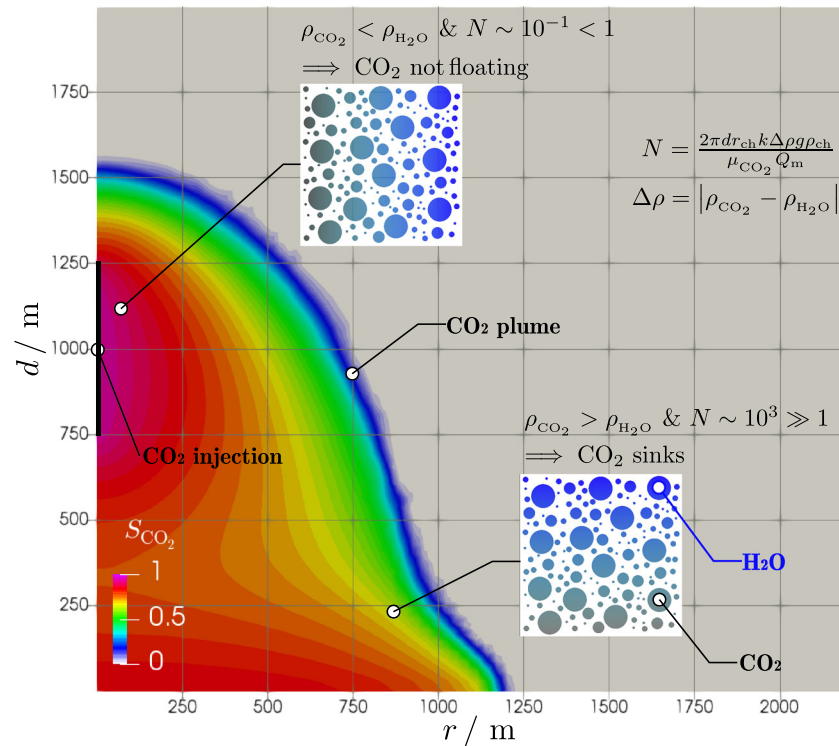
## 4. Discussion

### 4.1. Challenges

The coupling between the wellbore and the reservoir is important in storage formations with high temperature, like deep volcanic areas. The conflicting objectives of limiting cooling to minimize the risk of inducing seismicity in the long term (Parisio, Vinciguerra, et al., 2019) and of minimizing compression costs by lowering wellhead pressure can only be resolved with accurate optimization procedures. Since CO<sub>2</sub> density decreases with temperature, the lower the injection temperature, the higher the downhole injection pressure (Figure 2). Thus, a trade-off arises between the injection pressure and temperature at the wellhead. The optimum injection conditions are site specific and should be computed according to the characteristics of each site. The pressure and temperature

injection conditions at the wellhead are coupled to the injectivity of the reservoir and thus to the required pressure buildup at the downhole to inject a given mass flow rate. Given the highly nonlinearity of flow along a wellbore (Lu & Connell, 2014), the wellhead injection conditions will be determined by the injection mass flow rate and the reservoir transmissivity.

Injecting relatively cold CO<sub>2</sub> ( $T = 20^\circ\text{C}$ ) reduces the compression costs because of its higher density (Figure 2). The most energetically efficient option is to inject CO<sub>2</sub> in liquid state, that is,  $T < 31.04^\circ\text{C}$  (Vilarrasa et al., 2013), a solution that bears the consequence of cooling down the rock in the vicinity of the injection well. Cooling-induced thermal stress is inversely proportional to the injection temperature and is likely to enhance injectivity (Yoshioka et al., 2019) but also microseismicity by approaching failure conditions: Operators may therefore prefer to inject CO<sub>2</sub> at a relatively high temperature (40 ÷ 60°C). Heating CO<sub>2</sub> entails large energetic costs (Goodarzi et al., 2015), which in volcanic areas could be minimized by extracting heat from existing geothermal wells. Injecting hot also increases compression cost because the higher the injection temperature, the higher the required wellhead injection pressure. The energy spent to



**Figure 4.** CO<sub>2</sub> sinking mechanism. The numerically computed sinking profile of CO<sub>2</sub>, represented as the area with CO<sub>2</sub> saturation  $S_c > 1$ , is a consequence of the interplay between gravity and viscous forces as represented by the values of the gravity number  $N$ . Cold CO<sub>2</sub> injection does not increase CO<sub>2</sub> buoyant potential because thermal equilibrium is reached within a small region from the wellbore where viscous forces dominate over gravity forces. At the far field, CO<sub>2</sub> is in thermal equilibrium with the reservoir, becoming denser than water, and since gravity forces are greater than viscous ones, CO<sub>2</sub> has the tendency to sink.

compress the CO<sub>2</sub> should have a renewable source to comply with the objective of reducing CO<sub>2</sub> emissions. Unlike solar or wind resources, which provide time-fluctuating power output, geothermal energy best fits the purpose of providing a time-constant heat supply required for continuous CO<sub>2</sub> injection.

Combining geothermal energy production with geologic carbon storage is of particular interest to utilize the injected CO<sub>2</sub> and generate a synergy to maximize the cut of CO<sub>2</sub> emissions in volcanic areas. Exploiting a volcanic area for both geothermal and CO<sub>2</sub> storage purposes would foster subsurface characterization, reducing uncertainty and identifying the most suitable areas for both geothermal production and geologic carbon storage. CO<sub>2</sub> could be eventually used as working fluid once the CO<sub>2</sub> plume has grown enough (Randolph & Saar, 2011).

#### 4.2. Managing Risks

The CO<sub>2</sub> injection rates in deep volcanic areas can be of up to several Mt per year per well (Figure 3a). High injection rates induce pressure buildup and cooling that will in turn affect the geomechanical stability of faults and potentially induce seismic events. Pressure buildup is the main triggering mechanism in the short term and cooling dominates in the long term. The latter may limit the lifetime of injection projects if induced earthquakes become too frequent or of excessively high magnitude (Parisio, Vinciguerra, et al., 2019). The thresholds in frequency and magnitude of induced seismicity are site specific and depend on the local structural and tectonic features. Thresholds to induced seismicity, both in terms of magnitude and frequency, depend on the local conditions and on the consequences produced on the population and infrastructure: The risk might be low in isolated areas but unbearably high in densely populated volcanic areas around the world. In any case, induced seismicity risks should be minimized through subsurface characterization, continuous monitoring, and adequate pressure and temperature management.

The risks of CO<sub>2</sub> injection in volcanic areas are site specific and should be carefully assessed and evaluated prior to each potential development project. These risks are connected with the intrinsic risks of active volcanism, namely, CO<sub>2</sub> degassing, hydrothermal explosions, and magmatic eruptions—occurrences that could raise concerns about the feasibility of anthropogenic CO<sub>2</sub> injection. CO<sub>2</sub> degassing is naturally present in volcanic areas and usually has its origin at boiling aquifers with superheated steam, which is buoyant (Chiodini et al., 2001). For the injected CO<sub>2</sub> to leak and eventually reach the surface, it should reverse its sinking tendency and become buoyant. However, our proposal only considers injecting CO<sub>2</sub> in supercritical reservoirs, which are placed much deeper and at higher temperature and pressure than boiling aquifers. Yet, similarly to what happens in magma chambers, the denser fluid, that is, CO<sub>2</sub>, might migrate laterally outside of the storage formation and encounter different temperature and pressure conditions at which CO<sub>2</sub> becomes buoyant (Gudmundsson, 2020). Hydrothermal explosions are caused by spinodal decomposition from metastable states leading to fast reequilibration phenomena (Thiery & Mercury, 2009) and the relative risks can be increased by long-term fluid extraction in geothermal reservoir, where the pressure drop could bring the system closer to metastable states. We argue that injecting CO<sub>2</sub> will prevent excessive pressure drawdowns and will help maintain a safe distance in the fluid phase space from metastable and dangerous states, where explosive fluid demixing is possible. The risks of magmatic eruptions are strongly linked with the volcanic activity of a specific site. Consequently, volcanic centers with recent eruptive manifestation should be avoided as target areas of deep CO<sub>2</sub> injection. Avoiding recently active volcanic centers is seldom restrictive in terms of geographical development because supercritical resident brine can be potentially found at drillable depth in several parts of the world where volcanic manifestations are present (Elders et al., 2014). As an example, the Acochulco Caldera Complex has shown no sign of volcanic activity in the form of eruptions and lava flows since approximately 60,000 years ago (Sosa-Ceballos et al., 2018). Nonetheless, two wells drilled within the Caldera recorded a very high geothermal gradient, with approximately 300°C at 2-km depth (Calcagno et al., 2018).

The feasibility of this technology is strictly connected to the drilling technology available and to the possibility of reaching pressure and temperature above the critical point of water such that CO<sub>2</sub> would sink. For geothermal gradients of 30 K km<sup>-1</sup>, the critical point of water would be encountered at around 13-km depth, which is currently beyond the available drilling technology. In volcanic areas, because of the higher geothermal gradients, the critical point of water is located at the accessible depth of 3 ÷ 4 km (Friðleifsson et al., 2017). Isolating the lower part of the well through proper casing—a great technological challenge per se (Kruszewski & Wittig, 2018)—is also necessary to ensure that CO<sub>2</sub> is injected at the proper depth.

### 4.3. Perspectives of Technological Development

CO<sub>2</sub> injectivity is controlled by reservoir permeability, which is highly dependent on temperature. For example, fractured granite has a transition permeability (called elastoplastic), which depends on a threshold mean effective stress, itself a function of temperature (Watanabe, Numakura, et al., 2017). Above the threshold stress, permeability decreases drastically with increasing mean effective stress. In contrast, fractured basalt is stable until high temperature (>500°C) and at 450°C, the observed permeability depends on stress and ranges from 10<sup>-17</sup> to 10<sup>-16</sup> m<sup>2</sup> for a mean effective confining stress of up to 60 MPa (Watanabe, Numakura, et al., 2017). The mean effective stress in the crust strongly depends on the rheology (Meyer et al., 2019; Parisio, Vilarrasa, et al., 2019), and its determination at high depth and temperature remains uncertain. Considering that permeability measurements on laboratory specimens tend to underestimate natural permeability at the geological scale (Neuzil, 1994) and that during drilling of IDDP-2, all circulation fluid was lost (Friðleifsson et al., 2017), we believe that in situ permeability ranging from 10<sup>-15</sup> to 10<sup>-14</sup> m<sup>2</sup> is possible in the fractured basaltic crust (Hurwitz et al., 2007). Additionally, during injection, the fluid pressure opens up preexisting fractures, while cooling contracts the surrounding rock, generating an additional fracture aperture: Assuming a cubic relationship of transmissivity with fracture aperture (for which fracture permeability is expressed as  $k = w^2/12$ , where  $w$  is the fracture aperture), an increase of the fracture aperture of 1 order of magnitude implies an increase of the fracture transmissivity of 3 orders of magnitude. Stimulation techniques have also the potential to achieve higher permeability at depth (Watanabe et al., 2019; Watanabe, Egawa, et al., 2017).

We estimate that suitable injection sites will permit an injection rate ranging from 0.5 to 8 Mt yr<sup>-1</sup> per well (Figure 3a). Thus, for every 100 wells drilled worldwide in deep volcanic areas for combined geologic carbon

storage and geothermal purposes approximately 50 to 800 Mt of CO<sub>2</sub> would be stored each year without buoyancy-driven leakage risk. The number of injection wells that will become operative in the next decades is highly uncertain, but to put in perspective, 100 wells would provide a higher amount than what is currently being stored, representing between 1% and 8% of the total worldwide storage target, a nonnegligible contribution to mitigate climate change effects (IPCC, 2018). Our proposal is currently a blue-sky idea and several challenges need to be addressed in future works, including the exact deployment of the technology, more refined economical and costs/benefit analyses, predrilling geophysical exploration, site monitoring during operation, improvements, and adaptations of drilling technologies.

## 5. Conclusions

We show that storing CO<sub>2</sub> into reservoirs in which the resident water is in supercritical state will reduce the risk of buoyancy-driven CO<sub>2</sub> leakage. Even when CO<sub>2</sub> is injected much colder than the reservoir temperature, leading to CO<sub>2</sub> becoming locally buoyant, no buoyant forces arise around the wellbore and a sinking CO<sub>2</sub> plume develops away from the wellbore. The injectivity per wellbore is relatively high due to supercritical fluid mobility, while overpressure remains low. Continuous injection of CO<sub>2</sub> over a decade is safe, because cooling only affects a radius in the order of tens of meters from the injection wellbore. Over a longer time span, the expansion of the cooled region might increase local seismicity as faults and fractures respond to thermal induced strains, limiting project lifetime. Our analyses prove that injecting into reservoirs above the critical point of water would constitute a complementary solution to the problem of significantly reducing CO<sub>2</sub> emissions and would extend the current applicability of geologic carbon storage through the CO<sub>2</sub> sinking effect that hinders buoyancy-driven leakage to the surface.

## Conflicts of Interest

There are no conflicts to declare.

## Data Availability Statement

The calculations are easily reproducible and described in detail in section 2. The FEM code for computation of CO<sub>2</sub> injection can be downloaded freely online (at [https://deca.upc.edu/en/projects/code\\_bright](https://deca.upc.edu/en/projects/code_bright)). The input files for the numerical model can be accessed at the institutional repository Digital.CSIC, which practices FAIR principles (<https://digital.csic.es/handle/10261/196740>).

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