

Mineral Carbon Sequestration and Theoretical Constraints on CO₂ Removal

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Viktor Nesheim, April 29, 2016

Abstract

The growing scientific evidence establishing the effects of CO₂ emissions on the Earth's climate, together with the substantial difficulty in reducing our dependence on fossil fuels, have driven an increasing realization that carbon capture and storage (CCS) will likely have to play a key role in mitigating anthropogenic climate change. This paper begins by reviewing the literature surrounding carbon capture and storage technologies. We explain the traditional method of structural storage by injecting CO₂ into sedimentary basins, and investigate the increasing concerns regarding induced seismicity and leakage from structural CO₂ storage. We then turn to the more recently proposed method of mineral carbonation, which injects CO₂ into mafic rocks and induces mineral trapping through enhanced carbonation reactions, and evaluate its potential to mitigate the risks associated with both leakage and seismic triggering.

In the second part of the paper we develop a simple model to study the drawdown of CO₂ through mineral carbonation, and understand some of the conditions affecting the potential for mineral carbonation. We choose the hypothetical example of CO₂ drawdown matching current global emissions for the next 50 years and estimate the volume of peridotite needed, exploring a wide range of reaction conditions. We investigate the additional volume required to account for several limiting factors over time: armoring, reservoir clogging and seismic triggering. Our calculations find that variations in the adjustable parameters significantly affect the aforementioned limiting factors, and thus also the required rock volume. The "ideal" drawdown scenario of fast reaction rate and small grains requires a peridotite volume small enough for the Semail ophiolite in Oman to theoretically draw down all the CO₂. However, an "unfavorable" drawdown scenario of slow reaction rate and large grains requires a volume that in fact exceeds estimates of continental mass of peridotite.

Introduction

Scientific evidence establishing the effects of carbon dioxide emissions on climate change is rapidly growing (IPCC 2013). Yet, despite an increasing global consensus that rising carbon dioxide levels present a major threat to the Earth's climate, relatively little progress has been made to reduce our dependence on carbon-heavy fossil fuels. Fossil fuels continue to account for around 85% of the global energy supply, and CO₂ emissions keep rising (BP Statistical Review 2015). Although theoretically sufficient to meet the world's energy needs, carbon-free renewable and nuclear energy sources have proven difficult to scale up. Moreover, even if a sudden technological breakthrough were to enable us to dramatically cut CO₂ emissions immediately, atmospheric CO₂ levels have already reached a threshold where they are expected to have significant impacts on the world's climate and ecosystems.

The growing urgency of reducing carbon dioxide emissions has given rise to an increasing interest in the potential for carbon capture and storage to mitigate climate change. The IEA considers carbon capture and storage to be a key technology to achieve a low-carbon future and meet global emissions objectives (IEA 2012). The set of technologies offer the potential not just to reduce CO₂ emissions, but also to create negative emissions by removing excess CO₂ from the atmosphere. The remaining technological obstacles and lacking political willingness to reduce our hydrocarbon-dependence might make negative emissions become necessary in order to reach future stabilization levels (Lackner et al. 2012).

This paper will start by reviewing the literature surrounding carbon capture and storage technologies, both the traditional method of structural storage by injecting CO₂ into sedimentary basins, and the more recently proposed method of mineral carbonation, injecting CO₂ into mafic rocks and inducing mineral trapping through enhanced carbonation reactions. Subsequently, the paper will build on work by Yarushina and Bercovici to develop a model for CO₂ drawdown through mineral carbonation in a mafic host rock. The model will estimate the theoretical volume of mafic rock required for CO₂ drawdown to match current CO₂ emissions, exploring a range of conditions. The calculations will also demonstrate the effects from expected slowdowns in

reaction rate kinetics over time, as well as the implications of potential pore space clogging and seismic triggering on required reservoir volume.

1. Carbon Capture and Storage technologies: Literature review

1.1 Carbon Capture and Storage (CCS)

Carbon Capture and Storage (CCS) is an umbrella term for a broad range of technologies. Common to the technologies is that they involve capturing CO₂ either from ambient air or at some stage of a CO₂-emitting process, then pressurizing and transporting the CO₂ to a selected storage site, and ultimately injecting it into suitable geological formations where the CO₂ can be trapped safely on a geological time scale (Gibbins & Chalmers 2008).

The first of the three main stages is the capturing process, which generally separates the CO₂ produced in power plants or industrial processes. Three methods currently exist to capture the CO₂: pre-combustion capture removes the CO₂ from the fossil fuel before the combustion reaction is completed. Post-combustion capture separates the CO₂ from the exhaust of the combustion reaction, generally by using a solvent that absorbs the CO₂. Oxyfuel combustion separates oxygen from the air and then combusts the fossil fuel in oxygen diluted with recycled flue gas, producing mainly CO₂ and H₂O and allowing for easy purification.

Discussions regarding CO₂ capture are primarily concerned with capture from stationary point sources, as explained above, since this is currently the most economically and technologically feasible method. However, Lackner et al. and others have argued that given the necessity for large-scale operations in order for CCS to be an effective climate mitigation technology, the traditional point-source capture might have to be complemented with air capture (Keith 2009, Lackner et al. 2012, Goldberg & Lackner 2015). The authors call for a scaling up of resources devoted to take air capture technology from its current stage of infancy to becoming a commercially available method for reducing CO₂ concentrations in the atmosphere. Capturing CO₂ from ambient air would not only be an important option for dealing with emissions from mobile dispersed sources, it could also both act as an insurance against CO₂ leaking from storage

and allow for negative global CO₂ emissions (Lacker et al. 2012, Goldberg & Lackner 2015).

After capture, the CO₂ is transported to a suitable storage site, most commonly by ship or pipeline. In the cases where the CO₂ is injected into depleted oil and gas reservoirs, the existing pipeline infrastructure can potentially be re-used.

The last stage is the storage of carbon dioxide in the subsurface. Given that the injected CO₂ is supposed to remain stored on a geologic time scale, this is the stage with the greatest challenges associated with it. Following transportation to the chosen storage site, the CO₂ gets injected into porous geological formations under the Earth's surface, where the high pressure and temperature turn the CO₂ from its gaseous form into a 'supercritical' liquid. There are primarily three types of geological formations that are considered suitable for CO₂ storage; depleted oil and gas fields, deep saline formations (porous rocks filled with salty water), and mature oil and gas fields (where CO₂ injection can be used for enhanced recovery purposes) (Weir et al. 1995). While saline aquifers offer the greatest potential CO₂ storage capacity, depleted oil and gas reservoirs are most likely to be selected as storage sites, since extensive information from previous geological assessments is already available.

The storage mechanisms for the injected carbon dioxide change over time, and this has important implications for the risk of leakage (Johnson et al 2004). 'Structural storage' is the primary storing mechanism for CCS, and it refers to an impermeable layer of rock known as the cap rock, which traps the CO₂ and prevents it from migrating upwards. Over time some of the migrating CO₂ will become tightly trapped in the pore spaces of the host rock, in what is known as 'residual storage'. The CO₂ will also gradually start to dissolve in the surrounding salt water, which increases the density of the solution and causes it to sink towards the bottom of the reservoir. Finally, 'mineral storage' refers to the chemical reaction between the CO₂ and the host rock, which makes it bind permanently to the rock. Thus, the mobility of the carbon dioxide decreases over time, gradually reducing the risk of leakage.

1.2 Current status of CCS technology

Injecting CO₂ into oil and gas fields for enhanced recovery has already been pursued for a number of decades. First tried in Texas in 1972, there are now more than 100 active commercial CO₂ injection projects across the United States (DOE website). While most of the injected CO₂ has traditionally come from natural reservoirs, increasing attention is now being devoted to developing technologies that can produce and employ CO₂ from a variety of industrial applications. The most notable example of an enhanced oil recovery project using this technology is the Weyburn-Midale project in Canada, which since 2000 has injected 3 million tonnes of CO₂ per year. The injected CO₂ comes from both a gasification company and a rebuilt coal-fired power plant with carbon capture technology (MIT CCS project database 2016).

Commercial-scale CCS projects not intended for enhanced oil recovery are significantly less plentiful, and have a much shorter history. The perhaps best-known project is that at Sleipner, West of Norway, where around 1 million tonnes of CO₂ have been injected annually into the Utsira Formation since 1996 (Global CCS Institute, Sleipner website). Other important projects include the Norwegian Snøhvit project, which has sequestered CO₂ into a submarine sandstone reservoir since 2008 (Global CCS Institute, Snøhvit website), and BP's In Salah project in Algeria, which injected around 1 million tonnes of CO₂ per year since 2004. However, for reasons to which we will return later the In Salah project suspended further CO₂ injection in 2011.

While considerable experience had been gained regarding CO₂ injection through enhanced oil recovery projects, the aforementioned projects and their extensive geophysical monitoring and flow modeling have offered much operational experience and knowledge about the effectiveness of underground CO₂ storage over longer time periods (Arts et al. 2008). Perhaps even more importantly, they have played a key role in demonstrating the technical feasibility of large-scale commercial CCS. A variety of government-funded demonstration projects have also been carried out over the last couple of decades to study chemical and flow behavior of the CO₂ as it gets injected into the reservoirs. Yet, while small-scale demonstration projects can be helpful in addressing issues of process integration and to gain operational experience,

large-scale storage projects are necessary for monitoring, and capacity and risk assessments, since these factors are more directly related to the scale of the project (Benson et al. 2012).

Another heavily debated topic is the economic viability of CCS technologies. While CCS costs have decreased over time, recent cost estimates demonstrate the subsistent need for subsidies or high carbon prices in order to make CCS become economically practiced on a large scale (Benson et al. 2012). In this regard it should be noted that while the aforementioned projects have demonstrated the technical feasibility of large-scale CCs, the economic feasibility of particularly the Norwegian projects has been enabled by an unusually favorable set of conditions (Torp & Brown 2006). The gas extracted at the Norwegian gas fields contains around 4-9 % of CO₂ by volume, and this CO₂ needs to be removed before the gas can be processed into liquefied natural gas (LNG) and transported to the market. Thus, the costly process of capturing CO₂ does not become an additional cost with CCS. Moreover, the Norwegian government imposed a heavy CO₂ tax on offshore petroleum operations in 1991. These two factors together made CO₂ sequestration the least costly alternative.

1.3 Fluid injection and induced seismicity

A central concern associated with CO₂ storage through injection into porous reservoirs is the potential for earthquake triggering, and an exploration of the long history of literature establishing the mechanisms by which fluid injection can trigger seismicity is warranted. The idea that fluid injection has the potential of triggering seismic activity was first investigated in the 1960s, spurred by a significant increase in seismic activity following fluid injection into a disposal well at the Rocky Mountain Arsenal, near Denver, Colorado. The rapid surge in seismicity led geologists to suspect that the two occurrences were directly related, and in a famous paper from 1968, Healy et al. presented statistical evidence correlating the fluid injection and seismic activity (Healy et al. 1968). They found no evidence of significant pre-injection seismic activity, and given the narrow timeframe and the limited area in which the post-injection seismicity occurred, they calculated that the chance of a natural earthquake swarm this close to the disposal well would be an “extremely unlikely incidence.”

The pore-pressure mechanism – where an increase in pore pressure reduces the frictional resistance to faulting – was argued to be the only mechanism that could adequately explain the earthquakes, but could at the time not be established conclusively.

Further evidence of fluid injection's potential for triggering seismic activity was presented almost a decade later, when Raleigh et al. demonstrated that seismic activity could be controlled through variations in fluid injection pressures (Raleigh et al. 1976). By alternately injecting and removing water from a well penetrating a seismic area, and concurrently measuring the reservoir pressure in nearby wells, predictions could be made of the spatial distribution of pressure with the injection/withdrawal cycles. From measurements of the reservoir rock's frictional properties and in situ stress, the seismologists were able to compare their measurements with the predicted fluid pressure for earthquake triggering, and thus conclusively establish the effective stress hypothesis of the effect of fluid pressure on earthquake triggering.

A renewed interest in the potential for fluid injection to induce seismic activity has been noted particularly in the last decade, as a sharp increase in seismicity has been recorded in areas with high levels of wastewater disposal from unconventional oil and gas wells. Particular attention was given to the Oklahoma M_w 5.7 earthquake in 2011, which caused significant infrastructural damage and pushed the boundary for the hazard potential of fluid injection. Keranen et al. used subsurface data to investigate the faults that ruptured in the sequence and argued that wastewater injection into a depleted oil field had likely played a role in triggering the earthquake (Keranen et al. 2013). However, an extensive analysis by the Oklahoma Geological Survey (OGS), which included direct pressure measurements of the geologic formation, analyses of the earthquakes' orientation and comparisons with historical seismic activity in the region, argued that the earthquake sequence was most likely the result of natural causes (Keller & Holland 2013).

The lack of consensus surrounding the 2011 Oklahoma earthquake is reflective of the general debate surrounding the role of wastewater disposal in explaining the recent earthquake activity. While many geophysicists were quick to argue that there was a correlation between the wastewater disposal wells and

the recent earthquake activity (Zoback 2012, Ellsworth 2013), skeptics resisted the connection, pointing to the fact that in e.g. Oklahoma no significant injection sites were located within 20 kilometers of the epicenters (Hand 2014). In 2014, however, Keranen et al. presented new evidence that specifically linked also stronger and more distant earthquakes with the wastewater disposal wells (Keranen et al. 2014). By combining seismic recordings, rates and volume of wastewater injection, and hydrogeological models, the authors were able to model the water flow and show that wastewater injection could cause earthquake activity up to 35 kilometers away. Four of Oklahoma's highest-rate disposal wells could thus be accountable for as much as 20% of earthquakes in central United States.

The increasing literature establishing the mechanisms through which water injection can trigger seismic activity has also sparked growing concerns regarding the risks that induced seismicity pose for carbon sequestration technologies. While it has been suggested that CO₂ and water have different viscosity and bulk modulus, making CO₂ less likely to trigger seismic activity, Verdon and others have argued that fault reactivation is predominantly caused by pressure changes, which are determined primarily by the volume of the fluid rather than the type of fluid, and so probably produce similar induced seismicity (Verdon 2014, IEAGHG 2013). Nicol et al. examined induced seismicity at sites dominated by water injection and hydrocarbon extraction, and found that the induced earthquakes' rate and magnitude increase with total fluid volumes, rising reservoir pressure and rates of injection/extraction (Nicol et al. 2011). Given the high volumes and rates of injected fluid needed for commercial-scale CO₂ sequestration in order for it to offer meaningful potential in reducing global CO₂ emissions, they argue that high-magnitude induced earthquakes can be expected. Such high-magnitude inevitably pose a significant threat to the viability of CCS as an option for mitigating climate change.

Similarly, in an extensive report on the induced seismicity potential in various energy technologies from 2012, the National Research Council concluded that the historical evidence of fluid injection triggering seismicity implies that carbon sequestration "may have potential for inducing larger seismic events" (NRC 2012). Nevertheless, the report acknowledged the inherent lack of

information available to actually understand this potential, given the limited number of large-scale carbon capture and sequestration projects in operation.

1.4 Concerns regarding induced seismicity and CO₂ leakage

The primary concern related to induced seismicity from CO₂ injection is not damage caused by the earthquake activity itself, but rather the potential for subsequent geomechanical deformations to threaten the integrity of the sealing cap rock and create pathways for CO₂ leakage (Verdon et al. 2013). Examples of natural incidences such as the Lake Nyos disaster in 1986 have demonstrated the potentially detrimental effects associated with a sudden release of large quantities of carbon dioxide (Kling et al. 1987). However, given that the injected CO₂ is supposed to remain trapped in the storage reservoir for thousands of years, even small yearly leakage rates will rapidly accumulate and can render CCS projects non-viable. Van der Zwaan finds that a leakage rate of only 1%/year is too high for CCS to constitute a meaningful climate change mitigation option (van der Zwaan 2009).

Despite the apparent risks of earthquake triggering from CO₂ injection, seismic monitoring at CO₂ injection sites has been patchy at best. Neither Sleipner nor Snøhvit have seismic monitoring in place, and In Salah did not install microseismic arrays until several years after CO₂ had started (Verdon 2014). Indeed, at the In Salah site, injection into a water leg of a gas reservoir increased pore pressure and led to a rapid surge in microseismic activity in 2010, and analyses of geomechanical and seismic data led to the decision to suspend injection from June 2011. White et al. studied the geomechanical behavior of the reservoir and found that while there are no indications that the seal integrity has actually been compromised, monitoring showed that pressure – and probably also CO₂ – had migrated upwards into parts of the cap rock (White et al. 2014). The authors argue that the migration is probably a result of hydrofracturing in parts of the lower cap rock, potentially combined with interactions with preexisting faults. Similarly, a microseismic data analysis by Verdon et al. found that the seismic data is consistent with the inferences that the CO₂ injection stimulated a fracture zone extending into the overburden (Verdon et al. 2013).

The risk of induced seismicity and resulting leakage has been one of the main arguments among CCS-skeptics, and in 2012 Zoback and Gorelick went as far as to largely reject the potential for large-scale carbon sequestration altogether (Zoback & Gorelick 2012). The authors argue that the crust “is potentially active in the current stress field” nearly everywhere in the continental interiors, and both historical examples such as Colorado and the more recent example of Central United States have demonstrated that increasing pore pressure near preexisting potentially active faults risks earthquake triggering. Although larger faults can generally be detected during site characterization studies, even the largely undetectable small faults have the potential of threatening the seal integrity of CO₂ repositories by creating a hydraulic pathway. While the authors acknowledge that there are situations in which CCS technology can work well, the limited number of identifiable safe locations, in combination with the limitations that the critically stressed nature pose on the rate at which CO₂ can be safely injected, together reduce carbon sequestration potential to a level where it cannot make a significant impact for global warming. Moreover, currently existing small-scale pilot injection projects cannot accurately predict the stress build-up that will occur when implementing full-scale injection.

Zoback and Gorelick’s paper gained widespread attention, and spurred a vivid debate regarding the risk of induced seismicity and leakage with implementation of large-scale CCS technology. Juanes et al. criticized the misplaced focus on earthquake epicenters instead of hypocenters, pointing to the fact that CO₂ injection generally occurs at much shallower depths than most earthquake activity. The rheological properties of shallow sedimentary formations are much more ductile than the brittle basement rocks, thus allowing substantial deformations without establishing leaking pathways (Juanes et al. 2012). Vilarrasa & Carrera similarly argued that sedimentary formations into which the CO₂ would be injected are softer than the crystalline basement, and so are rarely critically stressed (Vilarrasa & Carrera 2015). Additionally, gradual dissolving of CO₂ into the brine reduces overpressure over time, and the fact that the initial injection phase is the least stable makes the risk of induced seismicity easy to avert through controlled injection rates. Yet, despite the aforementioned

criticisms, the increasing concerns regarding induced seismicity and CO₂ have put considerable pressure on the future of subsurface storage of CO₂.

1.5 Mineral carbonation as a potential CCS technology

Carbon storage through mineral carbonation has been proposed as a potential technology to mitigate the seemingly inevitable risks of leakage when storing CO₂ in its fluid or gaseous forms (Seifritz 1990, Lackner et al. 1995, Matter & Kelemen 2009, Andreani et al. 2009). As was explained earlier, when CO₂ is injected into large sedimentary basins, some of the CO₂ will bind chemically to the surrounding rock over time, in what is referred to as 'mineral storage.' However, studies suggest that this takes tens of thousands of years, if it occurs at all (Gilfillan et al. 2009). Discussions regarding mineral carbonation as a potential CCS technology rather refer to the injection of fluid or gaseous CO₂ into highly reactive mafic or ultramafic rocks (e.g. basalt or peridotite), which will immediately start chemically reacting with the injected CO₂ to produce mineral carbonates. This method of locking up the CO₂ as stable solid carbonates offers the potential of safe CO₂ storage on a geologic time scale.

While several minerals can be used for carbonation reactions, olivine exhibits the fastest known mineral carbonation rates and also has the highest molar proportion of divalent cations needed to form natural carbonate minerals (Kelemen et al. 2011). Rock composed of >40% olivine is called peridotite, and can be found across the globe, although primarily in oceanic crust and shallow mantle. Mg-olivine (forsterite), which is the mineral type that will be used in the calculations to follow, exothermically reacts according to the equation $Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2 + 95 \text{ kJ/mol}$, where 1 kg of Mg-olivine reacts with approximately 0.6 kg of dissolved CO₂ from fluid to produce 1.6 kg of magnesite and quartz.

Mineral carbonation technologies are broadly divided into in situ and ex situ. Ex situ methods involve quarrying and grinding the mafic rock, and then transporting it to a concentrated source of CO₂ – e.g. a fossil fuel-burning power plant – where it reacts with fluids at high temperature and pressure. However, as with other CCS technologies, questions have been raised about whether the costs will be low enough for industrial implementation (Mazzotti et al. 2005). In order

to avoid the costs of reaction vessels with high temperature and pressure, Schuiling & Krijgsman proposed inducing enhanced weathering by spreading fine-powdered olivine over forestland, farmland or beaches (Schuiling & Krijgsman 2006). Hangx and Spiers, however, argued that the technology would not be feasible on the scale needed, pointing to the economic, infrastructural and public health challenges associated with both the required grinding to get grain sizes small enough to obtain useful reaction rates, as well as the transportation of the olivine to the spreading sites (Hangx & Spiers 2009).

In situ mineral carbonation involves transporting the CO₂ to an area with large volumes of mafic rock, and injecting either supercritical CO₂ or a CO₂-rich fluid into the rock. Two primary in situ methods have been proposed for mineral carbonation for CO₂ storage; (1) raising the temperature of peridotite at depth to the optimal temperature for mineral carbonation, hydraulically fracturing the rock and injecting it with CO₂-rich fluids, and (2) hydraulically fracture a high-temperature rock volume in order to induce thermal convection of seawater through the rock (Kelemen & Matter 2008).

The first method requires initial costs of raising the temperature of the rock, but proponents argue that the exothermic heat output from the reactions later maintain the temperature and offset cooling from further fluid injections, and might even also heat adjacent rock volumes by diffusion. While there is also an initial cost of hydrofracturing the rock, once the initial fracturing has been performed the permeability and surface area can likely be maintained through reaction-driven cracking.

The second method offers an alternative that can enable us to achieve negative emissions, and also avoid the costs of CO₂ capture and transport. Carbonation reactions with the rock would remove most of the dissolved CO₂ from the water, and as the CO₂-depleted seawater returns to the surface, it will draw down atmospheric CO₂. While acknowledging the high cost of seawater pumping, Kelemen and Matter argue that regions of high heat flow are ideal as they can rely heavily on thermal convection to drive the water flow. In that case, the only associated costs would be drilling and hydrofracturing, which might make enhanced seawater convection the most economical mineral carbonation technology (Kelemen et al. 2011).

Various attempts have been made at estimating the mass of peridotite available at or near the Earth's surface, and consequently also the potential for mineral carbonation in natural peridotite (Kelemen & Matter 2008, Krevor et al. 2009). Ophiolites are slices of the Earth's oceanic mafic crust and shallow mantle that have been uplifted and exposed above sea level, and contain a significant amount of the world's peridotite. The Semail ophiolite in Oman is the largest in the world, and Kelemen and Matter have estimated that it contains around 5×10^{16} kg of peridotite within 3 km of the surface. They further project that peridotite weathering in Oman converts $10^4 - 10^5$ tons of atmospheric CO_2 to solid carbonate minerals every year (Kelemen & Matter 2008). To illustrate the large potential for carbon storage, adding 1 wt% CO_2 to the peridotite would consume around 7×10^{14} kg of CO_2 – which is roughly equivalent to the total increase in atmospheric CO_2 since the industrial revolution. The United States does not have a big ophiolite like the one in Oman, but Krevor et al. estimate that the mass of peridotite in the many smaller ophiolites together amounts to roughly the amount of peridotite in the Semail ophiolite (Krevor et al. 2009). Total global continental mass of peridotite in ophiolites is significantly larger, and assumed to be between 10^{17} and 10^{18} kg (Kelemen et al. 2011).

Kinetic data shows that the mineral plagioclase, which is the primary constituent of basalt, reacts with CO_2 more slowly than does olivine (Kelemen et al. 2011). However, basaltic rocks are more abundant on Earth's surface than peridotite – making up around 10% of the continents – and the CO_2 flux consumed by chemical weathering of basalt is estimated to account for 1/3 of the total CO_2 flux derived from silicate weathering at the Earth's surface (Dessert et al. 2003). The two field injection projects CarbFix in Iceland and BigSky Carbon Sequestration Partnership in Washington State are currently assessing the feasibility of carbon sequestration in basalt. The BSCP project injects pure CO_2 into a porous basaltic layer, where an impermeable cap rock prevents the CO_2 from escaping before it gets locked up through the carbonation reaction. In the CarbFix project, on the other hand, CO_2 is released into down-flowing water within the injection well. Once the CO_2 dissolves in the water it is no longer buoyant, and so the immediate solubility trapping reduces the risk of leakage and eliminates the need for an impermeable cap rock. CarbFix data after the first

years of injection show that nearly all of the injected CO₂ was carbonated within two years, at 20-50 degrees Celsius and 500-800 meter depth (Gislason et al. 2013). These results have significantly changed our understanding of the time scale of mineral carbonation and demonstrate the large potential of the CarbFix method. However, it should be noted that cost comparisons of the two projects show that the CarbFix method of dissolved water injection is currently twice as expensive as direct CO₂ injection at the BSCP site and in comparable sedimentary basins (Ragnheidardottir et al. 2011, Global CCS Institute 2011).

1.6 Mineral carbonation's potential to mitigate seismic risk

A major potential benefit associated with mineral carbonation for CO₂ storage is the reduced risk of leakage. However, work by Yarushina and Bercovici suggests that solidification of CO₂ through mineral carbonation not only reduces the risk of CO₂ leakage in case of seismic activity threatening the seal integrity, but also has the potential of mitigating the risk of induced seismicity itself (Yarushina & Bercovici 2013). Through a conceptual modeling of mineral carbonation in mafic rock over time, they illustrate how mineral precipitation increases frictional contact area between neighboring grains, reduces the effective fluid pressure and in total mitigates the risk of seismic triggering.

Yarushina and Bercovici's model assumes a reservoir consisting of a reactive, mafic host rock composed of identically sized grains, confined between an overlying caprock and an underlying basement rock. Lithostatic stress induces normal contact stresses between the grains, while local shear stresses are induced from shear stress present in the reservoir rock. A Mohr diagram is used to illustrate the stress tensor, with Mohr circles showing the stress state and the Mohr-Coulomb failure envelope delineating the line at which seismic triggering is expected. The distance between the initial circle and the failure envelope depends on the assumptions regarding the initial stress state.

Injecting a carbonic acid aqueous solution or supercritical CO₂ into the pore space causes the fluid pressure to increase. Thus the normal stress decreases, and the Mohr circle starts moving closer to the failure envelope. If there are no carbonation reactions, normal stresses will decrease until local stresses at the

grain contacts satisfy the Mohr-Coulomb friction law, at which point the rock fails and seismic slip occurs. When the injected CO₂ reacts with silicate minerals in the host rock, however, carbonate products are precipitated and the grain radius increases. The increasing grain-grain contact area alters the local stress state through a simultaneous reduction of both local normal and shear stresses, potentially avoiding the failure condition.

The authors develop Mohr diagrams for nine different scenarios – using three different values for both reaction rates and initial shear stress – and find that seismic risk is completely avoided in three scenarios; low shear stress and slow reaction rate, low shear stress and fast reaction rate, and moderate shear stress and fast reaction rate. In these cases, both reactions and pumping stop when the mineral precipitates have filled all the available pore space and the reservoir is clogged. Through an analysis of the grain radius, fluid pressure and contact stresses, the authors find that the most active stress reduction occurs during injection. Post injection, continued carbonation reactions cause the Mohr circles to migrate away from the failure envelope. Thus, if a seismic slip is not triggered during the active pumping stages, it will not occur afterwards either.

Yarushina and Bercovici's model also introduced the "critical pumping rate," which is the injection rate below which seismic triggering can be avoided. The critical pumping will depend on the reaction rate and the initial shear stresses. By graphing the pumping rate for which the Mohr-Coulomb friction law is satisfied with respect to time, the model demonstrates how the critical pumping rate must first decrease rapidly in order to avoid failure before grain growth becomes significant, but later can increase as the mineralization increases the grain-grain contact area. It follows that seismic triggering can be avoided with constant pumping as long as the pumping rate is below the minimum critical pumping rate.

2. Modeling CO₂ drawdown through mineral carbonation

2.1 Introduction

This second part of the paper aims to develop a simple theoretical model with which to study the potential for reducing atmospheric CO₂ through mineral carbonation using the highly reactive mineral olivine. The model will be used to estimate the amount of peridotite needed in order for CO₂ drawdown to match current global emissions, exploring a wide range of reaction conditions. The calculations will also account for the effects of expected slowdowns in reaction rate kinetics over time, as well as the potential problem of pore space clogging, and discuss the implications of these effects. Finally, building on earlier work by Yarushina and Bercovici, the paper will explore the limitations on fluid injection imposed by the risk of seismic triggering, and the subsequent effects on required peridotite. While the model is theoretical and simplifies the effects of various factors at play in real-life settings, it can still provide valuable insight into some of the conditions affecting the potential for mineral carbonation.

2.2 Mathematical model

The model assumes a peridotite host rock composed of grains of pure olivine. All grains are identical cubic-packed spheres of initial radius a . As the pore space becomes filled with supercritical CO₂ or a carbonic acid aqueous solution, the carbonation reaction causes grains to grow from precipitation of the reaction product at the free surface. The grain size evolution can be modeled for a grain of radius R , with growth rate (in cm/s):

$$\frac{dR}{dt} = k \left(\frac{b}{R}\right)^n \quad (1)$$

where k is the reaction rate parameter (in cm/s) and b is the reference grain size (in cm). The reaction rate exponent ($n > 0$) accounts for the slowdown in reaction kinetics with time, as is commonly observed in experiments (Kelemen et al. 2011). The mass of an individual spherical grain of radius R is thus given by

$$M = \frac{4}{3}\pi R^3 \rho \quad (2)$$

where ρ is the density of the grain in kg/cm³. Combining equations (1) and (2), it follows that the growth in individual grain mass at time t will be:

$$\frac{dM}{dt} = 4\pi R^2 \rho \frac{dR}{dt} = 4\pi R^2 \rho k \left(\frac{b}{R}\right)^n \quad (3)$$

The growth in grain mass corresponds to a drawdown of CO₂ given by the

$$\text{fraction } f = \frac{\text{Molecular weight (CO}_2\text{)}}{\text{Molecular weight (MgCO}_3\text{)}} = \frac{44.0 \text{ g/mol}}{84.3 \text{ g/mol}} = 0.522$$

Given that each grain is assumed to be a sphere within a cube of volume $(2a)^3$, a host rock of volume V will have $N = \frac{V}{8a^3}$ number of grains.

Total mass drawdown of CO₂ (in kg/s) can therefore be written as

$$\frac{dM_{\text{drawdown}}}{dt} = Nf \frac{dM}{dt} = \frac{V}{8a^3} f (4\pi \rho k b^n R^{2-n}) \quad (4)$$

Assuming that reference grain size $b =$ initial grain size a , the equation simplifies to

$$\frac{dM_{\text{drawdown}}}{dt} = \frac{\pi}{2} f \rho V k a^{n-3} R^{2-n} \quad (5)$$

where from equation (1) we know that grain radius R is given by the function

$$R^{n+1} = a^{n+1} + b^n (n+1)kt.$$

2.3 Discussion and results

The calculations below estimate the volume of host rock needed for a variety of drawdown scenarios, exploring the implications from varying certain adjustable parameters. While some of the parameters that affect the drawdown rate are scientifically given or show little room for variation, parameters such as

the grain size a , reaction rate k and reaction rate exponent n all vary depending on the host rock and the reaction conditions.

2.3.1 Zero-emission globe

In order to get a sense of the volume of rock required if mineral carbonation were to play a major role in reducing atmospheric CO₂-levels, an interesting starting point will be to estimate what volume of rock would be required to obtain a world of zero emissions, i.e. to ensure that the CO₂ drawdown rate matches the amount of CO₂ currently being emitted into the atmosphere. This condition can be expressed as

$$\frac{dM_{drawdown}}{dt} = \frac{dM_{emissions}}{dt}$$

which from equation (5) can be written as

$$\frac{\pi}{2} f \rho V k a^{n-3} R^{2-n} = \dot{M}_e \quad (6)$$

Immediately after supercritical CO₂ or a carbonic acid aqueous solution start being injected into the host rock, at $t = 0$, grain radius $R =$ initial grain radius a , and so the equation simplifies to

$$\frac{\pi}{2} f \rho V k a^{-1} = \dot{M}_e \quad (7)$$

The Global Carbon Project estimates that in 2014 global CO₂ emissions amounted to approximately 35.9 Gt CO₂, which translates to an emissions rate of 1.1384×10^6 kg/s (Le Quéré et al., 2015). Although the grain will be composed of a combination of olivine and magnesite while the mineral carbonation reaction is still ongoing, we assume the density of magnesite $\rho = 2.958$ g/cm³ for the entire grain.

The plot below shows the volume required for drawdown to match current emissions, plotted with respect to the changeable parameters k and a . Grain size can vary greatly depending on the physical and chemical conditions

under which the rock was formed. A host rock composed of smaller olivine grains will ensure faster mineral carbonation reaction, as relatively more rock is exposed to the CO_2 reactant. In this case we let grain size vary within the interval $0.05 \text{ cm} < a < 1 \text{ cm}$. The mineral carbonation reaction rate for olivine has been tested experimentally in a number of studies, and is a function of both temperature and pressure. We here assume reaction rate to be within the interval $44 \times 10^{-13} \text{ cm/s} < k < 44 \times 10^{-12} \text{ cm/s}$, consistent with experimentally obtained precipitation rates at neutral to alkaline conditions and 100-200 °C (Saldi et al. 2012).

The parameter k/a thus goes from what would be an unfavorable mineral carbonation scenario of big grain size ($a = 1 \text{ cm}$) and slow reaction rate ($k = 44 \times 10^{-13} \text{ cm/s}$) to an ideal mineral carbonation scenario of small grain size ($a = 0.05 \text{ cm}$) and high reaction rate ($k = 44 \times 10^{-12} \text{ cm/s}$). The plot includes two parallel graphs, one for molecular weight fraction $f = 0.522$ as calculated earlier, and another using the more conservative assumption of $f = 0.05$. This lower fraction roughly accounts for slower reaction if we are pumping in aqueous CO_2 rather than pure super-critical CO_2 .

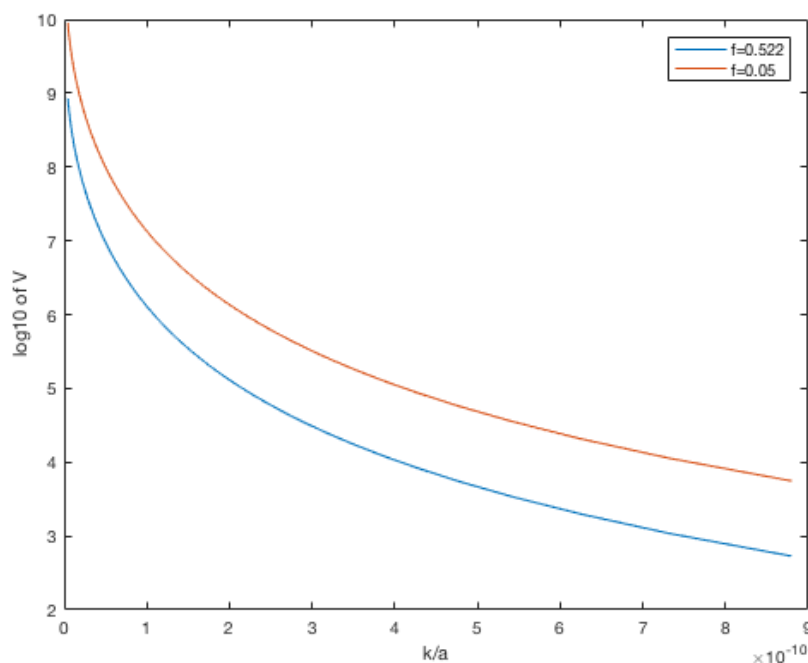


Figure 1

While the log scale makes the plot difficult to interpret in exact numbers, it is evident that the variations in parameters k and a have a significant effect on the required volume. The volume varies by several orders of magnitude across our selected k/a interval. For a molecular weight fraction of $f = 0.05$, the ideal condition of small grain size and fast reaction rate only requires a volume of $5.6 \times 10^3 \text{ km}^3$, while the unfavorable scenario requires a volume of $1.1 \times 10^6 \text{ km}^3$. Assuming a suitable reservoir depth to be 500 meters, the model estimates that the land areas required would be squares of $106 \times 106 \text{ km}$ and $1480 \times 1480 \text{ km}$, respectively.

From the drawdown equation we can deduce that both reaction rate and grain size linearly affect volume required, i.e. a doubling in reaction rate or halving of grain size will both reduce the volume required by a factor of 2.

2.3.2 Zero emissions until renewables take over

Figure 1 shows the volume required for CO_2 drawdown to match emissions at $t = 0$. Yet, we know that once the mineral carbonation reaction begins and the grains start to grow, the growth rate – and thus also the drawdown rate – slows down according to the reaction rate parameter n . Thus, if we want to calculate the volume required for drawdown to match emissions over a certain time span, we will have to account for this gradual reduction in drawdown rate – unless, of course, global CO_2 emissions happen to decrease at the same rate as the reaction rate.

Our model and calculations are motivated by a desire to understand what role mineral carbonation can potentially play in preventing atmospheric CO_2 -levels from rising and avoiding dramatic changes to the world's climate. Thus, an interesting calculation would estimate the volume of rock required to ensure net zero emissions up until the point when carbon-free energy technologies substitute for fossil fuels, given by the integral

$$\int_0^T \left(\frac{dM_d}{dt} - \frac{dM_e}{dt} \right) dt = 0 \quad (8)$$

where $\frac{dM_d}{dt}$ = drawdown rate, and $\frac{dM_e}{dt}$ = emissions rate. If we make the assumptions that CO₂-emissions remain constant up until renewables take over, and that this take-over occurs 50 years from now, we get

$$\int_0^T \left(\frac{\pi}{2} f \rho V k a^{n-3} R^{2-n} \right) dt = \dot{M}_e T \quad (9)$$

Given $R = (a^{n+1} + b^n(n+1)kt)^{\frac{1}{n+1}}$, we get:

$$\frac{\pi}{2} f \rho V k a^{n-3} \int_0^T \left((a^{n+1} + b^n(n+1)kt)^{\frac{2-n}{n+1}} \right) dt = \dot{M}_e T$$

$$\frac{\pi}{2} f \rho V k a^{n-3} \left(\frac{(a^{n+1} + b^n(n+1)kT)^{\frac{3}{n+1}} - a^3}{3b^n k} \right) = \dot{M}_e T \quad (10)$$

In order to illustrate the effects that the gradual slowdown in drawdown rate will have on the required volume, we make the calculation both for the ideal and unfavorable scenarios, again assuming molecular weight fraction $f = 0.05$ and reaction rate exponent $n = 3$.

- The ideal scenario ($a = 0.05 \text{ cm}$, $k = 44 \times 10^{-12} \text{ cm/s}$) gives 7,490 km³, which assuming a 500 m depth gives an area of 122 x 122 km
- The unfavorable scenario ($a = 1 \text{ cm}$, $k = 44 \times 10^{-13} \text{ cm/s}$) gives 1,117,478 km³, which again assuming a 500 m depth gives an area of 1495 x 1495 km.

We see that in the case where $n=3$, accounting for the gradual slowdown in reaction rates necessitates volume to increase by around 15% in the ideal case, but only by 1% in the unfavorable case. Raising the reaction rate exponent to 4 or 5 in the ideal case increases required volume to 9,400 km³ (25% increase) and 11,290 km³ (50% increase), respectively. For the unfavorable scenario, however, raising the reaction rate exponent only has a negligible impact on the volume, increasing required by 0.3% and 0.6%, respectively.

Thus, we notice that the ideal case of rapid drawdown becomes relatively more affected by the reaction rate slowdown exponent than does the unfavorable case, which has a much slower initial drawdown rate. In order to demonstrate why this is the case, we can turn back to equation (10)

$$\frac{\pi}{2} f \rho V k a^{n-3} \left(\frac{(a^{n+1} + b^n (n+1) k T)^{\frac{3}{n+1}} - a^3}{3 b^n k} \right) = \dot{M}_e T$$

which, assuming $a = b$, can be rewritten as

$$\frac{\pi}{6} f \rho V \left(\left(1 + \frac{(n+1) k T}{a} \right)^{\frac{3}{n+1}} - 1 \right) = \dot{M}_e T \quad (11)$$

Thus we note that the effects depend on the ratio k/a , and not on k or a individually. In the unfavorable scenario of slow reaction rate k and large grain size a , $\frac{(n+1)kT}{a} \ll 1$, and so by Taylor expansion we get

$$\dot{M}_e T \approx \frac{\pi}{6} f \rho V \left(1 + \frac{3}{n+1} \frac{(n+1)kT}{a} - 1 \right) = \frac{\pi}{2} f \rho V \frac{kT}{a}$$

which is simply the drawdown rate at $t = 0$ from equation (7) multiplied by the time T , showing no reduction in drawdown rate over time. For the ideal scenario of fast reaction rate k and small grain size a , on the other hand, $\frac{(n+1)kT}{a}$ takes on a much bigger value, and so the Taylor expansion becomes less accurate, with the drawdown rate deviating more relative to $t = 0$ as time increases.

Here it should be noted that our calculation shows the volume required for overall drawdown to match overall emissions over a time span of 50 years. However, this does not mean that drawdown matches emissions at any given point. On the contrary, a higher initial drawdown rate will be required to account for the gradual slowdown, since we assume volume to stay constant. Thus, it effectively follows that negative emissions would be required in the first years, i.e. actively removing CO₂ from the atmosphere through one of the previously proposed technologies.

2.3.3 Accounting for pore space clogging:

The above calculations assume that the grains can grow unrestrictedly during the entire time span, not accounting for the possibility of pore space clogging before 50 years. The host rock is composed of cubic-packed spheres of identical size, where the side of each cube is $2a$. Thus, the contact area between unit cells is $4a^2$. With grain radius R , the grain-grain contact area becomes $\pi(R^2 - a^2)$. If we interpret clogging to mean no permeability, the clogging condition can thus be expressed as the time t for which

$$4a^2 - \pi(R^2 - a^2) = 0 \quad (12)$$

where $R = (a^{n+1} + b^n(n+1)kt)^{\frac{1}{n+1}}$

For the ideal scenario ($a = 0.05 \text{ cm}$, $k = 44 \times 10^{-12} \text{ cm/s}$), again assuming reaction rate exponent $n = 3$, we find that clogging occurs after roughly 37.5 years. The ideal case with a higher reaction rate exponent ($n = 4$) increases expected clogging time from 37.5 to 48.8 years, and so has a significant effect on clogging time.

The clogging time is linearly related to both grain size a and reaction rate k , and so the unfavorable scenario of 20 times greater grain size and 10 times slower reaction rate, increases expected clogging time by a factor of 200. Thus, our model predicts that in the unfavorable scenario clogging is not relevant to our proposed time span.

When accounting for potential pore clogging, we thus notice that there are two competing effects at play. A smaller grain size exposes relatively more of the olivine to the CO_2 reactant and so causes less armoring, making less volume necessary to ensure high drawdown levels. However, the fast reaction – together with less initial pore space from tighter packing of the grain – also makes the pore space clog much faster, implying that over time additional host rocks would have to be found and new injection processes initiated. With a clogging time of 37.5 years for $n = 3$, the calculated volume in the ideal scenario would need to be increased by a factor of 1/3, giving us an area of 141 x 141 km. For the unfavorable scenario, on the other hand, no clogging will occur on any reasonable timescale.

2.3.4 CO₂ injection and induced seismicity

Turning to the much-debated risk of induced seismicity, the earlier literature review demonstrated that the mechanisms through which fluid injection can trigger seismicity raise major concerns regarding the CO₂ storage safety associated with CCS technologies. In this section we build on Yarushina and Bercovici's work suggesting that mineral carbonation can eliminate the risk of brittle failure by preventing local stresses at the grain contacts from satisfying the Mohr-Coulomb friction law that causes seismic slip. While the CO₂ injection decreases normal stress, the precipitation reaction causes a gradual increase in grain-grain contact area, which ensures a simultaneous reduction of both local normal and shear stresses. Thus, we can find a critical pumping rate under which seismic triggering can be avoided.

For a reservoir of normal contact stress $\tilde{\sigma}_n$ and local shear stress $\tilde{\tau}$, we have Mohr circle and failure envelope given by

$$y^2 + (p_f - \tilde{\sigma}_n)^2 = \tilde{\tau}^2 \quad \text{and} \quad y = \mu p_f,$$

where μ is the friction coefficient and p_f is total fluid pressure, which is assumed to increase monotonically through the function $p_f = p_i + Qt$, where p_i is initial fluid pressure and Q is the pumping rate.

Failure is present in cases when the Mohr circle intersects the failure envelope, i.e. when

$$(\mu p_f)^2 + (p_f - \tilde{\sigma}_n)^2 = \tilde{\tau}^2$$

for which the solutions are given by

$$p_f = \frac{\tilde{\sigma}_n \pm \sqrt{\tilde{\sigma}_n^2 - (1 + \mu^2)(\tilde{\sigma}_n^2 - \tilde{\tau}^2)}}{(1 + \mu^2)} \quad (13)$$

However, in order to find the point at which failure is just triggered, we want to find the values for which the Mohr circle is tangent to the failure envelope. This only occurs when the Mohr circle touches the failure line at one point, which requires that the radicand in the equation for p_f above is zero, i.e.

$$\tilde{\sigma}_n^2 - (1 + \mu^2)(\tilde{\sigma}_n^2 - \tilde{\tau}^2) = 0, \text{ for which we get}$$

$$\tilde{\sigma}_n = \pm \frac{\sqrt{1 + \mu^2}}{\mu} \tilde{\tau} \quad (14)$$

For normal and shear stresses, the force balance between the applied and contact stresses requires that

$$4a^2(\sigma_n - p_f) = \pi(R^2 - a^2)(\tilde{\sigma}_n - p_f) \text{ and } 4a^2\tau = \pi(R^2 - a^2)\tilde{\tau} \quad (15)$$

Combining equations (14) and (15) gives

$$p_f = \frac{\alpha}{(\alpha-1)} \sigma_n - \frac{\alpha}{(\alpha-1)} \frac{\sqrt{1+\mu^2}}{\mu} \tau, \text{ where } \alpha = \frac{4a^2}{\pi(R^2-a^2)}$$

Thus we get

$$t = \frac{p_f - p_i}{Q} = \frac{1}{Q} \left(\frac{\alpha}{(\alpha-1)} \sigma_n - \frac{\alpha}{(\alpha-1)} \frac{\sqrt{1+\mu^2}}{\mu} \tau - p_i \right) \quad (16)$$

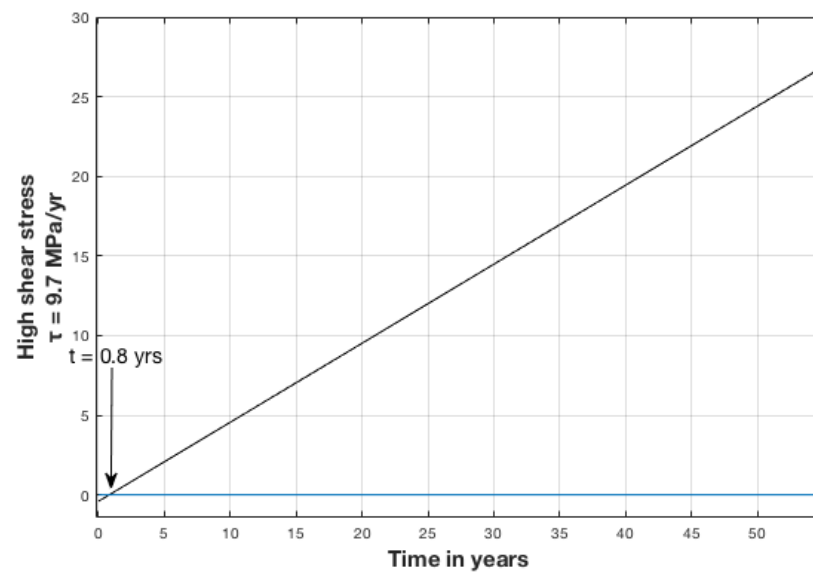
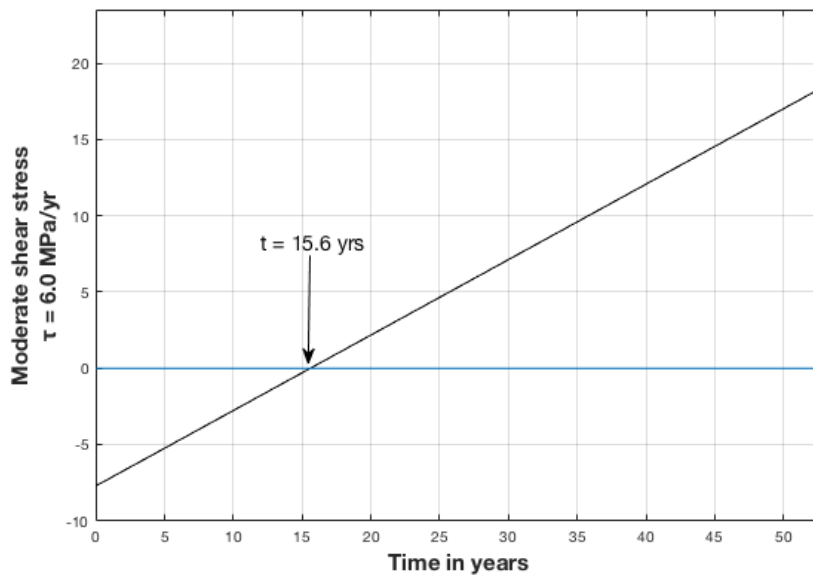
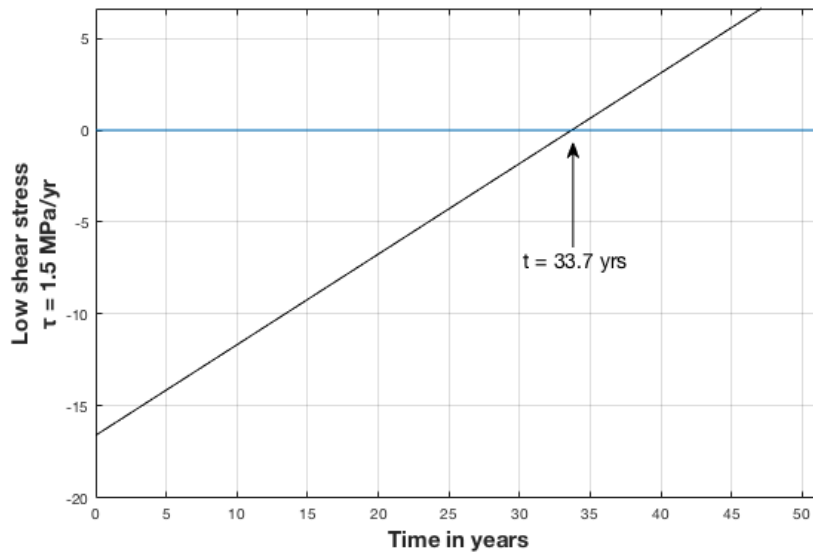
For any given set of reaction conditions, we can use equation (16) to find the time t for which seismicity is triggered. All calculations assume lithostatic stress $\sigma_n = 35 \text{ MPa}$, and initial fluid pressure $p_i = 16 \text{ MPa}$. This corresponds to an injection at approximately 1.2 km depth into rock of density 2.95 g/cm^3 , saturated with slightly over-pressured fluid of density 1.02 g/cm^3 (Yarushina & Bercovici 2013). As calculated earlier, clogging occurs after 37.5 years in the ideal scenario. We assume pumping rate $Q = 0.5 \text{ MPa/yr}$, to ensure that the final fluid pressure after 37.5 years does not exceed the lithostatic stress.

While our model assumes that the carbonation rates do not depend on the pumping rate, but instead solely require that the grains be surrounded by

abundant CO₂ at any point, a high injection pressure is needed to feed the CO₂ fluid into the pore space. Given a pumping rate of $Q = 0.5$ MPa/yr, we then calculate the time to failure in the ideal and the unfavorable scenarios, for low, moderate and high shear stresses.

For the ideal scenario, the fast reaction rate and the relatively greater amount of olivine exposed to the CO₂ reactant from smaller grain size ensures that the failure condition is never satisfied in either of the three stress cases. Thus, clogging becomes the only limiting factor for fluid injection over time.

For the unfavorable scenario, on the other hand, failure becomes a limiting factor for our CO₂ drawdown scenario. The plots below show that for all three investigated shear stress cases, ranging from low to high shear stress, the failure condition is reached within our 50-year time span, albeit at different times.



- In the low shear stress case ($\tau = 1.5 \text{ MPa/yr}$), failure occurs at 33.7 years
- In the moderate shear stress case ($\tau = 6 \text{ MPa/yr}$), failure occurs at 15.6 years
- In the high shear stress case ($\tau = 9.7 \text{ MPa/yr}$), failure occurs at 0.8 years

While we note that the high-stress scenario causes seismic triggering almost immediately, this case is less relevant, since a location with high shear stress (e.g. a fault zone) would not be selected for carbon storage. However, the estimated failure times in the low and moderate shear stress cases will have implications for our earlier calculations of volume required for CO₂ drawdown to match emissions for the next 50 years. If we assume that the above pumping rate of $Q = 0.5 \text{ MPa/yr}$ is required in order to feed the fluid into the pore space, then it follows that the volume would have to increase in order for CO₂ drawdown match 50 years worth of emissions before failure occurs. Thus, our revised calculations become:

$$\frac{\pi}{2} f \rho V k a^{n-3} \int_0^{\text{failure time}} \left((a^{n+1} + b^n (n+1) k t)^{\frac{2-n}{n+1}} \right) dt = \dot{M}_e T$$

- Unfavorable scenario ($a = 1 \text{ cm}$, $k = 44 \times 10^{-13} \text{ cm/s}$, $n = 3$) and low shear stress ($\tau = 1.5 \text{ MPa/yr}$) gives a total volume of 1,656,136 km³, which assuming a 500 m depth gives an area of 1820 x 1820 km.
- Unfavorable scenario ($a = 1 \text{ cm}$, $k = 44 \times 10^{-13} \text{ cm/s}$, $n = 3$) and moderate shear stress ($\tau = 6 \text{ MPa/yr}$) gives a total volume of 3,573,231 km³, which assuming a 500 m depth gives an area of 2673 x 2673 km.

While the two scenarios we have chosen to investigate are on each end of the k/a spectrum, there will be combinations of reaction rate, grain size and shear stress conditions that create so-called “boundary cases,” for which failure happens right before the mineralization picks up and increases the grain-grain contact area. In these cases, a faster reaction rate can either merely postpone the failure by some time, thus having only a small impact on the time of failure, or it can enable us to avoid seismic triggering altogether, thus offering a large benefit.

Modeling the stress state for a given reaction scenario can thus be valuable to evaluate whether it would be worth improving reaction conditions in order to avoid hitting the failure condition altogether.

2.3.5 Discussion of results

The above calculations have shown that in the 50-year drawdown scenario, injection restrictions are imposed in both the ideal and unfavorable scenarios, by clogging and seismic triggering respectively. In addition to implying that additional volume is needed for CO₂ drawdown to match emissions over 50 years, it presents us with two alternatives: the required volume increase can either be done by (1) increasing initial reservoir volume, or (2) dividing the CO₂ storage into several separate operations, where for example a new injection operation is started as the previous one becomes limited by clogging/failure. While increasing initial volume to enable all the CO₂ to be drawn down in one large operation is likely to reduce some of the costs associated with project initiation (see the earlier discussion on high fixed initial costs due to hydrofracturing and heating of the rock, but low variable costs associated with mineral carbonation, since the exothermic heat output makes the reaction self-sustaining – Kelemen & Matter 2008), it also implies that more of the CO₂ drawdown would have to happen through negative emissions, for which the associated CO₂ capturing is often more costly (see the earlier discussion on capturing CO₂ from ambient air – Lackner et al. 2012 – and the proposed CCS technology of creating negative emissions through seawater convection – Kelemen & Matter 2008). A cost-benefit analysis should therefore be carried out in order to decide which alternative is preferred.

Equation (16) would also enable us to plot the pumping rate for which the Mohr-Coulomb friction law is just satisfied with respect to time t , i.e. the “critical pumping rate” for which failure is just triggered. By knowing the critical pumping rate for any time t , we could theoretically tune the pumping rate to avoid failure, effectively making clogging the only physical upper limit on how long fluid can be pumped into the reservoir. Additionally, by riding along the failure envelope we could potentially maintain a sustained low level of fracturing, which would keep armoring down. Indeed, Kelemen and Hirth have found that

the volume change from hydration and carbonation can cause a positive feedback effect of fracture formation, which maintains or increases permeability and reactive surface area (Kelemen & Hirth 2012). However, the potential of riding along the failure envelope is indeed highly hypothetical, and extensive knowledge of the rock stresses would be required to prevent the fracturing from escalating, which could threaten the seal integrity of the reservoir.

In conclusion, our calculations show that limitations imposed by both clogging and induced seismicity require an increase in the initially estimated reservoir volume, although these limiting factors depend on the reaction conditions and do not necessarily coincide. In fact, the rapid carbonation in our idealized scenario results in rapid clogging, but eliminates the risk of induced seismicity at our selected pumping rate. On the other hand, an unfavorable scenario need not be concerned with a risk of clogging, but rather seismic triggering, with failure time depending on the reservoir shear stresses.

By investigating what we consider reasonable lower and upper boundaries for combinations of carbonation reaction rates and initial grain size, we find that required volume for CO₂ drawdown to match global emissions over a 50-year time period varies from roughly 10,000 km³ to 3.6 million km³ for reaction rate slowdown exponent $n = 3$. Kelemen and Matter estimated that the Semail ophiolite in Oman contains around 5×10^{16} kg of peridotite within 3 km of the surface, which given peridotite's density of around 3.3 g/cm³ corresponds to a volume of roughly 15,000 km³. Thus, our calculations suggest that under ideal reaction conditions the Semail ophiolite itself would be sufficient to draw down 50 years worth of global CO₂ emissions. Kelemen et al. estimated that total global continental mass of peridotite in ophiolites amounts to up to 10^{18} kg, which corresponds to a volume of roughly 300,000 km³. In other words, the amount of continental peridotite would not be nearly enough to draw down the CO₂ under unfavorable reaction conditions.

2.4 Conclusion

The last decades have seen an unprecedented rise in atmospheric CO₂ levels, and scientists have clearly established the mechanisms through which rising CO₂ levels can have devastating effects on Earth's climate. Yet, scaling up

carbon-free energy sources have proven difficult, and caused an increasing realization that CCS technology will likely have to play a key role if we are to reduce anthropogenic climate change. The enormous amount of mafic rock present at or near the Earth's surface gives mineral carbonation a huge CO₂ storage potential, and the technology is gaining increasing attention as concerns regarding induced seismicity and leakage from regular structural CO₂ storage have mounted.

In this paper we developed a simple model with which to study the drawdown of CO₂ through mineral carbonation. While the model is theoretical and simplifies the effects of various factors at play in real-life settings, it can still provide valuable insight into some of the conditions affecting the potential for mineral carbonation. We chose the hypothetical example of CO₂ drawdown matching current global emissions for the next 50 years and estimated the volume of peridotite needed, exploring a wide range of reaction conditions. We began by calculating the volume needed for drawdown to match emissions at $t = 0$, and then investigated the additional volume needed to account for several limiting factors over time: armoring, reservoir clogging and seismic triggering. Our calculations found that variation in the adjustable parameters reaction rate, initial grain size and reaction rate slowdown exponent all significantly affect the volume of reservoir rock required, both directly by affecting carbonation rates and indirectly through their effects on clogging and seismic triggering.

In an idealized scenario of fast reaction rate and small grain size, rapid clogging raises amount of volume necessary, but the estimated volume of $\sim 10,000 \text{ km}^3$ is still small enough for the Semail ophiolite to theoretically draw down all the CO₂. An unfavorable drawdown scenario of slow reaction rate and large grain size will not be limited by reservoir clogging, but rather from the risk of seismic triggering – both in cases of low, moderate and high shear stress. The estimated volume of ~ 3.6 million km^3 in the moderate shear stress case in fact exceeds estimates of continental mass of peridotite, illustrating the unfeasibility of implementing large-scale mineral carbonation storage under these reaction conditions. Yet, our model confirms that with the right reaction conditions mineral carbonation in peridotite exhibits an enormous potential for CO₂ storage.

Bibliography

- Andreani, M., Luquot, L., Gouze, P., Godard, M., Hoisé, E., B. Gibert, B. (2009). "Experimental Study of Carbon Sequestration Reactions Controlled by the Percolation of CO₂-Rich Brine through Peridotites." *Environmental Science & Technology*, 43 (4), 1226-1231, doi: 10.1021/es8018429
- Arts, R. J., Chadwick, A., Eiken, O., Thibeau, S., Nooner, S. (2008). "Ten years' experience of monitoring CO₂ injection in the Utsira Sand at Sleipner, offshore Norway." *First Break*, 26(1)
- Benson, S.M., Bennaceur, K., Cook, P., Davison, J., Coninck, H. de, Farhat, K., Ramirez, C.A., Simbeck, D., Surlis, T., Verma, P., Wright, I. (2012). "Global Energy Assessment - Toward a Sustainable Future." Cambridge University Press, Cambridge, United Kingdom, pp. 993 - 1068
- British Petroleum (2015), "BP Statistical Review of World Energy June 2015."
- Department of Energy – Office of Fossil Fuels. "Enhanced Oil Recovery."
<http://energy.gov/fe/science-innovation/oil-gas-research/enhanced-oil-recovery>
- Dessert, C., Dupre, B., Gaillardet, J., Francois, L., Allègre, C. (2003). "Basalt weathering laws and the impact of basalt weathering on the global carbon cycle." *Chemical Geology*, 202(3-4), 257-273, doi: 10.1016/j.chemgeo.2002.10.001.
- Ellsworth, W. (2013). "Injection-induced earthquakes." *Science*, 341(6142), doi: 10.1126/science.1225942.
- Gibbins, J., Chalmers, H. (2008). "Carbon capture and storage." *Energy Policy*, 32(12), 4317–4322.
- Gilfillan, S., Lollar, B., Holland, G., Blagburn, D., Stevens, S., Schoell, M., Cassidy, M., Ding, Z., Zhou, Z., Lacrampe-Couloume, G., Ballentine, C. (2009). "Solubility trapping in formation water as dominant CO₂ sink in natural gas fields." *Nature*, 458, 614-618, doi: 10.1038/nature07852
- Gislason, S., Broecker, W.S., Gunnlaugsson, E., Snæbjörnsdóttir, S., Mesfin, K.G., Alfredsson, H.A., Aradóttir, E.S., Sigfusson, B., Gunnarsson, I., Stute, M., Matter, J.M., Arnarson, M.Th., Galeczka, I.M., Gudbrandsson, S., Stockman, G., Wolff-Boenisch, D., Stefansson, A., Ragnheidardóttir, E., Flaathen, T., Gysi, A.P., Olssen, J., Didriksen, K., Stipp, S., Menez, B., Oelkers, E.H. (2014). "Rapid solubility and mineral storage of CO₂ in basalt." *Energy Procedia*, 63, 4561-4574, doi: 10.1016/j.egypro.2014.11.489
- Global CCS Institute (2011). "Economic Assessment of Carbon Capture and Storage Technologies: 2011 Update."
- Global CCS Institute. "Sleipner CO₂ Storage Project."
<http://www.globalccsinstitute.com/projects/sleipner%20co2-storage-project>
- Global CCS Institute. "Snøhvit CO₂ Storage Project."
<https://www.globalccsinstitute.com/projects/snøhvit-co2-storage-project>

- Goldberg, D., Lackner, K. (2015). "Creating negative emissions at remote CO₂ sequestration sites." *Greenhouse Gases Science & Technology*, 5, 230-240, doi: 10.1002/ghg.1489.
- Hand, E. (2014). "Injection Wells Blamed in Oklahoma Earthquakes," *Science*, 345(6192), 13-14, doi: 10.1126/science.345.6192.13.
- Hangx, S., Spiers C.J. (2009). "Coastal spreading of olivine to control atmospheric CO₂ concentrations: a critical analysis of viability." *International Journal of Greenhouse Gas Control*, 3(6), 757-767, doi: 10.1016/j.ijggc.2009.07.001.
- Healy, J. H., Rubey, W. W., Griggs, D. T., Raleigh, C. B., (1968). "The Denver Earthquakes: Disposal of waste fluids by injection into a deep well has triggered earthquakes near Denver, Colorado," *Science*, 161(3848).
- International Energy Agency (2012). "Energy technology perspectives 2012: pathways to a clean energy system."
- IEAGHG (2013). "Induced Seismicity and its implications for CO₂ storage risk." International Energy Agency Greenhouse Gas R&D Programme.
- IPCC (2013). "Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change," Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp, doi: 10.1017/CBO9781107415324.
- Johnson, J., Nitao, J., Knauss, K. (2004). "Reactive transport modelling of CO₂ storage in saline aquifers to elucidate fundamental processes, trapping mechanisms and sequestration partitioning." *Geological Society, London, Special Publications*, 233, 107-128, doi: 10.1144/GSL.SP.2004.233.01.08
- Juanes, R., Hager B. H., Herzog, H. (2012). "No geologic evidence that seismicity causes fault leakage that would render large-scale carbon capture and storage unsuccessful," *Proceedings of the National Academy of Sciences of the United States of America*, 109(52), E3623, doi: 10.1073/pnas.1215026109
- Kelemen, P. B., Hirth, G. (2012). "Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation," *Earth and Planetary Science Letters*, 345, 81-89.
- Kelemen, P. B., Matter, J. (2008). "In situ carbonation of peridotite for CO₂ storage," *Proceedings of the National Academy of Sciences of the United States of America*, 105(45), 17295-17300, doi: 10.1073/pnas.0805794105
- Kelemen, P. B., Matter, J., Streit, E., Rudge, J., Curry, W., Blusztajn, J. (2011). "Rates and Mechanisms of Mineral Carbonation in Peridotite: Natural Processes and Recipes for Enhanced, in situ CO₂ Capture and Storage," *Annual Review of Earth and Planetary Sciences*, 39, 545-576, doi: 10.1146/annurev-earth-092010-152509
- Keller, G. R., Holland, A. (2013). "Oklahoma Geological Survey evaluation of the Prague earthquake-sequence of 2011," *Oklahoma Geological Survey*.

- Keranen, K. M., Savage, H., Abers, G., Cochran, E. (2013). "Potentially induced earthquakes in Oklahoma, USA: Links between wastewater injection and the 2011 M_w 5.7 earthquake sequence," *Geology*, 41(6), 699-702,
- Keranen, K. M., Weingarten, M., Abers, G., Bekins, B., Ge, S. (2014). "Sharp increase in central Oklahoma seismicity since 2008 induced by massive wastewater injection," *Science*, 345(6195), 448-451, doi: 10.1126/science.1255802.
- Kling, G. W., Clark, M. A., Wagner, G. N., Compton, H. R., Humphrey, A. M., Devine, J. D., Evans, W. C., Lockwood, J. P., Tuttle, M. L., Koenigsberg, E. J. (1987). "The 1986 Lake Nyos gas disaster in Cameroon, West Africa." *Science*, 236(4798), 169-75.
- Krevor, S.C., Graves, C., Van Gosen, B., McCafferty, A. (2009). "Mapping the mineral resource base for mineral carbon-dioxide sequestration in the conterminous United States," *U.S. Geological Survey Digital Data Series 414*, 14 p.
- Lackner, K.S., Wendt, C., Butt, D., Joyce, E., Sharp, D. (1995). "Carbon dioxide disposal in carbonate minerals," *Energy*, 20(11), 1153-1170, doi: 10.1016/0360-5442(95)00071-N.
- Lackner, K. S., Brennan, S., Matter, J. M., Park, A.-H. A., Wright, A., & van der Zwaan, B. (2012). "The urgency of the development of CO₂ capture from ambient air." *Proceedings of the National Academy of Sciences of the United States of America*, 109(33), 13156-13162. <http://doi.org/10.1073/pnas.1108765109>
- Le Quéré, C, et al. (2015). "Global Carbon Budget 2015," Global Carbon Project, *Earth System Science Data*, doi: 10.5194/essd-7-349-2015
- Matter, J. M., Kelemen, P. B. (2009). "Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation," *Nature Geoscience*, 2, 837-841. doi:10.1038/ngeo683
- Mazzotti M, Abanades, JC, Allam, R, Lackner, K.S., Meunier, F. (2005). "Mineral carbonation and industrial uses of CO₂." In *IPCC Special Report on Carbon Dioxide Capture and Storage*, ed. B Metz, O Davidson, H de Coninck, M Loos, L Meyer, Cambridge Univ. Press, Cambridge, United Kingdom, pp. 319-38.
- MIT Carbon Sequestration Initiative (2016). "Weyburn-Midale Fact Sheet: Carbon Dioxide Capture and Storage Project." <https://sequestration.mit.edu/tools/projects/weyburn.html>
- National Research Council (2012). "Induced Seismicity Potential in Energy Technologies," The National Academies Press, Washington, D.C.
- Nicol, A., Carne, R., Gerstenberger, M., Christophersen, A. (2011). "Induced seismicity and its implications for CO₂ storage risk," *Energy Procedia*, 4, 3699-3706, doi: 10.1016/j.egypro.2011.02.302
- Ragnheidardottir, E., Sigurdardottir, H., Kristjansdottir, H., Harvey, W. (2011). "Opportunities and challenges for CarbFix: An evaluation of capacities and costs for the pilot scale mineralization sequestration project at Hellisheidi, Iceland and beyond," *International Journal of Greenhouse Gas Control*, 5(4), 1065-1072, doi: :10.1016/j.ijggc.2010.11.010

Rayleigh, C.B., Healy, J. H., Bredehoeft, J. D. (1976). "An experiment in earthquake control at Rangely, Colorado," *Science*, 191(4233), 1230-1237.

Saldi, G. D., Schoot, J., Pokrovsky, O., Gautier, Q., Oelkers, E. (2012). "An experimental study of magnesite precipitation rates at neutral to alkaline conditions and 100–200 °C as a function of pH, aqueous solution composition and chemical affinity." *Geochimica et Cosmochimica Acta*, 83, 93-109, doi: 10.1016/j.gca.2011.12.005

Seifritz, W. (1990). "CO₂ disposal by means of silicates." *Nature*, 345(6275), 486, doi: 10.1038/345486b0

Schuling R.D., Krijgsman P. (2006). "Enhanced weathering: an effective and cheap tool to sequester CO₂." *Climate Change*, 74(1), 349–354,

Torp, T. A., Brown, K. R. (2004). "CO₂ underground storage costs as experienced at Sleipner and Weyburn." In *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7)*, 531-540.

van der Zwaan, B., Smekens, K. (2009). "CO₂ Capture and Storage with Leakage in an Energy-Climate Mode." *Environmental Modeling & Assessment*, 14(2), 135- 148.

Verdon, J. P., Kendall, J. M., Stork, A. L., Chadwick, A., White, J., Bissell, R. (2013). "Comparison of geomechanical deformation induced by megatonne-scale CO₂ storage at Sleipner, Weyburn, and In Salah," *Proceedings of the National Academy of Sciences of the United States of America*, 110(30), E2762-E2771. doi: 10.1073/pnas.1302156110

Verdon, J. (2014). "Significance for secure CO₂ storage of earthquakes induced by fluid injection." *Environmental Research Letters*, 9, 064022, doi: 10.1088/1748-9326/9/6/064022

Vilarrasa, V., Carrera, J. (2015). "Geologic carbon storage is unlikely to trigger large earthquakes and reactivate faults through which CO₂ could leak," *Proceedings of the National Academy of Sciences of the United States of America*, 112(19), 5938-5943, doi: 10.1073/pnas.1413284112

Weir, G. J., White, S. P., Kissling, W. M. (1995). "Reservoir storage and containment of greenhouse gases." *Energy Conversion and Management*, 36(6-9), 531-534, doi: 10.1016/0196-8904(95)00060-Q.

White, J. A., Chiaramonte, L., Ezzedine, S., Foxall, W., Hao, Y., Ramirez, A., McNab, W. (2014). "Geomechanical behavior of the reservoir and caprock system at the In Salah CO₂ storage project," *Proceedings of the National Academy of Sciences of the United States of America*, 111(24), 8747-52. doi: 10.1073/pnas.1316465111

Yarushina, V., Bercovici, D. (2013). "Mineral carbon sequestration and induced seismicity," *Geophysical Research Letters*, 40(5), 814-818, doi: 10.1016/j.ijggc.2010.11.010

Zoback, M. (2012). "Managing the seismic risk posed by wastewater disposal." *Earth Magazine*.

Zoback, M., Gorelick, S. (2012). "Earthquake triggering and large-scale geologic storage of carbon dioxide," *Proceedings of the National Academy of Sciences of the United States of America*, 109(26), 10164-68, doi: 10.1073/pnas.1202473109