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"Neutralizing Carbonic Acid in Deep Carbonate Strata below the North Atlantic"

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Abstract: Our research is aimed at investigating several technical issues associated with carbon dioxide sequestration in calcium carbonate sediments below the sea floor through laboratory experiments and chemical transport modeling. Our goal is to evaluate the basic feasibility of this approach, including an assessment of optimal depths, sediment types, and other issues related to site selection. Through laboratory and modeling efforts, we are studying the flow of liquid carbon dioxide and carbon dioxide-water mixtures through calcium carbonate sediments to better understand the geomechanical and structural stability of the sediments during and after injection. Our modeling efforts in the first year show that the idea is feasible, but requires more sophisticated analysis of fluid flow at high pressure in deep sea sediments. In addition, we are investigating the kinetics of calcium carbonate dissolution in the presence of CO_2 -water fluids, which is a critical feature of the system as it allows for increased permeability during injection. Our experimental results from the first year of work have shown that the kinetics are likely to be fast enough to create dissolution which will affect permeability. However, additional experiments are needed at high pressures, which will be a focus for years 2 and 3. We are also investigating the possibility of carbon dioxide hydrate formation in the pore fluid, which might complicate the injection procedure by reducing sediment permeability but might also provide an upper seal in the sediment-pore fluid system, preventing release of CO_2 into the deep ocean, particularly if depth and temperature at the injection point rule out immediate hydrate formation. Finally, we are in the beginning stages of an economic analysis to estimate costs of drilling and gas injection, site monitoring as well as the availability of potential disposal sites with particular emphasis on those sites that are within the 200-mile economic zone of the United States.

Introduction:

Our research is aimed at investigating several technical issues associated with carbon dioxide sequestration in calcium carbonate sediments below the sea floor through laboratory experiments and chemical transport modeling. Our goal is to evaluate the basic feasibility of this approach, including an assessment of optimal depths, sediment types, and other issues related to site selection. Through laboratory and modeling efforts, we are studying the flow of liquid carbon dioxide and carbon dioxide-water mixtures through calcium carbonate sediments to better understand the geomechanical and structural stability of the sediments during and after injection. In addition, we are investigating the kinetics of calcium carbonate dissolution in the presence of CO_2 -water fluids, which is a critical feature of the system as it allows for increased permeability during injection. We are also investigating the possibility of carbon dioxide hydrate formation in the pore fluid, which might complicate the injection procedure by reducing sediment permeability but might also provide an upper seal in the sediment-pore fluid system, preventing release of CO_2 into the deep ocean, particularly if depth and temperature at the injection point rule out immediate hydrate formation. Finally, we are performing an economic analysis to estimate costs of drilling and gas injection, site monitoring as well as the availability of potential disposal sites with particular emphasis on those sites that are within the 200-mile economic zone of the United States.

This project is a collaboration between Dan Schrag and his group at Harvard University and Klaus Lackner and his group at Columbia University. In addition, there are several other collaborators, including Charles Harvey, Professor of Hydrology at MIT, who is playing a critical role in the project, and Bruce Watson from RPI who is working with the group on some high pressure experiments, also critical to our research plan. A rebudgeting request is being submitted separately report that will include small subcontracts to MIT for Prof. Harvey and to RPI for Prof. Watson.

RESULTS AND DISCUSSION: YEAR 1

In the first year of the project, both the Harvard group and the Columbia group have made substantial progress towards their individual goals, with substantial interaction along the way. Years 2 and 3 will see a growing synthesis of the experimental efforts at Columbia with the modeling studies at Harvard, coupled with the assistance of efforts at MIT and RPI. The most significant accomplishments of the first year was the development at Harvard of a simple model for CO2 injection into deep sea sediments that puts bounds on the extent of carbonate dissolution. The major results are that we now believe that carbonate dissolution will be an important effect in increasing the permeability of the sediment but there will be no karstification, and thus no danger of collapse of sediment and release of CO2 into the ocean. In addition, our physical models suggest that once injected into the sediment, the high-pressure carbon dioxide will slowly penetrate deeper in the sediment column, and will remain sequestered from the deep ocean for at least 100,000 years. This is an exciting result, and will be tested with additional work using 3-dimensional fluid flow models through collaboration with Charles Harvey at MIT. In addition, we are developing a collaboration with Schlumberger, which is moving their main research laboratory from Ridgefield, Connecticut to Cambridge, Massachusetts.

A major logistical goal for the first year of the project was successfully recruiting top graduate students and post-docs to work on the project. This has been accomplished. Dan Schrag now has two graduate students, one from Earth and Planetary Sciences, and one from the John F. Kennedy School of Government (who is studying the economics of this sequestration approach). In addition, Schrag has also recruited David Thompson, a post-doc who recently completed his Ph.D. in physics, who will also work on the project.

During the first year, we developed some simple box models to understand the behavior of the system and try to quantify the total amount of chemical reaction between CO_2 saturated pore-fluid and carbonate sediment. The application of these simple models led to some very important insights that are determining the immediate priorities of the project. First, a potential concern for long-term stability of the deposit was a concern on our original conception of the project, as we were concerned about the possibility of large scale leaching that might leave behind brine filled caverns that – as their content is naturally buoyant relative to the surrounding rock – would raise questions of geomechanical stability (Nunn and Meulbroek 2002). However, our calculations using our simple models have shown that such karstification is impossible during CO_2 injection because the system is essentially water limited. As CO_2 is injected at a pressure greater than 30 MPa, approximately 5% of the CO_2 will dissolve in the pore fluid. This means that for a given volume of CO_2 injected into the pore fluid, complete dissolution requires interaction with pore fluid in 20 times the pore volume – which requires substantial time for fluid flow to occur. Even after dissolution has occurred, only 3 to 5% of the host rock would actually dissolve – which is important for permeability during injection, but is not enough to create large caverns. This means that the benefits of carbonate dissolution (i.e., increased permeability) come without the risks of karst collapse and CO_2 escape. The modeling has also led to a refinement of our original idea for sequestration. A manuscript on discussing these ideas has been submitted for publication to the Proceedings of the National Academy of Sciences; a draft of this manuscript is attached to the end of this report.

We have also accomplished an intensive analysis of available core and borehole data from the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP). The data search was geographically limited to the western Atlantic, within 200 miles of the U.S. coastline. A database was developed and all available logs and key geochemical data from existing DSDP and ODP sites were included. The reservoir data comprise depth below seafloor, thickness of geologic units, lithology, carbonate content, porosity, bulk density, natural gamma ray, and resistivity. Based on this data survey we identified 16 sites, and approximately 30 geological units at these sites that may be used as future potential target layers for CO_2 disposal. Formation permeability data is missing at all of these sites. We have submitted a sample request to IODP to access plug samples for permeability, porosity and density testing. This data survey reveals that certain key data, such as formation permeability is missing. For this type of survey we will restrict sampling to 2 to 3 representative sites. Based on the database we are able to give an accurate petrophysical and geochemical description of a potential U.S. offshore, east coast CO_2 disposal sites. We can define the reservoir size, the fraction of the reservoir that can be used for sequestration and its accessibility by drilling. This information

will finally be incorporated into a basic economic analysis for deep-sea carbonate sequestration.

The main objective of the experimental program was to examine the reaction kinetics of deep sea carbonates in simulated brines of varying ratios of water and CO_2 as a function of P_{CO2}, temperature, pressure and rock characteristics (permeability, porosity, mineralogy and density). In addition, we study induced changes of the physical and chemical structure of the rock samples due to the neutralization reaction of carbonic acid. In the first year of the project we built (at Columbia) a flow-through system that can be used to perform dissolution experiments on core plugs. The system is not designed for high pressure and temperature. However, we have run low-pressure and low-temperature experiments in the first year of this project, followed by high-pressure (supercritical CO_2) experiments in the second and third year of the project. The collaborative efforts with Bruce Watson at RPI, who has extensive experience with high pressure experiments, will be very important in this effort.

With the low-pressure system we accomplished a series of flow-through experiments to acquire needed information on kinetics, permeability and porosity interrelationships. The experiments were run with carbonic acid and maleic acid and with core plugs from Cretaceous North Sea Chalk and Mississipian chalk. The North Sea chalk samples are used as a high-carbonate content endmember ($CaCO_3 > 80\%$), whereas the Mississipian chalk is the low-carbonate endmember ($CaCO_2 < 50\%$). The maleic acid was used as a carbonic acid proxy to simulate higher partial CO_2 pressures (10 to 100 bar). Dissolution rates of North Sea chalk as well as for the Mississipian chalk were calculated based on the calcium release, and changes in permeability and porosity were measured. Surprisingly, the permeability of the North Sea chalk samples decreased during the experimental run, although a small increase in the porosity occurred. This is inconsistent to what we expected and needs further research. We also observed the formation preferential flowpaths (i.e. wormholes) inside the chalk plugs during the flow-through experiments. The formation of wormholes has huge implications on fluid flow and transport in low-permeability deep-sea carbonates and therefore on CO_2 sequestration within these rocks. Their formation can significantly increase the permeability of deep-sea carbonates and results in "fingering" of the injected fluid. Further research in wormhole building is on-going.

In the coming months, we will conduct several series of long-term flow-through experiments with supercritical CO_2 in a high-pressure apparatus. The objective of these experiments is to simulate CO_2 injection and to study CO_2-water-rock reactions under in-situ conditions. Similarly to the low-pressure experiments we will perform these experiments on North Sea chalk and Mississipian chalk plugs. We plan to perform these types of experiments at the Schlumberger-Doll Research Laboratory in Ridgfield, Connecticut.

Research Plan for Years 2 and 3:

From the insights gained during Year 1, we have formulated a research plan for the second and third years that consists of five parallel research efforts, with many linkages between them. Our goal in these different efforts is to understand the short-term (i.e., injection time scale) behavior of CO_2 in deep sea carbonate sediments, the long-term behavior of the system (i.e., hundreds to million sof years), and the approximate cost from various regions in the U.S.

Numerical modeling of CO_2 injection: We are working right now on developing a deeper understanding of CO_2 flow at pressure and temperature in deep sea sediments using numerical codes of fluid flow in porous media. For this effort, we are establishing a collaboration with Schlumberger, as they have recently moved their research laboratory from Ridgefield, Connecticut to Cambridge, Massachusetts, and have extensive experience with this type of modeling. We will use the industry codes to study the physical behavior of the three fluids involved (CO_2 liquid, pore fluid, and CO_2 -saturated pore-fluid), and how the plume will migrate in the sediment column. However, some additional programming will be required to simulate chemical interactions connect with permeability changes. We are working on a variety of strategies to accomplish this, and we expect we will begin this effort in Year 3. Overall, the fluid-flow modeling will be useful in studying bit the behavior of the system during injection and also the long term fate of the repository. However, the chemical reactions will be especially important on these longer timescales.

Scaled experiments of CO_2 migration: Although the numerical codes we are using are well-tested by industry, the behavior of the low-viscosity CO_2 liquid in a higher viscosity pore fluid system at low temperature and high pressure is not well understood. Therefore, to complement the numerical modeling, we will perform a series of scaled experiments in Years 2 and 3 to try and understand the rates of migration of fluids over longer time scales. This effort will represent a major portion of the Ph.D. research of graduate student Kurt House, and will be done in collaboration Schrag and with Prof. Charles Harvey at MIT. Prof. Harvey has experience in these types of experiments, and also has access to several large centrifuges which are required for accelerating these experiments in the time domain.

Continued measurements of kinetics of carbonate dissolution: Over the next two years, we will extend the experiments measuring the kinetics of reaction between carbonic acid and calcium carbonate sediment to temperatures and pressures appropriate for the injection site. We will conduct several series of long-term flow-through experiments with CO_2 in a high-pressure apparatus. These experiments will be carried out at Columbia University. In addition, we will use stable isotopic tracers to refine the kinetic rate measurements, making measurements at the mass spectrometry facility at Harvard. The objective of these experiments is to simulate CO_2 injection and to study CO_2-water-rock reactions under in-situ conditions. Similarly to the low-pressure experiments we will perform these experiments on North Sea chalk and Mississipian chalk plugs, measuring the impact on porosity and permeability. We plan to perform these types of experiments at the Schlumberger-Doll Research Laboratory in Ridgfield, Connecticut.

Geologic and Economic Analysis of Deep Sea Carbonate Sequestration: In the next two years, we will follow up on our study of ocean drilling program cores, using detailed measurements of temperature, pore fluid chemistry, sedimentology, and various physical properties (porosity, grain size, etc.) to assess where the best sites for this type of sequestration are located. Already, we have identified several locations in the North Atlantic, within 200 miles of the U.S. coastline that would be ideal for this type of storage. We are also working with colleagues in economics at Harvard, and at the John F. Kennedy School of Government to develop a better economic estimate of the cost of this type of sequestration. In particular, graduate student Jeff Bielicki is studying the costs (both monetary and energetic) of transport of CO_2 through pipelines, and the accessibility of different types of sequestration

reservoirs to different electricity markets in the U.S. His preliminary findings are that sea floor sequestration is the best alternative for many densely populated regions in the Northeast.

Simulation of CO_2 storage in a high-pressure vessel: The final component of our project is a set of high-pressure experiments designed to observe the migration of CO_2 in carbonate sediment at temperature and pressure. These experiments are distinct from the high-pressure flow-through experiments described above as these will be used as another check on the numerical models to understand the migration of the CO_2 plume over short length scales. Overall, we expect that our parallel research efforts will lead to a clearer understanding of the feasibility of carbon dioxide injection into deep sea sediments. If we discover some unexpected obstacles, and we find that the results do not warrant a further development of this option, the final report will explain the nature of the hurdles that could not be overcome and what advances might change this conclusion. However, at this point, we believe that our preliminary results warrant a pilot-scale test of this approach to carbon sequestration. Therefore, we are working to define the issues that will have to be verified to perform a field experiment, moving one step closer to implementation of this strategy.

CONCLUSION:

Preliminary results from modeling and experiments suggests that injection of carbon dioxide in deep sea sediments below 3000 m water depth, and then 300 to 400 m deep within the sediment will provide for permanent storage of carbon dioxide. The critical advantages of this strategy are 1) that the reservoir capacity is near infinite; and 2) that the formation of hydrate and the density of CO2 make it impossible for the carbon to escape. The next two years of research will allow for detailed modeling of fluid flow in the ocean sediment system, and will provide results from high pressure experiments that will test some of the predictions from the models. We will also establish a collaboration with Schlumberger, who will be an excellent partner in planning for the next stages of designing a field experiment.

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Permanent Carbon Dioxide Storage in Deep Sea Carbonate Sediments

Kurt Z. House, Daniel P. Schrag, Charles F. Harvey, and Klaus S. Lackner

Abstract: Stabilizing the concentration of atmospheric CO_2 will require storing enormous quantities of captured anthropogenic CO_2 in near-permanent geologic reservoirs. Due to the subsurface temperature profile of terrestrial storage sites, CO_2 stored in these reservoirs is buoyant. As a result, the injected CO_2 can escape if the reservoir is not appropriately sealed. We show that CO_2 injection into deep sea sediments below 3000 m water depth and a few hundred meters of sediment provides permanent geologic storage even with large perturbations such as earthquakes. At the high pressures and low temperatures common in deep sea sediments, CO_2 resides in its liquid phase and is denser than the overlying pore-fluid. Additionally, CO_2 hydrate formation impedes the flow of $CO_2(l)$, and serves as a second cap on the system. The evolution of the CO_2 plume is described from the injection to the formation of CO_2-hydrates, and finally to the dilution of the $CO_2(aq)$ solution by diffusion. Dissolution of the carbonate host rock by the $CO_2(aq)$ solution will slightly increase porosity, which may cause large increases in permeability. Karst formation, however, is unlikely because total dissolution is limited to only a few percent of the rock volume. The total CO_2 storage capacity within the 200 mile economic zone of the U.S. coastline is enormous, capable of holding thousands of years of current U.S. CO_2 emissions.

Introduction

Supplying the energy demanded by world economic growth without affecting the Earth's climate is one of the most pressing technical and economic challenges of our time. The global climate/energy problem is particularly challenging because, although worldwide reserves and resources of conventional oil and gas are limited (1), coal reserves and resources are abundant and relatively inexpensive (2). Due to the abundance of coal and its value as a feed stock for a variety of synthetic fuels, hydrocarbons are likely to be the dominant energy source of the 21st century. The combustion of coal produces approximately twice as much CO_2 per unit energy as natural gas, and synthetic fuels derived from coal produce up to twice as much CO_2 per unit energy as fuels derived from conventional oil (3). Therefore, if the concentration of atmospheric CO_2 is to be stabilized within this century, it will be essential to have the capability to capture CO_2 from the combustion of fossil fuels and store it safely away from the atmosphere (4).

Several ideas have been proposed for the long-term storage of captured anthropogenic CO_2. These proposals include: storing CO_2 in various geologic formations (e.g., oil & gas fields (5), coal beds (6), and saline aquifers (7)); injecting CO_2 into the deep ocean (8, 9); and chemically transforming CO_2 in thermodynamically stable minerals (4, 10) or bicarbonate brines (11, 12). We describe storing CO_2 in deep sea carbonate sediments as a fourth storage option that combines beneficial elements of geologic storage, oceanic storage, and geochemical storage while addressing many of their drawbacks.

Storage of captured CO_2 in terrestrial geologic formations is a leading candidate for near term storage. All terrestrial geologic formations, however, face a common challenge. Due to the geothermal gradient in the continental crust, the temperature at injection is always greater than the critical temperature of CO_2. Under the high pressures (10 – 30 MPa) and high temperatures (330 – 400 K) of terrestrial storage sites, supercritical CO_2 is 40% to 70% less dense than the surrounding pore-fluid (13). This density contrast causes the buoyant CO_2 to migrate upward through any available conduit. As a result, all terrestrial-storage reservoirs must have impermeable layers (i.e., cap rocks) to prevent the release of buoyant fluids. Natural gas reservoirs have existed for millions of years, demonstrating that geologic formations can store buoyant fluids for long time periods. Over the last century, however, millions of wells have been drilled in most of the basins being considered for geologic storage, and each of these wells is a potential conduit for buoyant CO_2 to escape (14). The concern over leakage will require geologic storage sites to be monitored for centuries, and it is unclear who will be responsible for verifying the storage integrity over these time-scales.

Injecting CO_2 directly into the deep ocean, where most of it will dissolve as bicarbonate, is another option for CO_2 storage. Deep ocean injection can be seen as accelerating the natural oceanic uptake of CO_2, which would occur over many centuries (15). Unfortunately, due to ocean currents and local supersaturation, a large fraction of the injected CO_2 will be released to the atmosphere after a few hundred years (16). Additionally, concerns about the effects of CO_2 on marine ecosystems have led to widespread political opposition to direct ocean storage (17). Unless there is a significant change in the political climate, it is unlikely that direct ocean storage will be employed on large scales.

Chemically transforming captured CO_2 into bicarbonate brines or thermodynamically stable minerals is a third storage option. Forming bicarbonate brines through the dissolution of calcium carbonate has been suggested as a way to neutralize carbonic acid before ocean injection (11, 12). Separately, it has been proposed that $CO_2(g)$ be reacted with silicate minerals to form thermodynamically stable carbonate minerals (4). Mineralization—the most stable and permanent form of CO_2 storage—is an acceleration of the natural chemical weathering cycle (18). At surface temperatures, however, the reaction kinetics are very slow, and accelerating the kinetics to industrial rates with current technology costs 3 to 10 times more than terrestrial geologic storage (19).

Stable Storage of Liquid CO_2 at High Pressure and Low Temperature

Due to the high compressibility of $CO_2(l)$ relative to water, $CO_2(l)$ becomes denser than water at high pressures and low temperatures (Figure 1). These temperature-pressure regimes do not exist in terrestrial settings; they are, however, common in the deep ocean. When $CO_2(l)$ is injected into the ocean at a depth of 3000 m, it sinks, forming a lake of $CO_2(l)$ on the sea floor (20). As previously discussed, however, ocean currents will mix the injected $CO_2(l)$ causing a large fraction to be released to the atmosphere (16). To ensure that deep ocean currents will not mix the CO_2 into shallower regions, CO_2 can be injected below the seafloor. Furthermore, if the seafloor depth of injection is greater than ~3000 m, then the injected CO_2 will be denser than the ambient pore-fluid. The lower density pore-fluid acts as a buoyancy-cap on the system and ensures gravitational stability. The gravitational stability of the system in deep sea sediments is in contrast with terrestrial geologic storage where the high pressures and *high* temperatures cause the injected supercritical CO_2 to be gravitationally unstable. The buoyancy cap, provided by the pore water, serves the same purpose in deep sea sediments as a cap rock serves in terrestrial geologic formations. The buoyancy cap, however, is superior to a cap rock because conduits in a cap rock enable buoyant CO_2 to escape. In contrast, the gravitational stability provided by the buoyancy cap guarantees that fractures in the sediment column cannot serve as conduits for the CO_2, and even large geomechanical perturbations—such as earthquakes—cannot cause the $CO_2(l)$ to be released.

Storing CO_2 in deep sea sediments was first proposed by Koide et al (21) who considered storing CO_2-clay-ash solutions and $CO_2(l)$ below tens of meters of unconsolidated marine sediments. They identified three seafloor depth regimes for the storage of dissolved CO_2: 'shallow sub-seabed' (<300 m), 'deep sub-seabed' (300 m – 3700 m), and 'super deep sub-seabed' (>3700 m). In this study, we describe a different scenario then envisioned by Koide et al. (1997). Specifically, we consider injecting pure $CO_2(l)$ below at least 3000 m of ocean and several hundred meters of marine sediment. The key aspect of our study is to inject pure $CO_2(l)$ below the sediment layer where CO_2-hydrates form and below the sediment layer of less dense pore-fluid. As will be discussed below, the relative location of these sediment layers and the injected $CO_2(l)$ ensures permanent CO_2 storage.

The geothermal gradient, which various from .02ºC/m to .04ºC/m, controls changes in the density of $CO_2(l)$ injected into deep sea sediments by expanding and contracting the mobile $CO_2(l)$ until its density equals the density of the surrounding pore-fluid. Given a sea floor depth of 3500 meters and a geothermal gradient of .03 C/m, the injected $CO_2(l)$ becomes neutrally buoyant at ~200 m below the seafloor. Above the sediment depth of neutral buoyancy, the $CO_2(l)$

is denser than the ambient pore-fluid. We refer to this range between the seafloor and the sediment depth of neutral buoyancy the *negative buoyancy zone* (NBZ) (Figure 2).

To fully describe the fate of CO_2 injected below the sea floor, the chemical reactions between CO_2, seawater, and sediments must be considered. CO_2 that has been injected into deep sea sediments will slowly dissolve forming a $CO_2(aq)$ solution that is denser than the surrounding pore-fluid (22). At 30 MPa and 3ºC, the solution becomes saturated at a $CO_2(aq)$ mole fraction of ~5% (23). The CO_2 saturation concentration indicates that a given quantity of $CO_2(l)$ must interact with 20 times as much pore-fluid to fully dissolve. Therefore, during the injection, $CO_2(l)$ is the dominant phase.

In turn, the relatively low pH of the $CO_2(aq)$ solution drives the dissolution of carbonate minerals, which increases the density of the $CO_2(aq)$ solution and decreases pCO_2 by adding alkalinity to the pore-fluid creating a bicarbonate brine solution. The total dissolution of carbonate minerals will be relatively small; for a cubic meter of limestone of 60% porosity filled with CO_2-saturated pore-water in equilibrium with 30 MPa pCO2, approximately 3 kg or 0.75% of the rock will dissolve before the pore-fluid is saturated. Since CO_2 would be injected as a separate liquid phase, the host rock will not experience large fluxes of $CO_2(aq)$ near the injection well. Nevertheless, host rock dissolution may be important because minor increases in porosity have been shown to generate large increases in permeability (24-26). The exact relationship between porosity and permeability in carbonate sediment is highly variable (27) and further work is required to quantify whether carbonate dissolution will have a significant effect.

The pressures and temperatures necessary to compress $CO_2(l)$ to greater density than the pore-fluid are similar to the conditions necessary for CO_2-hydrates to form. CO_2-hydrates ($5.75H_2O \cdot CO_2$) are non-stoichiometric crystalline compounds that form at high pressures and low temperatures by trapping CO_2 molecules in hydrogen bonded cages of H_2O (28). These compounds occur in a 3-phase meta-stable equilibrium between $CO_2(l)$, $CO_2(aq)$, and hydrate (23).

We refer to the sub-seafloor region with low enough temperatures and high enough pressures for hydrate formation as the *hydrate formation zone* (HFZ). The HFZ extends from the seafloor downward into the sediment until the temperature rises past the boundary of the hydrate stability field. A comparison of the stability conditions for CO_2-hydrates (29) with the CO_2 buoyancy-depth relationship reveals that the HFZ overlaps to a great extent with the NBZ. Although the HFZ exists in submarine sediment at seafloor depths of ~400 m, $CO_2(l)$ does not become denser than seawater until a seafloor depth of ~2900 m. Below ~2900 m of ocean,

however, the thickness of the NBZ grows more rapidly then the thickness of the HFZ, and at seafloor depths below 4000 m, the NBZ is thicker than the HFZ (Figure 3).

The overlap of the HFZ and the NBZ present both implementation difficulties and storage opportunities. Hydrates are immobile crystals that clog the pore space and impede flow. As a result, hydrate formation will generate a self forming cap that limits the migration of CO_2 and enhances storage stability. On the other hand, if injection is within the HFZ, then hydrate formation will decrease permeability near the wellhead and may increase the energy required for injection. The optimal sediment depth of injection will depend on the relationship between depth and intrinsic permeability and on the degree to which hydrate formation affects the relative permeability of CO_2. The composition of the injection site below the HFZ may be either chalk or limestone. The intrinsic permeability of chalk and limestone ranges from 0.1 to 1000 mD (30). If the intrinsic permeability below the HFZ is lower than the relative permeability of $CO_2(l)$ to CO_2-hydrates, then no benefit is gained from injecting below the HFZ. Further work is needed to establish the effect of hydrate formation on permeability. We expect, however, that hydrate formation will cause sharp reductions in the relative permeability of $CO_2(l)$, and that locating the wellhead below the HFZ will be energetically favorable to locating it within the HFZ.

When the seafloor depth is shallower than 4000 m, the HFZ is thicker than the NBZ, and avoiding hydrate formation near the well head requires that the $CO_2(l)$ be injected below *both* the HFZ and the NBZ. $CO_2(l)$ injected below the NBZ is buoyant at the point of injection and will rise until it reaches the bottom of the HFZ. As the $CO_2(l)$ flows into the HFZ, it will form CO_2-hydrates, which will clog the pore space and form a cap that limits the upward migration of the remaining $CO_2(l)$ (31). If the hydrate cap does not form an impermeable seal, then some $CO_2(l)$ may flow within the HFZ to the bottom of the NBZ. Once that CO_2 reaches the bottom of the NBZ, it becomes neutrally buoyant and gravitationally stable. Injecting below both the HFZ and the NBZ takes advantage of both the buoyancy cap provided by the NBZ and the self forming hydrate cap provided by the HFZ.

If CO_2 were injected into sediment below a seafloor depth of 4000 m, where the NBZ is thicker than the HFZ, then it could be injected below the HFZ and directly into the NBZ. In such a configuration, it is unlikely that any hydrates will form, because the $CO_2(l)$ will percolate away from the HFZ to the bottom of the NBZ where it will reside beneath both the buoyancy cap and the hydrate cap.

Thermal Evolution of the Injected CO_2

As the CO_2 is pumped from the surface to the seafloor, heat will be transferred from the relatively warm CO_2 to the relatively cold ocean water. By the time the $CO_2(l)$ has traveled through the ocean pipeline to the seafloor, it will have thermally equilibrated with the ambient ocean water, and its temperature will be a few degrees Celsius. Beneath the seafloor, the sediment temperature increases by .02 to .04 ºC/m, but the relatively short period of time it takes $CO_2(l)$ to flow through the pipeline from the seafloor to the injection point is not long enough for the $CO_2(l)$ in the pipeline to thermally equilibrate with the sediment. As a result, the $CO_2(l)$ temperature at the injection point will be several degrees colder than the pore-fluid and cold enough to form CO_2-hydrates. The primary reason to inject $CO_2(l)$ below the HFZ is to avoid hydrate formation near the well head. Therefore, it will be necessary to control the $CO_2(l)$ temperature at the injection point by either heating the $CO_2(l)$ in the pipeline or insulating the ocean pipeline to keep the $CO_2(l)$ at higher temperatures.

During injection, the $CO_2(l)$ may be colder than the surrounding pore-fluid and host rock. Depending on the injection temperature, the $CO_2(l)$ may be positively, negatively, or neutrally buoyant near the wellhead. Over time, however, the $CO_2(l)$ plume will spread, and the regions of the plume farthest from the wellhead will reach thermal equilibrium with the pore-fluid. As heat is transferred from the pore-fluid and the host rock to the $CO_2(l)$, the $CO_2(l)$ will expand and rise to the bottom of the HFZ where CO_2-hydrates begin to form.

An interesting feature of this system is that the coefficient of thermal expansion for $CO_2(l)$ is high enough that, given a high enough permeability, a typical geothermal gradient will drive some convection within the $CO_2(l)$ (32). The onset of convection may be important in entraining additional water into the plume.

Long-Term Fate of CO_2 in Deep Sea Sediments

Over $\sim10^4$ years, $CO_2(l)$ injected below the seafloor will evolve in a way that ensures permanent storage (Figure 5). Initially, $CO_2(l)$ injected below the HFZ and the NBZ will flow upward until it reaches the bottom the HFZ. Given reasonable values for the intrinsic permeability, the relative permeability of $CO_2(l)$, and the geothermal gradient, we expect the injected CO_2 to flow toward the HFZ with a flow rate on the order of ~10 m/yr - ~100 m/yr. Once the $CO_2(l)$ reaches the bottom of the HFZ, CO_2-hydrates will form clogging pore channels and creating an impermeable cap. Additional $CO_2(l)$ flowing up from the wellhead will be physically trapped beneath the hydrate cap and will spread laterally extending the hydrate-cap and the area of the storage site.

As the $CO_2(l)$ flows by buoyancy driven advection, it will encounter larger and larger volumes of pore-fluid driving dissolution of the $CO_2(l)$ and forming $CO_2(aq)$. Pore-fluid saturated with $CO_2(aq)$ will sink because it will be denser than both the $CO_2(l)$ and the pristine pore-fluid (22). The sinking of the saturated pore-fluid will draw in additional water from outside the $CO_2(l)$ plume and drive the dissolution of the CO_2-hydrates. Eventually, the CO_2-hydrates will dissolve creating a dispersed plume of pore-fluid with high pCO_2. As the $CO_2(aq)$ saturated pore-fluid percolates downward through the sediment column, the solution's concentration will decline as it mixes with greater and greater volumes of water. Eventually, the buoyancy driven advection will cease as the density difference between the $CO_2(aq)$ solution and the pore-fluid vanishes. Once that occurs, further transport will only be accomplished through diffusion, and it will take over 10^6 years for the CO_2 to diffuse through a few hundred meters of sediment.

Storage Capacity

If the CO_2 storage site is 300 meters thick with 50% porosity and 50% residual water, then the total annual U.S. CO_2 emissions (~6 Gt of $CO_2(l)$) could be stored in a ~80 km^2 area. Figure 4 indicates that over 22% (1.3 M km^2) of the seafloor within the economic zone the continental U.S. is below 3000 m deep (33). That represents over 10^4 Gt of permanent $CO_2(l)$ storage.

Conclusion

Deep sea sediments at high pressure and low temperature provide a virtually unlimited and permanent reservoir for carbon dioxide captured from fossil fuel combustion. When injected below the ocean floor at an ocean depth greater than 3000 m, CO_2 will remain below a layer of more buoyant pore-fluid. Hydrate formation will also impede the upward flow of CO_2 as it cools along a geothermal gradient. Carbonate dissolution will play a minor role in the system, and may affect permeability within the reservoir. Over time-scales of thousands of years, the CO_2 will dissolve into the pore-fluid, and the $CO_2(aq)$ solution will remain denser than the overlying layer. Further transport can only be accomplished by molecular diffusion over millions of years. The permanence guaranteed by the double cap will enable $CO_2(l)$ to be stored without any investment in monitoring or verification technology. For these reasons, we propose that CO_2 storage in deep sea sediments at high pressures and low temperatures be considered along with other options.
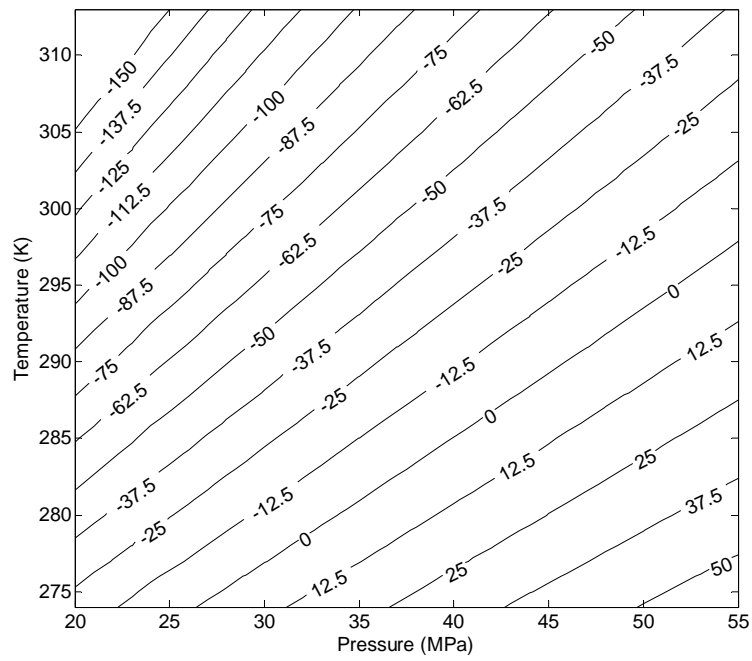
**Figure 1: Density difference between CO_2(l) and seawater as a function of temperature and pressure (13).**
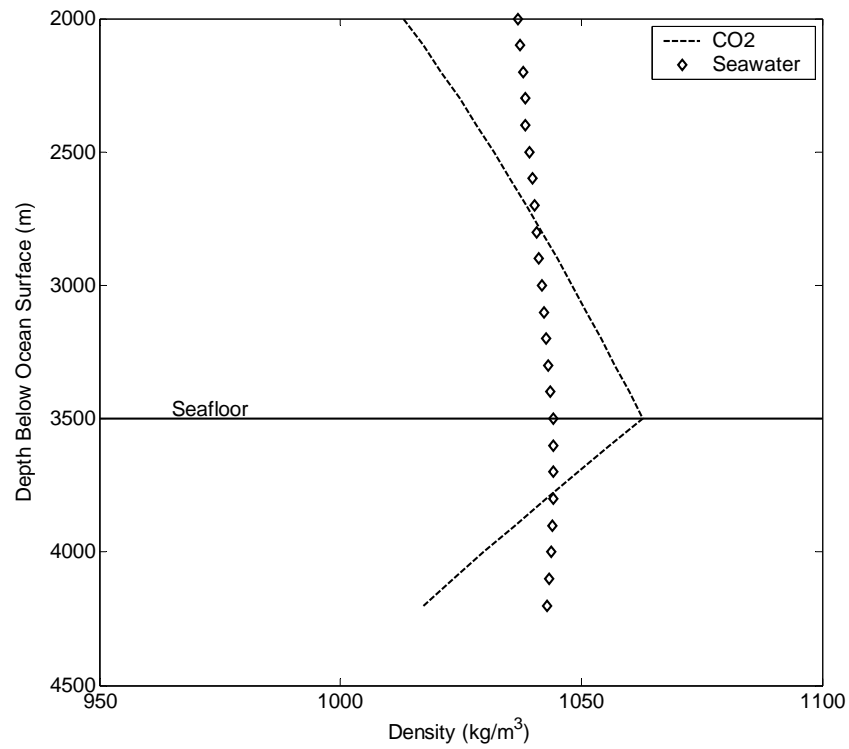
Figure 2: Since $CO_2(l)$ is more compressible than seawater, it becomes denser than seawater at ~3000 m.   Once below the seafloor, however, the geothermal gradient causes the $CO_2(l)$ to expand more rapidly than seawater. Eventually, the ambient temperature becomes hot enough that $CO_2(l)$ becomes less dense than the pore-fluid. (NOTE: A linear geothermal gradient of .03 ºC/m was assumed.)
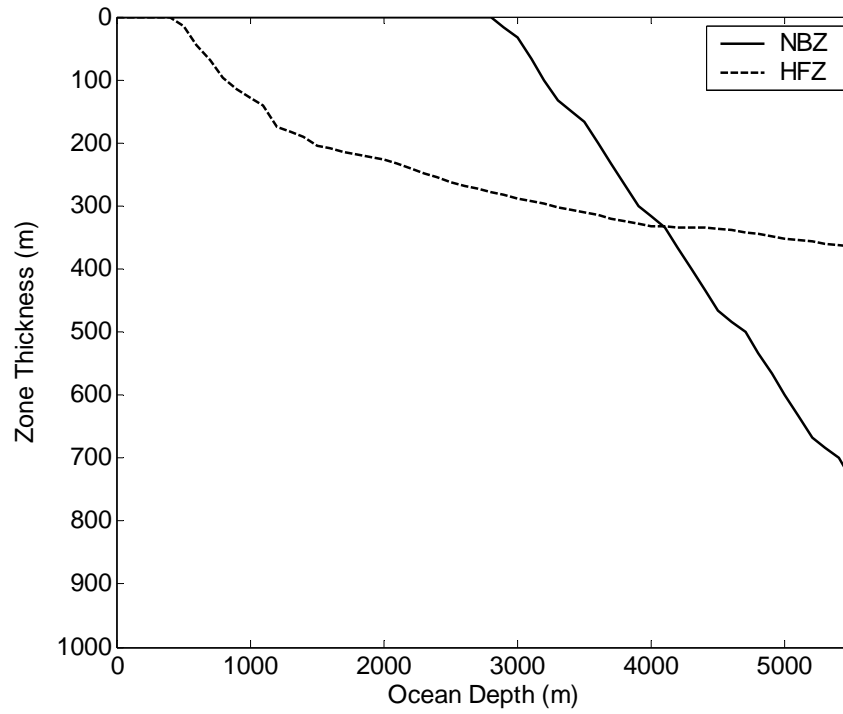
Figure 3: The thicknesses of the *Hydrate Formation Zone* (HFZ) and the *Negative Buoyancy Zone* (NBZ) as a function of the seafloor depth of injection. (NOTE: A linear geothermal gradient of .03 ºC/m was assumed.)
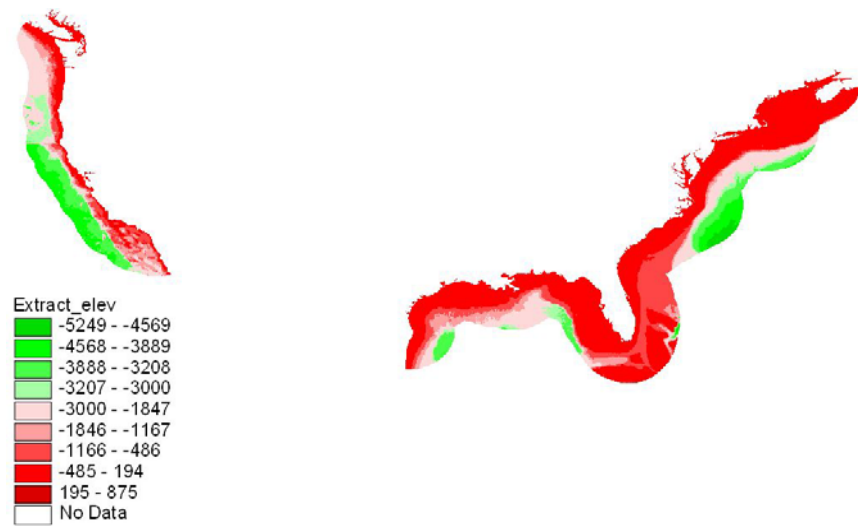
Figure 4: Over 22% of the seafloor within the 200 mile economic zone of the U.S. coast is below 3000 m deep. That represents over 1.3 M km^2 of potential CO$_2$ storage area.
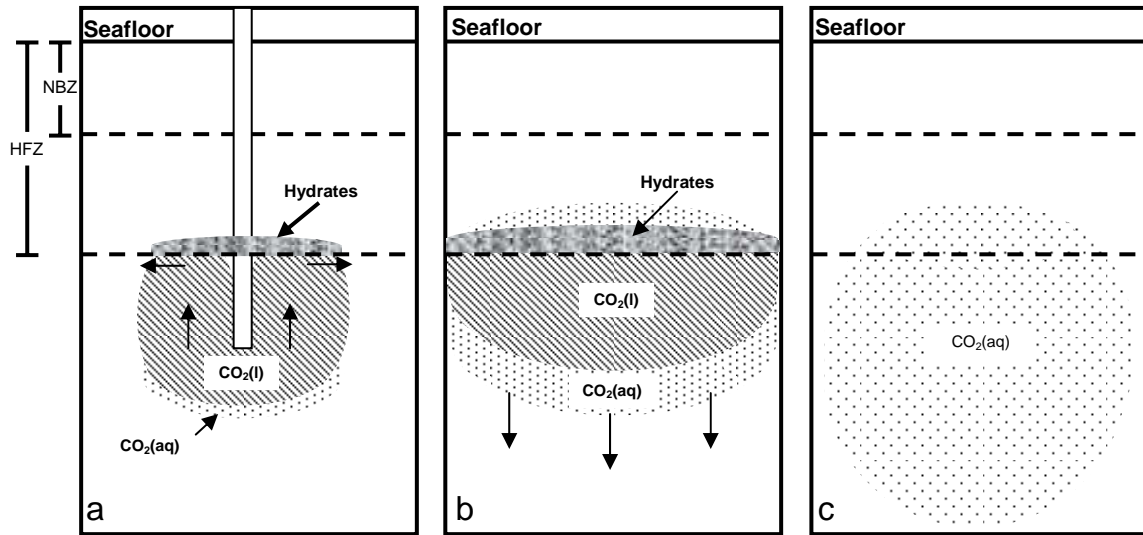
Figure 5: The long-term evolution of the injected CO_2: **a) On the injection time-scale (~1yr), small amounts of hydrate form as the top of the plume enters the HFZ. The hydrate that forms will impede the upward migration of $CO_2(l)$ and force the $CO_2(l)$ to flow laterally. b) After ~10^2 years, the self-forming hydrate-cap will have expanded laterally and trapped substantial quantities of $CO_2(l)$ below it. Simultaneously, the CO_2 saturated pore fluid will sink away from the HFZ by buoyancy driven advection. c) After 10^4 years, all the $CO_2(l)$ and CO_2-hydrates will have dissolved forming a $CO_2(aq)$ solution. The solution will percolate through the porous matrix until it has mixed with a large enough quantity of water to become neutrally buoyant. Once the solution is neutrally buoyant, further solute migration will only occur by diffusion.**

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