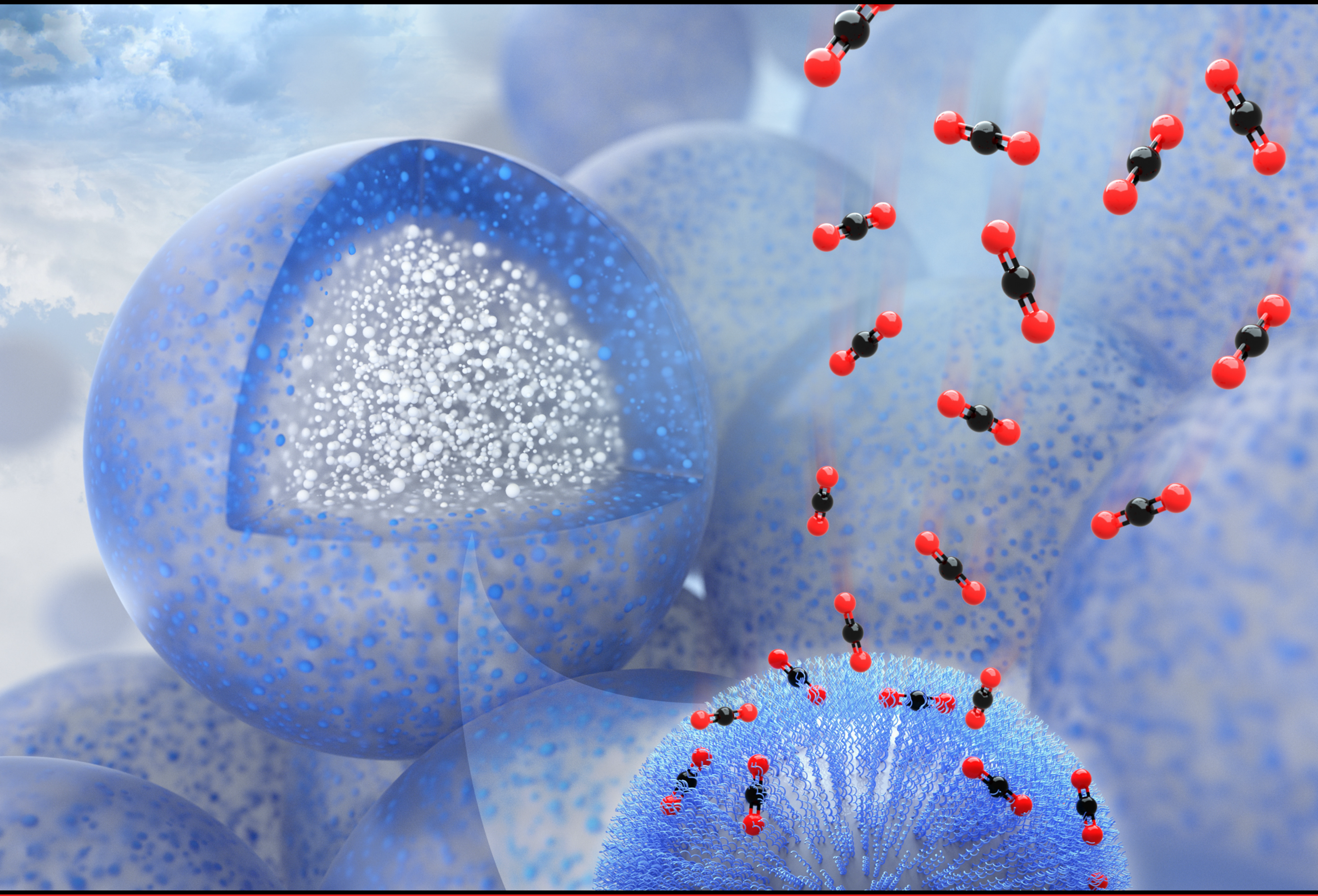
Basic Energy Sciences Roundtable

Foundational Science for Carbon Dioxide Removal Technologies



Report of the Basic Energy Sciences Roundtable
on March 2–4, 2022

Suggested citation: *Foundational Science for Carbon Dioxide Removal Technologies.* Basic Energy Sciences Roundtable report, US Department of Energy, Office of Science: Washington, DC, 2022. DOI: 10.2172/1894473.

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Report of the Basic Energy Sciences Roundtable on

Foundational Science for Carbon Dioxide Removal Technologies

March 2–4, 2022

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ABBREVIATIONS

AFM	atomic force microscopy
AI	artificial intelligence
ARPA-E	Advanced Research Projects Agency–Energy
BES	Office of Basic Energy Sciences
CDR	carbon dioxide removal
DAC	direct air capture
DFT	density functional theory
DIC	dissolved inorganic carbon
DOC	direct ocean capture
DOE	Department of Energy
EERE	Energy Efficiency and Renewable Energy
FECM	Office of Fossil Energy and Carbon Management
GCS	geological carbon sequestration
HPC	high-performance computing
IAP	interatomic potential
IPCC	Intergovernmental Panel on Climate Change
MD	molecular dynamics
ML	machine learning
MOF	metal–organic framework
NR	neutron reflectivity
PAA	poly(allylamine)
PRO	priority research opportunity
ROS	reactive oxygen species
SANS	small-angle neutron scattering
SAXS	small angle X-ray scattering
$scCO_2$	supercritical carbon dioxide
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
USAXS	ultra small angle X-ray scattering
WAXS	wide angle X-ray scattering
XRR	X-ray reflectivity

EXECUTIVE SUMMARY

Globally, the frequency of extreme climate events is increasing—with the rising levels of carbon dioxide (CO_2) in the atmosphere due to human activity believed to be a major contributor. The international consensus is that net carbon emissions must be eliminated to avoid significant negative consequences. Although reducing and capturing CO_2 at the source of generation is a critical strategy, recent reports from the Intergovernmental Panel on Climate Change conclude that carbon dioxide removal (CDR) from the environment will be essential to reducing CO_2 in the atmosphere. However, effective, economical, and secure methods for CO_2 removal on the massive scale that is required do not exist, nor does the foundational science needed for their development. Recognizing these challenges, the U.S. Department of Energy announced the Carbon Negative Shot—one of DOE's 8 Energy Earthshots—in 2021, setting the goal of removing CO_2 from the atmosphere and durably storing it at meaningful scales for less than \$100/metric ton of CO_2-equivalent within a decade.

A Virtual Roundtable on Foundational Science for Carbon Dioxide Removal Technologies was held in March 2022 to determine the fundamental knowledge base that must be developed to underpin the Carbon Negative Shot. The charge of this roundtable was to build on the strong foundations in fundamental research within the Office of Basic Energy Sciences, in coordination with existing research and development activities supported by the U.S. Department of Energy technology offices (e.g., Fossil Energy and Carbon Management, Energy Efficiency and Renewable Energy) and the Advanced Research Projects Agency-Energy. Participants were tasked with identifying critical needs for scientific understanding that could overcome scientific and technical barriers to development and implementation of CDR technologies, and to articulate opportunities for Office of Basic Energy Sciences–sponsored research to provide this foundational knowledge.

The advancement of these existing approaches to reducing atmospheric CO_2 could transform the technological landscape of CDR: (1) direct capture and concentration of CO_2 from ambient air and other dilute sources such as the oceans and other large bodies of water; (2) durable storage of carbon through mineralization and conversion through the synthesis of molecules and materials with useful functionality; and (3) sequestration in geologic formations deep underground. Innovations in these three areas rely on a molecular-level understanding of CO_2 interactions with interfaces in complex environments. Achieving this understanding requires the coupling of a variety of methods including novel operando experimental techniques, predictive theory and modeling, and data science. The foundational knowledge generated by this holistic approach can enable advances in multifunctional materials, mitigation strategies for degradation process, and overall control of CO_2 interactions with molecules, minerals, and materials. Research based on the priorities outlined in this report may lead to transformative advances in the understanding of CO_2 capture, conversion, and storage, and provide the scientific foundation for effective, efficient, and safe CDR technologies.

Priority Research Opportunities for Carbon Dioxide Removal Technologies

Master Interfacial Processes of CO_2 Transport and Reactivity across Multiple Length- and Timescales

Key question: How can we enhance or inhibit CO_2 reactivity and mass and energy transport by exploiting the coupling across interfaces between disparate phases?

CO_2 molecules crossing gas–fluid–solid interfaces via coupled physical and chemical reactions underlie all CDR processes. The driving forces for CDR at interfaces (pH, gradients in reactive species) decrease during operation, slowing capture kinetics, or worse, passivating surfaces of natural and synthetic materials. Incorporating a function that continuously regenerates reactivity could revolutionize efficacy of CDR media. Successful design and exploitation of next-generation CDR media that include regenerative capabilities requires an atomic- to macroscopic-level description of interfacial processes. Moreover, accurate descriptions of carbon capture and sequestration processes at interfaces must account for their inherent rough, multicomponent, and dynamic nature.

Create Materials that Simultaneously Exhibit Multiple Properties for CO_2 Capture and Release or Conversion

Key question: What design principles and synthetic methods can generate materials that simultaneously exhibit high binding affinity, low energy barrier to release or chemical conversion, and durability?

Creating new, high-performance materials is a key to reducing the energy required for capturing CO_2 from dilute sources and for converting CO_2 into valuable products with net-negative emissions. In particular, understanding the degradation and restoration pathways that impact function is essential to extending the lifetime of materials. At the same time, these materials must be designed to respond rapidly to incoming CO_2 and capture or convert it with high efficiency. The development of new synthetic approaches guided by analyses of in situ behavior can accelerate the discovery of materials with a transformative impact on CDR technologies.

Discover Unconventional Pathways for Energy-Efficient CO_2 Capture, Release, and Conversion

Key question: How can unconventional thermodynamics and kinetics be exploited to drive CO_2 binding and release or reactivity with low energy consumption?

CO_2 sorbents commonly use enthalpically driven processes for capture and are regenerated using thermal energy derived from fossil resources. With the rapid deployment of renewable energy, there is a unique opportunity to explore unconventional mechanisms for both processes, including electrochemical, electromagnetic, acoustic, entropic, and other alternatives, that can enable selective, energy-efficient capture and regeneration. A key challenge is to understand how these approaches can be used to decouple the strong CO_2 binding affinity required for efficient capture from the energy barrier to its subsequent release or conversion. To do so, new computational and experimental tools are needed to probe localized energy transfer and molecular reconfigurations at capture sites and across interfaces.

Control Multiphase Interactions Required for CO_2 Conversion into Minerals and Materials

Key question: What are the key multiphase interfacial structures, chemistries, and phenomena that control kinetics and mechanisms of CO_2 transformation into minerals and materials?

Rational tuning of multiphase physical and chemical interactions for CO_2 conversions into minerals and materials can enable scalable and durable CO_2 storage. Consideration of active sites, confinement, and mass transport is necessary to quantitatively determine, predict, and control the rates of catalytic transformations in chemically dynamic environments. Nongeologic mineralization strategies require an understanding of the roles of polynuclear species, amorphous or dense liquid precursors, and ion desolvation on carbonate mineralization rates, as well as the ability of biomimetic approaches to enhance both processes.

Achieve Predictive Understanding of Coupled Processes in Complex Subsurface Geologic Systems for Secure Carbon Storage

Key question: How can we integrate experimental and ambient data with physics-based modeling across time and length scales to understand and discover geochemical–geomechanical processes and create predictive models for long-term CO_2 storage security?

Subsurface geologic sequestration must store CO_2 for thousands of years in complex kilometer-scale formations that vary in lithology, groundwater chemistry, and structure. CO_2 storage will cause changes to the reservoirs that are not predictable. Understanding the processes relevant to prediction of long-term reservoir evolution requires data that capture this complexity. Field data provide an opportunity to validate experimental and computational methods that connect reservoir integrity to molecular-scale chemistry. Integration of geophysical signals with machine learning-driven simulations rooted in physics-based models can constrain the coupled geochemical–geomechanical processes, enabling more reliable forecasts of long-term reservoir performance.

INTRODUCTION

Globally, the frequency of extreme climate events is growing, with the increased levels of CO_2 in the atmosphere due to human activity believed to be a major contributor (**Sidebar 1**).[1] The international consensus is that net carbon emissions must be eliminated to avoid significant negative consequences. Although reducing and capturing CO_2 at the source of generation is a critical strategy, recent reports from the Intergovernmental Panel on Climate Change (IPCC) conclude that carbon dioxide removal (CDR) from the environment will be essential to reducing CO_2 in the atmosphere. However, effective, economical, and secure methods for CO_2 removal on the massive scale that is required do not exist nor does the foundational science for their development. Recognizing these challenges, the U.S. Department of Energy (DOE) announced the Carbon Negative Shot in November 2021 (**Sidebar 1**), setting the goal of removing CO_2 from the atmosphere and durably storing it at meaningful scales for less than \$100/metric ton of CO_2-equivalent within a decade.[2]

A suite of concurrent technologies is projected that could provide significant contributions to CDR. One option is biologically focused—removal and sequestration through growth of biomass with subsequent energy generation coupled to capture and sequestration. In addition, studies report three physical, chemical, and geochemical approaches that could transform the technological landscape: (1) Direct capture and concentration of CO_2 both from ambient air and other dilute sources, such as the oceans and other large bodies of water. (2) Durable storage of carbon through mineralization, which binds carbon dioxide as carbonates, as well as conversion through the synthesis of molecules and materials with useful functionality. (3) Sequestration in geologic formations deep underground. Basic research to identify and understand the fundamental principles governing carbon dioxide removal processes of capture, conversion, and storage is essential if these technologies are to be realized and “net-zero” and “negative” carbon emissions are to be achieved.

CO_2 Capture

A wide array of CDR approaches have been developed or are currently being studied (**Sidebar 2**). These approaches include using coastal habitats to increase carbon-removing biomass, direct air capture (DAC) of dilute CO_2, or improved forest management. The *CDR Primer*[3] provides an excellent overview of potential CDR approaches. This report will focus primarily on DAC and direct ocean capture (DOC). DAC technologies use solid sorbents to remove CO_2 from ambient air as it passes through a contactor. These sorbents often include amines or hydroxides to form carbamate or carbonate bonds, respectively, with CO_2 to enhance the capture ability. Since chemical bonds are formed during the capture process, thermal energy requirements to accomplish regeneration can be quite high. Some estimates[4] show that capturing 1 $MtCO_2$/y will require 180–500 MW of power. Next-generation capture materials should be designed with innovative properties that can utilize energy other than direct thermal heating for regeneration. Such designs will hinge on a fundamental understanding of what phenomena limit the energy efficiency, capacity, and durability of CO_2 capture systems; what the theoretical limits of various systems are; and what energy transfer mechanisms can be used to drive the separation processes.

Approximately 30% of the CO_2 emitted into earth’s atmosphere is captured by the world’s oceans. Thus, CO_2 exchange at the ocean/air interface represents an immense liquid-gas contact surface for carbon dioxide capture, with a mixing time of 2–4 months. Moreover, at the ambient ocean pH of 8.1, the predominant form of dissolved inorganic carbon is bicarbonate (HCO_3), which is concentrated 150 times by volume in ocean water relative to CO_2 in air, resulting in a HCO_3 concentration of 2 mM in ocean water. Thus, a process that can exploit this flux balance represents a globally accessible indirect method for CO_2 removal and sequestration. Although both biotic (plants, animals, organisms) and abiotic (nonliving chemical and physical factors) processes have been identified for CO_2 removal, this report will focus on abiotic approaches only.

Sidebar 1. DOE's Energy Earthshots: The Carbon Negative Shot

Total global carbon emissions have been increasing sharply over the past century. Since 1750, the consumption of fossil fuels and cement production have contributed to over 370 billion metric tons of carbon being released into the atmosphere; half of this release occurred just since the mid-1980s. Combustion of natural gas accounted for almost 20% of the total emissions from fossil fuels in 2011, reflecting a gradual increase in global natural gas use. With the clear rise in CO_2 emissions (**Figure S1**), an international consensus has been reached that technologies for accomplishing CO_2 removal from the environment are critical to reducing CO_2 levels in the atmosphere.

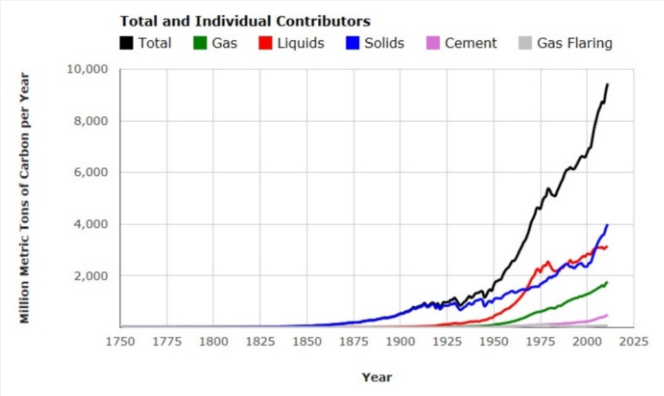

Figure S1. Annual global carbon emissions from fossil-fuel burning, cement manufacture, and gas flaring. Reprinted from the Carbon Dioxide Information Analysis Center.

In 2021, the U.S. DOE announced several new Energy Earthshots to accelerate scientific and technological breakthroughs that will enable clean energy solutions within the next decade (**Figure S2**). The Carbon Negative Shot, announced on November 5, 2021, sets the ambitious goal of capturing CO_2 from the atmosphere and durably storing it at gigaton scales for less than $100/net metric ton of CO_2-equivalent. Although progress has been made in the development of CDR technologies, effective, economical, and secure methods for removing and storing CO_2 do not yet exist on the massive scale that is required, nor does the foundational science needed for their development.

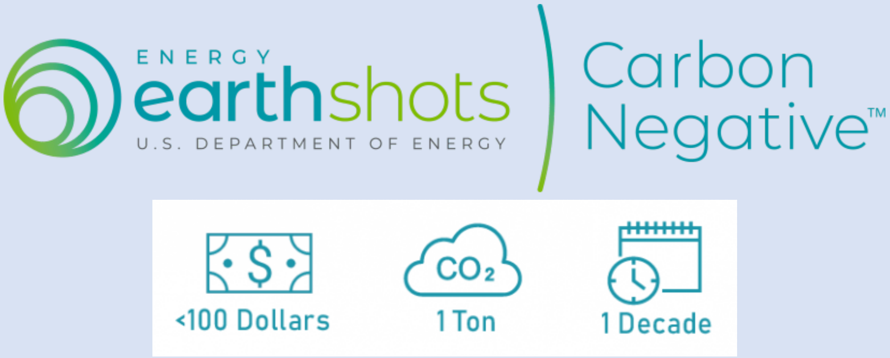

Figure S1. Carbon Negative Shot. Reprinted with permission of the U.S. DOE.

Achieving the Carbon Negative Shot goal can help spur innovation and position U.S. enterprises as leaders in research, manufacturing and deployment in a CDR industry that must have rapid, global ramp-up by midcentury. It can also position America to lead the way to net-zero on a global scale, eventually remove legacy greenhouse gas emissions from the atmosphere, create good-paying job opportunities that build on the skill sets of the fossil fuel workforce and ensure that climate and environmental justice for local communities remain a priority.

Sidebar 2. Carbon Dioxide Removal Technologies

Carbon dioxide removal (CDR) has a critical role in helping the United States address the climate crisis and achieve net-zero emissions by 2050. CDR refers to approaches that capture CO_2 directly from the atmosphere and store it in geological, biobased and ocean reservoirs or in value-added products to create negative emissions. To reach our global climate goals, gigatons of atmospheric CO_2 must be removed every year by midcentury, alongside aggressive decarbonization.

The massive volume of atmospheric CO_2 that must be removed requires a strong portfolio of multiple CDR approaches. A recent report[SR1] discusses different negative emissions technologies that include CO_2 mineralization, ocean alkalinity enhancement, soil carbon sequestration, improved forest management, afforestation and reforestation, coastal blue carbon, biomass storage, biomass energy with carbon capture and storage, direct air capture, and geological storage. This roundtable focused on identifying key opportunities where advances in foundational science could enable efficient direct air capture, ocean capture, mineralization, and combined capture/conversion processes.

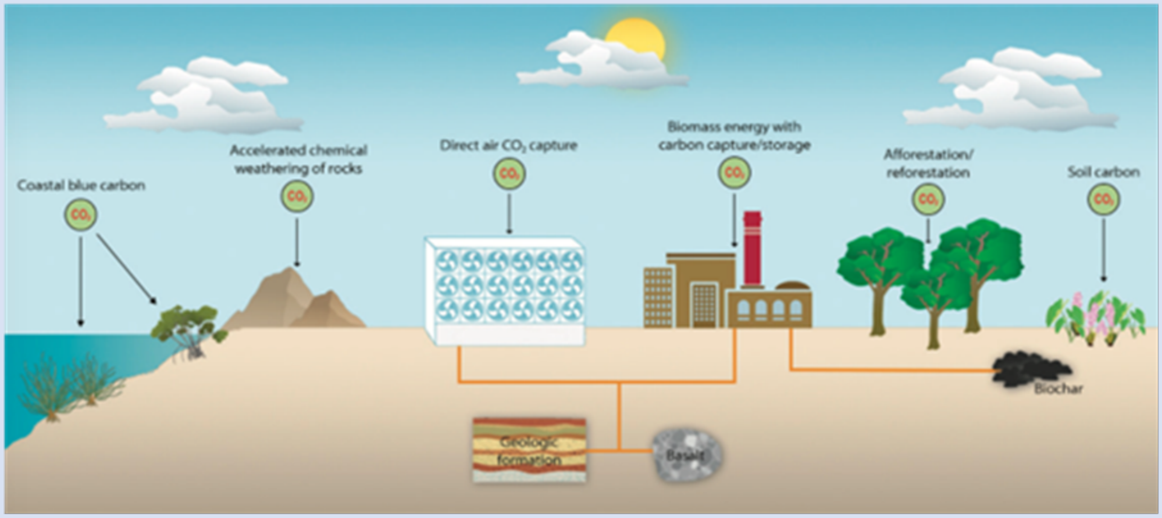

Figure S2. Negative emissions technologies. Reprinted with permission of the National Academies Press from National Academies of Sciences, Engineering, and Medicine, *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*. © 2019. Permission conveyed through the Copyright Clearance Center Inc.

Durable Carbon Storage

Converting captured CO_2 into a stable form represents both a necessity to prevent re-emission to the atmosphere and an opportunity to create valuable molecules and materials. Conversion of CO_2 into a mineral form is a direct way of achieving durable storage and benefits from the vast scale of the natural environment over which mineralization is possible. However, catalytic approaches to conversion, although technologically challenging, hold the potential for delivering functional products in return for the energy required to drive such processes. Whether it is transformed into minerals or functional products, conversion of CO_2 depends on the coupling of a diverse set of chemical reactions and transport phenomena at complex interfaces where disparate types of molecules or ions interact.

Strategies for promoting carbonate mineralization require an understanding of the controls on transfer rates from the vapor to the dissolved state, the chemical species that form as a consequence, and factors that determine rates of ion addition at the interface between the solution and forming mineral, both during nucleation and growth. These include the extent to which mineralization pathways are driven to pass through metastable dense liquid and amorphous precursor phases, the reaction pathways that lead to ion desolvation and attachment to the growing solid phase, and the ability of biomimetic approaches to accelerate these processes. The extensive existing body of literature provides a solid foundation for advancing the science of directed carbonate mineralization and lends clarity to the key knowledge gaps that must be bridged to achieve technologies at scale.

Catalytic processes to transform CO_2, which is a highly stable, nonpolar molecule, into valuable products involve three essential components: (1) the reactive center that binds and activates the CO_2 molecule, (2) a surrounding phase with reactants or solvents that is often in a confined space, and (3) a source of thermal, electrical, or photochemical energy. In general, the efficiency of these three components must be optimized to obtain active and selective catalysts. Thus, development of successful technologies requires an understanding of active site chemistry and reaction kinetics, the effects of both confinement and mass transport on conversion rates, and the mechanism and efficiency of energy input, all over a wide range of temperatures, pressures, and solvent environments. Owing to the disparate lengths and timescales that are characteristic of these various phenomenon as well as the inherent coupling between them, developing and linking multimodal, cross-scale experimental and theoretical approaches can play a vital role in accelerating the establishment of effective methods of CO_2 transformation into useful molecules and materials.

Geologic Sequestration

The total quantity of produced materials is dwarfed by the mass of carbon emitted into the atmosphere. Consequently, geologic sequestration is a necessary technology for achieving net-zero carbon emissions. Geologic sequestration, which complements direct capture, is achieved by compressing CO_2 to form a supercritical fluid and injecting it into subsurface geologic formations that are sufficiently porous to provide high storage capacity and deep enough to ensure the CO_2 remains supercritical. Over geologic time, the injected CO_2 will mineralize, but for the first hundreds to thousands of years, stability of the reservoir will be maintained by constraints on transport imposed by the overlying cap rock. Thus, successful sequestration technologies depend on an understanding of the coupling between geochemical and geomechanical processes.

Because future geologic sequestration sites will present extensive variations in lithology, groundwater chemistry, and structure, predictive models needed to ensure storage security cannot be based solely upon laboratory measurements on model systems. Establishing a network of field-scale subsurface measurement capabilities can provide an avenue for developing validated methods to bridge data and simulations from the field scale to the atomic scale accessed in the laboratory. Integrating geophysical signals from field measurements that can discern the signatures of reservoir evolution during CO_2 storage with multimodal measurements on representative rocks and fracture surfaces, as well as machine learning (ML)-driven physics-based simulations, will result in predictive models that can forecast long-term injectivity and security.

The Roundtable

The DOE Office of Basic Energy Sciences (BES) Roundtable on Foundational Science for Carbon Dioxide Removal Technologies was held March 2–4, 2022. Roundtable participants were charged with considering the scientific and technical barriers that limit those technologies identified in the National Academies study[4] as underexplored—DAC of CO_2 and carbon mineralization—and evaluating opportunities for BES research to provide fundamental knowledge that advances safe, durable geological storage. In its consideration of CO_2 capture, the roundtable was asked to expand beyond ambient air to consider other dilute sources that concentrate CO_2 from ambient air, such as large bodies of water (e.g., oceans). Consideration of durable storage of carbon expanded beyond mineralization, which binds CO_2 as carbonates, to consider CO_2 conversions in the synthesis of materials that could have useful functionality. Consideration of geological sequestration included evaluation of opportunities for fundamental research to elucidate the geochemical and geomechanical processes activated by CO_2 injection into geologic formations deep underground.

Planning and execution of the roundtable to establish the scientific research objectives for BES were coordinated with DOE programs that focus on more applied challenges in CDR, specifically, the Office of Fossil Energy and Carbon Management (FECM) , the Office of Energy Efficiency and Renewable Energy (EERE), and the Advanced Research Projects Agency-Energy (ARPA-E). This synergistic, cohesive, scientific, and technological effort encompassing multiple offices of DOE was needed to achieve the broad, impactful goals for the roundtable. The discussions at the roundtable focused on the foundational knowledge required to underpin advancement of the Carbon Negative Shot objective (**Sidebar 1**). The background for the workshop was established through the use of existing documents on CDR technologies, including the *CDR Primer*;[3] the National Academies reports on *Negative Emissions Technologies and Reliable Sequestration*,[4] *Gaseous Carbon Waste Streams Utilization*,[5] *A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration*,[6] and *A Research Agenda for Transforming Separation Science*;[7] as well as the *BES Basic Research Needs Workshop Report for Carbon Capture Beyond 2020*,[8] and IPCC's *Global Warming of 1.5°C*.[9]

Five priority research opportunities (PROs) were identified that build on foundational CDR studies and define the most compelling opportunities for future research in this space:

- Master interfacial processes of CO_2 transport and reactivity across multiple length- and timescales.
- Create materials that simultaneously exhibit multiple properties for CO_2 capture and release or conversion.
- Discover unconventional pathways and materials for energy-efficient CO_2 capture, release, and conversion.
- Control multiphase interactions required for CO_2 conversion into molecules, minerals, and materials.
- Achieve predictive understanding of coupled processes in complex subsurface geologic systems for secure carbon storage.

These five PROs represent the consensus of the roundtable on the foundational scientific advances required to reverse that trend and reach net-zero carbon emissions. The next section of this report provides in-depth discussion of the PROs.

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PRIORITY RESEARCH OPPORTUNITIES

PRO 1: Understand Interfacial Physicochemical Processes at Multiple Scales

The driving forces for CDR at interfaces (pH, gradients in reactive species) decrease during operation, resulting in slow capture kinetics, or worse, passivated surfaces of natural and synthetic materials. Incorporating a function that continuously regenerates reactivity could revolutionize efficacy of CDR media. Successful design and exploitation of next-generation CDR media that include regenerative capabilities requires an atomic- to macroscopic-level description of interfacial processes. Moreover, accurate descriptions of carbon capture and sequestration processes at interfaces must account for their inherent roughness, multicomponent, and dynamic nature.

1a. Summary

CO_2 molecules crossing gas–fluid–solid interfaces via coupled physical and chemical reactions underlie all CDR processes. Technologies that remove dilute CO_2 from air, stably contain CO_2 in underground sites, and harness mineralization in multiphase environments all depend on complex processes at interfaces. Interfaces include gas–liquid (basic solutions, ionic liquids), liquid–solid (subsurface of natural bodies of water or catalyst–fluid interactions) or gas–solid (sorbents such as metal–organic frameworks [MOFs], minerals, and metal oxyhydroxides). Gas–solid interfaces are affected by humidity and in some cases can be considered gas–liquid–solid interfaces where the liquid phase is on the order of a nanometer in thickness. Conditions known to drive CO_2 capture at these interfaces are usually tied to surface basicity but are also influenced by surface area and roughness, metal cations, and other species present.

Models from characterization of optimal interfaces for CO_2 capture are generally pristine in their "preoperating" conditions, but the process of interfacial CO_2 capture leads to evolution of the interface, often resulting in passivation. To better design and exploit interfaces for CO_2 removal, chemical processes beyond varying basicity could be considered. Innovation in integrated advanced instrumentation, experiments, and simulations would access more accurate descriptions of dynamic processes at carbon capture and removal interfaces, thus providing answers to the key scientific questions that limit design of effective interfaces.

1b. Key Scientific Questions

- How can we engineer and exploit reactivity at durable interfaces to capture carbon?
- How do we simultaneously tune reactive sites to enable thermodynamically favorable solid–gas, liquid–gas, and solid–liquid interactions at surfaces and in confined spaces?
- How can we design next-generation experiments and computational capabilities to capture multiscale coupled phenomena in carbon transformations?

1c. Scientific Challenges and Research Opportunities

The ability to manipulate reactivity at interfaces is crucial for control of carbon capture, both for achieving highly efficient capture and preventing degradation through interface passivation. The reactivity of carbon at an interface, as well as the ability of that interface to remain active ultimately depends on interfacial structure and chemistry. Yet, knowledge of interfacial structure and chemistry is limited and largely exists only for relatively ideal interfaces due to the difficulty of experimentally probing the interfacial region and simulating the complexity inherent to interfaces. These challenges create opportunities for interface design, in situ experimentation, and scale-aware simulations, and drive opportunities for developing a molecular level understanding of interfaces.

- Engineer interfacial reactive oxygen species for carbon capture.
- Develop scale-aware experiments that can tolerate or model rough and dynamic interfaces inherent to carbon transformations to study processes in situ and operando.
- Develop experimentally informed, scale-aware computational tools to link molecular-level phenomena controlling carbon transformations at multiple scales in architected and natural materials.
- Develop molecular-level understanding of how CO_2 capture processes are affected by interfacial structure and chemistry including (a) gas–fluid, fluid–fluid, and fluid–solid interfacial energies and (b) disjoining pressure (i.e., attractive interactions between two surfaces) and distinct chemistry in surface coatings by thin fluid films or neoformed solids.

Engineer interfacial reactive oxygen species for carbon capture

Some of the oldest, simplest, and least expensive solid materials that directly capture CO_2 from air in ambient conditions exploit reactive oxygen species (ROS, examples include O_2^- superoxide; O_2^{2-} peroxide, and OH^-). For example, potassium superoxide, used as an air scrubber for space travel, converts CO_2 to carbonate and releases O_2:

$$4KO_2\ (s) + 2CO_2\ (g) \rightarrow 2K_2CO_3\ (s) + 3O_2\ (g)$$

In another example of DAC of CO_2 via reactive oxygen species, isolation and characterization of a uranyl superoxide–peroxide compound allowed observation of rapid conversion to carbonate in ambient conditions,[1] and the reaction increases at higher temperature (**Figure 1-1A**).[2] In analogous d^0 transition metal chemistry, instability of vanadium peroxide anions and their conversion to carbonates in air has been noted (**Figure 1-1B**),[3] but these phenomena are not yet well-understood or well-documented. In a Fenton-type reaction, copper(II) decomposition of peroxide yielded formation of carbonate at the surface of formed nanoparticles.[4,5] All of these reactions represent stabilization of metastable molecules or materials by formation of carbonates via direct reaction with CO_2 in air or dissolved in solution from air, respectively, at the air–solid interface or liquid–solid interface. Yet, these reaction mechanisms and factors influencing the reaction pathways are poorly understood.

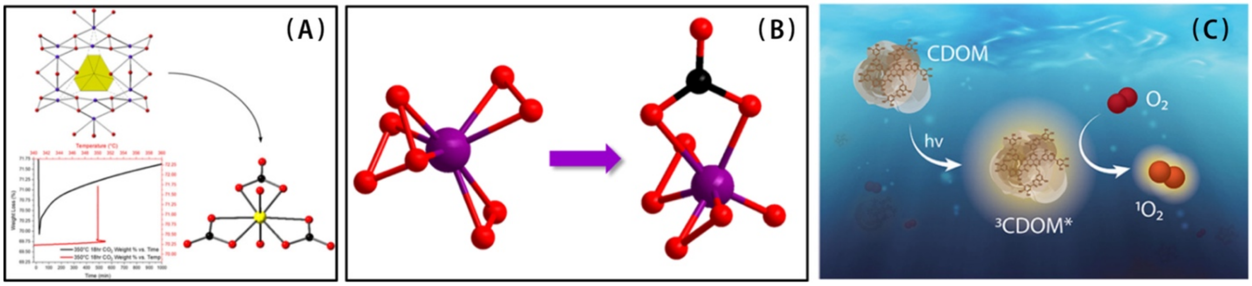

Figure 1-1. (A) Uranyl peroxide–superoxide conversion to uranyl carbonate via capture of CO_2 from air, and acceleration of the reaction with increased temperature. Adapted with permission from D. V. Kravchuk and T. Z. Frobes, *ACS Mater. Au*, 2 (1) 33–44 under CC BY 4.0. © 2022. (B) One step of conversion of tetraperoxovanadate to vanadyldiperoxidecarbonate via capture of CO_2 from air in ambient conditions. Unpublished figure courtesy of May Nyman, Oregon State University. (C) Formation of reactive oxygen species via UV exposure of chromophoric dissolved organic matter (CDOM). Reprinted with permission from R. Ossola et al., "Singlet Oxygen Quantum Yields in Environmental Waters," *Chem. Rev.* 121 (7), 4100–4146 under CC BY 4.0. © 2021.

There are many challenges to further elucidate and exploit simple and complex substances containing reactive oxygen species at interfaces for environmental carbon capture. For example, conversion to carbonates at the interface depletes reactive sites and renders the bulk of the material unreactive. This leads to an additional question: how can the reactive sites be regenerated after conversion to carbonates? Third, stable storage and shelf life of engineered carbon capture materials is a challenge in the case of extremely unstable (and thus reactive) ROS.

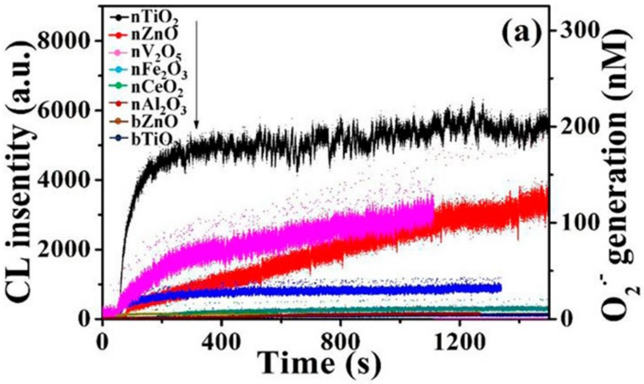

Figure 1-2. Superoxide photogeneration of metal oxide nanoparticles (n) and bulk (b) detected by luminol (left axis). Reprinted with permission from D. Wang et al., "Quantitative Analysis of Reactive Oxygen Species Photogenerated on Metal Oxide Nanoparticles and Their Bacteria Toxicity," *Environ. Sci. Technol.* 51 (17), 10137–10145. © 2017 ACS.

In engineered materials, there is opportunity to exploit photogeneration of ROS, which could both be a path to regenerating reactive CO_2 capture sites in real time and to create materials that produce reactive sites "on demand," to mitigate the problem of stable storage. The most well-known material for photogeneration of reactive oxygen species is titania, but there are many others (**Figure 1-2**),[6] including bismuth oxides, iron oxides, cerium oxide, zinc oxide, and various heterometallic compounds. Oxides and other materials with ROS photogeneration capabilities have been primarily studied and exploited for photocatalysis and antimicrobial function.[7] Yet, tailoring these and related hybrid materials toward DAC of CO_2 at the interface has been minimally explored. There is an opportunity to understand and design hybrid materials that harness interfacial reactive oxygen species for DAC of CO_2 using photoenergy input. Although this phenomenon has been observed in molecular analogs without photogeneration (highlighted above), it is yet to be specifically reported for robust oxide materials. Research challenges and questions to consider include (1) what role does redox activity of involved metals (including dopants and impurities) play in CO_2 capture exploiting

ROS? (2) How does atmospheric or liquid water affect processes? (3) What is the role of pH (solutions) or surface acidity/basicity on ROS? (4) How can hybrid multifunctional materials be designed that combine two or more properties and ultimately enhance carbon capture (i.e., basicity and ROS)?

In simulated natural systems, photochemical studies of phenolic organic compounds (natural organic matter or chromophoric dissolved matter, **Figure 1-1C**) suggest that ROS are photogenerated at the aqueous air interface in natural waters, photocatalyzed by sunshine.[8] It is now widely accepted that photogenerated free radicals via reduction of oxygen on sunlit surficial water are ubiquitous,[5] but the role of photoactivity in natural systems on CO_2 dissolution/carbonate formation has not been investigated. The role of reactive oxygen species that are photogenerated could also be considered as a strategy to enhance mineralization processes. DAC of CO_2 by mine tailings and fly ash rely on basicity of interfaces, including air–solid, liquid–solid, and air–liquid interfaces, and this is also true for engineered basic oxides, such as MgO or ZnO. The role of photogeneration of ROS at these interfaces has not been studied or considered. Could natural organic matter be added to natural systems to provide another pathway for carbon capture? Could mining sites containing metal cations that perform direct air capture of CO_2 in the laboratory under a variety of conditions be considered? (One such example is carnotite, $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$, which is mildly radioactive and promotes formation of ROS.) These approaches could provide an opportunity to understand and enhance carbon capture in mine tailings that are otherwise considered hazardous waste sites.

In summary, interfaces are inherently metastable, and formation and degradation (i.e., by CO_2 capture) of reactive oxygen species represents one surface stabilization process that could be harnessed, if understood. Recognition of other stabilization processes at interfaces could lead to new paradigms in CO_2 capture processes.

Develop scale-aware experiments that can tolerate or model rough and dynamic interfaces inherent to carbon transformations to study processes in situ and operando

Delineating dynamic CO_2 capture and transformation mechanisms at multiple scales requires step-change advances in tools or strategic use of these tools that can capture these multiphase chemical interactions. At the molecular scale, CO_2 capture and conversion often occurs via the formation of transient, metastable intermediate species. A fundamental understanding of the timescales associated with the evolution of these species and the physico-chemical parameters that lead to their formation is crucial for directing the evolution of specific reaction products. Examples of state-of-the-art instrumentation include broadband ultrafast time-resolved infrared spectrometry integrated with femto-/picosecond time-resolved resonance Raman, fluorescence, UV/visible/infrared transient absorption spectroscopy[9]; and X-ray and neutron scattering, absorption, and reflectivity. These measurements resolve the excited states and reaction intermediates in photochemical and radiolytic environments,[10,11] which is crucial for tuning these environments to form specific products. The timescales of these experimental studies are aligned with those of molecular scale simulations, which facilitates the development of experimentally validated models.

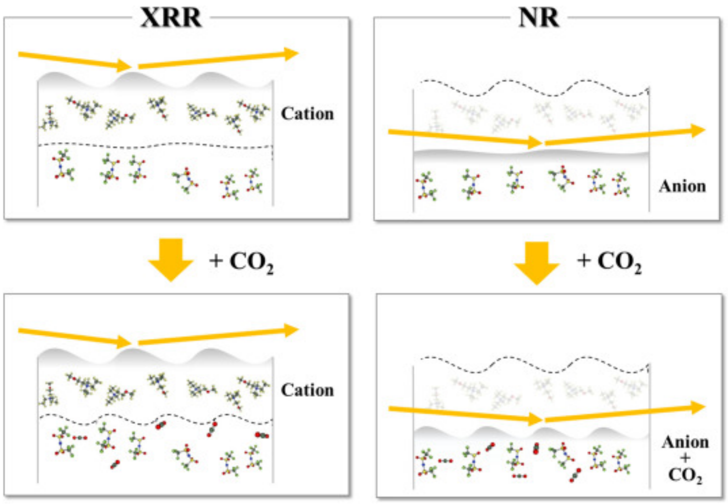

Figure 1-3. Model created from XRR and NR studies showing CO_2 absorbed into an ionic liquid selects the anion layer that underlies the air–cation interface. Reprinted with permission from H. Abe et al., "CO_2 Capture and Surface Structures of Ionic Liquid-Propanol Solutions," *J. Mol. Liq.*, 301. © 2020 Elsevier.

At length scales on the order of a few nanometers, resolving the organization and nanoscale transport behavior of fluidic molecules for carbon capture can inform approaches to tune specific separation pathways and direct preferential binding of specific species. **Sidebar 3** provides an example of combined neutron scattering and molecular dynamics to differentiate CO_2 molecular behavior on the walls of cylindrical silica pores from those in the interior of the pores, with resolution on the nanometer scale. X-ray reflectivity (XRR) and neutron reflectivity (NR) studies of ionic liquid air–cation–anion interfaces demonstrated that (1) the cation of the ionic liquid preferentially concentrates at the interface, and (2) the CO_2 selectively dissolves into the underlying anion layer (**Figure 1-3**).[12] Surface-enhanced Raman spectroscopy was used to model the water–copper electrode interface during CO_2 adsorption, followed by reduction to CO and then to ethylene with increasing negative potential (**Figure 1-4**).[13] Advances in imaging[14] can now validate multicomponent fluid flow behavior in nanopores and micropores using many-body dissipative particle dynamics models to validate mesoscopic, multicomponent fluid transport through porous matter.[15]

Sidebar 3. Differentiating Bulk and Surface-Adsorbed CO_2 in Mesoporous Silica Pores

Differentiating the conformation and interfacial association of CO_2 and captured forms such as carbonate or carbamate species in dynamic systems is challenging because the spectroscopic signals are subtle, they are hidden in the background averaged signal, or both. Gadikota et al.[SR1] was able to differentiate surface-adsorbed CO_2 from bulk CO_2 by exploiting in situ small-angle neutron scattering (SANS) of mesoporous silica materials (MCM-41 and SBA-15). Molecular dynamics (MD) simulations agreed with experiment in showing that CO_2 molecules at low pressure initially surface-sorb to the pore walls before filling the pore volume. Additionally, MD and SANS showed excellent agreement in determining the core (bulk) and shell (surface adsorbed) thickness, respectively, decreasing and increasing with increasing CO_2 pressure. These insights can inform the design of specific solid interfaces with desired functionality for tuning the thickness of interfacial fluids and directing preferential adsorption or displacement of specific species.

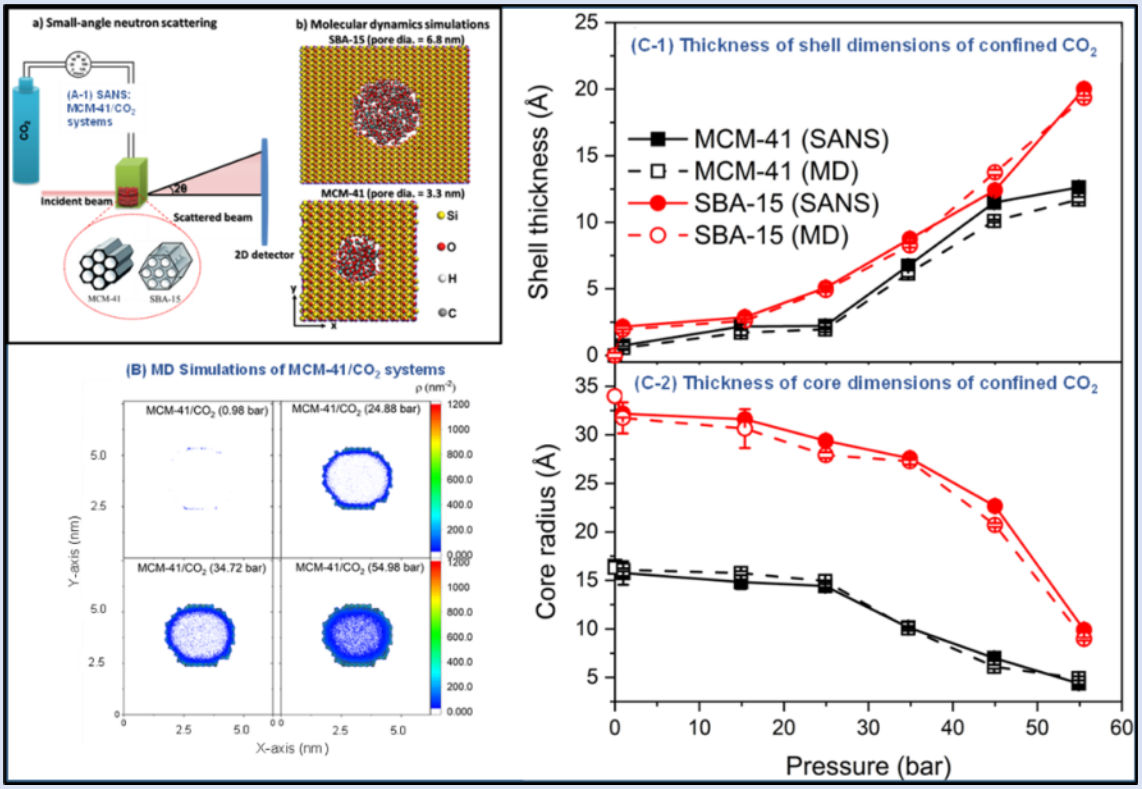

Figure S3. *Upper left,* Schematic representation of the experimental setup for SANS measurements for determining the organization of confined CO_2 molecules in the pores of MCM-41 (pore diameter of 3.3 nm) and SBA-15 (pore diameter of 6.8 nm) silica materials and snapshots of molecular scale simulations representing CO_2 molecules in silica nanopores. *Lower left,* Core-shell structures of confined CO_2 molecules are evident from classical molecular dynamics simulations. *Right,* The dimensions of the core and shell structures in MCM-41 with pore diameter of 3.3 nm and SBA-15 with pore diameter of 6.8 nm from SANS measurements (*solid lines*) and MD simulations (*dashed lines*) are shown. Reprinted with permission from S. Mohammed et al., "Resolving the Organization of CO_2 Molecules Confined in Silica Nanopores Using in Situ Small-Angle Neutron Scattering and Molecular Dynamics Simulations," *Environ. Sci. Nano.* 8 (7). © 2021 RCS. Permission conveyed through the Copyright Clearance Center Inc.

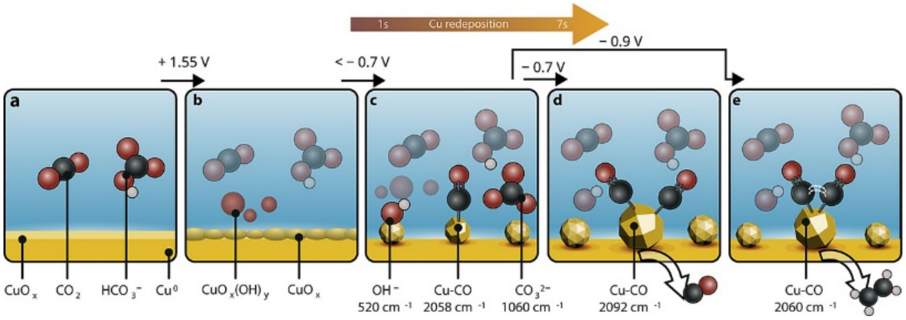

Figure 1-4. Species detected by surface-enhanced Raman spectroscopy during electrochemical reduction of CO_2 at Cu–electrode–water interface. Reprinted with permission from H. An et al., "Sub-Second Time-Resolved Surface-Enhanced Raman Spectroscopy Reveals Dynamic CO Intermediates during Electrochemical CO_2 Reduction on Copper," *Angew. Chem. Int. Ed.* under CC BY 4.0. © 2021.

Developing realistic limits on the kinetics of reactivity that can differ from thermodynamic estimates requires insights into the dynamic evolution of the structure and morphology of the solid interface during multiple cycles of CO_2 capture and conversion or carbon mineralization.

Advances in very small angle neutron scattering now enable the resolution of features ranging from 1 to 2,000 nm[16] in a single measurement. Similarly, advances in ultrasmall/small/wide angle X-ray scattering (USAXS, SAXS, WAXS) measurements can resolve features ranging from 1 Å to 5 µm as a single measurement in less than 3 minutes.[17] These operando X-ray scattering measurements can be used to resolve the structural and microstructural integrity of catalysts and sorbents in operation, identify metastable and stable carbonate phases and undesired secondary phases during mineralization, and identify the rate-limiting steps during CO_2 capture, conversion, and mineralization.

Atomic force microscopy (AFM) provides a natural technique for imaging at liquid–solid and gas–solid interfaces with molecular resolution. Recent advances in both resolution and speed now enable direct imaging of surface-adsorbed atomic species,[18] even in liquids, and observation of dynamic processes, such as polymer film formation,[19] at video rates (~50 images per second). The combination of AFM and measurements of surface potentials enhance the level of information obtained by providing a means of identifying adsorbed ionic species.[20] The ability to probe interfacial liquid structure at or between mineral surfaces has been augmented by AFM-based 3D fast force mapping, which provides a 3D image of solution structure at the atomic scale as seen by an AFM tip interacting with the surface.[20–25] Studies have been carried out at the interface of water with the surface of numerous materials, including muscovite mica,[20] calcite,[26] graphite and other 2D materials,[25] and boehmite (AlOOH).[20] The impact of electrolytes on water structure above muscovite and graphite was also investigated in these studies. More recently, measurements in ionic liquids have been used to examine their structuring near electrode surfaces.[27]

Transformative scientific advances in CO_2 removal can be realized by addressing the following research questions related to innovations in instrumentation, strategic interface design, and coupling experiment with simulations to elucidate spectroscopic signals: (1) What multimodal characterization advances can be achieved to delineate changes in the solid, aqueous and gas phase compositions during CO_2 removal at realistic conditions? (2) How can benchmarking experiments in high CO_2 environments (discussed above) be translated to dilute conditions with considerably weaker signals? (3) How can we harness experiments to validate computational models and parameterize force fields at representative conditions? (4) How can operando measurements be designed to link the evolution of specific chemical and physical properties to the structure and morphology of interfaces? How do we extract meaningful data from imperfect and evolving interfaces that are vulnerable to misinterpretation? (5) How can we design in situ and operando measurements to identify and tune the limiting steps during CO_2 removal processes at interfaces? (6) How can we design and harness model architected interfaces and materials to shed fundamental mechanistic insights into the evolution of fluid–surface interactions in real time to develop calibrated scientific insights?

Develop experimentally informed, scale-aware computational tools

Simulations of chemical phenomena exhibit an inverse correlation of system size and complexity with accuracy. Small, gas-phase molecular properties can be calculated precisely, as well or better than they can be experimentally measured. However, as spatiotemporal scales increase, necessary approximations limit accuracy. The challenge is to improve simulations at each scale so that they are accurate enough to be used at the system scale and flexible enough to handle changes in physicochemical properties of the system over time. These experimentally informed, scale-aware computational tools would be able to link molecular-level phenomena controlling carbon transformations at multiple scales in architected and natural materials.

There are several different approaches to link molecular-level phenomena to higher-scale observations and simulations. One approach is to use molecular simulations to obtain parameters such as site-specific pKa values that are not easily determined experimentally for use in continuum-scale thermodynamic models.[28] Another approach is to use a combination of experiment and simulation to establish mechanisms of reaction. For example, Miller et al.[29] studied oxygen exchange between H_2O and CO_2 as a function of H_2O film thickness on the mineral forsterite using infrared measurements, oxygen isotope tracers, and quantum chemical calculations. They learned that surface Mg^{2+} sites lower the barrier for carbonic acid formation. Placencia-Gomez et al.[30] and Miller et al.[31] used a combination of experiment and molecular dynamics simulation to examine Mg^{2+} adsorption and diffusion on forsterite surfaces covered in thin water films. The calculations provided a molecular level understanding of how H_2O film thickness dictates energy barriers for diffusive transport of adsorbed Mg^{2+} species required for the formation of $MgCO_3$.

Molecular simulations can also be used to test the assumptions inherent in thermodynamic constitutive equations. New thermodynamic expressions for describing mixed-phase systems (i.e., supercritical CO_2, $scCO_2$) that range from dry to partially water-saturated $scCO_2$ and over a wide range of temperature and pressure[32] have been developed for incorporation into reactive-transport codes to simulate two-phase flow and reaction over time. However, few data are available about how the ions in aqueous solution will affect the $scCO_2$ phase. Using classical molecular dynamics,[33] the solvation energies were compared for alkali and alkaline-earth metal cations in water and $scCO_2$, showing larger cations may partition readily into the $scCO_2$ phase, with a partial solvation sphere of water molecules (**Figure 1-5**). The combination of advances in ML techniques and exascale computing technologies makes it possible to address the decades-long challenge of scaling from atomic electronic structure calculations to continuum simulations at the macroscale (**Figure 1-6**).[35,36,37,38,39,40,41,42]

Once the more accurate, smaller scale calculations can be routinely performed on system sizes that overlap with the next larger scale, the next-level simulations can be parameterized and benchmarked to the next-level simulations at an accuracy comparable to the smaller scale. For example, machine-learning based DFT (ML-DFT) methods are being developed[33] that can extend the size of electronic structure calculations to 10^4 to 10^6 atoms, which overlaps the classical mechanical MD system size. Subsequently, parameterization of interatomic potentials based on ML methods (machine learning interatomic potential, or ML-IAP),[34] experimental data, and DFT results can be expanded to over 10^9 atoms, which overlaps the domain of lattice Boltzmann simulations. At each level, simulations can be compared to experimental observations at the same scale on systems designed to match experiment and simulation. The predictions of each level can be tested against results from smaller and larger scales as well (e.g., do molecular-scale diffusion coefficients or rate constants match those at pore scales?). System-scale models will not be expected to include the level of detail contained in smaller scale models; however, important parameters such as the change in Gibbs free energy (ΔG), rate constants, or interfacial tensions could be included. The result will be system-scale models that allow for longer term performance predictions and design capabilities that account for molecular mechanisms in the context of larger scale processes such as fluid flow and substrate changes.

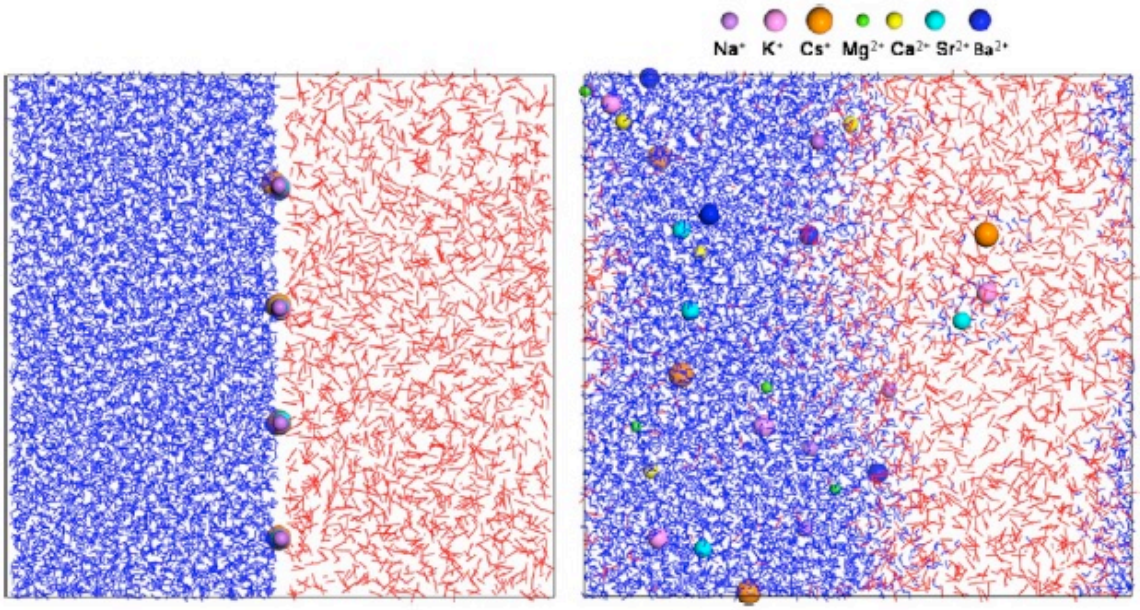

Figure 1-5. Initial configuration (*left*) and after 500 ps (*right*) of MD simulation cell of water (*blue*) supercritical CO_2 (*red*) system at 350 K and 20 MPa with alkali and alkaline earth metal cations positioned on the fluid–fluid interface. In this quick simulation, most of the cations diffuse into the water phase but K^+, Cs^+, and Sr^{2+} diffuse into the $scCO_2$ phase either partially or fully coordinated by water molecules.[32] Reprinted with permission from L. J. Criscenti and R. T. Cygan, "Molecular Simulations of Carbon Dioxide and Water: Cation Solvation," *Environ. Sci. Technol.* 47 (1), 87–94. © 2013 ACS.

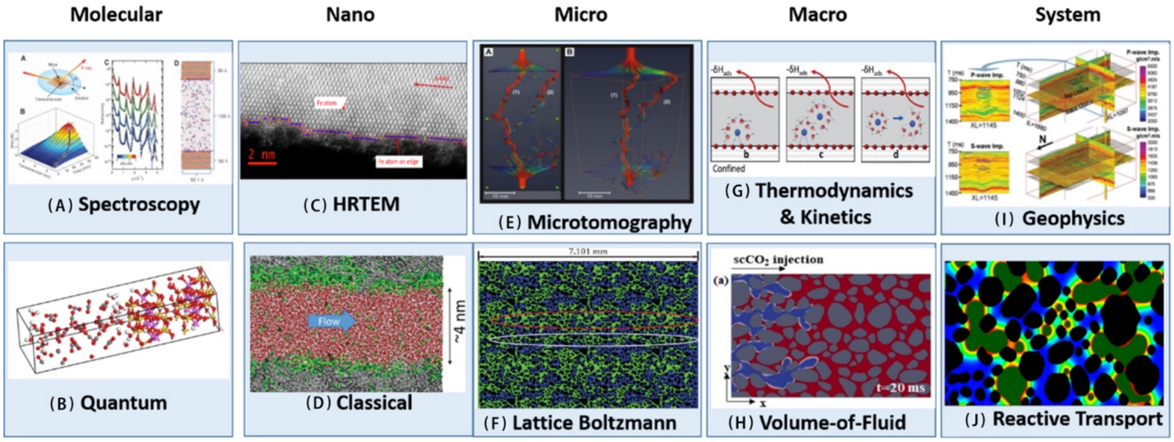

Figure 1-6. Range of scales probed by experimental techniques (*above*) and correlative computational methods (*below*). (A) Reprinted with permission from S. S. Lee et al., "Ion Correlations Drive Charge Overscreening and Heterogeneous Nucleation at Solid–Aqueous Electrolyte Interfaces," *P. Natl. Acad. Sci. USA* under CC BY-NC-ND 4.0.https://creativecommons.org/licenses/by-nc-nd/4.0/ © 2021. (B) Reprinted with permission from O. A. Ajayi and J. D. Kubicki, "Interfacial Energies of Supercritical CO_2 and Water with 2:1 Layered Silicate Surfaces: A Density Functional Theory Study," *Appl. Geochem.* 114. © 2020 Elsevier. (C) Adapted with permission from K. J. T. Livi et al., "Crystal Face Distributions and Surface Site Densities of Two Synthetic Goethites," *Langmuir* 33, 8924–8932; © 2017 ACS. (D) Reprinted with permission from T. A. Ho et al., "Supercritical CO_2-Induced Atomistic Lubrication for Water Flow in a Rough Hydrophilic Nanochannel," *Nanoscale* 10 (42), 19957–19963. ©2018 RSC. Permission conveyed through Copyright Clearance Center Inc. (E) Reprinted with permission from B. Callow et al., "Assessing the Carbon Sequestration Potential of Basalt Using X-Ray Micro-CT and Rock Mechanics," *Int. J. Greenh. Gas Con.* 70, 146–156. © 2018 Elsevier. (F) Reprinted with permission from Y. Chen et al., "Inertial Effects during the Process of Supercritical CO_2 Displacing Brine in a Sandstone," *Water Resour. Res*. 55 (12) under CC BY-NC 3.0. © 2019 AGU. (G) Reprinted from A. G. Ilgen et al., "Defining Silica-Water Interfacial Chemistry under Nanoconfinement Using Lanthanides," *Environ. Sci. Nano.* 8 (2). ©2021 RSC. Permission conveyed through Copyright Clearance Center Inc. (H) Reprinted with permission from S. Bakhshian, "Dynamics of Dissolution Trapping in Geological Carbon Storage," *Int. J. Greenh. Gas Con.* 112, 103520. © 2021 Elsevier. (I) Reprinted with permission fom A. Chadwick et al., "Quantitative Analysis of Time-Lapse Seismic Monitoring Data at the Sleipner CO_2 Storage Operation," *Lead. Edge* 29 (2), 113–240. © 2010 Society of Exploration Geophysicists. Permission conveyed through the Copyright Clearance Center Inc. (J) Reprinted with permission from L. Chen, "Pore Scale Study of Multiphase Multicomponent Reactive Transport during CO_2 Dissolution Trapping," *Adv. Water Resour. 116*, 208–218. © 2018 Elsevier.

Develop a molecular-level understanding of how CO_2 capture processes are affected by interfacial structure and chemistry

A recurrent theme in carbon capture and sequestration is the formation of fluid or solid coatings on reactive surfaces that restrict access or reduce reactivity. Opportunity exists to harness the energetics of these coatings to minimize or prevent these passivation effects. For example, interfacial energies dictate: (a) the thickness of adsorbed water films that influence CO_2 flow and mineralization in geologic storage formations,[29] (b) the preferential adsorption and reactivity of species at solid interfaces in multicomponent and confined porous environments, (c) the tendency of neo-formed solids (carbonates, salts, silicates) to coat and eventually occlude reactive surfaces,[36,44] and (d) the ability of mineral growth to expose fresh reactive surfaces by driving crack formation.[45] These insights could inform the design of interfaces for preferential solvation, separation, and crystallization pathways related to CO_2 mineralization. Thus, transformative advances in energy-efficient carbon removal could be realized by addressing knowledge gaps associated with molecular level interfacial structure and chemistry that prevent control over the energetics of interfacial processes, including:

- What is the energetic basis for tuning preferential adsorption and reactivity of species at solid interfaces in multicomponent and confined porous environments?
- How can we harness insights into energetic interactions to inform the design of interfaces for preferential solvation, separation, and crystallization pathways?

Preferential adsorption, organization, or displacement of specific molecules of interest at solid–gas or solid–liquid interfaces can be tuned by delineating the energetic interactions at the interface. Considering CO_2 injection for storage in depleted oil and gas reservoirs, computational studies have shown that preferential adsorption of CO_2 molecules over propane (same molecular weight) and toluene on silica surfaces is due to hydrogen interactions in silica nanopores, in addition to relative diffusion rates of the gas molecules.[46]

Weaker interactions (e.g., hydrogen bonding) vs. stronger interactions (e.g., covalent bonding) can be harnessed to tune specific interfacial functions of architected and natural materials (i.e., hybrid inorganic-organic materials can feature covalent and ionic interactions between CO_2 and the solid material).[47–49] Phase-changing nanofluids that enhance fracturing for heat mining can be developed by tuning hydrogen bonds between silica surfaces and functional polymer groups in the presence of CO_2, where higher CO_2 capacity of the silica–polymer compared to polymer alone is attributed to entropic effects (see **Sidebar 4**).[50]

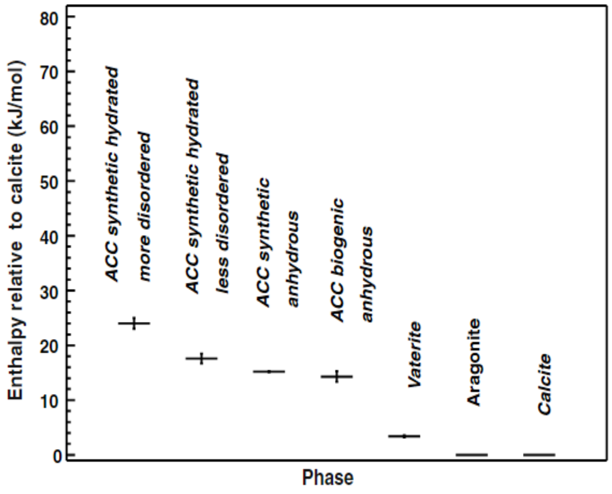

Figure 1-7. Relative energetic stabilities of different calcium carbonate phases with respect to calcite.[51] ACC refers to amorphous calcium carbonate. Reprinted with permission from A. V. Radha et al., "Transformation and Crystallization Energetics of Synthetic and Biogenic Amorphous Calcium Carbonate," *Proc. Natl. Acad. Sci. USA 107* (38), 16438–16443. © 2010.

In mineralization processes, interfacial energetic interactions play a crucial role in mediating the formation of specific solid carbonate phases. For example, for crystal sizes smaller than 100 nm, particle-size-dependent small variations in formation enthalpy (e.g., 1–10 kJ/mol) was proposed to explain the formation of metastable vaterite, aragonite, and then calcite (**Figure 1-7**).[51] Despite these insights, the influence of ligands, temperature, and multiple ionic species on the energetics of CO_2 solvation and crystallization in natural and engineered environments remain largely unresolved. Using energetic interactions as a basis to elucidate the formation of metastable versus stable carbonates can unlock fundamental scientific insights into solid-state and particle-size-dependent carbonate dissolution and reprecipitation mechanisms,[52] as well as enable predictive controls on carbon transformations.[52,53] These insights could inform the reaction-induced mechanical weakening and strengthening of natural and architected materials, and reactive transport behaviors across wide-ranging time and spatial scales.

Sidebar 4. Enhanced CO_2 Carrying Capacity in Nanofluids, Based on Interfacial Hydrogen-Bonding Interactions

Injecting neat CO_2 or CO_2-containing fluids in the subsurface serves the dual purpose of fracturing rocks to enhance fluid flow for heat mining or solution mining of metals from unconventional reservoirs and simultaneous storage of CO_2. Asgar and coworkers[SR2] compared CO_2 carrying capacity of aqueous poly(allylamine) (PAA) and aqueous SiO_2–PAA nanocomposites. The SiO_2–PAA demonstrated an almost threefold increase of CO_2 carrying capacity. On the macroscopic scale, the SiO_2–PAA solution undergoes gelation upon uptake of CO_2, whereas the PAA undergoes minimal change at room temperature (observed both by the eye and by SAXS data). Enhanced gelation of SiO_2–PAA on CO_2 uptake enables fracturing in the geologic formation. Combined SAXS and Fourier transform infrared spectroscopy data suggested the gelation and enhanced CO_2 carrying capacity was attributed to hydrogen bonding between interfacial Si–OH and the PAA amines, creating more rigid cages for CO_2 trapping.

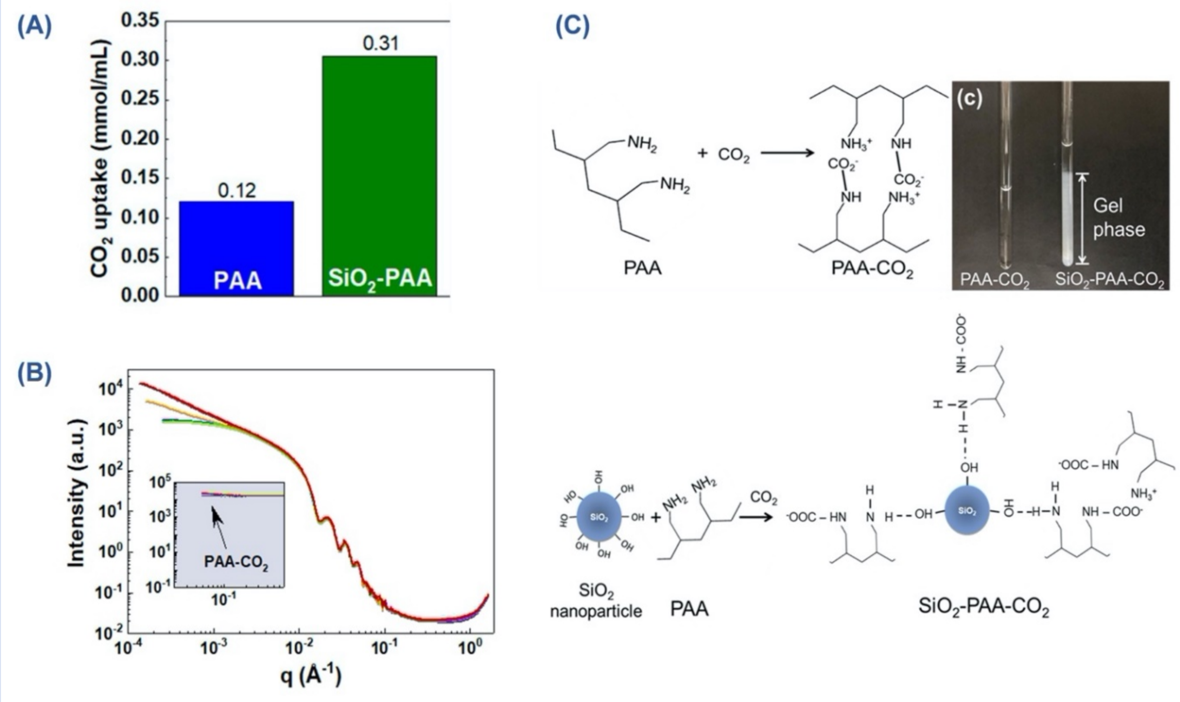

Figure S4. (A) CO_2 carrying capacity of PAA alone and as a composite with SiO_2 nanoparticles, SiO_2–PAA. (B) evolution of SAXS (small-angle X-ray scattering) spectra of SiO_2–PAA showing gel formation ($q < 0.004$ $Å^{-1}$) with increased CO_2 uptake. *Inset*, Analogous SAXS spectra for PAA alone, showing minimal changes with CO_2 uptake. (C) Proposed PAA–CO_2 (*top left*) and SiO_2–PAA–CO_2 interactions at the atomic level. *Upper right*, Photograph comparing PAA–CO_2 and SiO_2–PAA–CO_2 composites. Gel formation is evident in SiO_2–PAA–CO_2 composites at room temperature. Reprinted with permission from H. Asgar et al., "Designing CO_2-Responsive Multifunctional Nanoscale Fluids with Tunable Hydrogel Behavior for Subsurface Energy Recovery," *Energ. Fuel* 33 (7), 5988–5995. © 2019 ACS.

In the context of identifying emerging scientific needs, delineating the energetic interactions underlying nanoscale confinement and interfacial fluids on directing carbon transformations is crucial for developing predictive controls. These insights could inform the reaction-induced mechanical weakening and strengthening of natural and architected materials and reactive transport behaviors across wide-ranging temporal and spatial scales.

1d. Potential Impacts

Interfacial processes are a ubiquitous feature of all carbon removal technologies. Thus, recognition of poorly characterized but ubiquitous interfacial processes (i.e., formation and degradation of reactive oxygen species) could lead to new paradigms in CO_2 capture chemistries and beyond. The scope for improvement in characterization of complex and dynamic interfaces in both natural and engineered CDR materials could inspire next generation experimental design and instrumentation—both on the benchtop and at user facilities—for in situ X-ray, neutron, and vibrational spectroscopies, as well as scanned probe imaging. Improved computational techniques will link scales from the atomic level to the full system level, where all scales are important in both engineered and natural processes for CO_2 removal. These advances may be critical for defining approaches to tuning specific bonding behavior and interfacial energetics that could be harnessed to direct carbon transformations in multiphase chemical environments.

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1f. Sidebar References

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PRO 2: Create Materials that Simultaneously Exhibit Multiple Properties for CO_2 Capture and Release or Conversion

Creating new, high-performance materials could be key to reducing the energy required for capturing CO_2 from dilute sources and for converting CO_2 into valuable products with net-negative emissions. In particular, understanding the degradation and restoration pathways that impact function could be essential to extending the lifetime of materials. At the same time, materials must be designed to respond rapidly to incoming CO_2 and capture or convert it with high efficiency. The development of new synthetic approaches guided by analyses of in situ behavior could accelerate the discovery of materials with a transformative impact on CDR technologies.

2a. Summary

An essential endeavor for achieving energy efficiency in dilute-source CO_2 capture and conversion lies in the synthesis of durable new materials that can simultaneously meet multiple performance metrics. Accordingly, the development of fundamentally new synthetic approaches and the realization of new classes of materials could lead to important breakthroughs in CDR technologies. In particular, approaches to creating new materials with a high surface area are critical for enabling effective contact with the extremely low levels of CO_2 present in air and bodies of water, as well as for establishing catalysts that deliver a high conversion yield. Since durability is of key importance, learning to synthesize new porous framework materials built of strong inert bonds and establishing methods for then installing functional sites for capture or conversion is of particular importance. Further, the realization of new types of functional groups or metal sites that adsorb or activate CO_2 is of interest, as well as control of outer-sphere interactions that can be used to enhance performance. Relevant synthetic methods might include novel approaches to solid-state synthesis (including mechanical grinding and chemical vapor deposition), solution-based materials assembly, high-throughput synthesis, and even molecular reaction chemistry.

2b. Key Scientific Questions

- Can we synthesize new materials that meet multiple performance characteristics simultaneously as required to enable efficient dilute-source CO_2 capture or conversion?
- Can we develop a fundamental understanding of degradation and restoration pathways that enable the design of separation materials and catalysts with extended lifetimes?
- Can we develop in situ tools with high spatiotemporal resolution that enable an understanding of materials assembly and performance?
- Can we accelerate the discovery of separation materials and catalysts through ML and artificial intelligence (AI)?

2c. Scientific Challenges and Research Opportunities

As discussed in more detail in the following sections, key opportunities to be explored include:

- Design and synthesis of robust materials that can remove CO_2 from dilute sources (air or water) with a high swing capacity, fast uptake and release, and a high capture fraction.

- Creation of long-lived catalysts with high activity for the selective conversion of CO_2 into valuable products with net-negative emissions.
- Assemblage of structured forms of separation materials and catalysts for enabling processes with improved mass transport, low pressure drop, and enhanced energy efficiency.
- Development and application of in situ tools, computational methods, or a combination of both approaches for understanding the assembly and dynamic behavior of new separation materials and catalysts.

Design and synthesis of robust materials that can remove CO_2 from dilute sources

Unlike the development of materials for a typical process where under normal operating conditions the feed composition, temperature, and pressure are within a tight window, DAC has to operate efficiently under conditions that vary widely both geographically and temporally. Although the CO_2 concentration in air is currently 414 ppm and may change slowly, rising in the short term before eventually falling over many decades, other factors such as relative humidity and temperature can vary widely in the space of a few hours. Additionally, the price and lifetime of DAC materials have been identified as the major economic barriers to its implementation.[1] Therefore, it can be beneficial if DAC materials operate effectively for long durations (over many thousands of cycles for adsorbents) and are robust enough to tolerate these changes in operating conditions as well as potential degradation mechanisms.

Adsorbents: For effective CDR using solid adsorbent based processes, the DAC process must, in addition to being robust, have high productivity. This entails three characteristics: (1) the material must have a high swing capacity (i.e., a high capacity under adsorption conditions and a low capacity under desorption conditions); (2) the material must have fast intrinsic adsorption and desorption kinetics; and (3) the contactor must enable fast mass transfer in both the adsorption and desorption steps to expedite the transfer of CO_2 from air to the material and back. As previously mentioned, an additional feature is the ability for this process to be repeated over many cycles with minimal material degradation so that performance is maintained. The development of new adsorbents for DAC could therefore take all of these factors into account to synthesize improved materials that can be employed in DAC processes.

Understanding sorbent degradation mechanisms such as chemical poisoning (e.g., irreversible urea formation),[2] especially in conditions of low humidity adsorption or desorption, and oxidation of amines[3] along with the effects of temperature and humidity on the mechanisms will be critical in the design of materials that are more robust under expected process conditions. Other factors such as catalytic degradation by metals from airborne pollutants or metals inherently present as impurities in the sorbent synthesis also need to be studied and ways to mitigate them found.[4] Given the immense scale of DAC sorbents that will likely be needed, the sorbents could benefit from long lifetimes or from the ability to regenerate/heal in situ as removal and transportation of huge amounts of sorbent for regeneration could be impractical.

For DAC to be a negative emission technology, the CO_2 will most likely need to be sequestered, which will require high CO_2 product purity for efficient compression and storage. Capture fraction in DAC is as critical as it is in carbon capture and storage (CCS), where a higher capture fraction per cycle increases the productivity of the process and reduces the energy penalty per ton of CO_2 captured.[1] Strong, selective binding of CO_2 is required to achieve high capture fractions of CO_2 from air where the CO_2 is such a minor component. Thus, materials with high capture fractions (>75% from air) that can produce high purity CO_2 (>95%) while also being robust need to be developed (**Sidebar 5**).

Understanding co-adsorption of water on sorbents is also critical to consider when developing new DAC adsorbents. The concentration of water can be over three orders of magnitude higher than the concentration of CO_2, making selective adsorption of CO_2 problematic if water and CO_2 are competing for the same binding sites. For some sorbents such as hydrophilic zeolites, water binds strongly and selectively over CO_2 and effectively poisons the sorbent, whereas with some amine-based solid sorbents the presence of water can improve performance.[5] Because of the profound effects of humidity on DAC sorbent capacity, kinetics, and lifetime, there are clear limitations to using standard laboratory single-component equilibrium capacity measurements to evaluate materials for a real DAC process. In addition, CO_2 adsorption onto a sorbent can change the water affinity, further complicating the use of single-component measurements. A greater focus on measuring accurate multicomponent CO_2/H_2O isotherms over a wide concentration and temperature range needs to be prioritized to understand the effect of humidity on adsorbent performance, and for use in process modeling, which requires accurate isotherms as an input. One potential benefit of water co-adsorption that can be explored is in situations where the co-adsorbed water from air can be used to offset the expected large water use/loss from DAC sorbent processes and can possibly even be a source of clean water for agricultural use or human consumption (potentially after further purification) in water-scarce regions. However, even with the potential beneficial aspects of water adsorption, an excess of adsorbed water that has to be cycled on and off with the CO_2 with each cycle will add a large parasitic energy penalty. Therefore, it is critical to have a fundamental understanding of the effect of water on these materials in DAC processes, so that adsorbents can be designed to fit specific DAC applications (**Sidebar 6**).

Membranes: Although membrane separation of O_2 from air has been studied extensively in the context of O_2 production and N_2/CO_2 membrane separations are well developed for postcombustion CO_2 capture, materials to achieve DAC are less developed.[6,7] Studies suggest that the very small CO_2 chemical potential driving force requires multistage separations with prohibitively high compression costs, unless very thin (nanometers thick) ultraselective membranes can be developed.[8] Therefore, for membrane-based DAC, new materials and thin film formation and surface modification methods are required to manufacture low-cost, high–surface area membranes with ultrathin and CO_2-ultraselective layers (**Figure 2-1**).[9,10] Innovations are also required on how to couple the operation of such membranes with active (e.g., by reaction) removal of CO_2 on the membrane permeate side to sustain high permeation–driving force.

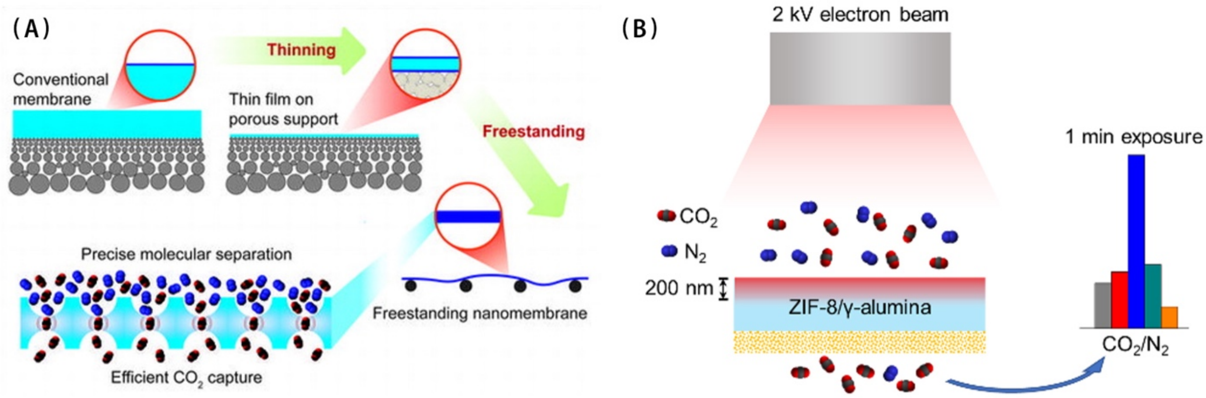

Figure 2-1. (A) Concepts for ultrathin selective layer formation using membrane thinning and free-standing membranes and (B) surface modification methods using irradiation methods. (A) Reprinted with permission from R. Selyanchyn and S. Fujikawa, "Membrane Thinning for Efficient CO_2 Capture," *Sci. Technol. Adv. Mater.* under CC BY 4.0. © 2017. (B) Reprinted with permission from Miao et al., "Electron Beam Induced Modification of ZIF-8 Membrane Permeation Properties," *Chem. Commun.* 2021, *57*, 5250–5253. Permission conveyed through Copyright Clearance Center Inc.

Sidebar 5. Cooperative Adsorption

Although materials and liquids that can take up large amounts of CO_2 from dilute sources typically have isolated binding sites, it is also possible to create porous materials that bind CO_2 in a way that activates a neighboring site, leading to cooperative adsorption akin to that encountered for O_2 uptake in hemoglobin. An initial example of this was realized with the diamine-appended MOF mmen-Mg_2(dobpdc). In this MOF, CO_2 insertion into a metal–amine bond prompts a cascade reaction to form 1D ammonium carbamate chains running along the pore surface.[SR1,SR2] An important consequence of such a cooperative mechanism is the step-shaped CO_2 adsorption isotherms, which can lead to high separation capacities with small changes in pressure or temperature relative to the Langmuir-type isotherms displayed by traditional adsorbents (**Figure S5**). The realization of new materials displaying cooperative adsorption of CO_2 at conditions relevant to its effective capture from air or water could potentially reduce the energy associated with such a separation. Here, new mechanisms for cooperative CO_2 adsorption are of interest, including mechanisms that might lead to a more robust cooperativity that propagates in 2D or 3D.

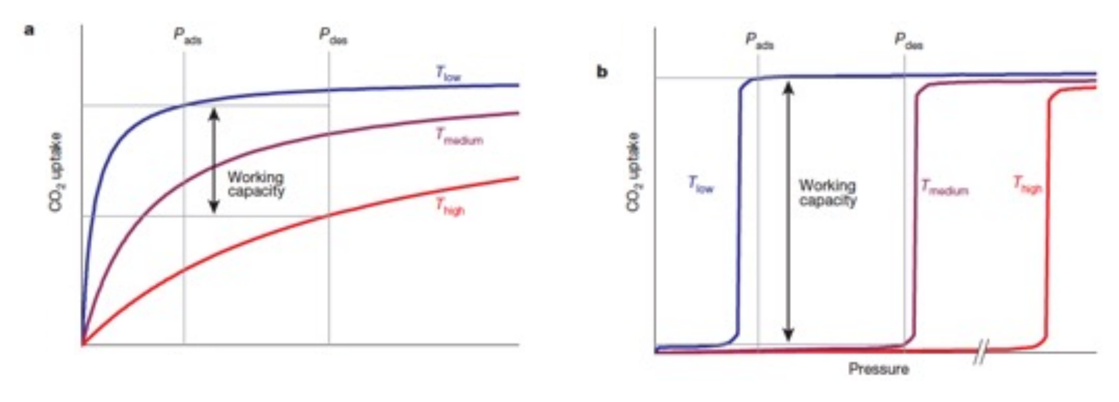

Figure S5. Idealized CO_2 adsorption isotherms for (A) a traditional adsorbent with a Langmuir-type profile and (B) a cooperative adsorbent with a step-shaped (or sigmoidal) profile. The double-headed arrows indicate the working capacity (i.e., the amount of gas removed per adsorption/regeneration cycle) for a separation performed using a temperature swing process in which selective adsorption occurs at P_{ads} (below 415 ppm for air) and T_{low} (ambient air temperature) and desorption is performed at P_{des} and T_{high} (A) or T_{medium} (B).[SR1] Reprinted with permission from T. M. McDonald et al., "Cooperative Insertion of CO_2 in Diamine-Appended Metal–Organic Frameworks," *Nat.* 519, 303–308. © 2015 Springer Nature.

Creation of long-lived catalysts with high activity

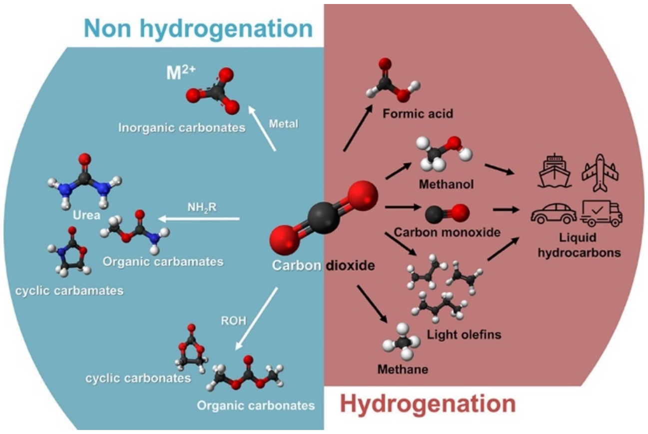

Figure 2-2. High-valued fuels and chemicals produced by catalytic conversion of CO_2 selectively; however, one of the grand challenges for designing long-lived catalysts is reducing the rate of deactivation while preventing active site loss during multiple regeneration cycles. Reprinted with permission from E. C. Ra et al., "Recycling Carbon Dioxide through Catalytic Hydrogenation," *ACS Catal.* 10 (19), 11318–11345. © 2020 ACS.

Catalyst development must take into account several overarching criteria for practical implementation of carbon capture and utilization, which include the design of long-lived catalysts from earth-abundant materials that are capable of handling large-scale CO_2 conversion (gigaton quantities).[11] The economic feasibility of these processes relies on the products of the catalytic reactions having value, which precludes CO_2 conversion to methane, but allows for a broad class of reaction pathways leading to value-added chemicals or intermediates, fuels, plastics, or novel building materials (**Figure 2-2**).[12] The selection of reaction pathways for CDR should focus on processes leading to overall net negative CO_2, using examples that combine catalyst design with life cycle analysis as a guide for pursuing practical solutions.[13] Catalysts can be designed with one or more active sites for CO_2 conversion by chemical, biochemical, photochemical, electrochemical, photo-electrochemical, plasma processes, or a combination thereof. Criteria for catalyst design and optimization will naturally involve the synthesis of materials with enhanced activity and selectivity. The magnitude of catalysts that must be manufactured to sufficiently handle large-scale (gigaton/year) CO_2 conversion requires that these materials be designed from earth-abundant elements as both active sites and supports. Achieving high activity and selectivity are critical not only for optimal carbon utilization but also for mitigating downstream separation costs. The overall design could focus on a singular reaction or may account for hybrid processes (e.g., chemical looping) where combinations of two or more reactions may be used to enhance CO_2 utilization. To this end, multifunctional catalysts may be required wherein two or more active sites operate in tandem to convert CO_2 to intermediates (syngas, methanol, etc.) that are subsequently upgraded to the desired final product(s). Synthesis of a single catalyst that possesses multiple active sites could be desirable in lieu of optimized contacting sequences of multiple catalysts, each possessing a single functional group. Design criteria may also include ways to achieve exceptional performance under more favorable operating conditions, such as low temperatures and pressures, while also allowing flexibility to handle diverse CO_2 feedstocks where the quantity or nature of impurities can either poison catalysts or have other deleterious effects on their overall performance.

Developing nanoporous catalysts for these reactions involves several challenges to occlude active metals (single atom or nanoparticles), bimetallics, or metal oxides within confined pores. Synthetic methods requiring the least number of steps is desirable. Important considerations may include the interactions between the support (framework) and occluded extra-framework species, which may prove to be critical for long-term stability of active sites and the enhancement of catalytic activity. Shape selectivity is dependent upon the nature of the porous network, which can be a limiting factor for the production of smaller products (e.g., small olefins, oxygenates) owing to the difficulties of placing extra-framework species within highly confined geometries. Maintaining stability of these sites with prolonged reaction times and regeneration cycles will be critical. Moreover, mass transport limitations of these porous materials present a ubiquitous problem because of longer internal diffusion path lengths, leading to increased rates of deactivation (e.g., coking); solutions that reduce these limitations are needed. To this end, these problems require a holistic approach that accounts for multiple factors such as active site design and methods to synthesize nanosized or hierarchical porous materials to maximize catalyst activity, selectivity, and lifetime.

Assembling structured forms of separation materials and catalysts

As with other technologies that rely on nanoporous materials, scale up is a major hurdle in successful implementation of new DAC technologies. Once durable, high-performance materials are designed and synthesized for CO_2 capture and conversion, they could be formed into practical contactors to prevent attrition from high-rate industrial gas flows.

Upon formulation into a desired configuration (**Figure 2-3**), the physicochemical and textural properties may undergo changes, thereby affecting the separation and catalytic performance of the shaped materials relative to their parent analogs in powder form.[14,15,16,17] These changes may arise from strong interparticle/intercrystalline interactions or active phase–binder interactions, which could dictate the formation, extent, and size of meso/macropores upon shaping, as well as the tortuosity of the structure. This is particularly important from a transport perspective because diffusion through these pores can have a dominating effect on the overall mass transfer and accessibility of the active sites. Although generating such pores can increase porosity and the mass transfer rate, it can compromise the mechanical robustness and durability of the structured form. Understanding the relative implications of such trade-offs can enable identification of the best assembling strategy and selection of suitable additives.

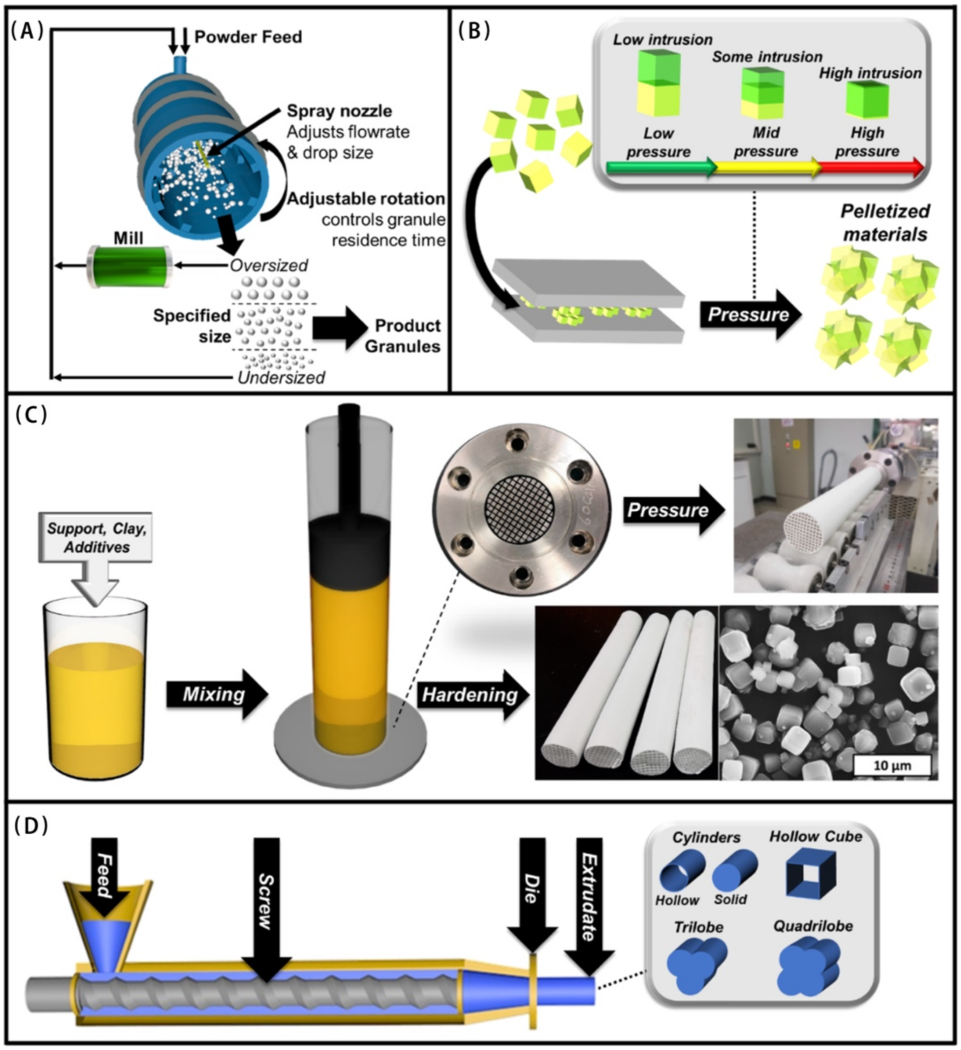

Figure 2-3. Schematic of traditional (A) granulation, (B) pelletization, (C) hydraulic pressure extrusion, and (D) hydraulic screw extrusion methods for adsorbent and catalyst geometric processing. (A, B, D) Reprinted with permission from S. Lawson et al., "Recent Advances in 3D Printing of Structured Materials for Adsorption and Catalysis Applications," *Chem. Rev.* 121 (10), 6246–6291. © 2021 ACS. (C) Reprinted with permission from J. Y. Lee et al., "Investigation on Long Term Operation of Thermochemical Heat Storage with MgO-Based Composite Honeycombs," *Energies* 12, 1262. © 2019. Ojuva et al., "Mechanical Performance and CO_2 Uptake of Ion-Exchanged Zeolite a Structured by Freeze-Casting," *J. Eur. Ceram. Soc.* 35, 2607−2618. © 2015.

Sidebar 6. Electrochemically Modulated Sorption Processes

In contrast to the traditional sorption processes for CO_2 capture and release based on temperature or pressure swings, electrochemically modulated processes rely on changes in the oxidation state of redox-active species to control the uptake of CO_2. The modulation can be either *direct*, in which the redox-responsive component also serves as the primary sorption agent, or *indirect*, in which the redox active species modulates the sorbent environment to change the affinity of an electrochemically inert capture agent for the CO_2. An example of direct activation is quinone species in aprotic media that, when in a reduced state, form adducts with CO_2, but not when oxidized (**Figure S6**).[SR3] These redox species can either be immobilized on electrode substrates for typical swing operations or in solution for continuous flow operations within electrochemical cells. In protic systems, indirect modulation is predominant because the reduced quinones become protonated, the solution becomes more alkaline, and the CO_2 is absorbed as bicarbonate or carbonate ions. Other pH modulation options include the use of intercalation electrodes (e.g., MnO_2, TiO_2, NiHCN) where protons intercalated within the crystal structure are released when the electrode is subjected to an oxidizing potential, and reintercalated under reducing conditions. Similarly, divalent metal cations released into carbamate solutions can form amine–metal complexes, thereby displacing and releasing the CO_2. The successful implementation of these approaches will depend on the development of robust electrode structures that are resistant to oxidative degradation and morphological changes during operation, that have narrow potential swings between reduced and oxidized states (to minimize energetics), and that have small diffusional and electrical resistances. The preparation of these electrodes, normally by drop casting, dip coating, or spray coating, will require careful consideration of ink formulations, substrates and binders, and electrolytes required for ionic conductivity. Innovative electrode configurations will assist with reducing required overpotentials and overall transport and reaction rates with enhanced productivity and selectivity.

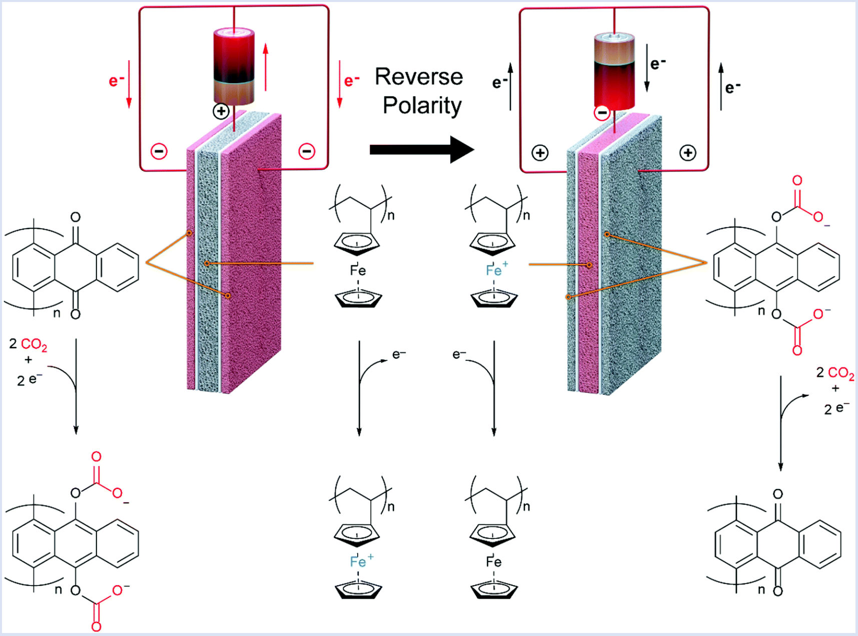

Figure S6. Schematic of a single electro-swing adsorption electrochemical cell with porous electrodes and electrolyte separators. The outer electrodes are coated with poly-1,4-anthraquinone composite and can capture CO_2 on application of a reducing potential via carboxylation of quinone and release the CO_2 on reversal of the polarity. The inner polyvinylferrocene-containing electrode serves as an electron source and sink for the quinone reduction and oxidation, respectively. Reprinted with permission from S. Voskian and T. A. Hatton, "Faradaic Electro-Swing Reactive Adsorption For CO_2 Capture," *Energy Environ.* under CC BY-NC 3.0. © 2019.

Moreover, the sorbent/catalyst materials that consist of organic components may undergo irreversible structural transformations during processing or post-thermal treatment steps. Leaching of active sites to the binder particles may also take place in the formulated structure. Fundamental research is needed to gain atomic/molecular understanding of the changes at the interfaces, particularly in relation to the possible implications in CO_2 capture and conversion, and to establish structure–property–function relationships for structured forms. Understanding such relationships would enable the discovery of suitable formulation methodologies that render the structured form mechanically robust while exhibiting comparable capture and conversion performance to that of the parent analog.

Complementing the fundamental research on the synthesis of durable, high-performance materials with those aimed at assessing the relative kinetics and thermodynamics of CO_2 capture and conversion in structured forms in early stages of development will provide the foundational science to support the eventual scale-up and implementation of such materials at large scale.

Developing and applying in situ tools and/or computational methods

The development and application of in situ physical measurement techniques and ML-based computational methods could greatly facilitate the discovery of new high-performance materials for dilute-source CO_2 capture and conversion. Such tools could provide insights into the conditions governing the nucleation and growth of a solid and potentially—through application of ML and real-time variation of the reaction conditions—even control over the formation of a specific product structure or crystal form. The progress of the synthesis could be followed with advanced imaging/visualization techniques such as X-ray diffraction computed tomography (XRD-CT), confocal fluorescence microscopy (CFM), or MRI, which can provide 2D or 3D distribution of various phases during assembly and formulation. Additionally, in situ tools could be used to provide detailed information about changes in a material during its operation throughout a CO_2 removal process, following the course of both capture and regeneration. Similarly, such experiments may allow changes to a catalyst to be followed throughout the CO_2 conversion reaction. In both cases, the studies may reveal critical degradation and restoration pathways, as well as specific operating conditions that should be avoided, thereby facilitating the design of new materials with improved performance. Investigating the consequences of potential impurities or variations in the feed streams, such as particulates or relative humidity in air, competing adsorbates and fouling agents in bodies of water, or poisonous contaminants in the CO_2 source could be particularly important for ensuring a long lifetime for the capture material or catalyst.

Depending on the material and its form, a wide range of characterization methods—including AFM, transmission electron microscopy, and infrared, Raman, nuclear magnetic resonance, and X-ray absorption spectroscopies—could provide the critical understanding leading to improvements in performance. In particular, the development of new types of sample cells that allow the system to be probed under realistic conditions, improvements in spatial and temporal resolution of the methods, and the ability to bring multiple such in situ probes to bear simultaneously may be of value in gaining this understanding. Further, computational approaches that apply AI or ML algorithms could effectively use the data emerging from such experiments to accelerate the discovery of improved materials.[18] Validation of these computational methods through comparison with extensive experimental data may even then allow confidence in predictions for radically new materials synthesis targets worthy of pursuit.

2d. Potential Impacts

Cost, energy, and physical space requirements are all critical, intertwined factors that impact the viability of CDR technologies being implemented at scale. Successes resulting from the research areas outlined in this PRO could lead to the development of durable, high-performance materials with increased energy efficiency that could significantly reduce the cost of CDR processes and enable the scale up and implementation of CO_2 capture and conversion technologies. Additionally, improvements in material performance and lifetime can lead to reductions in the quantity of material needed to achieve target reductions, thereby reducing the size of contactors and the overall environmental impact of CDR processes.

In addition, the development of new approaches to synthesis and materials design can have a broad impact in many areas beyond the CDR community and can lead to advances in materials used in other separation and catalytic processes. The development of advanced characterization tools, particularly those that can also be coupled to computational methods such as ML and AI, can accelerate the discovery of separation materials and catalysts for applications in CDR and beyond. In particular, this research can improve the understanding of interfacial reactivity, transport, and degradation mechanisms for materials and provide a better understanding of the interactions and reactivity of CO_2 with materials and interfaces under dynamic conditions and in complex environments.

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PRO 3: Discover Mechanisms and Materials for Efficient Energy Transfer and Management in CO_2 Capture, Release, and Conversion

CO_2 capture sorbents are commonly regenerated by thermal energy derived from fossil resources. With the rapid deployment of renewable energy, there is a unique opportunity to explore unconventional mechanisms (e.g., electrochemical, electromagnetic, acoustic, and other alternatives) for selective, energy-efficient regeneration of sorbent materials that can be integrated with CO_2 conversion. A key challenge is to understand how these approaches can be used to decouple the strong CO_2 binding affinity required for efficient capture from the energy barrier to its subsequent release or conversion. To do so, new computational and experimental tools could enable investigations that probe localized energy transfer and molecular reconfigurations at capture sites and across interfaces. These advances could enable improved thermal management and energy efficiency for CDR.

3a. Summary

Approaches to DAC include aqueous alkaline bases, humidity-swing quaternary ammonium-based anion-exchange resins, and solid-supported amines, with fewer technologies based on electrochemical and membrane separations.[1] DAC using aqueous alkaline bases requires regeneration temperatures of 800–900°C, which constitutes most of the energy required for CO_2 removal (6–9 GJ per ton of CO_2). Aqueous amines have milder regeneration temperatures (~120°C); however, their reaction enthalpies, on the order of −80 kJ/mol of CO_2, are still demanding, especially when coupled with the evaporation of both the amine and water. Therefore, innovative heat integration schemes have been carried out to reduce the parasitic energy consumption of CO_2 capture technologies. However, the volatility and toxicity of amines limit their use in open systems. Solid-supported amines are more promising but present mass transport and durability limitations. The current state of the field necessitates improved solvents/sorbents with high CO_2 selectivities and capacities, fast transport, new regeneration mechanisms or improved energy requirements for thermal regeneration, and long-term stability.[2] With the availability of affordable renewable electricity (e.g., solar), new regeneration methods can be less energy intensive. Thus, next-generation CO_2 capture materials should possess innovative properties that can use energy other than direct thermal heating.

DOC and removal of CO_2 is an emerging research area for dilute capture of CO_2 (**Sidebar 7**). The world's oceans are the largest global carbon sink, storing 50 times more carbon than the atmosphere.[3] Total carbon in the shallow ocean water layer exists as dissolved inorganic carbon (DIC), which mostly takes the form of bicarbonate (HCO_3^-) at the native ocean pH of ~8.1.[4] The increase in DIC has followed linearly the increased atmospheric CO_2 concentration and has resulted in a linear decrease in pH, corresponding acidification of the shallow ocean. By volume, DIC in ocean water is ~120 times more concentrated than CO_2 in the atmosphere.[4,5] Depending on wind speed and ocean currents, the timescale for the mixing between the atmospheric CO_2 and ocean water can be as short as 2–4 months, resulting in net CO_2 drawdown from the atmosphere.[6] DOC may be able to exploit emerging offshore energy resources such as wind and wave power, and it may also have unique access to offshore sequestration sites, potentially making it possible to capture CO_2 from the ocean on a large scale at low cost.

Sidebar 7. Direct Ocean Capture

Oceans have absorbed about 40% of all anthropogenic carbon emissions to date because of equilibration between CO_2 in the atmosphere with the carbonate system in ocean water that takes place on a short timescale (<1 year).[SR1] Total carbon in the shallow ocean water layer exists as DIC, which mostly takes the form of bicarbonate (HCO_3^-) at the native ocean pH of ~8.1.[SR2] Various approaches to DOC of CO_2 are being explored, including both biotic and abiotic routes. Biotic approaches include carbon storage in coastal wetlands and salt marshes containing seagrasses and mangroves, harnessing the ocean's natural processes for upwelling and downwelling of seawater between the shallow ocean and the deep ocean. Abiotic approaches include alkalinity enhancement when dissolved solid minerals are added to ocean water resulting in an increase of pH and precipitation of stored carbon in solid form and electrochemical pH swing processes that acidify ocean water to a pH ~4–5, shifting the DIC equilibrium from bicarbonate toward dissolved CO_2 (aq), which can then be extracted as gaseous CO_2.[SR3]

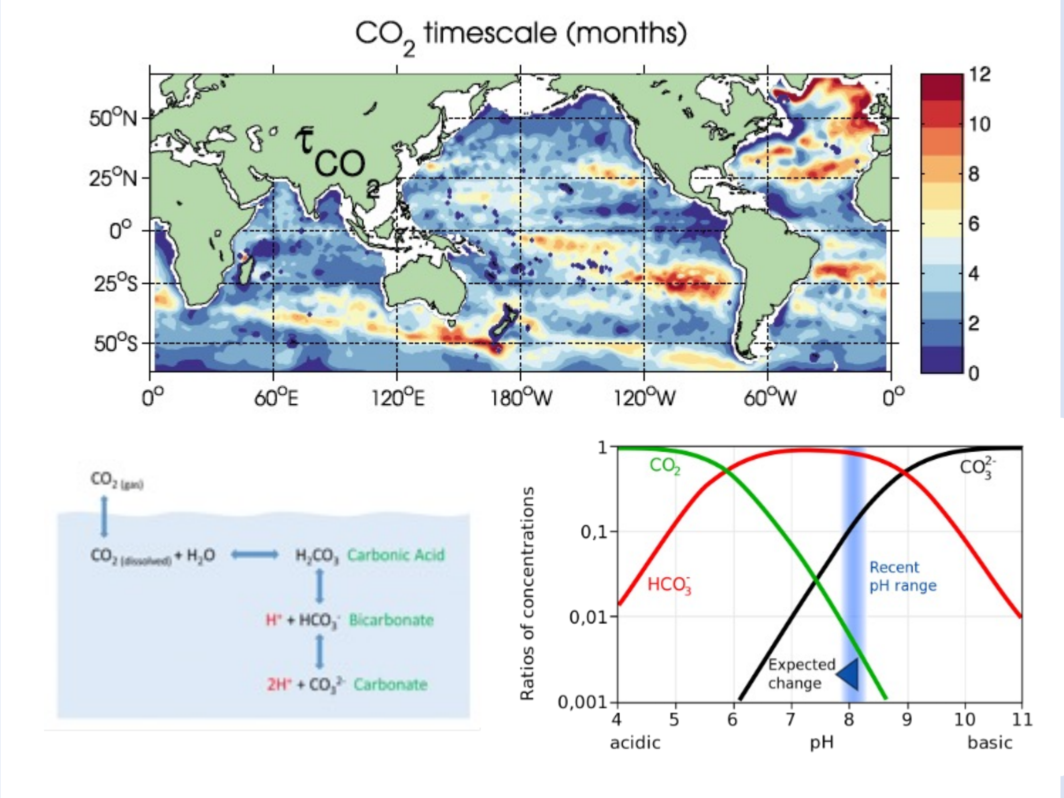

Figure S7. *Top,* Global map of the mixing time for CO_2 at the atmosphere–ocean boundary.[SR1] Reprinted with permission from D. C. Jones et al., "Spatial and Seasonal Variability of the Air-Sea Equilibration Timescale of Carbon Dioxide," *Glob. Biogeochem. Cycles*, *28* (11), 1163–1178. © 2014 AGU. *Bottom left,* Products formed upon absorption of CO_2 into seawater.[SR4,SR5] Reprinted with permission from P. Webb, *Introduction to Oceanography*, Roger Williams University under CC BY 4.0. © 2021. *Bottom right,* Ratios of bicarbonate and carbonate species in seawater as a function of pH. Adapted with permission from *Ocean Acidification due to Increasing Atmospheric Carbon Dioxide*. © 2019 Royal Society.

CO_2 capture processes are frequently based on molecular interactions that involve CO_2 sorption and subsequent release of CO_2 at a later stage. There are fundamental limitations of the thermodynamics and kinetics of such a process (i.e., a sorbent with high affinity for CO_2 can overcome kinetic limitations due to a favorable thermodynamic driving force); however, the thermodynamics later become commensurately unfavorable when CO_2 release is desired, requiring substantial energy to regenerate the sorbent. Instead of releasing the CO_2, another approach is to convert it to a desired carbon-based product directly from the sorbed intermediate.

Multifunctional sorbents that absorb CO_2 and catalyze its conversion via thermal and nonthermal routes provide new approaches.[7] **Figure 3-1** illustrates the concept of using chemically functional sorbents to capture and convert CO_2 via photochemical and electrochemical approaches. A potential benefit of a capture-conversion process is the direct production of a carbon-based product within a single unit, without having to transport or store the CO_2, effectively a reactive separation. There are many possible means to accomplish this, with much room for scientific creativity.

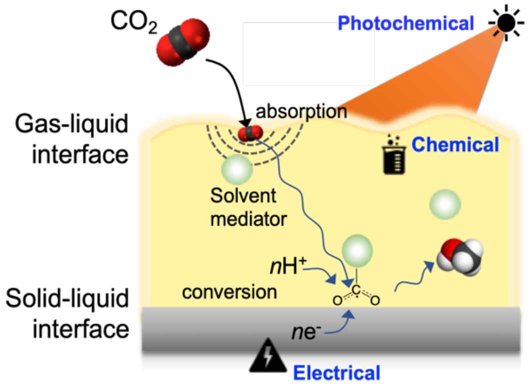

Figure 3-1. Illustration of capture and conversion of CO_2 by multifunctional sorbents by nonthermal approaches such as photochemical and electrochemical. Unpublished figure courtesy of Burcu Gurkan.

3b. Key Scientific Questions

- How do we gain fundamental understanding of unconventional energy transfer mechanisms within complex CO_2 capture materials and systems?
- How do we design composites or multifunctional materials with tailored morphologies that selectively capture CO_2 and enable the efficient transfer energy to and from the target site to capture and release CO_2 at a high rate?
- How do we develop theory and experimental tools to investigate localized heat, mass, and electron transfer behaviors from bulk to interfaces?
- How do we tailor interfacial electrochemical and thermal processes for efficient energy transfer and management?
- How can CO_2 conversion be leveraged to more efficiently regenerate sorbents?

3c. Scientific Challenges and Research Opportunities

Enabling efficient DAC, ocean capture, or combined capture/conversion processes at a volume and scale that is needed to impact CDR technologies depends on solving a key fundamental challenge: decoupling CO_2 binding energy from the energy barrier needed for its release or conversion. Compared to conventional fossil energy sources that produce heat for sorbent regeneration, renewable energy such as solar or wind provides carbon-free electrons for the capture, release, and conversion of CO_2. If CO_2 capture and sorbent regeneration systems can operate under isothermal conditions, the parasitic energy consumption required for DAC and DOC would be significantly reduced, and the overall energetics could be greatly improved. A key scientific challenge is to determine the most effective mechanisms to transfer different forms of energy to the target sites to release, convert, or release and convert CO_2 while managing heat throughout the capture materials and systems. To address this challenge, three research opportunities are identified:

- Investigate different types of unconventional energy transfer (e.g., electrochemical and light modulation, resistive heating, magnetic induction heating, microwave heating, plasma, light, acoustics) in terms of their targeted capture and release of CO_2
- Design and synthesize multifunctional CO_2 capture materials that respond to thermal and unconventional energy transfer mechanisms and that can combine capture and conversion
- Develop experimental, spectroscopic, and computational tools and methodologies to provide new insights into heat, mass and electron transfer and management across multiple length scales in the bulk and at interfaces

Investigate different types of unconventional energy transfer in terms of their targeted capture and release of CO_2

The development and deployment of DAC and DOC systems are unique compared to the point source CO_2 capture processes. They are often modular in their design and scaled out (i.e., adding more components in parallel to spread out a load) rather than scaled up (i.e., making a component bigger or faster so that it can handle more load). The distributed deployment of DAC and DOC systems leads to great opportunities to use distributed renewable energy sources for carbon capture and storage as well as conversion. The renewable electricity from solar and wind can be used to generate unconventional energy transfer mechanisms, such as electrochemical and light modulation, resistive heating, magnetic induction heating, microwave heating, and plasma heating, as well as light and acoustic activations (**Sidebar 8**). Each of these unconventional energy transfer mechanisms calls for innovative materials and systems design for targeted capture, release, and conversion of CO_2. Some of these methods involve targeted heating of the CO_2 binding sites, whereas other approaches involve chemical modulation of captured CO_2 via electrochemical or light activation.

Electrochemical and photochemical approaches can provide nonthermal modulation of the CO_2 sorption capacity and can either provide a direct activation/deactivation of the capture moieties or can influence the binding capacity through indirect means. The direct electrochemical approach exploits the complexation of an electroactive moiety directly with the CO_2 upon its activation by electrochemical reduction, with subsequent release of the CO_2 when the agent is reoxidized on reversal of the applied cell voltage. The redox-active component can be immobilized on an appropriate conductive substrate bathed with a suitable electrolyte (typically an ionic liquid), and the capture and release can be affected in a typical adsorptive swing mode. The redox-active compound can also be used in solution in a continuous flow mode, with the activated nucleophile capturing the CO_2 in the absorber and releasing the gas upon oxidation in the anode chamber of an electrochemical cell.[8]

In the indirect electrochemical approach, the actual CO_2 speciation in solution is itself not redox- or photoactive but rather is affected by changes in the surrounding medium due to the release of another species that affects the CO_2 capacity of a chemical sorbent.[8] An example of such a process is the competitive complexation of a metal ion such as Cu^{2+} with an amine to disrupt the carbamate bond and release the CO_2. There are interesting studies on the development of novel electrolyte systems that can tune the reaction and transport behaviors at the electrode–electrolyte interfaces (e.g., electrolyte containing amine-functionalized nanoparticle organic hybrid materials[9]). The introduction of the metal ions can be via the electrodissolution of the copper anode in an electrochemical cell. The amines themselves are regenerated for cycling back to the absorber as the copper is plated out on the cathode.

Sidebar 8. Types of Electromagnetic Radiation

CO_2 desorption involves an endothermic process of breaking chemical bonds (e.g., carbamate), in which a temperature swing is typically used. Sorbents are heated up to 80–120°C, requiring significant thermal energy input and residence time. Thus, the development of more efficient heating or energy transfer mechanisms, particularly based on renewable electrons, could provide a paradigm shift in the development of CO_2 capture and conversion technologies. There are a number of nonthermal energy transfer approaches, including radiation heating, resistive heating, and electrochemical activation, that can be employed for carbon capture. For instance, magnetic induction has been used to generate heat based on Néel and Brownian relaxation mechanisms,[SR6] when magnetic materials are in an alternating magnetic field. Recent studies have shown that various solid sorbents including zeolites[SR7] and MOFs[SR8] containing iron oxide (Fe_3O_4) can be regenerated and release CO_2 via magnetic induction heating. Light can also be employed to control the CO_2 capture and release process when CO_2 sorbents are combined with photothermal agents.[SR9] CO_2 capture and conversion via plasma treatment instead of conventional heating was also recently reported.[SR10] Microwave energy can also be used to deliver targeted heating to CO_2 binding sites and effectively release CO_2 from liquid sorbents such as ionic liquids[SR11] and from solid sorbents with accelerated desorption kinetics and enhanced cycling stability.[SR10, SR12]

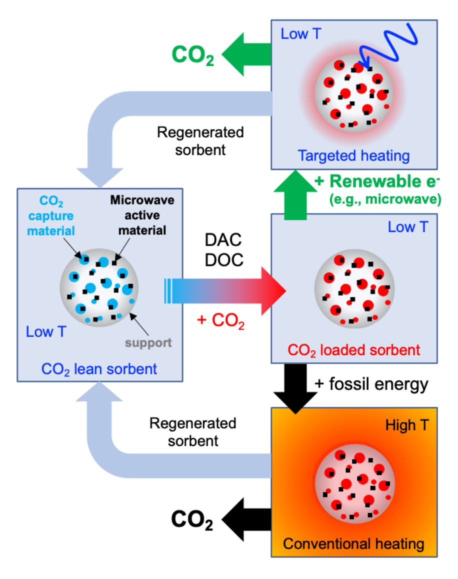

Figure S8. Microwave attenuation leads to heating of materials, where the penetration depth of the microwave is a function of material properties and can influence the design of multifunctional sorbent materials and form factors, as well as reactor design. Ideally, targeted heating will allow the release of CO_2 with a minimum temperature increase inside the sorbent regenerator. Unpublished figure courtesy of Burcu Gurkan.

Other indirect approaches generally result in modulation of the pH in an aqueous solution and changes in the speciation of the CO_2, with lower pHs (<6) favoring formation of molecular CO_2 over the bicarbonate (pH ~8) or carbonate (pH >9) ions formed when CO_2 is absorbed under alkaline conditions.[10] This modulation can be achieved in several ways: (1) Water splitting in the anode chamber of an electrodialysis unit generates protons that can migrate through a cation exchange membrane to acidify the CO_2-laden feed from the absorber and thereby release the CO_2. Similarly, stream acidification can be attained with bipolar membranes in an electrodialysis stack.[11] (2) Redox-active compounds such as quinones become protonated upon electrochemical reduction in an aqueous environment, and the solution, which is now alkaline, can absorb CO_2 effectively in the form of bicarbonate ions. On oxidation of the quinone species, the protons are released, and the enhanced acidity of the solution allows for liberation of the CO_2. (3) When used as electrodes, intercalation compounds such as certain metal oxides (MnO_2, TiO_2, etc.) are able to absorb protons under sufficiently negative potentials and release these protons under oxidizing conditions. Thus, the pH can be modulated by reversing an applied voltage across the electrochemical cell, thereby altering the solution capacity for the CO_2.

Photochemical modulation of CO_2 capture and release may be feasible using molecular photoswitches (i.e., photochromic molecules that undergo reversible conversion between their stable and metastable isomers when triggered by light of appropriate wavelength). Photoresponsive capture agents that have some affinity for CO_2 in one state may release the CO_2 when steric constraints are imposed upon changes in configuration. The configurational changes in molecular photoswitches[12] induced by irradiation with light of appropriate wavelengths are often accompanied by a commensurate change in pH and can therefore be used to regulate CO_2 sorption/desorption. Photoswitches have been used in many areas of research including catalysis, biology, and material science because of their changes in structural geometry and chemical properties upon irradiation. Several examples of photochromic compounds include azobenzene, spiropyran, thioindigo, and diarylethene.[12]

In the various approaches described, there is some latitude in the selection of the sorbents and the solutions for a given absorption system. In direct ocean capture DOC applications, however, the CO_2 must be removed from a prescribed solution, and additives would not be feasible. Thus, all DOC applications to date rely on pH modulation in either electrodialysis, electrodeionization, or water electrosplitting operations. Depending on whether the solution treated is acidified or alkalized, CO_2 can be recovered either in gaseous form or as a $CaCO_3$ precipitate.[10] An alternative approach for pH modulation is to use the intercalation compounds (e.g., NiHCN) or reactive electrode materials (e.g., Bi) to regulate the pH of the feed solution without direct water splitting.

Design and synthesize multifunctional CO_2 capture materials that respond to thermal and nonthermal energy transfer mechanisms and that can combine capture and conversion

It is imperative to consider the existing chemistry of materials commonly used in CDR and question the viability of these materials to respond to nonthermal energy transfer mechanisms. Amines are ubiquitous with carbon capture because of the near 100-year-old approach of applying acid–base chemistry to chemical capture of CO_2, most of which has been regenerated thermally since the year 1930. Aqueous and nonaqueous amines alone are not responsive to light, electricity, or redox processes. For this reason, additives have been introduced to amines to make them susceptible to nonthermal energy transfer mechanisms to release CO_2. In some embodiments, electrolytes have been added to solvents to make them more conductive for pH or other electrochemical modulation and allow coupled CO_2 capture and electrochemical conversion.[8,13,14,15] In other embodiments, nanoparticles such as iron oxides[16,17] or carbon black[18] have been added to aqueous amines and CO_2-binding organic liquids (CO_2BOLs) so that they absorb actinic light, resulting in highly localized heating at the nanoparticle surface and promoting bubble formation and CO_2 release without heating of the bulk fluid (**Figure 3-2** *left*).[19,18] Lastly, recent advances have shown redox-active species such as nitrate salts of pyridinyl radicals could be used to promote electrochemical capture and release via redox cycle (**Figure 3-2** *right*).[8] In most of these now bifunctional systems, the ability to modulate CO_2 loading by nonthermal means relies on additives to be responsive to stimuli, as the chemistry of sorbents is mostly limited to amines.

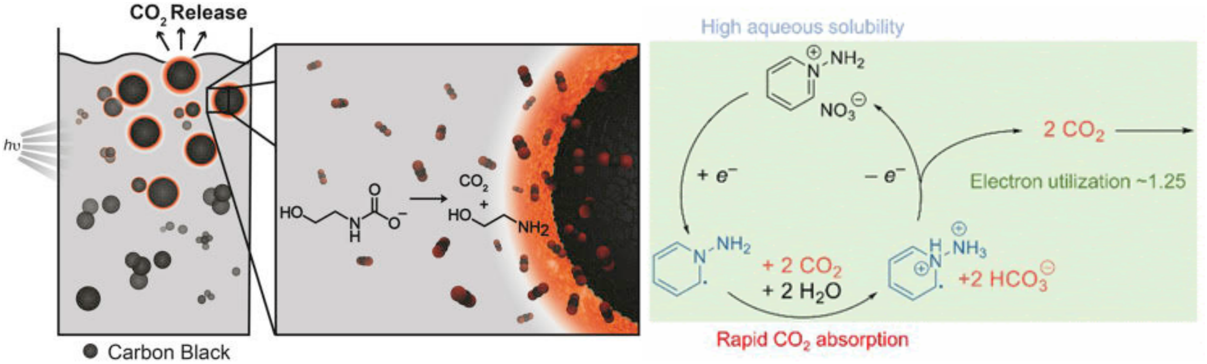

Figure 3-2. *Left,* Addition of carbon black to 5 M monoethanolamine solutions enables photothermal effect via absorption of actinic light, resulting in a high local temperature near the nanoparticle surface and CO_2 release without heating of the bulk fluid. Reprinted with permission from S. A. Goetz et al., "Surface Modification of Carbon Black Nanoparticles Enhances Photothermal Separation and Release of CO_2," *Carbon* 105, 126–135. © 2016 Elsevier. *Right,* Redox-modulated CO_2 capture using pyridinyl radicals. Reprinted with permission from H. Seo et al., "Electrochemical Carbon Dioxide Capture and Release with a Redox-Active Amine," *J. Am. Chem. Soc.* 144 (5), 2164–2170. © 2022 ACS.

In the future, expansion beyond antiquated acid:base chemistry between amines and CO_2 would be transformational. Novel chemistries and more efficient processes capable of modulating CO_2 by nonthermal means could be achieved by applying the principles of redox-active materials, stimuli-responsive frustrated Lewis pairs, photosensitive molecular cages, or coupled electrocatalytic conversions of CO_2 in capture media. The DAC and DOC materials often come in different form factors (e.g., encapsulated solvents,[20] polymer beads, electrospun fibers, ceramic monoliths), so the selection of shell or substrate materials will also play an important role in unconventional energy transfer and mass transfer.

Table 3-1 summarizes recent examples of CO_2 capture materials designed for nonthermal energy transfer (i.e., microwave, magnetic induction, acoustic, light, and plasma). For each energy transfer mechanism, different functional materials have been incorporated into CO_2 capture sorbent to achieve enhanced energy efficiencies. For example, Fe_3O_4 particles can significantly improve the magnetic induction heating of solid sorbents such as zeolites and MOFs.[16,17] Fe_3O_4 is also microwave active.

Another option to enhance the efficiency of nonthermal energy transfer during the sorbent regeneration and CO_2 conversion is the co-sorption of other molecules that are active under different energy transfer modes. For example, water is a great microwave-active molecule. Thus, the sorption of small quantities of water during CO_2 capture may lead to effective release of CO_2 via microwave heating. Further, the materials design of supports (e.g., monoliths) and reactors could also be tailored for different energy transfer mechanisms to maximize the overall energy efficiency and minimize the energy loss. For example, microwave, which has longer wavelengths (**Sidebar 8**), requires innovative reactor designs (e.g., fluidized bed reactor or moving bed reactor) to address standing waves issues that create hot spots. As discussed here, the unconventional energy transfer mechanisms can provide a paradigm shift in the way CO_2 loaded to the DAC and DOC materials is released and converted using renewable energy. Consequently, future research could focus on the novel design and synthesis of materials and systems that can effectively transfer energy through materials and across the interfaces. Innovative reactor designs could provide opportunities to address the limitations of different energy transfer mechanisms (e.g., fluidized bed or moving bed reactor to address standing wave issues creating hot spots).

Table 3-1. Examples of CO_2 Capture Materials Developed for Different Unconventional Energy Transfer Mechanisms[16–26]

Heating source	Purpose	Sorbent	Control parameters	Performance
Microwave	CO_2 desorption	Monoethanolamine (MEA) aqueous solution	✓ MEA concentration ✓ Initial power of microwave ✓ Temperature (70–90°C) ✓ Time	✓ 50 wt% MEA solution: 13% increase CO_2 cyclic capacity ✓ 15% decreate energy consumption (compared with 30 wt%)
	CO_2 desorption	MEA aqueous solution	✓ Temperature (70–90°C) ✓ Time ✓ Cycles	✓ 23% (70°C), 50% (90°C) CO_2 recovery ✓ Rapid heating, low regeneration temperature, fast recovery
	Synthesis MOF for CO_2 capture	MOF-5 ($Zn_4O(BDC)_3$)	✓ Isothermal (microwave) ✓ Temperature ramping ✓ N-methylpyrrolidone (NMP) washing	✓ Higher quality crystal structure ✓ CO_2 uptake three times greater than conventional synthesis
Magnetic induction heating	CO_2 desorption	Fe_3O_4/NPC* (*nitrogen-doped mesophorous carbon)	✓ Fe_3O_4 weight percent (10, 15, 20%) ✓ Current (5, 10, 15 A) ✓ Temperature (110, 140°C)	✓ Adsorption: 2.64 mmol CO_2/g solvent ✓ Saturation magnetization: 15.51 emu/g sorbent ✓ Desorption: 3.27 mg CO_2/g sorbent/s ✓ Energy efficiency: 79.2%
	CO_2 desorption	Composite of Fe_3O_4 and 13X-AP zeolite	✓ Mass ratio (13X-AP:Fe_3O_4 = 9:1 or 8:2) ✓ Applied current (49.4–171 A) ✓ Temperature (30–250°C)	Average desorption rate (up to 95% deposition) ✓ under 171 A: 156.8 mg CO2/g sorbet/min ✓ under 49.4 A: 4 mg CO_2/g sorbent/min
	CO_2 desorption	Fe_3O_4@HKUST-1	✓ Synthesis temperature ✓ Magnetic flux density (12.5–30 mT)	Desorption efficiency: ✓ 75% at 65°C ✓ 94.5% at 130°C

Table 3-1. Examples of CO_2 Capture Materials Developed for Different Unconventional Energy Transfer Mechanisms (continued)

Heating source	Purpose	Sorbent	Control parameters	Performance
Acoustics	CO_2 capture	Activated carbon inside fluidized bed (lab scale)	✓ Sound intensity (125–140 dB) ✓ Sound frequency (20–300 Hz)	✓ 0.37 mmol CO_2/g sorbent at ambient temperature pressure (10 vol% dry CO_2) ✓ 20% increase compared with orginal case
	CO_2 capture	Biochar (pine)	✓ Ultrasound power (475 W, 700 W) ✓ Ultrasound activation time (30 s, 1 min, 3 min) ✓ Activation agent ratio (for amine concentration change)	✓ Max adsorption capacity: 2.79 mmol CO_2/g sorbet (at 70°C, 15 CO_2 vol% ✓ Significant enhancement compared with raw biochar (0.3 mmol/g)
Light	CO_2 capture	Foam (polyethyleneimine) + photothermal agent	✓ NIR irradiation	✓ When polyethyleneimine foam (0.45 g) is in a glass reactor full of CO_2 (30 vol%) and CH_4 (70 vol%), CO_2 decreases to 20 vol% at room temperature in 310 min
Plasma	CO_2 conversion	Hydrotalcite (packed bed)	✓ Ignition of plasma (target: CO_2 conversion to syngas)	✓ Average conversion of CO_2 during the detectable CO production period is 41.14%

Develop experimental, spectroscopic, and computational tools and methods to provide new insights into heat, mass, and electron transfer and management across multiple length scales

There is a tremendous opportunity to develop novel methods and processes to capture, release, and convert CO_2. Understanding heat, mass, and electron transfer and management across multiple length scales will be essential to inform improved strategies. Many techniques are available today that can contribute to this effort and could be leveraged extensively. There is also ample room for further method development to understand these phenomena in new and important ways. Key to this effort is the combination of experimental and computational efforts that should be combined to produce the deepest understanding of the physical and chemical processes at play (**Figure 3-3**).

In reality, CO_2 capture, release, and conversion are processes that occur at the molecular length scales and at timescales on the order of femtoseconds to seconds. Real technology, of course, operates at much larger length- and timescales (e.g., meters and minutes and beyond). Substantial fundamental science and engineering questions may need to be addressed to reconcile these vast differences in length- and timescale. New approaches offer opportunities. **Figure 3-4** depicts experimental length and timescales (*left*) that reflect reality as well as a range of computational methods to address them.[15,27–30] Each domain of length- and timescale could benefit from new approaches to achieve greater accuracy, precision, and speed of measurement/calculation to provide new insights. Connecting these domains is equally important, stitching together the length and timescales across orders of magnitude to inform improved processes. Physics-based modeling will be essential, both at the quantum- and continuum-levels. Data science and ML should also be leveraged to provide new insights. Recognizing the diversity of emerging ideas in the space of CO_2 capture, release, and conversion, there is a great opportunity to develop new methods and approaches both in experiment and computation to address the many phenomena at each length- and timescale, in addition to coupling them into integrated systems.

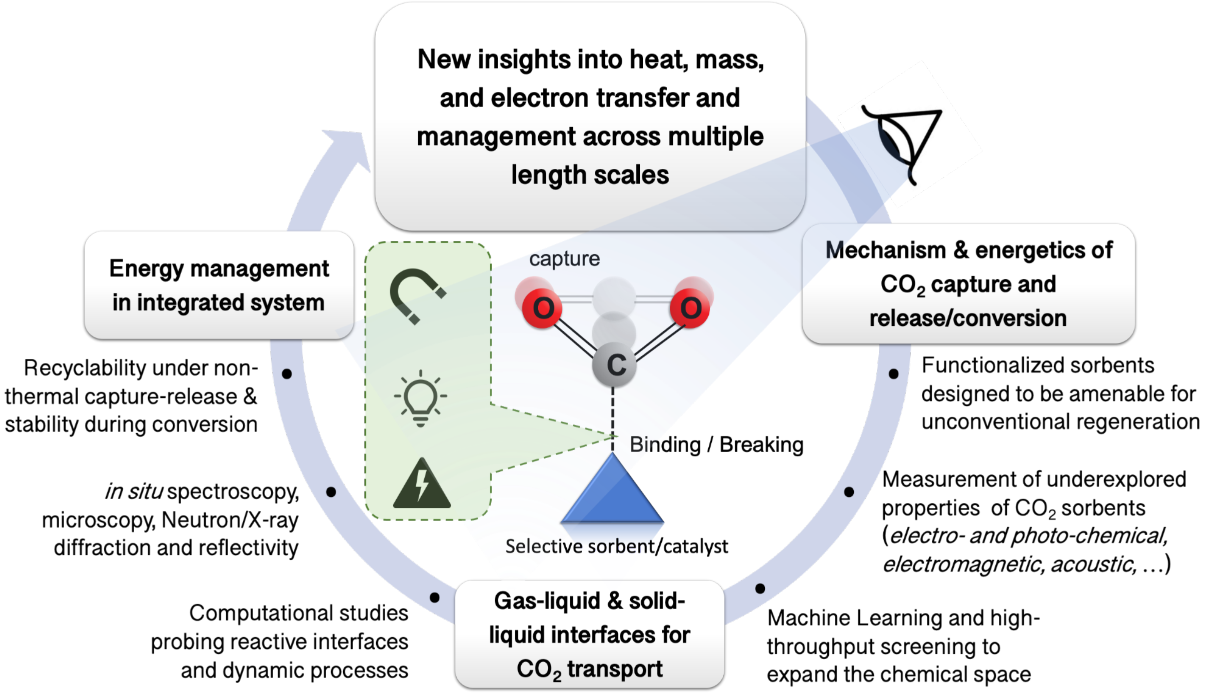

Figure 3-3. Vision of a research framework that synergizes advanced experimental, spectroscopy, and computational tool and methods toward the discovery of mechanisms and materials for efficient energy transfer and management in CO_2 capture, release, and conversion. Unpublished figure courtesy of Burcu Gurkan.

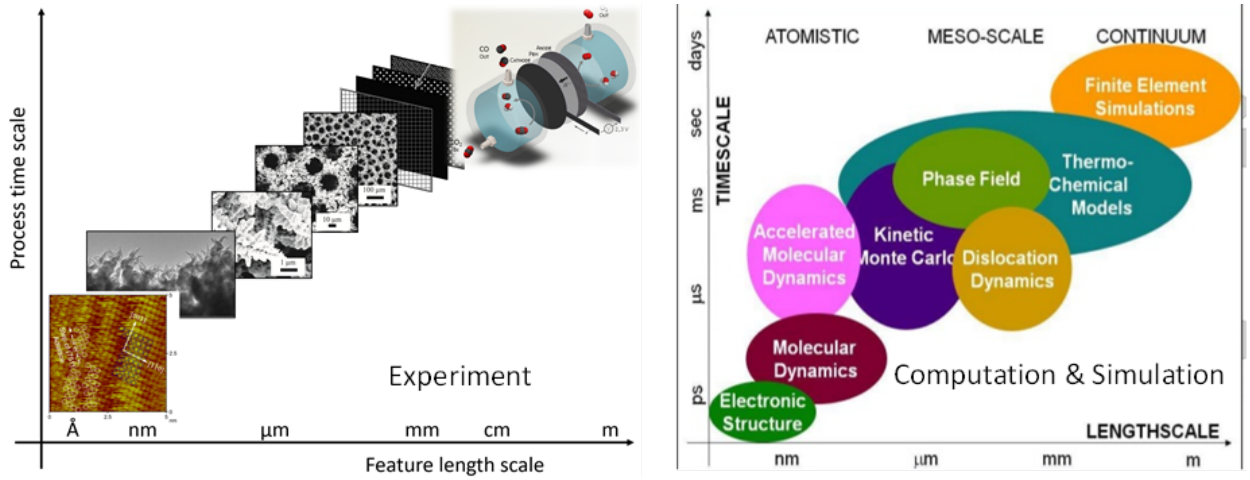

Figure 3-4. High-performance systems require controlling phenomena at multiple length- and timescales. Efforts to combine experiment, computation, and simulation can help to uncover key knowledge that enables improved processes. *Left, from bottom to top,* Adapted with permission from C. Haun et al., "Engineering Cu Surfaces for the Electrocatalytic Conversion of CO_2," *Proc. Nat. Acad. Sci.* 114, 5918–5923 (2017). Adapted with permission from L. B. Sheridan et al., "Growth and Electrochemical Characterization of Carbon Nanospike Thin Film Electrodes," *J. Electrochem. Soc.* under CC BY-NC-ND 4.0. © 2014. Adapted with permission from S. Sen et al., "Electrochemical Reduction of CO_2 at Copper Nanofoams," *ACS Catal.* 4, 3091–3095. © 2014 ACS. Reprinted with permission from R. D. McKerracher et al., "A Review of the Iron–Air Secondary Battery for Energy Storage," *ChemSusChem* 80, 323–335. © 2015 Wiley. Reprinted with permission from C. Tatin et al., "Efficient Electrolyzer for CO_2 Splitting in Neutral Water Using Earth-Abundant Materials," *Proc. Nat. Acad. Sci.*, 113, 5526–5529 (2016). *Right*, Reprinted with permission from M. Stan, "Discovery and Design of Nuclear Fuels," *Mater. Today*. 12 (11), 20–28 under CC BY 4.0. © 2009.

Discovery of unconventional approaches for the regeneration of sorbents and subsequent conversion of CO_2 can be advanced by improved understanding of dynamic processes that take place both in the bulk and at interfaces. It is also relevant to understand the polarizability, dielectric loss behavior, and electrochemical stability of the media that is used to capture, release, and convert CO_2. In situ experimental techniques that are capable of interrogating the bulk and gas–liquid interfacial structure from molecular to mesoscale during CO_2 absorption and desorption and away from equilibrium, are essential. Studies aimed at understanding bulk behavior need to be complemented by interfacial understanding. Therefore, in-situ experimental techniques that can probe the solid–liquid and solid–liquid–gas interface upon electric, electromagnetic, and light stimuli with nanometer-scale resolution are needed.

The specific challenge in this area is the buried nature of these interfaces. With the use of operando synchrotron-based X-ray techniques and in situ atomic-scale scanning transmission electron microscopy (STEM), advancements have been made toward understanding charge transfer kinetics and overall reaction mechanisms at electrified interfaces.[31] The application of these and similar techniques such as grazing incidence X-ray absorption spectroscopy and X-ray diffraction to study CO_2 electroreduction in aqueous electrolytes revealed that the oxide layer is reduced to metallic copper and that copper electrocatalyst goes under a dynamic surface reconstruction in the presence of CO_2.[32] This finding was useful in explaining the hysteresis in the previously measured product distribution between the anodic and cathodic sweeps in CO_2 conversion. In another example, by using advanced transient optical and X-ray absorption spectroscopy and in situ diffuse reflectance spectroscopy, the key reaction intermediates and rate-limiting step in the photocatalytic conversion from CO_2 to CO with a newly designed covalent organic framework were identified.[33] Also a deeper understanding of thermal conversion processes[34] involving the hydrogenation of captured CO_2 may be of interest as long as the H_2 is produced with low carbon intensity. The adaptation of advanced surface techniques for in situ external stimulation of CO_2 absorption, release, and conversion with the newly developed materials/catalysts and multifunctional liquids can be instrumental in the development of the next-generation technologies for CO_2 removal.

3d. Potential Impacts

CDR technologies from dilute sources require copious amounts of thermal and mechanical energy, limiting widespread adoption. An enhanced understanding of interfacial energy transfer and interconversion processes could revolutionize the ability to couple mass and energy transport to interfacial and kinetic processes, allowing for the design of bespoke multifunctional materials and morphologies across multiple length scales. New computational and experimental tools that can probe the interfaces and localized and bulk phenomena can provide a robust scientific framework on which to design and build innovative materials and, in turn, transformative reactive separations among other energy-related processes. The use of unconventional methods for regeneration of sorbents allows processes that avoid time and energy-intensive thermal regeneration of sorbents, which currently account for 80% of the energy demand for DAC. Improved integration of capture, conversion, and durable sequestration may provide sizable reductions in energy demands for DAC or DOC, where selective and rapid capture can be done in parallel with conversion. Here, integrated systems can be designed to offset endothermic sorbent regeneration with an exothermic conversion, while also bypassing mechanical compression of CO_2 for carbon storage offering potential to lower operating expenditure and capital expenditure. The concepts discovered as a part of this research could greatly benefit DAC and DOC among other (e.g., marine) CDR processes, facilitating more widespread adoption. Similarly, these concepts could greatly influence other energy-intensive separations and catalytic conversions. Ultimately, the fundamental science provides a strong foundation on which to build, opening new avenues to achieve the Carbon Negative Shot and enable CDR at meaningful scales for less than $100/net metric ton of CO_2-equivalent.

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PRO 4: Control the Multiphase Physical and Chemical Interactions of CO_2 Required for Conversions into Molecules, Minerals, and Materials

Rational tuning of multiphase physical and chemical interactions for CO_2 conversions into minerals and materials can enable scalable and durable CO_2 storage. Consideration of active sites, confinement, and mass transport is necessary to quantitatively determine, predict, and control the rates of catalytic transformations in chemically dynamic environments. Nongeologic mineralization strategies require understanding the roles of polynuclear species, amorphous or dense liquid precursors, and ion desolvation on carbonate mineralization rates, as well as the ability to exploit biomimetic approaches to enhance both processes.

4a. Summary

The capture and conversion of CO_2 involves pairing of a diverse set of chemical reactions and transport phenomena through complex interfaces where different types of molecules or ions interact (**Figure 4-1**). Rational tuning of multiphase physical and chemical interactions for converting CO_2 into molecules, minerals, and materials could enable scalable and durable CO_2 storage. Systematic experimental and theoretical studies can advance our fundamental understanding of the selective transformations of CO_2 into minerals or materials with desired properties or novel interfaces, allowing the coupling of CO_2 capture and conversion. Considering the active site, confinement, and mass transport, it is necessary to quantitatively determine, predict, and control the rates of nucleation, growth, and dissolution of solid phases in chemically dynamic environments (multiple ions, phases/interfaces, organics), at a wide range of temperatures and pressures, and in a range of solvents, in an efficient, combinatorial manner. Developing and linking multimodal, cross-scale approaches with experimental, theoretical, and data science tools can promote effective chemical transformations of CO_2.

Design and optimization of cost-effective technologies for the capture, use, and storage of CO_2 requires fundamental knowledge and control of multiphase physical and chemical interactions associated with the conversion of the molecule into high-value chemicals, minerals, and materials. The conversion processes can occur in timescales from nanoseconds to millennia, involving processes covering length scales from those of atoms to nanostructures to rocks (**Figure 4-1**). Although many types of man-made compounds, such as metal oxides, sulfides, carbides, metal-exchanged zeolites, and MOFs, have shown great potential for trapping or converting the molecule through reversible binding or catalytic reactions, the process of carbon mineralization involves irreversible formation of solid carbonate minerals through reaction of CO_2 with rocks rich in calcium or magnesium. A scientific foundation for CO_2 conversion into molecules, minerals, and materials must address this range of timescales, length scales, and disparate materials and processes.

4b. Key Scientific Questions

- What are the key interfacial structures, chemistries, and phenomena that control the kinetics and mechanisms of CO_2 transformation into minerals and materials?
- How can the rates of nucleation, growth, and dissolution of minerals in dynamically complex environments be quantitatively determined for precise prediction and control?

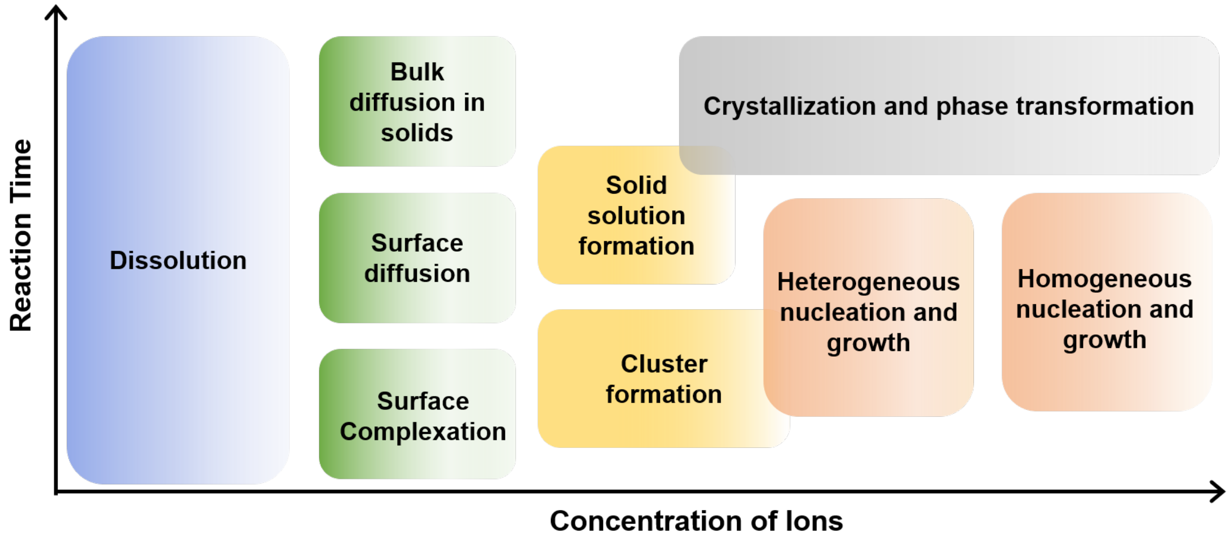

Figure 4-1. Dissolution, nucleation, precipitation, and phase transformation of minerals and materials at a wide range of timescales and concentrations (chemical potentials) of the systems. Unpublished figure courtesy of Young-Shin Jun, Washington University in St. Louis.

4c. Scientific Challenges and Research Opportunities

The key questions cited above drive the scientific challenges that underlie this PRO. First, the structural factors and physicochemical mechanisms that control binding of CO_2 at interfaces, and that govern its transformation into organic and inorganic materials with desirable properties, need to be identified, both to manipulate natural transformation processes and develop synthetic molecules and materials for this purpose. Then, accurate prediction and control of the resulting rates of transformation in chemically complex environments must be achieved at a wide range of temperatures and pressures, and in a range of solvents, in an efficient, combinatorial manner. To rationally design energy-efficient processes, interfacial phenomena that control CO_2 sequestration should be tightly integrated with its continuous transformation, removal of the resulting products, and regeneration of active sites. Addressing the following scientific challenges can open distinct opportunities for advancing the foundational science of CDR:

- Understanding the binding and conversion of CO_2
- Optimizing components and parameters of photoelectrochemical systems for CO_2 conversion into fuels and chemicals
- Designing interfaces to enhance CO_2 solvation, speciation, and crystallization
- Discovering molecularly integrated pathways for CO_2 capture and conversion
- Elucidating multiphase transformations using multimodal approaches
- Harnessing computational and data science tools

Understanding the binding and conversion of CO_2

CO_2 is a stable, nonpolar molecule that can be transformed into materials with a desired functionality or value using catalytic processes (**Figure 4-2**). These processes involve three essential components: (1) the reactive center that binds and activates the CO_2 molecule, (2) a surrounding phase with reactants or solvents, and (3) a source of thermal, electrical, or photochemical energy.[1,2,3] In general, the efficiency of these three components is optimized to obtain active and selective catalysts. Future work could involve studies examining in a systematic way fundamental aspects of the bonding of CO_2 to materials, such as metal oxides, sulfides, and carbides, metal-exchanged zeolites, and MOFs, etc., that have shown significant potential for binding and transforming the molecules. Even on well-studied catalytic materials, the nature of active sites for CO_2 binding and conversion is not well understood.[4] These surfaces often also evolve as a function of time, **Figure 4-3**. Thus, understanding the nature of the catalytic binding and activation sites and how they evolve under reaction conditions is critical for improving the efficiency of catalytic CO_2 conversion processes.

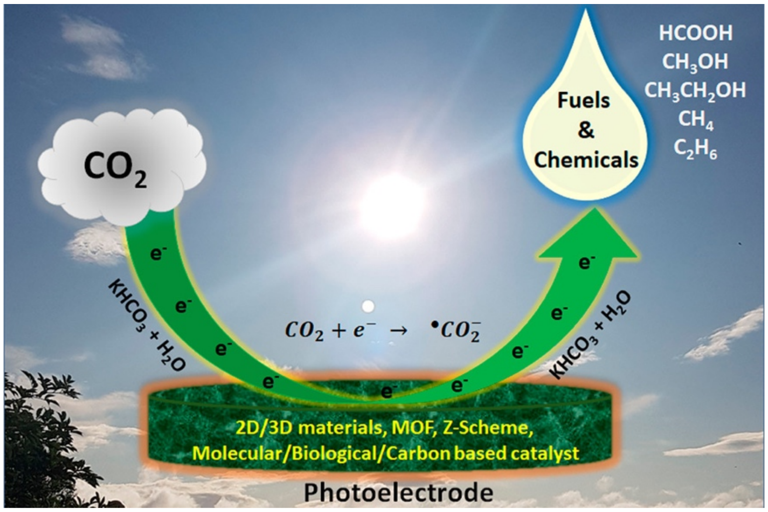

Figure 4-2. Schematic for the photoelectric conversion of CO_2 into fuels and value-added products under solar light irradiation. Reprinted with permission from V. Kumaravel et al., "Conversion of Carbon Dioxide (CO_2) into Fuels and Value-Added Products," *ACS Energy Lett.* 5, 486–519. © 2020.

Time-resolved in situ or operando studies are necessary to validate models for binding and selective conversion. However, there is a lack of comprehensive studies on the phenomena or mechanisms that can be used to control the selective catalytic conversion of CO_2 by combining thermal, electro- and photo-chemical approaches (**Sidebar 9**).[3,5]

Bioinspired approaches, by which catalytic CO_2 conversion is achieved using various enzymes, deserve attention.[6,7] The enzymes can be present in solution, in a membrane, or immobilized on mesoporous structures. They can be combined to transform CO_2 into a range of organic molecules. For example, using the three enzymes formate-, formaldehyde- and alcohol dehydrogenase, CO_2 is converted into formate, then formaldehyde, and finally methanol.[7] However, cascading enzymatic reactions, even though very appealing, require significant improvements to be useful for handling large amounts of CO_2.[6]

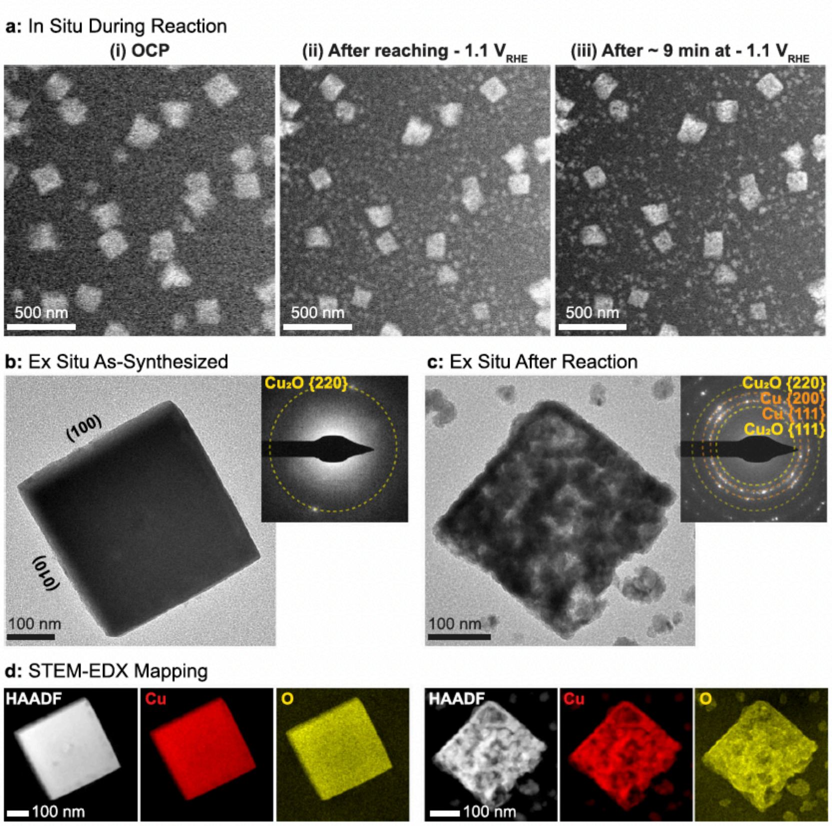

Figure 4-3. Morphology of Cu_2O cubes and their evolution during electrochemical reduction of CO_2 using ex situ TEM imaging and electron diffraction (*upper right inserts*) and STEM energy dispersive X-ray maps of the same cubes showing the copper and oxygen signals. Adapted with permission from P. Grosse et al., "Dynamic Transformation of Cubic Copper Catalysts during CO_2 Electroreduction and its Impact on Catalytic Selectivity," *Nat. Commun.* 12 (1), 1–11 under CC BY 4.0. © 2021.

Optimizing components and parameters of photoelectrochemical systems for CO_2 conversion into fuels and chemicals

The dissociation energy for breaking a C=O bond in CO_2 is higher than 750 kJ/mol, which means that the barrier to breaking the bond is 300 times greater than thermal energy at room temperature. Thus, the conversion of the molecule is a challenging task. The transformation of CO_2 into fuels and chemicals can be achieved by thermocatalytic, electrochemical, photochemical, and photoelectrochemical processes. The reaction of CO_2 with hydrogen can lead to methanol or other oxygenates, but the source of the hydrogen determines the carbon neutrality of the process, and in general, thermocatalytic approaches have a high operation cost and are not environmentally friendly.[2] Pure electrochemical and photochemical approaches have low efficiencies, and recent studies suggest that combined photoelectrochemical processes are the best option for the conversion of CO_2 into liquid fuels.[1,3]

Figure 4-4 shows a scheme for the transformation of CO_2 and the splitting of water in a photoelectrochemical process.[3] The generation of H^+ species is not an easy objective, and the products of the reduction of CO_2 depend on the nature of the catalyst used and the applied voltage. The way in which CO_2 binds to the cathode (monodentate binding through oxygen or carbon, or bidentate bonding via O,O or C,O) can affect the final products and selectivity of the process.[3] This and the electrical conductivity of the material are taken into consideration when optimizing the performance of a photoelectrochemical process.[5] In situ studies can be used to determine the chemical evolution of the electrodes with time and how it correlates with the bonding configuration and reduction mechanism for CO_2.[8]

Sidebar 9. Quantifying Reactive Surface Area from Field to Molecular Scale

The discovery that surface areas across scales can be described as fractals[SR1–SR3] opens up the possibility that constitutive laws can be generated that describe interfacial phenomena from field to molecular scales. The connection between surface dissolution reactions with porosity and permeability in basalts demonstrated the benefits of connection across scales so as to predict long-term processes such as weathering,[SR4] which is relevant to the dissolution and precipitation necessary for subsurface carbon storage security. However, the definitions of “reactive surface area” are different for the molecular and macro scales. Reactive sites on surfaces must be quantified to model chemical reactions at the molecular level,[SR5] whereas surfaces in contact with flowing fluid defines reactive surface area at the macro scale.[SR6] Recent work[SR7] has shown that it is possible to quantify reactive surface area on the macroscopic scale. Hence, it should be possible to upscale the surface roughness factor (SRF) and reactivity to the continuum scale with constitutive laws such as $F = aSRF^b$, where F is the correction function, a is a flow-reaction parameter, and b accounts for nonlinear surface area–reaction rate behavior.[SR8] ML techniques have been applied to predict adsorption behavior based on molecular-scale information on the surfaces,[SR9] so the challenge and opportunity here is to apply these methods to the complex surfaces and solutions involved with the dissolution/precipitation reactions required to mineralize CO_2 into carbonate minerals in the subsurface to ensure long-term safe sequestration.

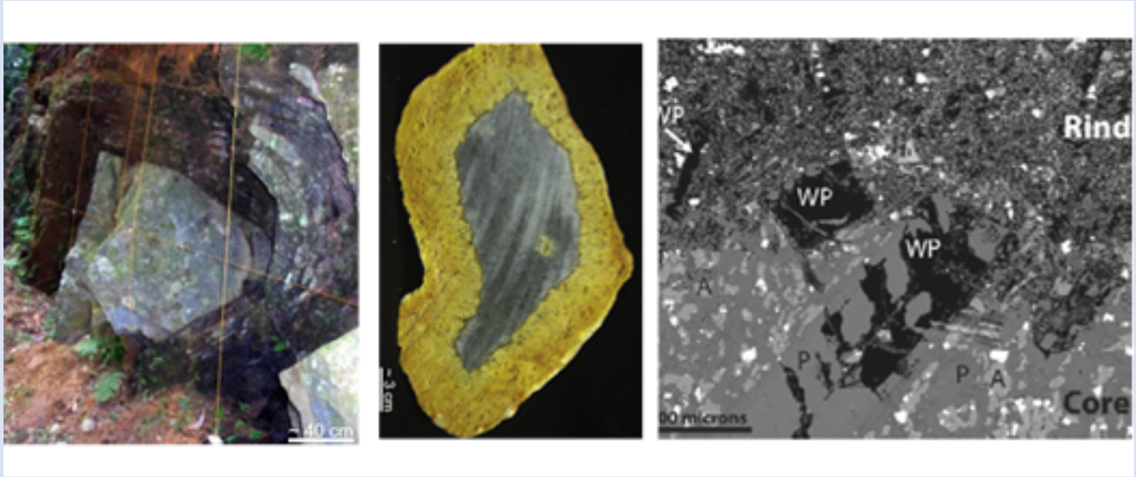

Figure S9. *Left*, Field scale fracturing and surfaces. *Middle*, Hand specimen interface between fresh and weathered basalt. *Right*, Micron-scale porosity and surface roughness. *Left and middle,* Reprinted with permission from A. K. Navarre-Sitchler et al., “Porosity and Surface Area Evolution during Weathering of Two Igneous Rocks,” *GCA* 109, 400–413. © 2013 Elsevier. *Right,* Reprinted with permission from A. K. Navarre-Sitchler et al., “Evolution of Porosity and Diffusivity Associated with Chemical Weathering of a Basalt Clast,” *J. Geophys. Res. Atmos.* 114. © 2009 AGU.

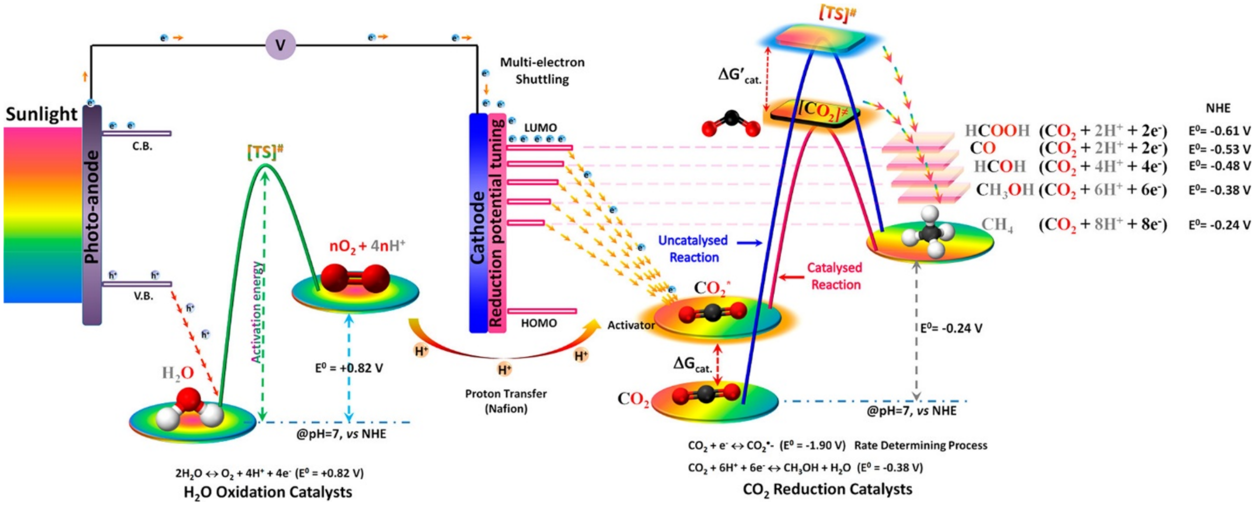

Figure 4-4. Thermodynamic energy diagram for the splitting of water and the conversion of CO_2 under different reaction conditions with electricity and light as sources of energy. Adapted with permission from A. U. Pawar et al., "General Review on the Components and Parameters of Photo-Electrochemical System for CO_2 Reduction with In Situ Analysis," *ACS Sustainable Chem. Eng.* 7, 7431–7455. © 2019 ACS.

Designing interfaces to enhance CO_2 solvation, speciation, and crystallization

A better understanding of coupled processes of dissolution of reactive solids and precipitation of new carbonate phases is critical for effective CO_2 mineralization. Having the ability to predict the dissolution kinetics of solids that provide metal ions to convert CO_2 to solid forms is necessary for facilitating CO_2 removal by these coupled processes. Although extensive studies have examined dissolution rates of a wide range of mineral phases, discrepancies between laboratory-based dissolution data and field-scale data on mineral dissolution still remain. In particular, the heterogeneity of mineral chemical composition, distribution of reactive sites and defects, and confinement effects can play significant roles in controlling the dissolution. The formation of passivation layers on mineral surfaces can significantly decrease mass transfer at interfaces, further reducing CO_2 mineralization. At the same time, the dissolution of mineral surfaces and the cracking and detachment of passivation layers can create or expose new reactive sites or surfaces. Many mineral dissolution processes would consume protons, increasing the system pH values. This could facilitate CO_2 dissolution/solvation in the aqueous systems. Hence, the ability to predict the dissolution process could enable mechanistic controls of the extent and the transport of precursor molecules for CO_2 mineralization. In particular, consideration of mineral crystallography can provide a fundamental principle for predicting dissolution kinetics (**Figure 4-5**). To properly capture the reactivities of multimineralic systems in the prediction of dissolution rates, the mineral composition of specific rocks and their distributions in rocks should be determined.[9]

Understanding crystallization pathways at the atomic level, in chemically complex media and on a wide range of substrates, is of foundational importance for CO_2 storage. There are still significant knowledge gaps regarding robust kinetic data of nucleation, growth, aggregation, and phase transformation that are necessary to determine whether classical nucleation theory describes processes with sufficient accuracy, or to what degree classical and nonclassical pathways involve precursor phases.[10,11] This greatly limits the ability to predictively model CO_2 conversion to solid phases and their phase transformations in all but the simplest scenarios. Furthermore, there is significant interest in designing pathways that result in final materials that are far-from-equilibrium in terms of structure or composition, and are thus more functional and of higher value than those in the ground state.[12–15] Biologically controlled processes, such as biomineralization, serve as important sources of inspiration.[10,16] Complemented by a profound understanding of the energy landscape and synthesizability of well-known and novel solid phases, these insights can greatly aid in accelerating scalable and durable carbon storage.

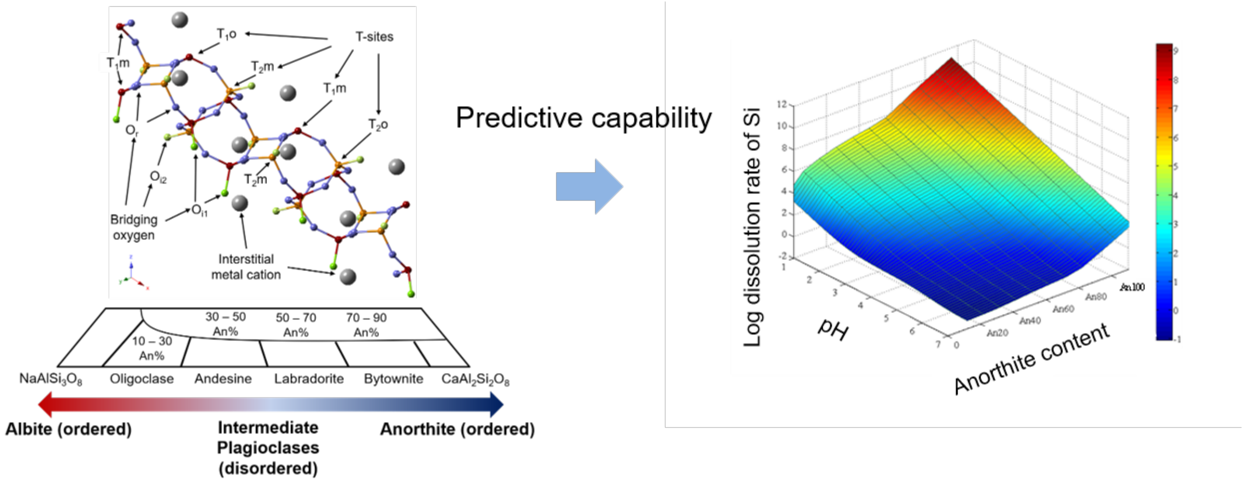

Figure 4-5. Plagioclase minerals are highly reactive aluminosilicates and are abundant in basalt as well as in minerals from deep saline aquifers. Fast dissolution of plagioclases can provide metal ions to form metal carbonate solids to store CO_2. This image illustrates that the crystallographic information of these plagioclase minerals can be used to predict the dissolution rates of each mineral with varied anorthite contents at different pHs. *Left*, Reprinted with permission from Y. Yang et al., "A Mechanistic Understanding of Plagioclase Dissolution Based on Al Occupancy and T–O Bond Length," *Phys. Chem. Chem. Phys.* 15, 18491–18501 © 2013 Royal Society of Chemistry. Permission conveyed through Copyright Clearance Center Inc. *Right,* Reprinted with permission from Y. Yang et al., "Effects of Al/Si Ordering on Feldspar Dissolution," *GCA* 126, 595–613. © 2014 Elsevier.

To obtain accurate mechanistic and kinetic information of crystallization, in situ techniques such as liquid-cell transmission electron microscopy[17] and grazing incidence small- and wide-angle X-ray scattering[18] (**Figure 4-6**) are poised to provide fundamental insights into mechanisms at interfaces. Atom probe tomography at cryogenic temperatures is a powerful, emerging tool that could help determine structure and chemical composition of nascent, disordered, and chemically complex phases at solvated interfaces with atomic scale resolution and chemical sensitivity for low atomic number elements.[19]

In parallel to mechanistic investigations at very high spatial or temporal resolution, determining the effective rates of nucleation, spinodal decomposition, growth, aggregation, and dissolution over a wide range of conditions, using, for instance, X-ray scattering (**Figure 4-6**),[18,20] microfluidic,[21,22] or other parallelizable assays is essential. Comprehensive kinetic data sets obtained through systematic experimental and theoretical investigations and ML/data mining approaches can aid in identifying additives that enhance or retard precipitation of specific phases, control polymorphs, tune rates, or enable steering of processes toward more valuable materials. An integral aspect of this opportunity is the systematic analysis of biological processes (biomineralization), identifying the design principles of biologically controlled mineralization that already occurs at a global scale and applying these principles to effective control of carbon mineralization.

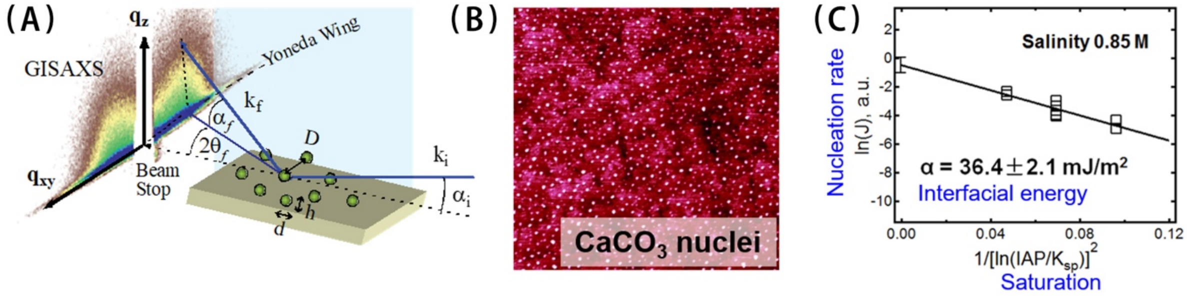

Figure 4-6. In situ observation of $CaCO_3$ nucleation and growth to control metal mineralization. (A) Reprinted with permission from Y.-S. Jun et al., "In Situ Observations of Nanoparticle Early Development Kinetics at Mineral–Water Interfaces," *Environ. Sci. Technol.* 44, 8182. © 2010 ACS. (B) Adapted with permission from Q. Li et al., "Dynamic Transformation of Cubic Copper Catalysts during CO_2 Electroreduction and its Impact on Catalytic Selectivity," *Comm. Chem.* under CC BY 4.0. © 2018. (C) Adapted with permission from Q. Li and Y.-S. Jun, "Salinity-Induced Reduction of Interfacial Energies and Kinetic Factors during Calcium Carbonate Nucleation on Quartz," *J. Phys. Chem. C* 123. © 2019 ACS.

Discovering molecularly integrated pathways for CO_2 capture and conversion

An important aspect of maximizing the net fixation of carbon is to tightly integrate capture and conversion of CO_2. Conversion here could mean chemical transformation/reduction to carbon monoxide, syngas, or small molecules (e.g., methanol, ethylene) all the way to their subsequent transformation to polymers and carbonates and the formation of sparingly soluble salts.

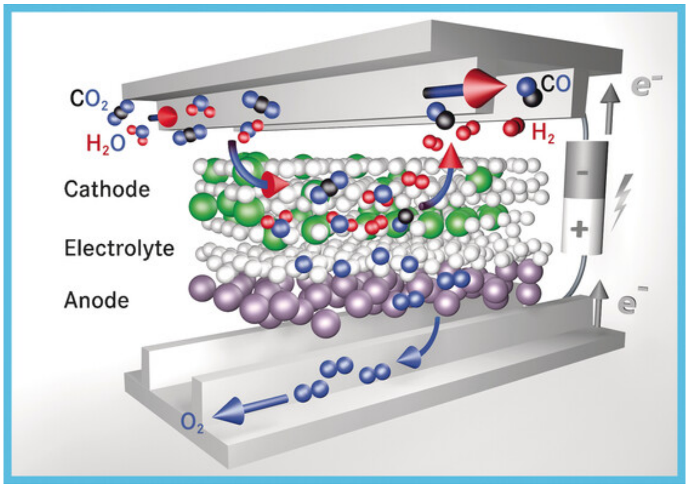

Figure 4-7. Coupling CO_2 and H_2O high-temperature electrolysis to form syngas using sustainable—but intermittent—energy sources such as wind or solar. Reprinted with permission from S. R. Foit et al., "Power-to-Syngas: An Enabling Technology for the Transition of the Energy System?" *Angew. Chem. Int. Ed.* 56, 5402–5411. © 2017 Wiley.

CO_2 capture and conversion pathways, which involve the reduction of carbon for producing fuels and chemicals, are energy intensive. However, recent progress using photo- and electron-assisted reduction driven by carbon-neutral energy sources may greatly improve efficiency. For instance, in artificial photosynthesis, photochemical oxidation of water is coupled to electrochemical reduction of CO_2. In principle, this enables the use of sustainable solar energy to generate high-value products such as syngas.[23] Similarly, in electron-assisted conversion, carbon-neutral energy sources, even intermittent ones, can be used to reduce CO_2. At high temperature, CO or syngas can thus be produced (**Figure 4-7**).[24] At low temperature, a slate of valuable chemical feedstocks, including methanol, ethanol, and ethylene, are accessible. Although potentially transformative, activity, selectivity, and stability of the electrode catalysts are limiting factors, and at low temperature, product selectivity remains a challenge.

Advances in electrocatalysts can be harnessed to develop photo-assisted and electron-assisted approaches to accelerate carbon mineralization with integrated H_2 evolution as analogs to thermochemical approaches. Specific examples include harnessing photons and electrons to selectively precipitate solid carbonates from water streams with a wide range of dissolved metal compositions. Scientific opportunities exist in synthesizing novel materials for accelerating carbon removal with inherent H_2 recovery.

In addition, CO_2 capture and conversion pathways that involve producing calcium and magnesium carbonates via thermodynamically downhill approaches are less energy-intensive compared to pathways that involve CO_2 reduction. To integrate CO_2 capture and mineralization, a key scientific challenge arises due to the low solubility of CO_2 in water. To address this challenge, CO_2 capture solvents such as amino acids (e.g., sodium glycinate) and amines have been used to increase the concentration of (bi)carbonate species. As a result, CO_2 capture and conversion to produce solid calcium and magnesium carbonates can be enhanced significantly (**Figure 4-8**). The solvents are regenerated as the dissolved (bi)carbonate species are depleted and solid carbonates are formed. The key advantages of this approach include the use of temperatures below 80–90°C where CO_2 capture and carbon mineralization, relatively fast timescales of 1–3 hours as opposed to days, and rapidly regenerated solvents as an alternative to the use of acids and bases that are rapidly consumed.[25] Future research directions include development of novel solvents for integrated CO_2 capture and carbon mineralization that are highly selective for CO_2, are rapidly regenerated, and remain robust through multiple cycles of operation.

Carbon mineralization can also be harnessed as an integrated pathway for the reactive separation of CO_2 in the water–gas shift reaction for producing H_2 shown here: $CO + H_2O \rightarrow CO_2 + H_2$. Although it is well known that oxides and hydroxides of calcium and magnesium sorb CO_2 and thermodynamically enhance H_2 yield, the direct use of earth-abundant calcium- and magnesium-bearing silicate minerals remains infrequent.[25] Future research directions include developing thermodynamically downhill routes for deconstructing renewable bioderived molecules to produce H_2 with inherent carbon removal via carbon mineralization. Delineating the rate-limiting step in these multiphase coupled chemical reaction environments is a crucial consideration for accelerating these approaches.

Novel synthetic sorbents that can absorb CO_2 from the atmosphere at gas–liquid interfaces and enhance the bicarbonate concentrations can unlock biobased pathways for carbon removal via algal growth. Significant scientific opportunities lie in the design of next generation of solvents and sorbents that can accelerate CO_2 uptake and transfer while being efficiently regenerated when coupled to a conversion pathway. The design of new materials and chemical pathways can conserve water, minimize sorbent loss and degradation, and enable energy- and atom-efficient CO_2 capture and conversion.

Multimodal approaches to elucidating multiphase transformations

The catalytic conversions and mineralization processes described above are usually far from being static and involve simultaneous changes in the structural and electronic properties of the system as a function of time, involving events that go from timescales of nanoseconds to days or years. When focusing on spatial resolution, characteristic length scales range from meters to angstroms or picometers. The systems under study can have multiple phases coexisting in a 3D space (**Figures 4-3** and **4-7**). Images detailing the interaction of CO_2 with materials that can be used for the storage/conversion of the molecule (**Figure 4-9**) are very rare but could enable a valid theoretical modeling during the design or optimization of removal processes.

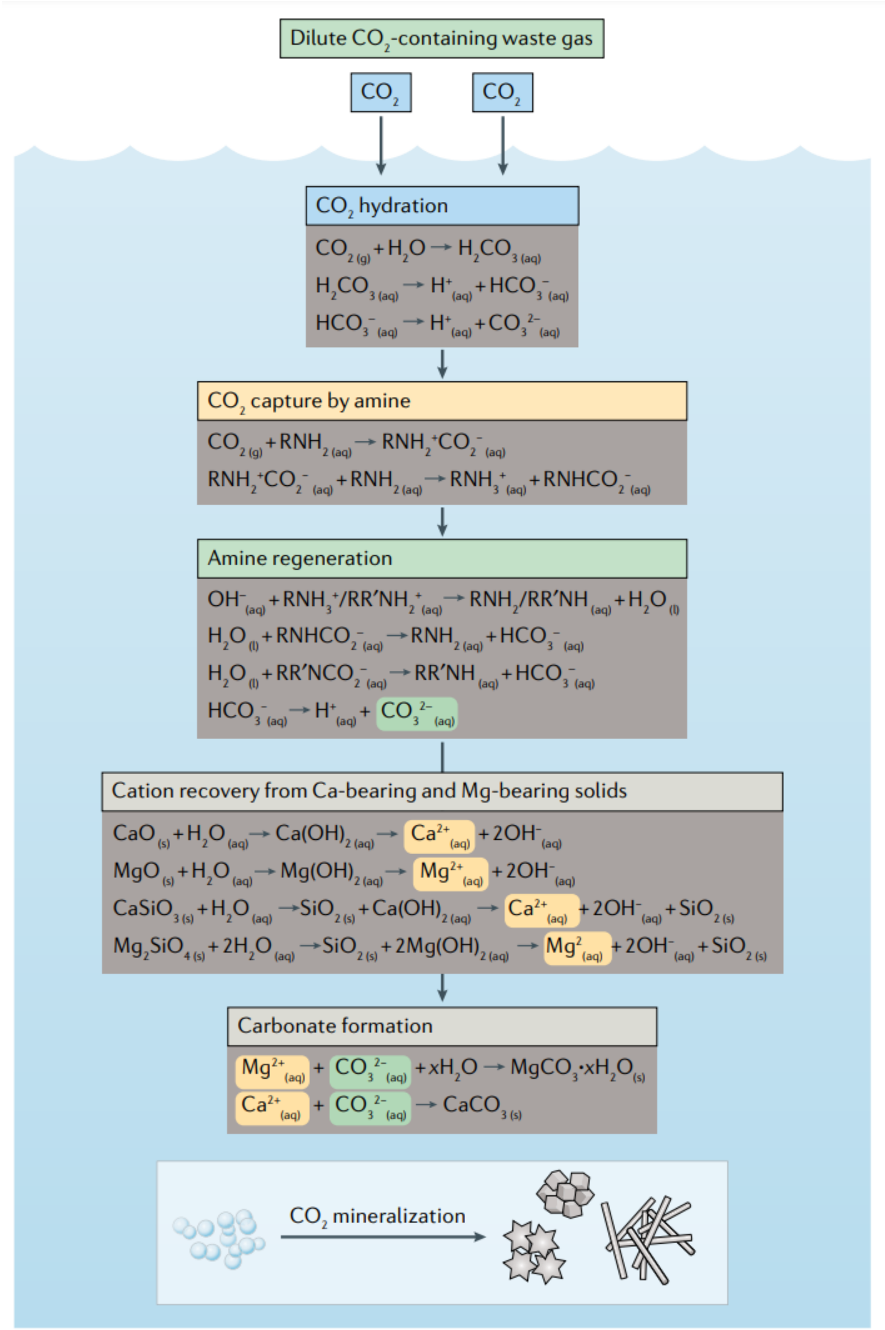

Figure 4-8. The aqueous alkaline-amine-looping approach for CO_2 mineralization. In principle, all reactions are reversible. CO_2 first undergoes partitioning from the gas to the aqueous phase, where it can be captured by an amine to give a carbamate (in the case of primary amines). The carbamate can readily be converted back into the amine and the CO_3^{2-} ions that form combine with dissolved Ca^{2+} and/or Mg^{2+} to give $CaCO_3$ and $MgCO_3{\cdot}xH_2O$. Reprinted by permission from G. Gadikota, "Multiphase Carbon Mineralization for the Reactive Separation of CO_2 and Directed Synthesis of H_2," *Nat. Rev. Chem.* 4 (2), 78–89. © 2020 Springer Nature.

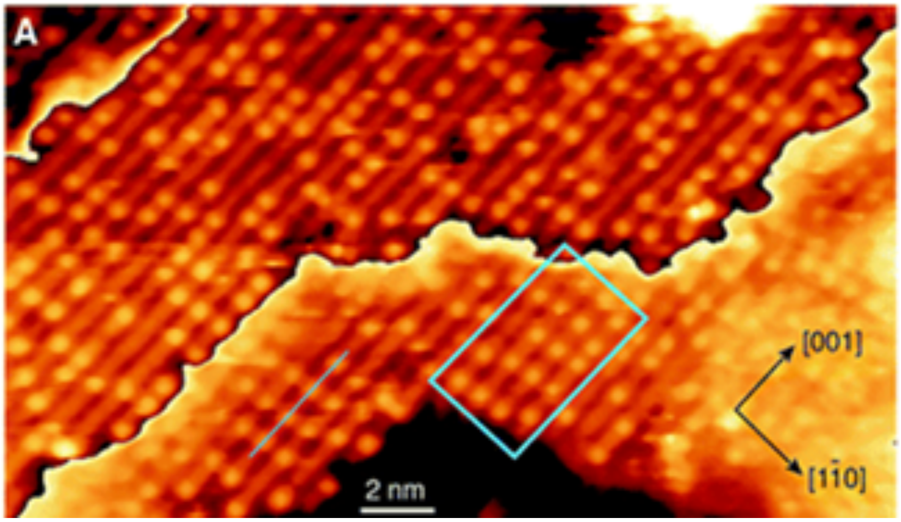

Figure 4-9. Scanning tunneling microscopy image of the rutile $TiO_2(110)$ surface under 0.53 Torr CO_2 at 300 K (24 × 14 nm^2). The small blue rectangle shows the adsorbate spacing relative to the titania substrate. Reprinted with permission from R. C. E. Hamlyn et al., "Imaging the Ordering of a Weakly Adsorbed Two-Dimensional Condensate," *Phys. Chem. Chem. Phys.* 20, 13122. © 2018. Permission conveyed through Copyright Clearance Center Inc.

In general, there is a need to develop and link multimodal cross-scale approaches to elucidate the dynamics of multiphase chemical transformations underlying durable carbon storage.[26–30] Based on the challenges discussed in the previous sections, the ideal tool for a detailed study of targeted processes for CO_2 storage should have high sensitivity and facilitate the fast acquisition of data in a millisecond timescale with a spatial resolution in the range of nanometers or smaller and simultaneously monitor the properties of the reactive centers and the environment around them. At the present time, no single technique can accomplish all of these tasks.

Recently, a large number of in situ/operando methods have been used to study the manipulation of CO_2 through catalytic and mineralization processes: Fourier-transform infrared spectroscopy, Raman spectroscopy or surface-enhanced Raman spectroscopy, small angle and wide angle X-ray scattering with transmission (SAXS/WAXS) or grazing incident modes (**Figure 4-6**), X-ray absorption spectroscopy (XAS), X-ray diffraction and scattering (**Figure 4-5**), ambient-pressure X-ray photoelectron spectroscopy, a combined transmission X-ray microscopy and X-ray tomography, transmission electron microscopy, AFM, scanning tunneling microscopy, and transmission electron microscopy (TEM) (**Figure 4-3**).[26–29,31,32] This type of research is very useful for obtaining fundamental knowledge, but the studies can be separated into those that follow a time-resolved mode to examine fast phenomena and reaction rates while giving a spatial average of the sample properties and those that provide high spatial resolution at the atomic or nanometer level in a more or less static mode. Efforts should be made to overcome this characterization gap.

Harnessing computational and data science tools

In recent years, computational studies have pointed to new directions for CO_2 storage and conversion. Screening approaches that combine ML with calculations based on density functional theory and microkinetic modeling or experimental measurements have been used to identify electrocatalysts for effective CO_2 reduction (**Figure 4-10**). Screening large search spaces is still nontrivial, but these approaches can minimize the cost of separate experimental and theoretical searches and point to novel catalytic materials to be used in thermal, electro-, and photochemical transformations of CO_2. In the area of CO_2 storage, ML methods can be used to identify precursors and processing conditions that enhance the efficiency of forming minerals and other materials.[33–35]

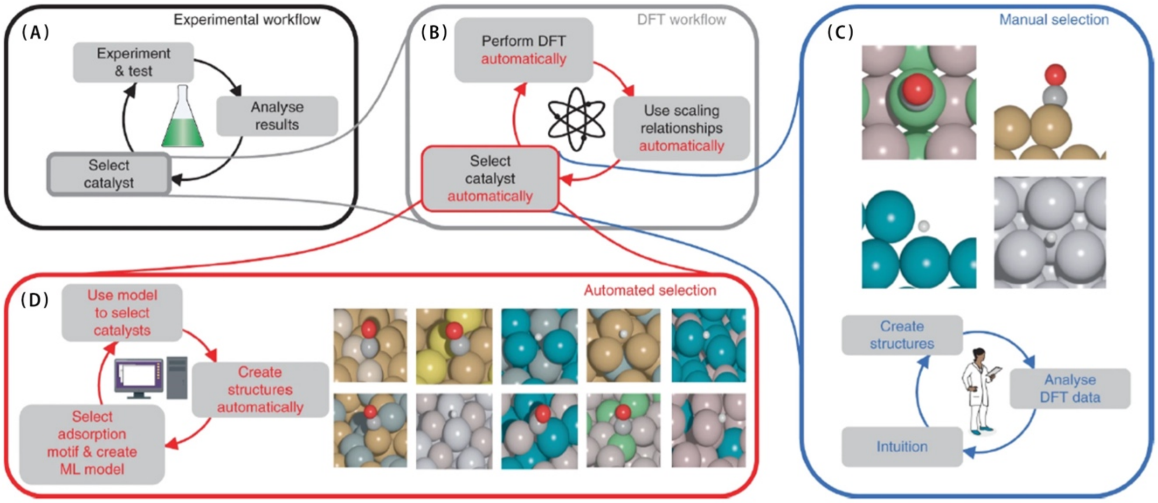

Figure 4-10. Workflow for automating theoretical materials discovery. Reprinted with permission from K. Tran and Z. W. Ulissi, "Active Learning across Intermetallics to Guide Discovery of Electrocatalysts for CO_2 Reduction and H_2 Evolution," *Nat. Catal.* 1, 696. © 2018 Springer Nature.

A primary goal of data science approaches to CDR research should be the de novo design of materials from a data-driven approach informed by targeted experimental and theoretical results. There is a need to design, develop, and implement experiments and theoretical models specifically intended to integrate computational and data science tools to create data-driven solutions.[34,36] These tools may leverage visualization, AI, ML, deep neural networks, and deep learning, among other approaches. The main task is to identify smart processes for smart storage and utilization.

4d. Potential Impacts

Successful execution of the CDR research outlined here has the potential to impact the broader understanding of chemical catalysis, coupled reactions, and mineralization processes, as well as the use of in situ measurement methods and data science tools. Addressing the scientific challenges and research opportunities can lead to a new conceptual framework for the effective binding and conversion of CO_2 into minerals and materials. This framework could enable rational design of novel methodologies for CO_2 conversion and storage and advance the fundamental understanding of carbon transformations for carbon removal from both point sources and nonpoint sources, such as air and oceans. The proposed development of characterization and computational tools for multiphase chemical transformations could directly translate to other scientific investigations of related problems of molecular binding, chemical conversion, and mineralization. The results of this research can be the development of transformative technologies for CO_2 conversion and storage that offer novel, low-cost pathways to durable carbon storage at the gigaton scale using renewable energy sources, aiding in the realization of the Carbon Negative Shot's goals for CO_2 removal.

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PRO 5: Integrated System Observatories for Carbon Storage Security

Subsurface geologic sequestration can store CO_2 for thousands of years in complex kilometer-scale formations that vary in lithology, groundwater chemistry, and structure. CO_2 storage will cause changes to the reservoirs that are not predictable. Understanding the processes relevant to prediction of long-term reservoir evolution requires data that capture this complexity. Field data provide an opportunity to validate experimental and computational methods that connect reservoir integrity to molecular-scale chemistry. Integration of geophysical signals with ML-driven simulations rooted in physics-based models can constrain the coupled geochemical–geomechanical processes, enabling more reliable forecasts of long-term reservoir performance.

5a. Summary

Future regional CDR geologic sequestration hubs could vary in lithology, groundwater chemistry, and structure. All will require that injected CO_2 remain underground for more than 1,000 years. Establishing a network of field-scale subsurface measurement capabilities dedicated to providing long-term predictability is an opportunity to develop validated methods to bridge data and simulations from the field to atomic scales and vice versa. New signals and ML-driven physics-based simulations can provide constraints on coupled geochemical–geomechanical processes to forecast long-term injectivity, security, and CO_2 mineralization. The resulting predictive models can increase storage security for regional sites and optimize carbon sequestration.

5b. Key Scientific Questions

- How can processes, data, and modeling be integrated across time and length scales to bridge the gap and create predictive models for long-term carbon storage security?
- Can geophysical signals identify coupled geochemical–geomechanical feedbacks that affect long-term storage security, and can we understand these signals at each scale?
- How can we optimize the use of subsurface rock–fluid systems for predictive design of efficient and secure storage?

5c. Scientific Challenges and Research Opportunities

To answer the above questions, three scientific challenges must be tackled, each of which offers an opportunity to impact CDR. An ongoing challenge is validation during predictive modeling of CO_2 subsurface storage security, particularly with capabilities intended to bridge information and processes across scales, and for anticipating rates and interactions in complex systems with geological heterogeneity. A network of field-scale subsurface measurement capabilities could address this challenge by providing access to regional subsurface systems to record data from field-scale monitoring of sequestration sites in diverse lithologies, structure, and fluid chemistry to combine with insight from laboratory experiments to understand the geochemical–geomechanical coupled response of rock during long-term carbon storage.

A current challenge in constraining CO_2 subsurface storage performance is that laboratory measurements and model predictions of small-scale processes that dominate coupled geochemical–geomechanical processes in geologic sequestration do not match field observations or are below the resolution of field-scale measurements. Combined laboratory imaging modalities applied to rock and fracture surfaces would provide an opportunity to enable the quantification of dynamic coupling among geochemical–geomechanical processes in samples that are more representative of CDR field conditions. X-ray, neutron scattering, MRI and other geophysical modalities would provide orthogonal information on the mechanical and chemical alterations of polymineralic surfaces, heterogeneous rheology, and fluid chemistry in 3D and real time. These new multimodal data sets would provide new approaches to reduce the uncertainties in the application of laboratory-calibrated geochemical and geomechanical models to subsurface lithologies exposed to complex fluid chemistries. Additionally, insight about the effect of this dynamic coupling on geophysical and geochemical signals could be gained that can be used to monitor subsurface sites and to enable tailored metal carbonation at specific targeted locations to improve the efficiency and safety of geologic carbon sequestration.

Extrapolation of coupled processes beyond the domain of the measurement space (rock vs reservoir, boundary conditions, lithology, longer timeframes) is currently not possible. Recent advances in data science, AI, ML and high-performance computing (HPC) offer an opportunity to extract useful information from multiple data streams to monitor evolving rock–fluid systems, to learn how to extrapolate information beyond domains, and to accelerate physics-based modeling from the atom-to-field scale to optimize carbon storage and mineralization through reservoir management of temperature, pressure, and chemistry. This would require the development of unsupervised neural networks methods that can learn the physics from a few or nonexistent (and potentially noisy) data sets, to discern the signatures of reservoir evolution during CO_2 storage.

Field-scale subsurface measurements capabilities for "slow science"

Linking the macroscopic system response of geologic carbon sequestration in the field to microscale process models has challenged scientists over the last decade. Key aspects of CO_2 behavior in the subsurface relevant to geological carbon sequestration (GCS) security, such as the rates of dissolution in the aqueous phase and the rate of carbonate mineralization, often vary by several orders of magnitude from preinjection modeling studies. Although process-driven approaches have attempted to estimate silicate mineralization rates in GCS-relevant rock samples based on microscale structural/chemical characterization, few have been successful,[1,2] and these results have been challenging to use for the prediction of the response and state of CO_2 over longer length and timescales.

Given the heterogeneity and scale of natural geologic systems (**Figure 5-1**), significant opportunities exist to improve our understanding of geologic carbon storage by complementing upscaling (or process-driven) approaches with downscaling investigations. Such scientific approaches start with highly instrumented sites providing field-scale subsurface measurements that can capture the complexity of geologic systems at the reservoir scale while providing sufficient information to probe fundamental questions about the parameters relevant to the prediction of long-term system evolution. Recent advances in high-resolution in situ geophysical and geochemical sensing approaches provide a wealth of data capable of probing transformations in larger rock volumes. In parallel, advances in fully coupled thermo-hydro-mechanical-chemical forward and inverse models[3] provide a path forward for extracting parameters such as mineralization rates from diverse information sources. This combination of improved sensing and inversion offers a path for both recovering scaled parameter estimates for GCS processes, as well as validating upscaled predictions from first principles and laboratory-based studies.

Dedicated subsurface scientific measurement capabilities also fill a gap by extending observation timescales of GCS systems beyond a typical project lifetime. The value of monitoring data sets often scales with duration and continuity when large-scale changes are being investigated, as has been thoroughly documented by researchers studying global climate change. Scientific targets for such measurements include improved constraints on field-scale mineralization rates for reactive formations and geochemical/hydrogeological coupling processes that affect CO_2 fate in the reservoir.

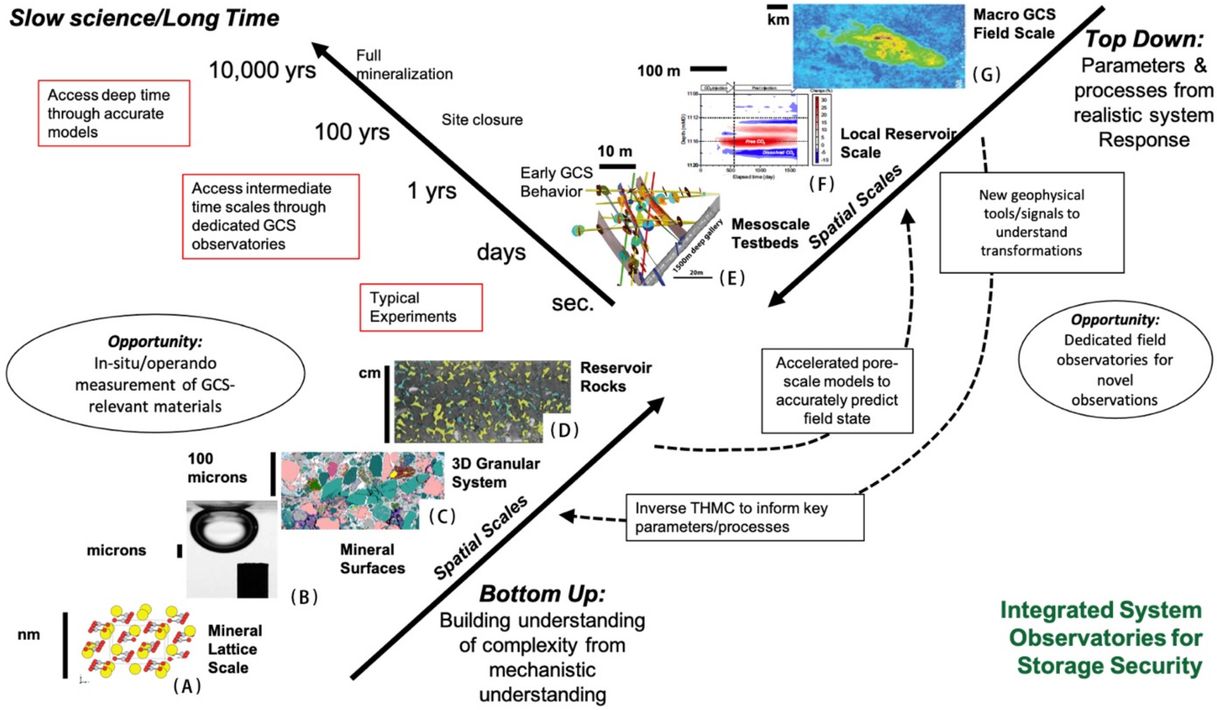

Figure 5-1. Building understanding of geological carbon storage by combining top-down and fundamentals-driven research. (A) Reprinted with permission from R. Chang et al., "Tuning Crystal Polymorphisms and Structural Investigation of Precipitated Calcium Carbonates for CO_2 Mineralization," *ACS Sustain. Chem. Eng.* 5 (2), 1659–1667. Permission conveyed through Copyright Clearance Center Inc. © 2017. (B) Reprinted with permission from J. Wan et al., "Contact Angle Measurement Ambiguity in Supercritical CO_2–Water–Mineral Systems," *Int. J. Greenh. Gas Control* 31, 128–137. ©2014. Permission conveyed through the Copyright Clearance Center Inc. (C) Reprinted with permission from L. E. Beckingham et al., "Evaluation of Accessible Mineral Surface Areas for Improved Prediction of Mineral Reaction Rates in Porous Media," *GCA* 205, 31–49. © 2017 Elsevier. (D) Reprinted with permission from M. Voltolini et al., "Visualization and Prediction of Supercritical CO_2 Distribution in Sandstones during Drainage," *Int. J. Greenh. Gas Control* 66, 230–245 under CC BY-NC-ND 4.0. © 2017. (E) Reprinted with permission from H. S. Viswanathan et al., "From Fluid Flow to Coupled Processes in Fractured Rock," *Rev. Geophys.* 60 (1) under CC BY-NC-ND 4.0. © 2022. (F) Reprinted with permission from S. Mito and Z. Xue, "Post-Injection Monitoring of Stored CO_2 at the Nagaoka Pilot Site," *Energy Procedia 4*, 3284–3289 under CC BY-NC-ND 4.0. © 2011. (G) Reprinted with permission from R. A. Chadwick et al., "4D Seismic Quantification of a Growing CO_2 Plume at Sleipner, North Sea," *Pet. Geol. Conf.* 6 (1), 1385–1399. © 2005.

In this context, mesoscale (borehole ~1–100 m) experiments have particular advantages, providing a sufficient rock volume to sample property heterogeneity, including lithologic, structure, hydrogeologic, and geochemical, while still allowing for detailed characterization, instrumentation, and monitoring at relatively low cost. Recent geothermal and nuclear waste experiments have used mesoscale testbeds to greatly improve our understanding of complex fractured systems.[4,5] Ongoing studies are using similar field-scale subsurface capabilities to probe GCS-related problems dynamically, including the reactivation of faults due to fluid injection,[6] which highlights the potential for such capabilities to perform small-scale manipulations during hypothesis testing. Another related opportunity is the development of field-scale subsurface science capabilities (1 per proposed regional hub) coupled to large commercial GCS operations. By providing science-driven subsurface capabilities coupled to industrial-scale subsurface perturbations, GCS-related processes and rates could be investigated at appropriate pressure-temperature states and forcings that differ significantly in potential geochemical reactions from the requirements for enhanced geothermal energy projects or nuclear waste isolation. These measurement capabilities needed for the next step beyond scientific drilling programs include state-of-the-art in situ observations to constrain the state and security of injected CO_2 over time.

The following research objectives would be enabled by the capabilities outlined above:

1. Determining how fluid flow through serial lithologies can be used to accelerate carbon mineralization in the appropriate rock unit.
2. Developing ambient noise monitoring techniques and interpretation methods to perform long-term imaging of subsurface storage to monitor injectivity, mineralization, and leaks
3. Determining if carbon mineralization increases porosity to enhance dissolution or seals fractures to enhance caprock integrity
4. Developing new downhole tools to identify chemical signatures of mineralization or other trapping mechanisms
5. Developing a framework to better constrain reservoir simulations with information from subtle changes in geophysical signatures

Impact of small-scale processes on long-term subsurface storage

Geologic CO_2 sequestration depends on our ability to predict reservoir integrity over 1,000 years and across kilometer-scale subsurface reservoirs. However, the chemical and physical processes that affect long-term storage occur on smaller spatial and shorter temporal scales and are distributed across the reservoir. Consequently, when managing, engineering, and monitoring natural systems, knowledge of the molecular, nano, and micro scales is critical to the identification of evolving conditions to assess storage safety. A current challenge is that laboratory observations and model predictions of chemical reaction kinetics and coupled processes based on small-scale systems (e.g., grains, cores) can be inaccurate by 100–1,000 times when compared to field observations[7] or below the resolution of field-scale measurements. The reasons for such disparities are complex and multifold. One main source of uncertainty is the inherent material and structural heterogeneities of geological units together with the complexity of the thermal-chemical-mechanical feedback at subsurface conditions. Therefore, laboratory-scale experiments are needed that can determine: (1) the impact of the mineral and lithology heterogeneity, structural roughness, and fluid confinement encountered at the field scale on reaction rates, kinetics and coupled processes, and (2) the geophysical and chemical signatures that are produced and can be scaled to field monitoring.

Transport properties and mechanical strength of a CO_2 underground repository are expected to exhibit substantial spatiotemporal variability in response to mechanical, chemical, and thermal loads. Existing laboratory-calibrated models often failed to "scale up" because of the lack of experimental constraints on effects of feedback and coupling between the processes controlling rock deformation in real time in heterogeneous rock. A recent study demonstrated the value of multimodal imaging by combining 3D X-ray microscopy and MRI to image and extract both the pore structure and the fluid velocity field in the pore structure of rock cores.[8] Neutron and X-ray beamline technologies are two other sensing modalities that provide a tremendous opportunity to develop new experimental strategies that enable quantification of the 3D spatial and temporal evolution rock more representative of field site geomaterials (i.e., fracture surfaces and rock with heterogenous mineralogy, rheology, and microstructures under in situ conditions). Combined sensing techniques can also enable identification of potential geophysical signatures of this evolution. Neutrons are an ideal probe for visualizing hydrogenous fluids in geological systems as rocks composed of silicates and carbonates are reasonably transparent to neutrons. At the same time, the X-rays readily reveal the microstructure of the denser solid matrix. A recent study using neutron tomography recorded the time-resolved wormhole formation in limestone samples.[9] The results reveal the importance of the interplay between the generation of fluid pathways (by dissolving carbonate rocks) and transition to multiphase flow (by mixing CO_2 released from dissolution) in potential CO_2 injection. Imaging reactive samples can shed light on heterogeneous alteration,[10] fingerprint mechanisms of porosity evolution,[11] and quantify the stress and strain evolution during fluid-induced fracturing (**Figure 5-2**).[12,13]

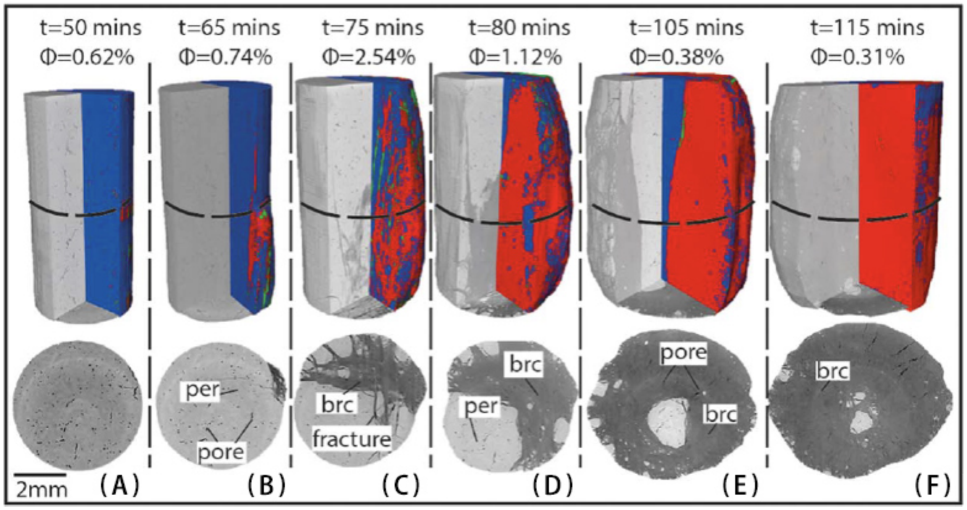

Figure 5-2. Synchrotron X-ray microtomography reveals the feedback between reaction-induced fracturing and hydration of periclase. *Blue*, periclase. *Red*, brucite. *Green*, pore space. Reprinted with permission of X. Zheng et al., "Effects of Confinement on Reaction-Induced Fracturing during Hydration of Periclase," *Geochem. Geophys. Geosy.* 19, 2661–2672. © 2018 AGU.

Application of emerging beamline capabilities enable us to probe multigrain and multiphase material microstructures in 3D and real time. By adding the dimension of time evolution and elucidating the coupled physical and chemical processes at subsurface conditions, the in situ experimental studies could revolutionize testing and calibration of geomechanical models and identification of geophysical signatures of alteration for better assessments of the security and efficiency of CO_2 sequestration.

Opportunities also exist to apply recent advances in AI and ML to help integrate data across scales and among computational and experimental results at each scale. In relation to increasing the realism of smaller scale laboratory and simulation studies, ML can be used to parameterize models based on data and calculations using increasingly accurate methods. For example, density function theory (ML-DFT)[14] and interatomic potentials (ML-IAPs)[15] can be used in classical MD simulations based on quantum mechanics and spectroscopic information, which would be accurate and account for chemical reactions. Creating such IAPs and adapting MD codes to new exascale computing capabilities can allow for expansion of molecular simulations into spatiotemporal domains covered by methods such as lattice Boltzmann techniques. In such a manner, one could build each spatiotemporal scale upon accurate information provided at smaller scales to progress up to the field scale (upscaling).

Addressing the challenge of upscaling would benefit from the following research objectives:

1. Determining reaction rates for polymineralic or heterogeneous mineral fracture surfaces under stress, temperature, and pressure conditions and gradients experienced in subsurface sequestration over long time frames
2. Determining the geomechanical controls on geochemical reaction rates and conversely the geochemical controls on geomechanical deformation, slip and fracture propagation
3. Identifying geochemical and geophysical signatures that can differentiate pore-scale processes such as carbon mineralization from propagating fractures or other failure mechanisms caused by coupled geochemical–geomechanical processes, and determine which of these signatures can be scaled up
4. Determining how carbon mineralization contributes to seismic versus aseismic slip
5. Determining how geomechanical relaxation rates and geochemical reaction rates are similar or differ under confined conditions
6. Determining how to integrate geochemical and geophysical signatures to inform and constrain predictive models

AI for signature identification and model acceleration

Performance assessment of geologic carbon sequestration sites is challenging because the noisy data sets from monitoring these deep, complex sites make it difficult to constrain predictive models. In addition, small-scale factors such as heterogeneity, relative permeability, and reaction rates that are currently oversimplified in reservoir-scale calculations often control key metrics such as injectivity, capacity, CO_2 trapping and mineralization rates. For more accurate assessments a more rigorous multiscale approach is required.

Data science methods such as AI and HPC have the potential to transform signature science and predictive multiscale simulation both of which are critical for assessing the security of geologic carbon sequestration sites. Subsurface monitoring uses a range of techniques to characterize and monitor the perturbations to subsurface geologic systems from pressures, temperature, and geochemical interactions that can occur during the injection and storage of CO_2. Interpreting these data sets is challenging because noisy data streams, uninformative channels, and multiple data types need to be co-interpreted. Recent advances in deep machine learning and AI have created numerical approaches to separate overlapping sources of noise, identify information rich channels, distill information from noise, and discern new signals in low signal-to-noise ratio data sets in precisely these kinds of complex situations to discern controlling mechanisms.[16–18] AI approaches can be a critical element in the development of long-term monitoring of CDR subsurface sites based on ambient noise wavefield interactions with evolving subsurface systems.

Decision makers and regulators require uncertainty bounds on numerical predictions and forecasts of CDR storage to make sound technically defensible assessments of injectivity, capacity, leakage and mineralization over 1,000 years. Accurate predictions require the incorporation of pore-scale processes (10^{-9} to 10^{-3} m) into reservoir-scale (10^{2} to 10^{3} m) calculations.[19] For example, 3D simulation of geochemical processes for a 1 km^3 reservoir would require 10^{28} simulation cells for a nanoscale resolution, which is currently not possible without quantum computing. HPC reservoir models have been developed to simulate complex thermo-hydro-mechanical-chemical processes that control the evolution of a carbon sequestration site.[5] However, these models are difficult to constrain because of a lack of observational data (opportunity 1), and these models do not account for critical pore-scale geochemical–geomechanical processes (opportunity 2). Although pore-scale simulators have shown good agreement with laboratory experiments, they are computationally expensive,[20] and not suitable for reservoir-scale research questions. Previously it was not possible to include pore-scale processes into reservoir-scale simulators because of the computational demands (CPU, cores, time). However, recent work has shown that multiscale neural networks (**Figure 5-3**) have the potential to mimic and replace pore-scale simulators with 3–4 orders of magnitude speedup in computation time.[21] These accelerated models have the potential for pore-scale processes to be incorporated into HPC reservoir models to enable a paradigm shift for performance assessment of geologic carbon sequestration.

The nature of this challenge and the resulting opportunities for capability development justify the following research objectives:

1. Developing AI and HPC mathematical framework and computational methods to incorporate pore-scale processes that include geochemical–geomechanical coupling in response to changes in fluid chemistry, mineralization, pressures, temperatures, and stress to achieve prediction for long-term storage performance and security.
2. Acquiring data on multiple appropriate scales to validate new models that incorporate processes from smaller scales.
3. Developing AI and data fusion methods to identify relevant information channels, relevant signal components, and cointerpretation of multiple diverse sensors data streams to constrain simulations at the larger scales.

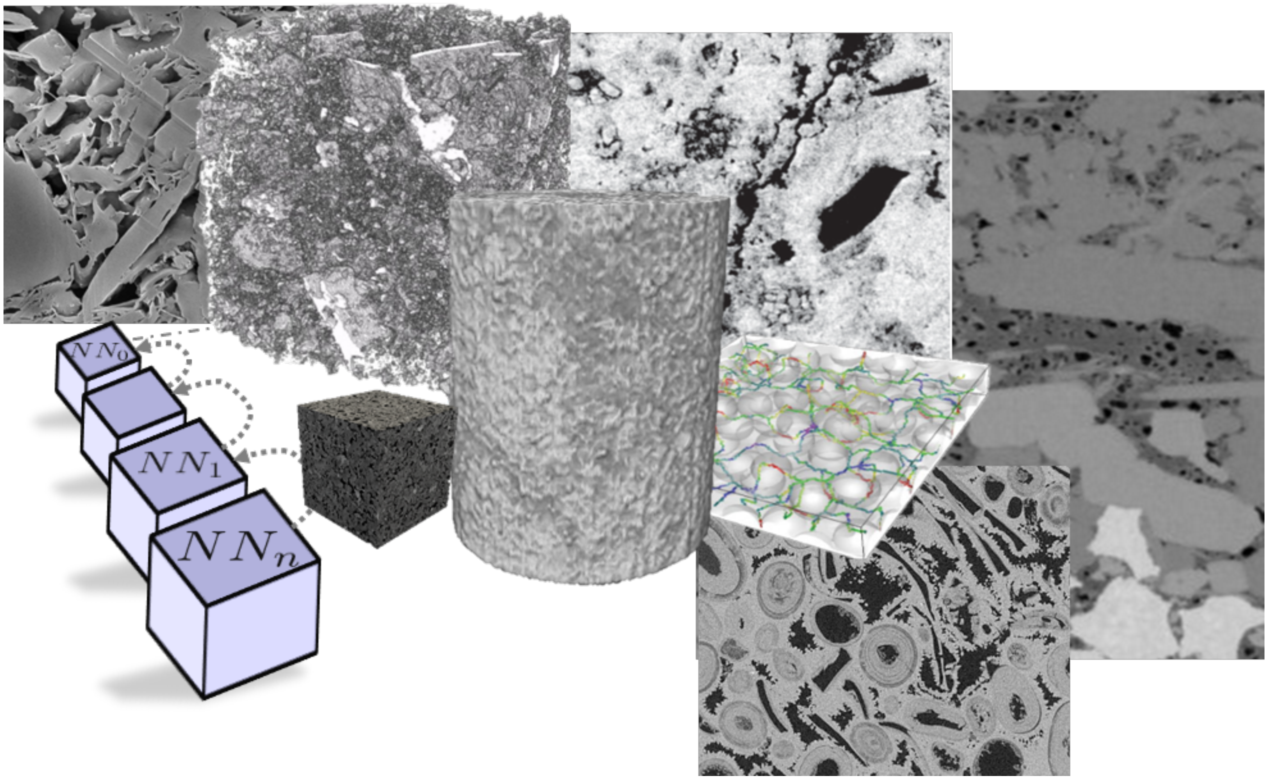

Figure 5-3. Emulating detailed pore-scale simulations with multiscale neural networks to accelerate these calculations by orders of magnitude will allow for accurate macroscopic properties to be used in reservoir calculations. *Bottom left*, Reprinted with permission from J. E. Santos et al., "Computationally Efficient Multiscale Neural Networks Applied to Fluid Flow in Complex 3D Porous Media," *Transport in Porous Media* 140 (1), 241–272. © 2021 ACS. *Top right*, Reprinted with permission from Santos, J. E. et al., "Modeling Nanoconfinement Effects Using Active Learning," *J. Phys. Chem. C*. 124 (40), 22200–22211. © 2020 ACS. Unpublished images courtesy of H. Viswanathan and J. Santos.

5d. Potential Impacts

Subsurface CO_2 storage is challenging because the reservoirs are composed of heterogeneous materials and contain complex fluids. Although past studies of geochemical alterations on monomineralic surfaces of microscale particles have been essential for obtaining reaction rates, the values are often found to be nonrepresentative of the behavior observed at field sites. Another challenge for any geologic site is the range of length scales and timescales over which processes occur and alter the integrity of a system. Pore-scale simulations are now fairly accurate in reproducing laboratory measurements,[2] but accurate bridging to larger scales has not been achieved. The proposed combination of dedicated subsurface observatories for long-term CO_2 related in situ experiments, laboratory studies dedicated to delineating timescales and signatures of geochemical-geomechanical coupling, and AI-enhanced signature discernment and accelerated physics-based modeling could lead to a new ability to address diverse subsurface geologies, to select which sites will be most efficient and secure, to perform economical long-term monitoring, and to accelerate mineralization for permanent trapping or decelerate mineralization to ensure good injectivity near the wellbore. Transformative advances in transferring information across scales (from the field-to-atom and back again) that have been groundtruthed can establish much needed constraints on predictive modeling.

Regional subsurface CDR geologic sequestration hubs could vary in lithology, groundwater chemistry, and structure. These reservoirs will require that CO_2 remain underground with leakage less than 1% per 1,000 years.[22] CDR technologies such as performance assessment models are poorly constrained, which leads to large uncertainties in the predictions required by decision makers. The proposed future research directions have the potential to affect CDR technologies through the development of constrained models to provide decision makers with scientifically and technically sound forecasts that are based on real-time data acquired with new measurement techniques. These performance assessment models can be more accurate and enable optimization of multiple heterogeneous field sites for durable storage pathways at different regional hubs. The goal of accurate metrics with uncertainty bounds to ascertain injection capacity, leaks, and amount of mineralization can be realized with these research directions. In addition, understanding thermo-hydro-mechanical-chemical feedbacks could allow operators to engineer fluids to better control reservoir behavior ensuring self-sealing of caprocks and wellbores and accomplish this through accelerated mineralization that would greatly reduce leakage risks. In this manner, the capability can be developed to tailor long-term subsurface carbon sequestration sites based on the regional geology at locations around the nation and the planet.

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CLOSING REMARKS

This report provides a detailed description of current knowledge gaps, scientific and technical challenges, and foundational science needs for the successful development and implementation of CDR technologies. Five PROs are identified that are designed to address scientific and technical barriers associated with controlling CO_2 transport and reactivity at interfaces, making durable materials that efficiently capture and convert CO_2 into long-lived and useful products, and achieving secure underground CO_2 storage. These opportunities provide a cogent framework for greatly accelerating the design and development of materials and chemical processes required for atmospheric CO_2 reduction. Such progress can enable synthesis of innovative multifunctional materials; elucidation of degradation processes and pathways to their mitigation control of CO_2 interactions with molecules, minerals, and materials, and prediction of the evolution of CO_2 and its products in complex geologic settings. Research based on the priorities outlined here can greatly advance the understanding of CO_2 capture, conversion, and storage, and provide the scientific foundation for effective, efficient, and safe CDR technologies.

APPENDIX A. BACKGROUND AND CHARGE—ROUNDTABLE ON FOUNDATIONAL SCIENCE FOR CARBON DIOXIDE REMOVAL TECHNOLOGIES

March 2–4, 2022 (Zoom virtual meeting)

Background

Recent reports from the Intergovernmental Panel on Climate Change[1] (IPCC) indicate that carbon dioxide removal (CDR) will be essential to achieve net-zero carbon emissions by 2050.[2] CDR is defined in the IPCC report as:

> "Anthropogenic activities removing CO_2 from the atmosphere and durably storing it in geological, terrestrial, or ocean reservoirs, or in products. It includes existing and potential anthropogenic enhancement of biological or geochemical sinks and direct air capture and storage, but excludes natural CO_2 uptake not directly caused by human activities."

CDR approaches are clearly described in the *CDR Primer*,[3] which parallel negative emissions technologies (NETs) outlined in a recent National Academies consensus study.[4] The National Academies study made one major recommendation (italics added to emphasis areas relevant to this activity):

> "The nation should launch a substantial research initiative to advance negative emissions technologies (NETs) as soon as practicable. A substantial investment would (1) improve existing NETs (i.e., coastal blue carbon, afforestation/reforestation, changes in forest management, uptake and storage by agricultural soils, and bioenergy with carbon capture and sequestration) to increase the capacity and to reduce their negative impacts and costs; (2) *make rapid progress on direct air capture and carbon mineralization technologies, which are underexplored*, but would have essentially unlimited capacity if the high costs and many unknowns could be overcome; and (3) *advance NET-enabling research on biofuels and carbon sequestration that should be undertaken anyway as part of an emissions mitigation research portfolio*."

This Roundtable on Foundational Science for Carbon Dioxide Removal Technologies is a step toward development of the knowledge base that could underpin such a research initiative. The intent of this roundtable is to build on the strong foundations in fundamental research within BES, in coordination with existing research and development activities supported by the DOE technology offices (e.g., Offices of Fossil Energy and Carbon Management (FECM) and Energy Efficiency and Renewable Energy(EERE), and the Advanced Research Projects Agency-Energy (ARPA-E)), to identify critical needs for scientific understanding that can overcome scientific

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[1] Intergovernmental Panel on Climate Change, https://www.ipcc.ch/.

[2] Intergovernmental Panel on Climate Change (IPCC). Global Warming of 1.5°C; Intergovernmental Panel on Climate Change, 2018. https://www.ipcc.ch/sr15/.

[3] Wilcox, J.; Kolosz, B.; Freeman, J. *CDR Primer*. **2021**. https://cdrprimer.org/.

[4] National Academies of Sciences, Engineering, and Medicine. **2019**. *Negative Emissions Technologies and Reliable Sequestration: A Research Agenda*. Washington, DC: National Academies Press. DOI: 10.17226/25259.

and technical barriers to development and implementation of CDR technologies, and to articulate opportunities for BES-sponsored research to provide this foundational knowledge. This foundational knowledge is anticipated to underpin advancement of the Carbon Negative Shot[5] objective to "remove CO_2 from the atmosphere and durably store it at meaningful scales for less than \$100/net metric ton of CO_2-equivalent (CO_2e) in 1 decade."

Roundtable Charge

This roundtable, organized by BES in coordination with FECM, EERE, and ARPA-E will consider scientific and technical barriers that limit those technologies identified in the National Academies study as underexplored—direct air capture (DAC) of CO_2 and carbon mineralization—and will evaluate opportunities for BES research to provide fundamental knowledge that advances safe, durable geological storage. Consideration of CO_2 capture will expand beyond ambient air to consider other dilute sources that concentrate CO_2 from ambient air, such as large bodies of water (e.g., oceans). Consideration of durable storage of carbon will expand beyond mineralization, which binds carbon dioxide as carbonates, to consider CO_2 conversions in the synthesis of materials that could have useful functionality. Consideration of geological sequestration will evaluate opportunities for fundamental research to elucidate the geochemical and geomechanical processes activated by CO_2 injection into geologic formations deep underground. The roundtable will engage participants in discussions of technological and scientific challenges and fundamental science opportunities in these areas by considering the following questions.

Carbon Capture from Dilute Sources

- What phenomena limit the energy efficiency, capacity, and durability of CO_2 capture systems, and what are the theoretical limits of various systems?
- What energy transfer mechanisms can be used to drive processes in separation systems, such as regeneration of capture media or acceleration of processes that influence capture rates (e.g., mass transport)?
- To what extent is the direct use of thermal energy a viable driving force for CDR, considering low-carbon heating possibilities such as those employing geothermal, solar, or nuclear energy?
- What physical and chemical mechanisms lead to degradation of performance and limit the service lifetime of separations media?
- How can synthesis and assembly processes be designed to incorporate resiliency under operating conditions into CO_2 capture and separations media?

Durable Carbon Storage

- What phenomena influence the rates of CO_2 phase change reactions, such as conversion to solid carbonate materials?
- What are possible targets for discovery science that will lead to innovations in production of durable materials from CO_2? What are the opportunities for data science/machine learning in this assessment?

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[5] Carbon Negative Shot, https://www.energy.gov/fecm/carbon-negative-shot.

- How do we identify novel synthetic pathways to convert CO_2 to durable materials, which may also have targeted functionality?
- How can CO_2 capture and conversion processes be coupled to enhance CO_2 removal?

Geological Sequestration

- How well understood are the geochemical mechanisms of supercritical CO_2 interactions with natural mineral systems? What are the conditions for stabilization vs. destabilization of the mineral phases?
- How well understood are the possible geomechanical responses of rock formations undergoing chemical reaction with supercritical CO_2? How do the chemical transformations influence structural changes in the natural materials?

The objective of these discussions will be to identify priority research opportunities (PROs) for fundamental science that will accelerate progress in developing current CDR technologies, as well as to reveal opportunities for novel technologies with improved functionality.

Participants

Chairs:	Krista Walton (Georgia Tech) and Jim DeYoreo (PNNL)
Estimated size:	Approximately 30 participants plus additional observers

- Participants will include scientists and engineers from academia, DOE national and federal laboratories, and industry
- Representatives from DOE, other Federal agencies, and DOE national labs will be invited as observers
- Informational presentations will be given on the status of CDR technologies
- Background information will be based on body of existing assessments and reports (no additional factual status document will be created)

Breakout Panels

Day 1	Participants will discuss the 3 focus areas described above in separate panels. Participants on a crosscut panel will initially meet with the other panels and then convene together to identify common research opportunities emerging from the other panels.
Day 2	Participants convene in panels focused on developing selected PROs.

APPENDIX B. ATTENDEES—ROUNDTABLE ON FOUNDATIONAL SCIENCE FOR CARBON DIOXIDE REMOVAL TECHNOLOGIES

Roundtable Co-Chairs

Krista Walton, Georgia Institute of Technology
James DeYoreo, Pacific Northwest National Laboratory

Plenary Speakers

Jennifer Wilcox, FECM, "The Role of CDR and Carbon Capture in Meeting Net-Zero Carbon Goals"
Jingguang Chen, Columbia University, "Challenges in Achieving Net-CO_2 Reduction via Catalytic Conversion of CO_2"
Don DePaolo, Lawrence Berkeley National Laboratory, "Issues and Research Needs for Geologic CDR and Sequestration of CO_2"

Invited Roundtable Participants

Carbon Capture from Dilute Sources Panel (Panel Lead: Jeff Long, University of California, Berkeley)

Harry Atwater, California Institute of Technology
Stephanie Didas, Lawrence Berkeley National Laboratory
T. Alan Hatton, Massachusetts Institute of Technology
Alissa Park, Columbia University
Fateme Rezaei, Missouri University of Science and Technology
Simon Weston, ExxonMobil

Durable Carbon Storage Panel (Panel Lead: Jose Rodriguez, Brookhaven National Laboratory)

Geeshma Gadikota, Cornell University
Tom Jaramillo, SLAC
Derk Joester, Northwestern University
Eranda Nikolla, Wayne State University
Jeff Rimer, University of Houston
Charles Webster, Mississippi State University

Sequestration Panel (Panel Lead: Laura Pyrak-Nolte, Purdue University)

Jonathan Ajo-Franklin, Rice University
Ian Bourg, Princeton University
Young-Shin Jun, Washington University in St. Louis
R. M. Pollyea, Virginia Institute of Technology
Hari Viswanathan, Los Alamos National Laboratory
Wen-Lu Zhu, University of Maryland

Crosscutting Research Panel (Panel Leads: James Kubicki, University of Texas at El Paso, and May Nyman, Oregon State University)

Louise Criscenti, Sandia National Laboratory
Burcu Eksioglu Gurkan, Case Western Reserve University
David Heldebrant, Pacific Northwest National Laboratory
Nadine Kabengi, Georgia State University
Eric Pierce, Oak Ridge National Laboratory
Michael Tsapatsis, Johns Hopkins National Laboratory

U.S. Department of Energy (DOE) Participants

Mark Ackiewicz, FE
David Babson, ARPA-E
Shawn Chen, BES
Bruce Garrett, BES
Kerry Hochberger, BES
Linda Horton, BES
Mike Markowitz, BES
Dan Matuszak, BES
Raul Miranda, BES
Kathryn Peretti, EERE-AMO
Jim Rustad, BES
Andy Schwartz, BES
Michael Sennett, BES
Kelly Visconti, S4

Invited Observers

Peter Agbo, LBNL
Chris Bradley, BES
Wade Braunecker, NREL
Greg Fiechtner, BES
Nichole Fitzgerald, EERE
Jessica Garner, ORNL
Craig Henderson, BES
Emily Huckabay, ORNL
Santa Jansone-Popova, ORNL
Kourosh Kian, S4
Amishi Kumar, FECM
John Litynski, FECM
Di-Jia Liu, ANL
Gail McLean, BES
Thomas Moore, LLNL
Karl Mueller, PNNL
Long Qi, Ames NL
Hanny Rivera, WPTO
Ian Robinson, ARPA-E
Ian Rowe, EERE
Viviane Schwartz, BES
Raj Singh, LANL
Craig Taatjes, SNL
Elizabeth Troein, ARPA-E
Lucun Wang, INL

APPENDIX C. AGENDA—ROUNDTABLE ON FOUNDATIONAL SCIENCE FOR CARBON DIOXIDE REMOVAL TECHNOLOGIES

Platforms: Zoom and Teams (panel discussion and report writing)
March 2–4, 2022
****All times indicated are Eastern****

Day 1: March 2, 2022

10:30–10:45 AM	Log-in
10:45–10:55 AM	Welcome Professor Geraldine Richmond, Undersecretary for Science and Innovation
10:55–10:57 AM	Roundtable charge Dr. Bruce Garrett, Director, Chemical Sciences, Geosciences, and Biosciences Division, Basic Energy Sciences (BES)
10:57–11:00 AM	Welcome from roundtable chairs and introductions of speakers Professor Krista Walton, Georgia Institute of Technology Dr. James DeYoreo, Pacific Northwest National Laboratory
11:00–11:30 PM	The role of CDR and carbon capture in meeting net-zero carbon goals Dr. Jennifer Wilcox, Principal Deputy Assistant Secretary (PDAS) for the Office of Fossil Energy and Carbon Management
11:30–12:00 PM	Challenges in achieving Net-CO_2 reduction via catalytic conversion of CO_2 Professor Jingguang Chen, Columbia University
12:00–12:30 PM	Issues and research needs for geologic CDR and sequestration of CO_2 Dr. Don DePaolo, Lawrence Berkeley National Laboratory
12:30–1:00 PM	Discussion
1:00–1:15 PM	Workshop goals and logistics—Roundtable chairs
1:15–1:30 PM	Break (15 minutes)
1:30–3:30 PM	Breakout session I—Science focus (panels use Teams) Panel 1: Carbon Capture from Dilute Sources—Jeffrey Long, Lawrence Berkeley National Laboratory Panel 2: Durable Carbon Storage—Jose Rodriguez, Brookhaven National Laboratory Panel 3: Sequestration—Laura Pyrak-Nolte, Purdue University Panel 4: Crosscutting Research—James Kubicki, University of Texas, El Paso, and May Nyman, Oregon State University Crosscut panelists will directly participate and interact on other panels: 1:30–2:30: Crosscut panelists contribute to other three panels 2:30–3:30: Crosscut panelists convene to discuss and coordinate ideas across the other three panels
3:30–4:00 PM	Break (30 minutes)—Panel leads finalize presentations on PROs from panel discussions
4:00–5:00 PM	Plenary session I—Panel reports on PROs (15 minutes per panel, including clarifying Q&A)

5:00–5:45 PM	Plenary discussion of PROs—Roundtable chairs Discussion of common emerging ideas for PROs, synergy between PROs presented, PROs that could be consolidated
5:45PM	Adjourn—Panel leads and chairs meet to consolidate input into 4–5 PROs for further development

Day 2: March 3, 2022

10:45–11:00 AM	Log-in
11:00–11:15 AM	Plenary session II—Roundtable chairs Presentation of final PRO topics, PRO discussion leads, and reassignment of participants to PRO topics
11:15–2:00 PM	Breakout session II—PRO development Participants report to PRO breakout rooms for discussions and development of PROs and PRO presentations
2:00–2:30 PM	Break (30 minutes)—PRO discussion leads finalize presentations on PROs
2:30–3:30 PM	Plenary session III—PRO Presentations (10–15 minutes/PRO including clarifying Q&A)
3:30–4:30 PM	Plenary discussion of PROs—Roundtable chairs Discussion of gaps (areas not covered) within PROs and overlap between PROs
4:30–4:45 PM	Closing remarks—Chairs and BES
4:45 PM	Roundtable adjourns

Report writing session for Roundtable Chairs, PRO leads, designated writers after 15 minute break

5:00–5:30 PM	Overview/discussion of report and brochure—Editorial lead, ORNL Discuss report structure and content, writing logistics, etc.
5:30–6:00 PM	Writing assignments—Roundtable chairs
6:00 PM	Writing session ends—Breakout rooms available for writing sessions until 8 PM

Day 3: March 4, 2022

Roundtable Chairs, PRO leads, designated writers (optional)

10:45–11:00 AM	Log-in
11:00–11:15 AM	Check in on writing assignments/progress
11:15 AM–2:00 PM	Writing/editing session—Breakout rooms available for chairs and PRO writers
2:00 PM	Writing session ends

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DOI: 10.2172/1894473

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