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# Harvesting, storing, and converting carbon from the ocean to create a new carbon economy: Challenges and opportunities

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Ever-increasing anthropogenic CO<sub>2</sub> emissions have required us to develop carbon capture, utilization, and storage (CCUS) technologies, and in order to address climate change, these options should be at scale. In addition to engineered systems of CO<sub>2</sub> capture from power plants and chemical processes, there are emerging approaches that include the Earth (i.e., air, Earth, and ocean) within its system boundary. Since oceans constitute the largest natural sink of CO<sub>2</sub>, technologies that can enhance carbon storage in the ocean are highly desired. Here, we discuss alkalinity enhancement and biologically inspired CO<sub>2</sub> hydration reactions that can shift the equilibrium of ocean water to pump more carbon into this natural sink. Further, we highlight recent work that can harvest and convert CO<sub>2</sub> captured by the ocean into chemicals, fuels, and materials using renewable energy such as off-shore wind. Through these emerging and innovative technologies, organic and inorganic carbon from ocean-based solutions can replace fossil-derived carbon and create a new carbon economy. It is critical to develop these ocean-based CCUS technologies without unintended environmental or ecological consequences, which will create a new engineered carbon cycle that is in harmony with the Earth's system.

## KEYWORDS

climate change, direct ocean capture, ocean acidification, carbonate, alkaline thermal treatment

## Introduction

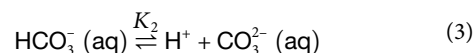
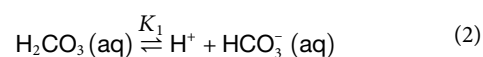
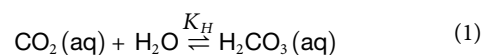
Ever-rising global anthropogenic carbon emissions accounted for 40 GtCO<sub>2</sub> y<sup>-1</sup> in 2020 (Friedlingstein et al., 2020) and thus it is critical to effectively manage carbon through natural and engineered systems to address climate change (Caldeira et al., 2018; Watson et al., 2020; National Academies, 2019; National Academies, 2022; Kelemen et al., 2020). During the past few decades, significant effort has been devoted to capturing CO<sub>2</sub> from industrial point sources such as coal-fired and natural gas-fired power plants. While the world moves towards the rapid decarbonization of industrial sectors, negative emission technologies (NETs)

provide an important pathway to capture historically emitted CO<sub>2</sub>. For example, technologies that can directly capture CO<sub>2</sub> from the atmosphere, called direct air capture (DAC), are currently in development (Sanz-Perez et al., 2016). DAC is challenging because of the very low concentration of CO<sub>2</sub> in air (i.e., ~420 ppm in air (Tans and Keeling, 2021) compared to 3–15% in flue gas of power plants (Songolzadeh et al., 2014)) and demands unique requirements such as a low pressure drop and high oxidative thermal stability. There have been significant advancements in the design and scale-up of air contactors, and efforts are currently focused on the development of more efficient and selective DAC materials and regeneration methods. (Sanz-Perez et al., 2016). CO<sub>2</sub> captured from the atmosphere with DAC can be considered “non-fossil carbon” and can be used to produce chemicals, materials, and fuels using renewable energy. Thus, DAC holds promise to not only provide a pathway towards a negative emission technology, but also to create a new carbon economy that is not based on fossil resources.

Historically emitted CO<sub>2</sub> can be found in three places in the environment—the air (*ca.* 420 ppm gaseous CO<sub>2</sub>), the Earth (e.g., mineral carbonates and CO<sub>2</sub> in soil), and in the ocean. A surprisingly untapped source of carbon can be found in the Earth’s oceans. The ocean is the largest natural sink of CO<sub>2</sub> and is thought have absorbed at least 2.5 PgC yr<sup>-1</sup> of anthropogenic carbon from 1994–2007 (Watson et al., 2020). In 2019, the Global Carbon Budget found that oceans absorbed 2.6 GtC yr<sup>-1</sup> (Friedlingstein et al., 2020). Within oceans, most human-made CO<sub>2</sub> is found at shallow depths (<1,000 m) (Caldeira et al., 2018), and with the continued increase in CO<sub>2</sub> concentration in the atmosphere, the pH of the shallow ocean is significantly lower than at deep levels leading to ocean acidification (DeVries et al.,

2017; Caldeira et al., 2018). Importantly, the concentration of inorganic carbon in oceans (0.099 kgCO<sub>2</sub> m<sup>-3</sup>) is 125 times higher than the concentration of CO<sub>2</sub> in air (Khawiwala et al., 2013; Sanz-Perez et al., 2016; Patterson et al., 2019), which suggests that direct ocean capture (DOC) of CO<sub>2</sub> in ocean or seawater that does not interfere with marine aquatic life (Eisaman et al., 2018; Fuss et al., 2018) is another important pathway for carbon capture technologies (Sharifian et al., 2021; Terlouw et al., 2021). Carbon captured by the ocean is distributed and converted to different forms including dissolved inorganic carbon and marine biomass, as illustrated in Figure 1.

Carbon dissolved in ocean or seawater primarily consists of carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>). Carbon dioxide dissolution into ocean water is controlled by the partial pressure of carbon dioxide in the atmosphere and the pH and alkalinity of water. Once dissolved in ocean water, carbon dioxide is in equilibrium with bicarbonate (pK<sub>a</sub> = 5.9) (Mojica Prieto and Millero, 2002) and carbonate (pK<sub>a</sub> = 9.1) (Mojica Prieto and Millero, 2002) following Eqs. 1–3



Thus, at a typical oceanic surface pH of 8.2, most dissolved carbon is speciated as HCO<sub>3</sub><sup>-</sup>, not dissolved carbon dioxide. This is more clearly seen in Figure 2, which plots the speciation of CO<sub>2</sub> in seawater at different pH values. While HCO<sub>3</sub><sup>-</sup> is the predominant carbon species at ocean water pH, CO<sub>2</sub> can be evolved if the pH is lowered. The total alkalinity of ocean water can be measured to

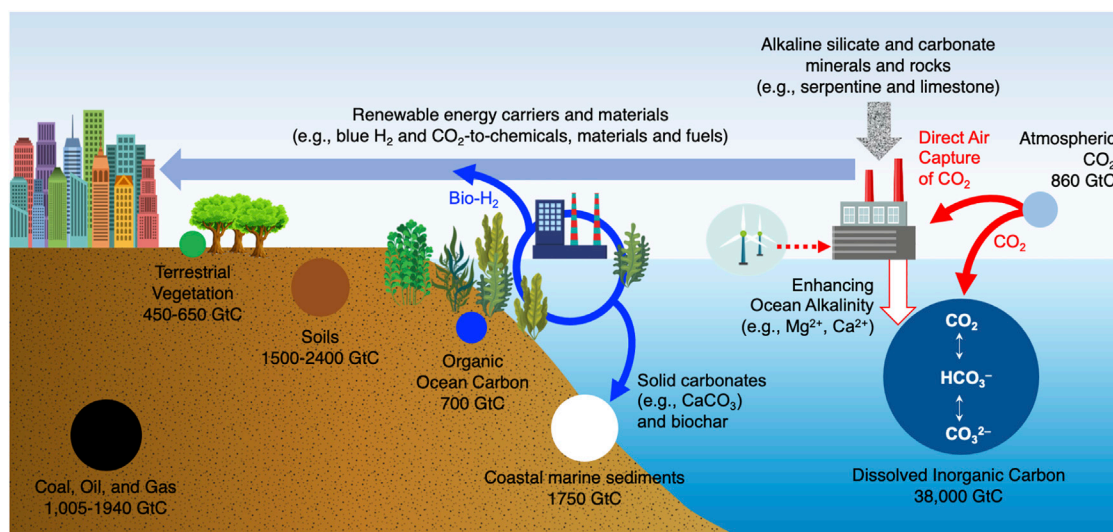


FIGURE 1  
Distribution of carbon on Earth (data used from the Global Carbon Budget, 2020 (1)).

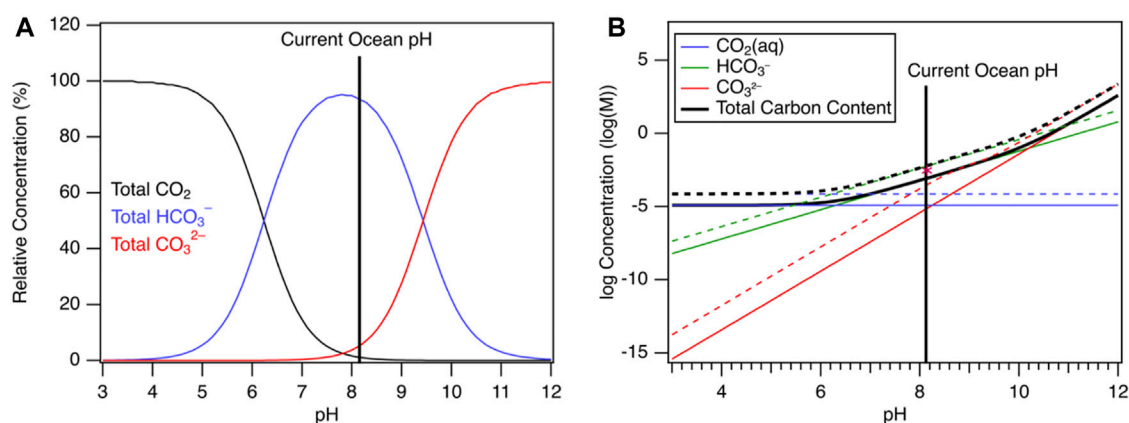


FIGURE 2

(A) Bjerrum plot showing the speciation of dissolved inorganic carbon in a background of seawater (Riebesell et al., 2010) at fixed total carbon concentration at 25°C (B)  $\text{CO}_2$  speciation vs pH for pure (solid lines) and seawater (Riebesell et al., 2010) (dotted lines) at fixed partial pressure in an open  $\text{CO}_2$  system at 25°C. Calculations were performed with ChemEQL (Müller, 2015). The asterisk denotes the total carbon content of water as calculated in Ref. (Riebesell et al., 2010).

determine the extent of carbonate dissociation. Total alkalinity ( $A_T$ ) is defined as the proton deficiency in a solution relative to a baseline. As the alkalinity of ocean water increases, more dissociation of carbonic acid and bicarbonate occur and more carbonate is produced. Thus, the addition of alkalinity into the ocean would increase the total  $\text{CO}_2$  uptake by the ocean.

As shown in Figure 1, carbon in the ocean can also be used by aquatic life like marine biomass, corals, and shellfish. Because of climate change, the marine biome is rapidly transforming and the health of aquatic life is threatened. Thus, direct ocean capture (DOC) and utilizing marine biomass for energy and material production have emerged as unique engineered solutions for climate change mitigation because they provide a sustainable carbon balance in the ocean that is important for the Earth's stability. Here, we discuss how oceans store, capture, and convert  $\text{CO}_2$  and how ocean-based technologies can be developed to harvest non-fossil carbon from the ocean to create a new carbon economy.

## Storing carbon in the ocean

As discussed, the ocean is the largest natural sink for carbon. Below, we suggest several avenues that accelerate and increase  $\text{CO}_2$  uptake by the ocean including added alkalinity and enzymatic catalysis.

## Enhanced carbon sequestration in the ocean via added alkalinity

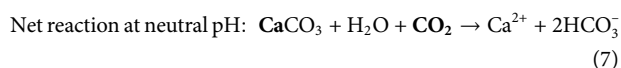
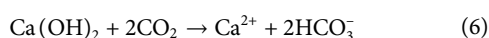
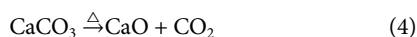
The ocean can capture and store  $\text{CO}_2$  as carbonates on geologic time scales. Unfortunately, the anthropogenic  $\text{CO}_2$

emission rate is too fast for the ocean to keep up with, and thus, there is an imbalance of carbon leading to ocean acidification. In order to restore the ocean's pH balance while storing more carbon in the ocean, several methods have been considered. These technologies rely on the formation enthalpies of adding aqueous metal ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  to bicarbonate and carbonate-rich ocean water (Renforth and Henderson, 2017). The ocean already contains  $0.010 \text{ mol kg}^{-1} \text{ Ca}^{2+}$  and  $0.052 \text{ mol kg}^{-1} \text{ Mg}^{2+}$ , but its capacity for additional alkalinity is vast (Riebesell et al., 2010). An additional source of alkaline metals can be found in earth-abundant minerals and rocks such as limestone ( $\text{CaCO}_3$ ), ultramafic rocks (e.g., olivine ( $(\text{Mg,Fe})_2\text{SiO}_4$ ), and serpentine ( $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ )). These can be mined, processed, and dissolved to obtain  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , (Renforth et al., 2013; La Plante et al., 2021), and their addition to the ocean water results in the capture and subsequent transformation of atmospheric  $\text{CO}_2$  to bicarbonate (dominant carbon species at pH 8.2) and carbonate ions.

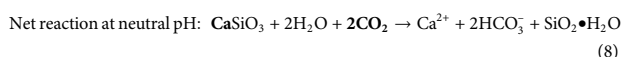
An early example of this technology used  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$  which easily dissolve and increase the bicarbonate concentration in ocean water (Kheshgi, 1995). Most  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$  are currently produced from Earth abundant limestone ( $\text{CaCO}_3$ ) (Kenny and Oates, 2007; Kantzas et al., 2022), but they can also be derived from industrial alkaline wastes such as mine tailings, waste-to-energy ashes, iron and steel slag, and waste concrete (Renforth, 2019; Bui Viet et al., 2020; Gadikota, 2021; Hong et al., 2021; Rim et al., 2021). Since limestone already contains one carbon per calcium, a maximum of only 1 mol of additional  $\text{CO}_2$  can be captured by producing bicarbonate solutions from  $\text{CaCO}_3$ . On the other hand, if calcium and magnesium-bearing silicate minerals such as olivine, (Gadikota et al., 2014), serpentine, (Park et al., 2008), wollastonite, (Zhao

et al., 2013), pyroxenes, and plagioclase feldspar are used, the CO<sub>2</sub> capture and storage capacity of this reaction can theoretically be doubled, since those alkaline metals are extracted without any attached carbon. In reality, the CO<sub>2</sub> capture capacity of these silicate-bearing minerals would be slightly less than two because the calcium or magnesium to CO<sub>2</sub> ratio would depend on the source of alkalinity and pH of the oceanwater. If magnesium and calcium ions are added into the ocean, the overall equilibrium shown in Figure 2 will shift and additional CO<sub>2</sub> will be captured from the air into the ocean. Example reactions of calcium-bearing minerals are given below (Eqs. 4–8).

From carbonate minerals:



From silicate minerals without carbonate phases:



Magnesium-bearing minerals would undergo similar reactions capturing and storing CO<sub>2</sub>. One challenge is that silicate minerals are generally less reactive than carbonate minerals in ocean water, and thus, the process is often kinetically limited. Other recent work has shown that industrial wastes such as fly ash, steel slag, and cement dust can also be used for ocean alkalinity enhancement (Gadikota et al., 2020).

In all of these reactions, the rate-limiting process is thought to be mineral dissolution. *Ex-situ* mineral dissolution can significantly accelerate Ca<sup>2+</sup> and Mg<sup>2+</sup> leaching from different sources (on a time scale of hours or less) (Gerdeemann et al., 2007; Gadikota et al., 2014). Alkaline calcium- and magnesium-rich solutions can be added to the ocean at desired locations, though this *ex-situ* technology would require the construction of engineered reactor systems and infrastructure. Mineral dissolution processes often use chemicals including acids and ligands to accelerate the calcium and magnesium leaching process. A few emerging technologies have been proposed, including the production of acid (e.g., HCl) from the ocean water via electrolysis using renewable energy (House et al., 2007). The strong acid produced can rapidly dissolve minerals to be added to the ocean (Rau, 2008; Rau et al., 2013). The use of this “renewable” acid in ocean-based solutions will also be discussed in the later section on the electrochemical recovery of CO<sub>2</sub> from the ocean.

*In-situ* mineral dissolution utilizes the ocean surface to perform mineral dissolution, and it is often limited in terms of mineral dissolution rates since mixing and reaction temperatures are bound by the environmental conditions, and chemical additives cannot be used. Thus, it is important to select

the appropriate approach for different regions and varied mineral compositions (i.e., *in-situ* versus *ex-situ*). The CarbFix project in Iceland has shown that alkaline metals can be effectively liberated in water saturated with CO<sub>2</sub> and ultimately form solid carbonates (Snæbjörnsdóttir et al., 2020). A similar approach can be used to tune the ocean alkalinity. CarbFix2 is investigating this approach using captured CO<sub>2</sub> from water treatment plants for mineralization using seawater (Snæbjörnsdóttir et al., 2020; Carbfix, 2022). A complementary approach, sCS<sup>2</sup> (single step carbon sequestration and storage), which involves electrolytic precipitation of carbonates from CO<sub>2</sub> and seawater may also provide interesting ocean based solutions (La Plante et al., 2021). Another noteworthy project is from the CarbonSAFE program in the United States, which aims to inject CO<sub>2</sub> into ocean basalt at Cascadia Basin (Goldberg et al., 2018).

One important challenge for alkaline addition technologies is the energy efficient delivery of large quantities of alkaline-bearing materials (e.g., CaO, Ca(OH)<sub>2</sub>, Ca-silicates, etc.) to acidified ocean water. We believe that new and innovative offshore technologies and existing transportation systems can address some of the fundamental issues in ocean-based CO<sub>2</sub> sequestration. For instance, shipping lines (Hassellöv et al., 2013) are major contributors to ocean acidification, and thus, it has been proposed that one method to combat localized acidification is to carry minerals and carbonates on tankers to different parts of the ocean (Butenschön et al., 2021; Caserini et al., 2021). For this use it would be important to control the rate of alkaline addition to the ocean water to ensure that local change in pH and alkalinity will not harmfully impact local ecosystems. Local changes for *in situ* carbonation approaches would likely also affect the carbonate chemistry of seawater, which could have important and/or unknown implications for calcifiers.

Another potential issue with mineral addition to ocean water would be increased local concentrations of unwanted dissolved species. This is critical for alkaline industrial wastes containing nickel (serpentine mine tailings), iron and cerium (iron and steel slag), and a wide range of heavy metals like zinc, iron, and lead (waste-to-energy plant ashes). These metal ions could have unwanted and potentially toxic effects to life found in ocean water (Hartmann et al., 2013; Montserrat et al., 2017; Fuss et al., 2018). For example, low concentrations of nickel (~0.3 μM) are known to be cytotoxic to *Mytilus edulis* (blue mussel) (Montserrat et al., 2017). Thus, any impurities detrimental to the environment and the eco-system should be removed from these waste materials before they are added to ocean water. An *ex-situ* approach that first produces relatively pure calcium- and magnesium-bearing materials derived from silicates or alkaline industrial wastes would greatly improve the environmental friendliness of the proposed alkaline addition technology. Furthermore, the *ex-situ* approach will minimize the mass of alkaline materials that must be delivered to different ocean sites by separating out impurities and non-alkaline materials from the feedstock.



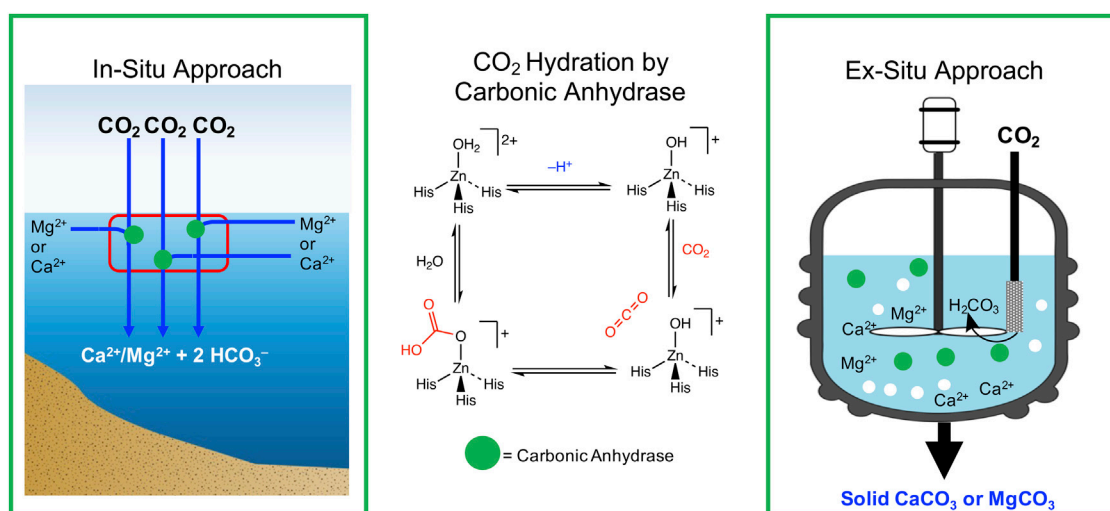


FIGURE 3

Illustration of how carbonic anhydrase can be used to increase alkalinity in both an *in-situ* and *ex-situ* approach. The middle panel of the figure describes the proposed mechanism for CO<sub>2</sub> hydration (His = histidine).

## Biologically inspired technologies using carbonic anhydrase

Carbonic anhydrases are a metalloenzyme family that biologically catalyze CO<sub>2</sub> hydration and dehydration. They are found in all mammals, plants, algae, fungi, and bacteria (Elleuche and Poggeler, 2009). Carbonic anhydrases play a key role in the ocean's carbon balance by accelerating rate limiting steps of CO<sub>2</sub> ocean uptake. They also are involved in CO<sub>2</sub> homeostasis, biosynthetic reactions, lipogenesis, ureagenesis, and calcification, among other processes relevant to life in the ocean (Supuran, 2016). In nature, carbonic anhydrases are found in five different classes,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\zeta$ . The active site of carbonic anhydrases contains a tetrahedral metal (II) ion prosthetic group coordinated with three histidine side chains and a water molecule. This provides access to a metal hydroxide active species that can bind CO<sub>2</sub> and produce a metal bicarbonate complex. In most carbonic anhydrases, Zn<sup>2+</sup> is the catalytically active metal ion, though Fe<sup>2+</sup> and Cd<sup>2+</sup> are thought to be central to some carbonic anhydrases. Co<sup>2+</sup> has also been observed to substitute Zn<sup>2+</sup> with little activity loss. Carbonic anhydrases are thought to mediate the hydration of CO<sub>2</sub> through the mechanism proposed in Figure 3, shown with a Zn<sup>2+</sup> metal center. Here, a tetrahedral Zn<sup>2+</sup> aquo complex is deprotonated, forming a highly nucleophilic zinc hydroxide active site. Diffusion of CO<sub>2</sub> into the active site and nucleophilic attack on CO<sub>2</sub> generates the Zn<sup>2+</sup> bicarbonate. Further displacement of the bicarbonate with water allows the completion of the enzymatic catalytic cycle.

For CDR/NET technologies, carbonic anhydrase is useful because it helps improve the rate of CO<sub>2</sub> uptake by catalyzing

the rate of CO<sub>2</sub> hydration which is often the rate limiting step in these reactions. The reaction can also operate in the reverse direction. Thus, several groups have shown that carbonic anhydrase can catalyze the dissolution of calcites in seawater to enhance the rate of alkalinity addition into the ocean (Liu et al., 2005; Li et al., 2009; Xie and Wu, 2013; Subhas et al., 2017). In these systems, CO<sub>2</sub> is bubbled into a solution containing the carbonic anhydrase enzyme and calcite particles. The carbonic anhydrase rapidly equilibrates dissolved CO<sub>2</sub> with that in the gas phase (i.e., atmosphere), resulting in a reactive system that is limited by gas exchange kinetics. The rapid dissolution of CO<sub>2</sub> by carbonic anhydrase provides additional protons for the calcite dissolution. Thus, calcite precipitation may be minimized as carbonic anhydrase catalyzes CO<sub>2</sub> hydration reaction. One of the challenges associated with natural carbonic anhydrase is its thermal and long-term stability, and thus there are efforts to encapsulate and immobilize carbonic anhydrase and to incorporate it into innovative reactor designs such as a monolithic reactor and a fluidized bed reactor (Patel et al., 2013; Patel et al., 2014a; Patel et al., 2014b; Boucif et al., 2020; Fabbicino et al., 2021; Verma et al., 2021).

Another emerging area of research is biologically inspired catalysis mimicking carbonic anhydrase. Small molecule chemistry has been explored to synthesize homogenous metal catalysts with significantly improved thermal stability compared to natural carbonic anhydrase, which can thermally denature under the conditions required for CO<sub>2</sub> adsorption and desorption (Kozioł et al., 2012). The coordination center of Zn<sup>2+</sup> in the carbonic anhydrase active site has been modeled by several groups using various amine and tris(pyrazolyl)borate ligand systems (Kimura et al., 1990; Looney et al., 1993; Schrodt et al., 1997; Khan et al.,

2012; Koziol et al., 2012; Floyd et al., 2013; Liu et al., 2013; Verma et al., 2021). In principle, these systems are thought to react with CO<sub>2</sub> using the same mechanism as shown in Figure 3. Other types of mono, dinuclear, and trinuclear complexes, including molecules with copper or nickel centers, have also been used to capture CO<sub>2</sub> (Verma et al., 2021), (Bernauer et al., 2002; Kolks et al., 2002; Appel et al., 2005; Verdejo et al., 2008; Mateus et al., 2011). One of the best studied catalysts in this area is the 1,4,7,10-tetraazacyclododecane Zn(II) (zinc cyclen), which, because of its low molecular weight, only shows a 5-fold lower activity than natural carbonic anhydrase (Koziol et al., 2012). Zinc cyclen is found to remain active at industrially relevant temperatures as high as 75°C (Koziol et al., 2012).

## Harvesting inorganic and organic carbon captured and stored in the ocean

In order to achieve deep decarbonization and address climate change, we need to go beyond zero emission technologies and develop a multifaceted set of NETs (Negative Emission Technologies). Further, we need to create a new carbon economy that is not based on fossil carbon, and it would be closely integrated with a new hydrogen economy. The locations and scale of different types of carbon are shown in Figure 1. With the rapid deployment of renewable energy including off-shore wind and its significantly reduced cost, we now have a great potential to harvest inorganic ocean carbon and convert it to high value chemicals, materials, and fuels. The direct recovery of carbon from ocean water can be achieved via different chemical and biological pathways. There are a number of interesting studies that focus on cultivating and harvesting marine biomass. Marine biomass is attractive for energy and chemical production because it utilizes the large ocean surface and does not require land use.

To convert and utilize inorganic carbon that is stored in the ocean, an equilibrium shifting approach, where acid is directly added to carbonate-rich water to shift its equilibrium back to CO<sub>2</sub> (see Eqs. 1–3, Figure 2), is often used. An electrochemical acidification cell employs an ion-exchange membrane with an applied voltage to trade sodium ions for protons (Willauer et al., 2011). As a result, acid (e.g., HCl) and base (e.g., NaOH) can be produced using renewable electricity, and they can be used to either capture or release CO<sub>2</sub> from the ocean by shifting equilibrium. In these systems, hydrogen gas is also evolved as a byproduct, and thus, the carbon and hydrogen economies can be effectively integrated.

## Tandem capture and conversion of ocean carbon to chemicals, fuels, and materials

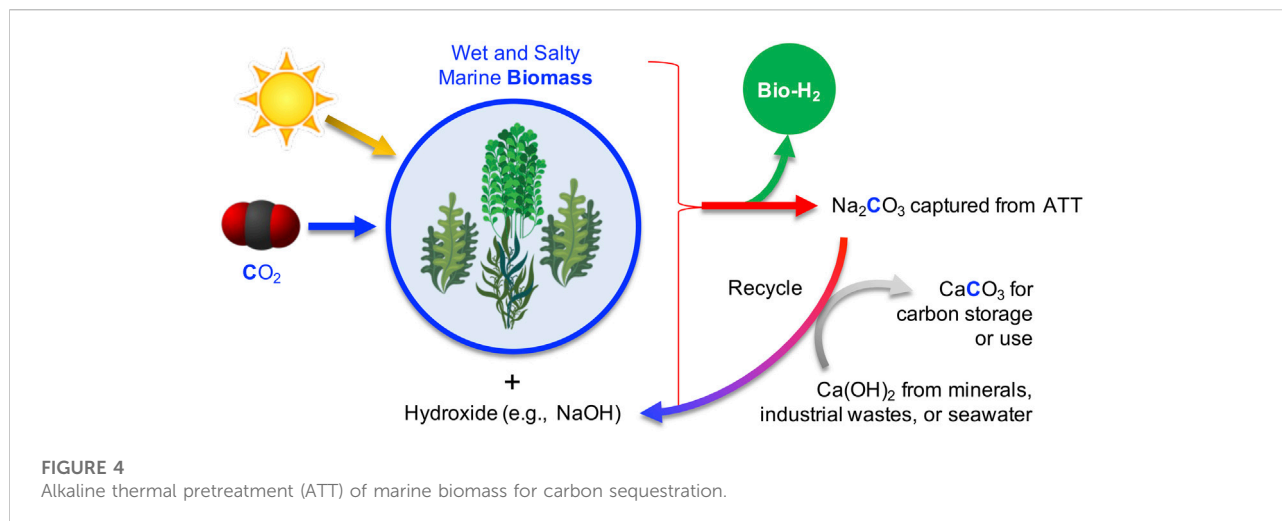
A number of innovative electrochemical systems have been employed to capture and convert CO<sub>2</sub> stored in the ocean. As

bicarbonates and carbonates become CO<sub>2</sub> via electrochemical equilibrium shifting, they are converted to low molecular weight carbon products (C<sub>1</sub> or C<sub>2</sub>). For example, Digdaya et al. recently reported an innovative approach to capture and convert dissolved carbon in the ocean to CO with total Faradaic efficiencies up to 95% (Digdaya et al., 2020). Their device operates using a bipolar membrane electrodialysis cell. There, ion transport through the membranes generates a proton gradient (as discussed above), acidifying the ocean water and liberating CO<sub>2</sub>. Dissolved CO<sub>2</sub> is then reduced using Ag or Cu electrodes. The silver catalyst system was found to be highly selective for CO production. Other examples of these types of electrochemical systems use bipolar membranes to facilitate the electrolytic conversion of CO<sub>2</sub> derived from ocean carbonates and bicarbonates into low carbon products, including CO (Li et al., 2019; Lees et al., 2020) and formate (HCO<sub>2</sub><sup>−</sup>) (Li et al., 2020). With copper electrodes, a wide array of reduction products are found, including larger carbon containing products like ethanol, propanol, and acetate (Digdaya et al., 2020). These organic compounds as fuels or chemical feedstocks can play a role in a new carbon economy.

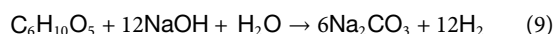
## Conversion of carbon in marine biomass to chemicals, fuels, and materials

During the last several years, there has been a growing movement to use algae, microalgae, and seaweed biomass to produce biofuels (Sayre, 2010; Zhao and Su, 2014). Among the advantages of biomass are its high production efficiency, available cultivation area that does not compete with current land use, and ability to capture and convert CO<sub>2</sub> and carbonates dissolved in aqueous environments. Seaweeds, which have myriad uses and are cultivated on large scales, can sequester seven times the carbon dioxide of terrestrial lignocellulosic biomass (not normalized) (Zhang et al., 2020). These types of marine and salt water biomass have active bicarbonate pumps that can concentrate and dehydrate bicarbonates with carbonic anhydrases. The CO<sub>2</sub> captured in this biological process is then converted to sugars via photosynthesis. The need for efficient cultivation and harvesting of marine biomass in the open ocean has led to innovations in automated robotic systems (Zereik et al., 2018). Off-shore biomass conversion systems are also being considered (Nassar et al., 2020).

Marine biomass can be converted into high-energy liquid fuels or chemicals that can be directly used in the current carbon economy. There are a number of biomass conversion technologies including anaerobic digestion, gasification, and pyrolysis. Compared to terrestrial biomass, the water and salt contents of marine biomass are significantly higher, and thus, their conversion pathways are limited. Thus, innovative technologies that can directly work with wet and salty biomass, such as seaweed, are desired.



Recently, we have demonstrated a unique approach that converts seaweed to bio-hydrogen (Zhang et al., 2020). Our alkaline thermal treatment (ATT) of wet, brown seaweed with NaOH and a Ni/ZrO<sub>2</sub> catalyst produced bio-hydrogen, while suppressing the formation of CO<sub>x</sub> at moderate temperatures (<500°C) under ambient pressure. In this process, we use solar energy stored in marine biomass to produce bio-derived H<sub>2</sub>, while the carbon and nutrients (e.g., N, P, etc.) will return to the ocean as dissolved species. This innovative reaction scheme produces bio-derived hydrogen, while marine biomass is converted to solid carbonates, as illustrated in Figure 4. By using Ca(OH)<sub>2</sub> derived from alkaline industrial wastes such as iron and steel slags and fly ash rather than freshly mined limestone (CaCO<sub>3</sub>), the ATT reaction can be performed with reduced overall energy requirement, while treating solid wastes and minimizing their landfill requirement. A net equation is shown in Eq. 9. The integration of two chemical reaction loops, alkaline thermal treatment of marine biomass and carbon mineralization, allows a new pathway towards a negative emission bioenergy production, since carbon from marine biomass can be sequestered into the ocean as bicarbonates. Other technologies that maximize carbon atom efficiencies and provide long-term carbon storage should be investigated. These new pathways might be useful not only to produce existing chemicals and materials, but to produce new chemicals and materials through highly integrated innovative technologies.



An important emerging area that can be directly tied with the ATT technology is the recovery of strategically important critical elements that are found dilute concentration in the ocean or in marine biomass. While the absolute concentration of many rare Earth elements (REEs) found in seawater are often quite low (31.8–168 pmol L<sup>-1</sup> found in the western Pacific Ocean) (Deng

et al., 2017), those REE concentrations found in biomass, like seaweeds can be significantly higher. Those REE contents are highest for La and Ce, but can be found from 1–100 ng g<sup>-1</sup> in a variety of seaweeds. Moreover, the concentration of REEs in ash derived from seaweeds is significantly higher, such that the concentrations of La and Ce can rise above 100 ng g<sup>-1</sup> (Fu et al., 2002; Piarulli et al., 2021). In the ATT reaction outlined above, in addition to net CO<sub>2</sub> storage in the form of carbonates, we also produce biochar residues from marine biomass with concentrated REEs and other critical elements at levels similar to unconventional resource streams (e.g., waste-to-energy ashes or steel/iron slag). An interesting future direction would be to integrate the ATT production of H<sub>2</sub> and storage of CO<sub>2</sub> with downstream leaching and separation steps to recover rare Earth elements like Ce or La from these materials.

As shown above, H<sub>2</sub> can also be produced through electrochemical means from seawater (see Tandem Capture and Conversion Section). Electrochemical approaches also hold promise as NETs that can produce H<sub>2</sub> (Rau and Baird, 2018; Rau et al., 2018). The question for which process will ultimately provide a higher impact on CO<sub>2</sub> concentrations is still undecided, and clearly both technologies are worth pursuing. The ATT strategy shown here, we believe, holds enormous promise. Solar concentrators could be used to heat the reactions, which rely on fairly modest temperatures. Moreover, we see the potential for not only negative-emission H<sub>2</sub> production, but also the concentration of elements of strategic importance to future clean energy innovations.

## Final remarks

Oceanic carbon capture, conversion, and storage offer an enticing alternative route to address urgent climate change at scale. The present level of engineered CO<sub>2</sub> uptake by the ocean,

outside of adding alkalinity and using an electrochemical acidification process, is underexplored. Thus, significant effort should be devoted to addressing critical challenges and opportunities in this area, while creating a better environment for marine life and restoring the Earth's carbon balance. With the rapid increase in affordable renewable energy, we now have synergistic opportunities to capture, convert, and store organic and inorganic carbon in the ocean and replace fossil-derived carbon. Innovative electrochemical systems allow tandem reactions that convert CO<sub>2</sub> derived from bicarbonate and carbonates to value-added products (e.g., CO and formate). In another approach, alkaline thermal treatment can produce bio-hydrogen and store carbon in solid carbonates.

Including the environment into the system boundary of engineered solutions often has undesired consequences, particularly when deployed at large industrial scales. There could be local spikes in ocean pH, a significant rise in metal concentrations leading to harmful algal plumes and increased toxicity. Thus, it is critical to consider all the short-term and long-term environmental and ecological impacts of each engineered solution before it is implemented at a large scale. Further, the deployment of these ocean-based carbon management solutions requires innovative technological development of systems. These include the efficient transportation of materials to the site and reactors that may have to operate in a distributed mode with renewable energy. The automation and process intensification would be very important for such technology development. The use of marine industries, such as container shipping lines, to access large areas of the ocean to deploy CCUS technologies (e.g., added alkalinity) are potential synergistic options. These ocean-based CCUS solutions are great examples of how we can work with the ocean to develop a new carbon economy, while creating a better planet for all.

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## Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

## Author contributions

HV and AHP conceived of and wrote the manuscript.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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