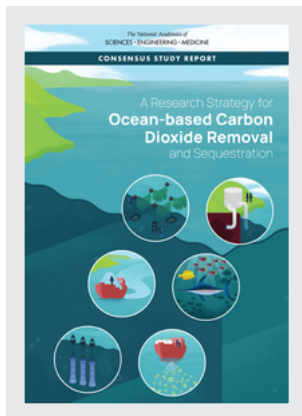


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## A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration (2021)

### DETAILS

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## 7

**Ocean Alkalinity Enhancement****7.1 OVERVIEW**

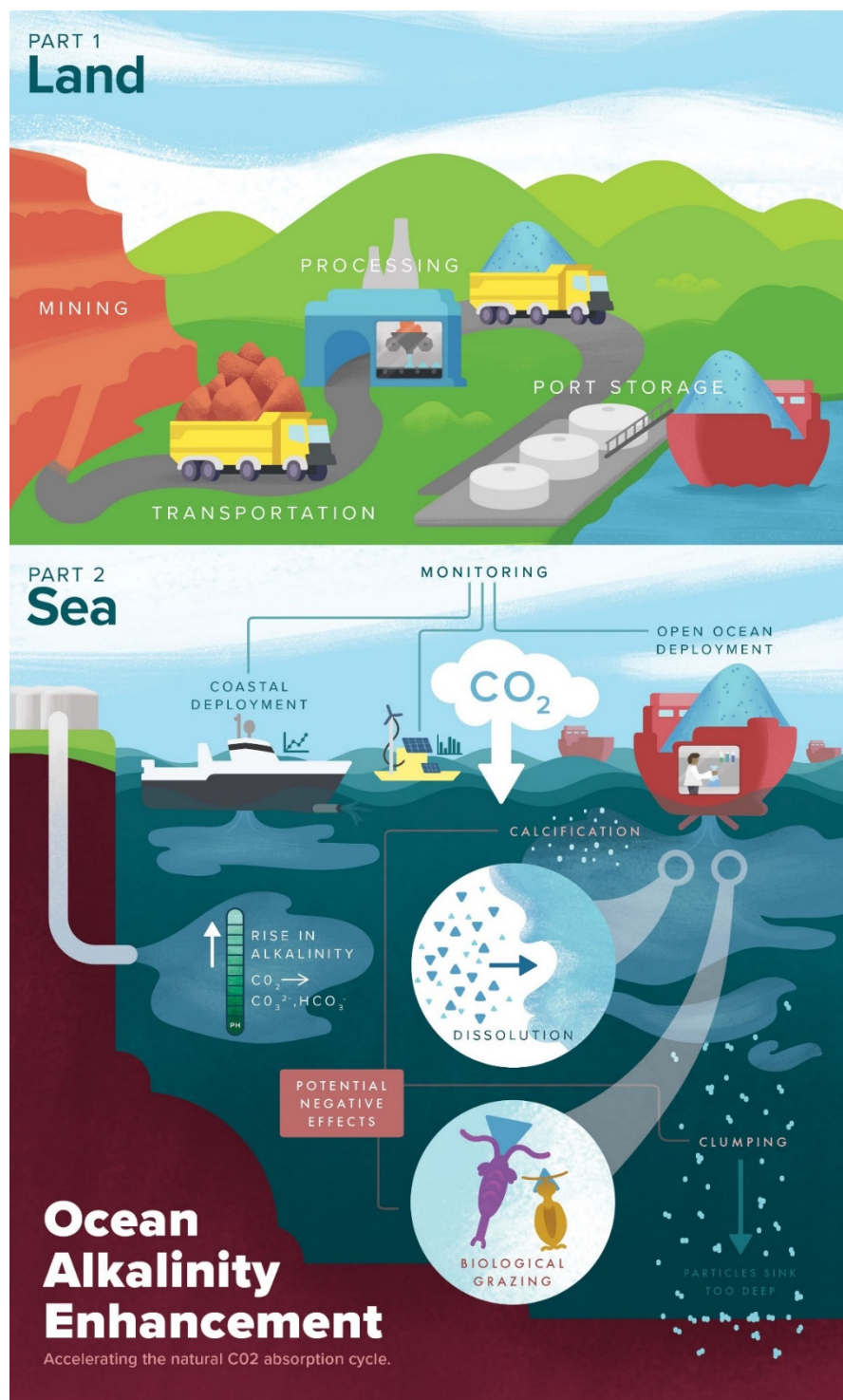
Current concern about the accelerated rate of CO<sub>2</sub> diffusion from the atmosphere into the surface ocean has prompted the marine scientific community to explore ocean carbon dioxide removal (CDR) approaches. Land-based CDR methods such as afforestation or bioenergy with carbon capture and storage have received much attention recently. However, meeting climate mitigation targets with land-based CDR alone will be extremely difficult, if not impossible, because the ocean governs the atmospheric CO<sub>2</sub> concentration and acts as the natural thermostat of Earth, simply because the ocean contains more than 50 times as much carbon as the atmosphere (Sarmiento and Gruber, 2002). One proposed ocean-based CDR technique is ocean alkalinity<sup>1</sup> enhancement (OAE) (Figure 7.1), also termed enhanced weathering (EW), proposed by Kheshgi (1995). This approach is broadly inspired by Earth's modulation of alkalinity on geological timescales. Adding alkalinity *via* natural or enhanced weathering is counteracted by the precipitation of carbonate, which reduces alkalinity and, in today's ocean, is driven almost entirely by calcifying organisms. For example, on geologic timescales, the dissolution of alkaline silicate minerals plays a major role in restoring ocean chemistry via addition of alkalinity to the ocean and conversion of CO<sub>2</sub> into other dissolved inorganic carbon (DIC) species (Archer et al., 2009). To date, most attention has been paid to terrestrial EW applications (Köhler et al., 2010; Schuiling and Tickell, 2010; Hartmann et al., 2013), with potential co-benefits in addition to CO<sub>2</sub> removal including stabilization of soil pH, addition of micronutrients, and crop fertilization (e.g., Manning, 2010). When applied to the ocean, EW of minerals is achieved by adding large amounts of pulverized silicate or carbonate rock or their dissolution products, which adds alkalinity to the surface ocean and thereby “locks” CO<sub>2</sub> into other forms of DIC, which is expected to promote atmospheric CO<sub>2</sub> influx into the ocean. Specifically, following alkalinity addition, CO<sub>2</sub> is converted into bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) and carbonate ions (CO<sub>3</sub><sup>2-</sup>) and these chemical changes lead to a rise in pH (Kheshgi, 1995; Gore et al., 2019). Therefore, this approach has the potential to not only remove atmospheric CO<sub>2</sub> but also counteract ocean acidification and thus contribute to the restoration of ecosystems threatened by it.

OAE involves the dissolution of large amounts of naturally occurring silicate (Schuiling and Krijgsman, 2006; Köhler et al., 2010), carbonate minerals (Kheshgi, 1995; Rau and Caldeira, 1999; Caldeira and Rau, 2000; Harvey, 2008; Rau, 2011), and mineral derivatives or other alkaline materials, such as some industrial waste products (Figure 7.1). Dissolution may either occur in the ocean, following processing, grinding, and dispersal of mineral, or it might be achieved in chemical reactors on land or on board ships (Figure 7.1). Another OAE approach is the generation of sodium hydroxide (NaOH) electrochemically (electrodialytically or electrolytically) resulting in the drawdown of atmospheric CO<sub>2</sub> into bicarbonate (Rau, 2008).

Natural increases in ocean alkalinity via rock weathering can lead to the removal of at least 1.5 moles of atmospheric CO<sub>2</sub> for every mole of dissolved magnesium (Mg)- or calcium (Ca)-based minerals (e.g., wollastonite, olivine, and anorthite) and 0.5 mole for carbonate minerals (e.g., calcite and dolomite) (see *Dissolution of Naturally Occurring Minerals* below). These processes are responsible for a net removal of 0.5 billion tons of CO<sub>2</sub> per year from the atmosphere (Renforth and Henderson, 2017).

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<sup>1</sup> Alkalinity can be defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors over proton donors in seawater (Dickson, 1981).

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**FIGURE 7.1** Steps and potential impacts of ocean alkalinity enhancement in coastal and open-ocean environments. (Part 1) Mining and transportation and required infrastructure at ports for storage of alkaline products. (Part 2) Addition of minerals or alkaline seawater (via prior dissolution of minerals or addition of NaOH generated electrochemically) to coastal waters through pipelines and ships, and to open-ocean waters through ships; monitoring of the carbonate system through autonomous measurements on buoys and flow through systems aboard ships; potential impacts of alkalinity addition.

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Based on modeling studies, adding large amounts of alkalinity globally could be an effective CDR method (Ilyina et al., 2013; Keller et al., 2014) that has the potential to promote CO<sub>2</sub> uptake from the atmosphere while mitigating ocean acidification. Some of the proposed minerals are abundant in Earth's crust, but the costs, logistics, and environmental footprints of mining, industrial transformation (e.g., the conversion of limestone into quicklime via calcination), pulverizing, and transporting minerals require careful consideration when designing OAE deployments in open ocean and coastal locations (Figure 7.1). Of particular concern are the local environmental impacts and the CO<sub>2</sub> release associated with a considerable increase in mining, industrial transformation, and transportation activities required for large-scale deployments of minerals (see Sections 7.3 and 7.4). Like other CDR approaches and negative-emissions technologies, OAE must be examined carefully after experimental validation to determine its potential benefits and environmental and social side effects (both intended and unintended), as well as assessment of the geographic boundaries for its deployment. The vast majority of results on OAE impacts on chemical and biological processes come from modeling studies, and there is therefore an urgent need to generate empirical data from laboratory and mesocosm studies, and to explore these questions in small field trials. This chapter brings together the state of knowledge on OAE and explores the feasibility potential and anticipated limitations of this CDR approach.

According to criteria described in Chapter 1, the committee's assessment of the potential for OAE as a CDR approach is discussed in Sections 7.2–7.7 and summarized in Section 7.8. The research needed to fill gaps in understanding of OAE as an approach to durably removing atmospheric CO<sub>2</sub> is discussed and summarized in Section 7.9. Although OAE and electrochemical approaches are explored in separate chapters, there are intrinsic commonalities in the methods.

### 7.2 KNOWLEDGE BASE

The ocean absorbs up to ~30 percent of the CO<sub>2</sub> that is released to the atmosphere through physicochemical processes and, as atmospheric CO<sub>2</sub> increases, equivalent levels of CO<sub>2</sub> are measurable in the surface ocean within timescales of months to years, causing ocean acidification. Briefly, as CO<sub>2</sub> diffuses in seawater, it combines with H<sub>2</sub>O to form carbonic acid (H<sub>2</sub>CO<sub>3</sub>), which dissociates into bicarbonate ions (HCO<sub>3</sub><sup>-</sup>) and protons (H<sup>+</sup>), causing ocean acidification. A proportion of the excess protons combine with carbonate ions (CO<sub>3</sub><sup>2-</sup>) to form more HCO<sub>3</sub><sup>-</sup>. The concentration of carbonate in the ocean is governed by the global alkalinity cycle (Broecker and Peng, 1982). Essentially, the production of calcium carbonate (CaCO<sub>3</sub>) in the surface ocean exceeds the supply of alkalinity from rivers. To maintain the balance of alkalinity fluxes, only a fraction of carbonate production can be removed from the ocean by burial, which is governed by the depth of the saturation horizon (where precipitation equals dissolution, dictated by inorganic carbon thermodynamics<sup>2</sup>), defined as the depth where the saturation state of the carbonate mineral is 1 (7.1):

$$\Omega = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] / K_{\text{sp}} \quad (7.1)$$

Where  $K_{\text{sp}}$  is the solubility product constant.  $\Omega$  values of 1 suggest a fluid in thermodynamic equilibrium with the mineral;  $\Omega < 1$  at greater ocean depths indicates undersaturation, and based on inorganic carbon thermodynamics, mineral dissolution should exceed precipitation. On the other hand,  $\Omega > 1$  at shallower depths indicates oversaturation, and mineral precipitation is promoted with respect to

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<sup>2</sup> In some CaCO<sub>3</sub>-producing organisms, some organisms have been found to maintain calcification in undersaturated waters ( $\Omega < 1$ ). In addition to mechanisms that promote low levels of H<sup>+</sup> such as proton pumps and physical proximity of processes that remove H<sup>+</sup>, such as photosynthesis in calcifying algae (Bergstrom et al., 2019), the extent to which the shell or skeleton is covered by an organic layer can provide protection against dissolution (Ries et al., 2009). This is a common feature in most calcifiers; for example, the epicuticle in crustacea and echinoids, periostracum in mollusks, ectoderm in corals, and utricles in calcifying algae that cover the biomineral provide some protection against dissolution (Ries et al., 2009).

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dissolution. On timescales longer than millennia, carbonate compensation adjusts the alkalinity of the global ocean, counteracting any changes in atmospheric CO<sub>2</sub>.

Carbonate chemistry conditions are critical to the functioning and ecological fitness of calcareous organisms, and this is exemplified in two water basins of contrasting carbonate properties: the Black Sea, with carbonate chemistry conditions comparable to those in the open ocean, and the Baltic Sea, which harbors low-alkalinity waters (Müller et al., 2016). Interestingly, while the Black Sea displays seasonal blooms of the calcareous plankton coccolithophores (Iglesias-Rodriguez et al., 2002; Kopelevich et al., 2014) and the sediments are covered by thick layers of calcareous ooze (Hay, 1988), the Baltic Sea does not harbor coccolithophores. In the Black Sea, it is also possible that the selection for coccolithophores might be partially forced by the decline in silicate following the construction of a dam on the Danube and other rivers that deliver nutrients to the basin. This was reported as a likely factor shifting an ecosystem dominated by the silicate-dependent diatoms and dinoflagellates into a coccolithophore-dominated system (Mihnea, 1997).

Only a small fraction of the total DIC pool in seawater is in the form of CO<sub>2</sub> gas that can exchange with the atmosphere. Adding alkalinity to seawater can be beneficial because it shifts the partitioning of inorganic species, lowering the concentration of CO<sub>2</sub> gas in seawater. Indeed, increasing alkalinity shifts CO<sub>2</sub> into other DIC species such as HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, the main forms of seawater alkalinity, consequently, decreasing the partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>). If this process occurs at the ocean surface, air–sea flux of CO<sub>2</sub> will be enhanced, resulting in net oceanic CO<sub>2</sub> uptake. Globally, atmosphere–ocean upper mixed layer equilibration occurs on timescales of months to a year, although many factors (e.g., mixing and wind speed) will affect the exchange rate and there could be localized effects that accelerate this exchange. However, while alkalinity addition consumes CO<sub>2</sub> from the ocean surface, replenishment via air–sea flux can take place very slowly, possibly on timescales of years, depending on the oceanographic properties of the location where deployments take place (Harvey, 2008; Feng et al., 2017; Bach et al., 2019). Therefore OAE can possibly lead to severe carbonate chemistry perturbations until equilibration with air takes place. In the Mediterranean Sea, OAE simulations applying a constant and steadily rising discharge relative to the surface pH trend of the baseline scenario attaining comparable quantities of annual discharge by the end of the alkalization period suggest nearly doubling the CO<sub>2</sub> uptake after 30 years (Butenschön et al., 2021).

The implications are twofold—the method has the potential to promote atmospheric CO<sub>2</sub> uptake by the ocean and mitigate acidification and its negative biological and long-term biogeochemical consequences. For example, an increase in CO<sub>3</sub><sup>2-</sup> concentrations increases the calcium carbonate saturation state of seawater, which is central to promoting and maintaining precipitation of calcium carbonate in organisms that produce shells, exoskeletons, and plates of carbonate such as some planktonic organisms, corals, and shellfish. OAE has potential benefits over other CDR schemes although empirical data are necessary to determine the effectiveness, risks, and side effects. Advantages include “permanent” CO<sub>2</sub> sequestration on timescales of millenia or longer in the absence of processes that remove the added alkalinity; not requiring long-term storage of large quantities of CO<sub>2</sub>; and, in addition to its application as a CDR method, possible lessening of some of the effects of ocean acidification. OAE can also represent a source of nutrients (see Hartmann et al. 2013) including silicate and some beneficial (e.g., iron [Fe] and magnesium) micronutrients, although the potentially toxic effect of metals such as nickel (Ni) (Montserrat et al., 2017), leached from olivine, is of concern. The main unknown is how OAE deployments would alter the biogeochemical cycling of elements on local and planetary scales and the repercussions of these alterations on marine ecosystems given the permanence of these chemical changes.

### Learning from the Past

The development of paleo proxies has enabled paleoreconstruction of seawater pH and the carbonate system (e.g., Foster, 2008; Wei et al., 2021); however, understanding the paleorecord of seawater alkalinity is challenging because alkalinity is poorly constrained. The balance between mineral weathering, which increases alkalinity, and the largely biotic precipitation of carbonate, which decreases

## *Ocean Alkalinity Enhancement*

alkalinity, is the primary mechanism governing seawater alkalinity. The silicate rock weathering hypothesis postulates that over timescales of a million to hundreds of million years, there is a negative feedback between the tectonic uplift of mountains and the amount of CO<sub>2</sub> in Earth's atmosphere. The mechanism driving this process is the increasing tectonic uplift of mountains that intensifies erosion on steep slopes, thus enhancing the rate of chemical weathering, which consumes atmospheric CO<sub>2</sub>, thus cooling the Earth. Ocean drilling science programs aim to test this hypothesis to improve forecasts of how this negative feedback that regulates atmospheric CO<sub>2</sub> can be used to predict whether the Earth system can regulate the rapid and vast amounts of anthropogenic carbon and over specific timescales (Koppers and Coggon, 2020).

Two periods of apparent contrasting alkalinity—the Pleistocene and the Paleocene–Eocene—are discussed by Renforth and Henderson (2017) to illustrate past forcings leading to shifts in alkalinity. During the last glacial period, in the Pleistocene (20 kya ago), high alkalinity is expected to have increased oceanic CO<sub>2</sub> removal and thus decreased atmospheric *p*CO<sub>2</sub> (a significant cause of glacial cooling). A combination of factors including lower glacial sea level leading to less continental shelf area for carbonate reef formation, thus decreasing coastal CaCO<sub>3</sub>, and probable erosion and dissolution of old reefs (CaCO<sub>3</sub> + CO<sub>2</sub> → Ca<sup>2+</sup> + CO<sub>3</sub><sup>2-</sup>), would increase CO<sub>3</sub><sup>2-</sup> and global ocean alkalinity (Opdyke and Walker, 1992). A physical process in the deep ocean driven by alterations in ocean circulation in the Atlantic resulting in slow-moving deep waters comprising significantly more remineralized CO<sub>2</sub> would reduce deep-water pH, thus shoaling the lysocline, consequently adding alkalinity by dissolution of CaCO<sub>3</sub> (Boyle, 1988; Sigman et al., 2010; Renforth and Henderson, 2017).

The minor and trace element contents (ratioed to calcium) of biogenic carbonates have been used for paleoclimate reconstructions and, specifically, the uranium/calcium (U/Ca) ratio of biogenic carbonates has been used as a proxy for seawater CO<sub>3</sub><sup>2-</sup>, particularly for the deep ocean where temperature changes are modest. Experimental calibrations indicate that U/Ca in corals and foraminifera are negatively correlated with seawater [CO<sub>3</sub><sup>2-</sup>] or pH (Russell et al., 2004; Anagnostou et al., 2011; Inoue et al., 2011; Raitzsch et al., 2011; Keul et al., 2013; Raddatz et al., 2014; Allen et al., 2016). However, the correlation between U/Ca and seawater [CO<sub>3</sub><sup>2-</sup>] is largely an outcome of alterations in the rates of the alkalinity pump, but can be confounded by the calcification strategy used by individual calcifiers (Chen et al., 2021). At present, it appears that a multiproxy approach combining stable isotopes and trace element/Ca ratios can only provide partial understanding of the biological mechanisms to be able to use these tracers for paleoceanographic reconstructions.

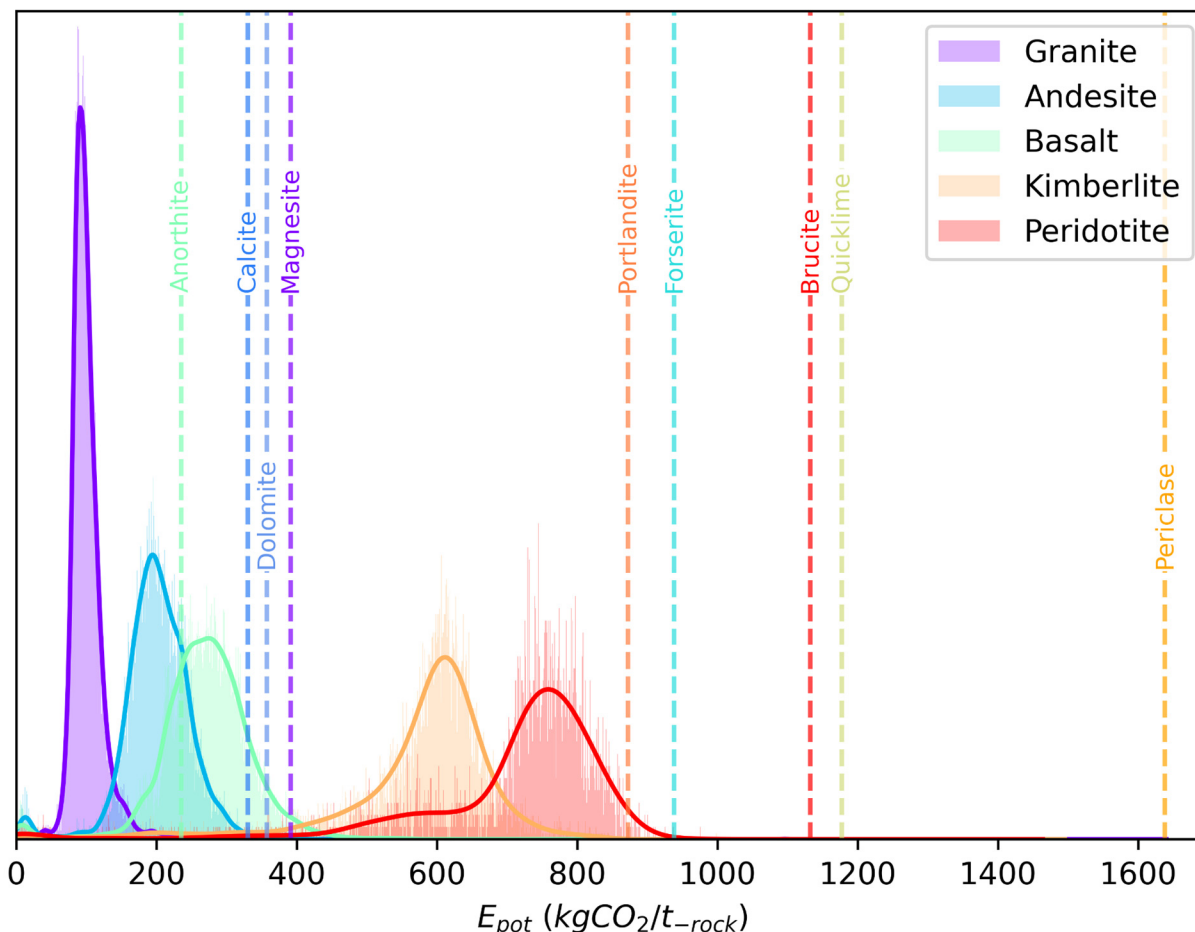
### **Dissolution of Naturally Occurring Rocks and Minerals**

The overall approach proposed with OAE is to accelerate the slow geological process of mineral dissolution in seawater by increasing the reactive surface area of the minerals through pulverizing the alkaline rock into small particles. The hope with this approach is to lock CO<sub>2</sub> away from the atmosphere via conversion into proton acceptors (mainly HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>) over proton donors (Wolf-Gladrow et al., 2007) in a semipermanent fashion. Three main methods, in addition to electrochemical approaches (reviewed in Chapter 8), are currently being considered to enhance alkalinity in seawater: the dissolution of naturally occurring silicate-based minerals such as olivine, accelerated limestone weathering (Rau and Caldeira, 1999), and dissolution of calcium carbonate derivatives—quicklime (calcium oxide, CaO) or portlandite (calcium hydroxide, Ca(OH)<sub>2</sub>)—in the surface ocean. Dissolution of other minerals such as chalk, calcite, or dolomite also affect seawater pH and total alkalinity on timescales of months. The impact of mineral addition is specific to the mineral itself and technology. The theoretical maximum potential of a rock or mineral (*E*<sub>pot</sub>, kg CO<sub>2</sub>/t<sub>rock</sub>) to convert CO<sub>2</sub> into bicarbonate can be estimated by equation 7.2 (see Renforth, 2019):

$$E_{\text{pot}} = \frac{M_{\text{CO}_2}}{100} \left( \alpha \frac{M_{\text{CaO}}}{M_{\text{CaO}}} + \beta \frac{M_{\text{MgO}}}{M_{\text{MgO}}} + \varepsilon \frac{M_{\text{Na}_2\text{O}}}{M_{\text{Na}_2\text{O}}} + \theta \frac{M_{\text{K}_2\text{O}}}{M_{\text{K}_2\text{O}}} + \gamma \frac{M_{\text{SO}_3}}{M_{\text{SO}_3}} + \delta \frac{M_{\text{P}_2\text{O}_5}}{M_{\text{CaO}}} \right) \cdot 10^3 \cdot \eta \quad (7.2)$$

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where  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  are the elemental concentrations of calcium, magnesium, sulfur (S), phosphorus (P), sodium (Na), and potassium (K), expressed as oxides,  $M_x$  is the molecular mass of those oxides. Coefficients  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$ , and  $\theta$  consider the relative contribution of each oxide ( $\alpha$ ,  $\beta$ ,  $\epsilon$ , and  $\theta$  are equal to 1,  $\gamma$  is equal to  $-1$ , and  $\delta$  is equal to  $-2$  for the pH range of the ocean);  $\eta$  is molar ratio of  $\text{CO}_2$  to divalent cation sequestered during EW (equivalent to 1.4–1.7 for the ocean's temperature, pressure, and salinity ranges).  $E_{\text{pot}}$  values for common rock types is presented in Figure 7.2. Given the size of the rock resource, there may be scalable potential in the extremes of the distribution.

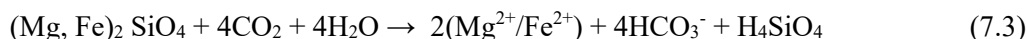


**FIGURE 7.2** Enhanced weathering potential of common rock types derived from oxide data from GEOROCK database (<http://georoc.mpch-mainz.gwdg.de/georoc/Start.asp>). Histogram frequency (vertical axis) bars were generated using 1,000 bins across the horizontal axis scale to generate frequency of carbon capture potential for each rock type. Given that the total size of the samples varied ( $n = 10,839$ , 8,747, 10,337, 5,431, and 3,226, for granite, andesite, basalt, kimberlite, and peridotite, respectively) frequency was normalized to each total such that the vertical axis represents proportional frequency. The lines represent a Gaussian kernel density estimation fit of the histogram. The potentials for the pure minerals magnesite ( $\text{MgCO}_3$ ), calcite ( $\text{CaCO}_3$ ), dolomite [ $\text{CaMg}(\text{CO}_3)_2$ ], forsterite ( $\text{Mg}_2\text{SiO}_4$ ), anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ), quicklime ( $\text{CaO}$ ), portlandite [ $\text{Ca}(\text{OH})_2$ ], and brucite [ $\text{Mg}(\text{OH})_2$ ] were calculated by expressing their Mg and Ca composition as oxides and using equation 2. The efficiency factor  $n$  (equation 2) was assumed to be 1.5 for silicates and 0.75 for carbonates (Renforth and Henderson, 2017).

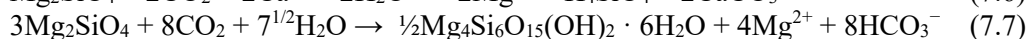
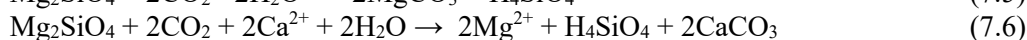
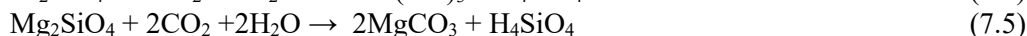
*Ocean Alkalinity Enhancement***Silicate Minerals and Rocks (Olivine, Basalt)**

Alkaline, silicate rock dissolution is an important process that consumes excess CO<sub>2</sub> and restores seawater chemistry on geologic timescales (Archer et al., 2009). This has inspired the idea of speeding up dissolution by crushing rock and pulverizing into small particles to enhance dissolution. The acceleration of silicate weathering generates stable dissolved calcium and magnesium bicarbonates accompanied by the release of metals.

Olivine-rich rocks are abundant and vary in composition and are among the most abundant minerals—*forsterite* and *fayalite* (Fe<sub>2</sub>SiO<sub>4</sub>). The most abundant olivine-rich rocks contain 30–50 percent Fe (Deer et al., 2013). *Forsterite* is among the most desirable mineral constituents due to its high reactivity and relative high concentration in cations (e.g., Oelkers et al., 2018). The weathering of olivine in seawater can be described by



In the case of pure *fayalite* (equation 7.3) and *forsterite* (equations 7.4–7.6), the dissociation of olivine leads to the following products (see Griffioen, 2017, for details):



Equations 7.5 and 7.6 describe weathering reactions in environments where carbonate precipitation occurs and have a 1:2 molar ratio of olivine to CO<sub>2</sub> compared to 1:4 in equation 7.3. The secondary precipitates are important to consider because the efficiency of CO<sub>2</sub> removal declines when secondary precipitates are developed. For instance, the rise of pH in response to the above reactions can result in calcite precipitation and the concomitant release of CO<sub>2</sub> in the ocean via the following reaction:



The release of CO<sub>2</sub> by this reaction diminishes the efficiency of OAE via olivine by roughly a factor of two compared to that without secondary precipitation.

The effect of microbes appears to be unclear and likely minor, but some studies indicate decreasing dissolution rates. Possibly, this is because of the presence of mineral coatings, and the effect microbes have on the oxidation and/or complexation of metals (Seiffert et al., 2014; Oelkers et al., 2018). Numerous studies have illustrated that thin layers of amorphous silica can establish on the olivine surface, slowing its dissolution (e.g., Wang and Giammar, 2013). The selective colonization of minerals from experiments exploring aqueous environments seems to be governed by the need of specific microbes to harvest nutrients from the dissolving olivine (e.g., Shirokova et al., 2012).

Although it is widely accepted that *forsterite* dissolution rates always exceed those of most other silicate minerals, this is a misconception because the relatively rapid dissolution rates are reported to occur under acidic conditions (Oelkers et al., 2018). Indeed there are limited options to enhance the rates of *forsterite* dissolution for EW, and the only processes that appear to significantly augment *forsterite* dissolution rates are increasing *forsterite* surface area (through grinding), decreasing seawater pH, and the presence of some organic ligands at neutral to basic conditions (Wogelius and Walther, 1991; Oelkers et al., 2018). In an analysis of the cost of grinding, Hangx and Spiers (2009) estimated over 60 kWh of energy would be required and >30 kg CO<sub>2</sub> emitted when finely ground olivine is produced to consume 1 ton of CO<sub>2</sub>. The effect of the aqueous organic species in an aqueous solution on dissolution rates can be a result directly from the interaction of the organic species with the bonds that need to be broken to dissolve the mineral (Olsen and Rimstidt, 2008), or indirectly by changing the pH of the water (see Oelkers et al.

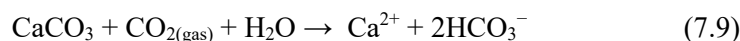


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(2018). It appears that because of very low dissolution rates per unit surface area, silicate minerals in general need to be pulverized to  $\leq 1 \mu\text{m}$  to dissolve on relevant timescales as elevated ocean pH slows dissolution rates (GESAMP, 2019). The combination of secondary mineral precipitation and the limited routes to enhance dissolution rates of olivine are challenging issues in using EW of olivine as a CDR approach.

**Limestone**

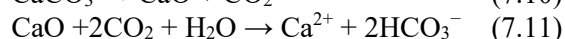
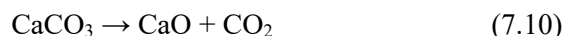
Harvey (2008) proposed the idea of adding powdered calcium carbonate ( $\text{CaCO}_3$ ) mineral (limestone) to seawater as a CDR protocol. Similar to olivine,  $\text{CaCO}_3$  dissolution kinetics in seawater is expected to be slow for supersaturated conditions ( $\Omega > 1$ ) and the release of alkalinity on short timescales only takes place under  $\text{CaCO}_3$  undersaturation, and therefore this is an inefficient method to apply to the surface ocean. Limestone dissolution has been proposed as a potentially desirable method to apply to  $\text{CO}_2$ -rich waste gas streams where seawater and elevated  $\text{CO}_2$  and limestone could facilitate the conversion of  $\text{CaCO}_3$  into bicarbonate:



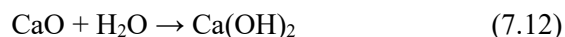
The dissolution rates of whole-shell biogenic carbonates increase with decreasing  $\text{CaCO}_3$  saturation state, decreasing temperature, and fluctuate predictably with respect to the relative solubility of the calcifiers' polymorph mineralogy: (high-Mg calcite [mol% Mg > 4]  $\geq$  aragonite > low-Mg calcite [mol% Mg < 4]) the implications being that OA and temperature will continue to increase dissolution of biogenic carbonate shells and skeletons (Ries et al., 2016). The role of physics on the fate of the particles is exemplified in an experiment releasing limestone particles smaller than  $10 \mu\text{m}$  in surface waters, where horizontal eddy diffusion appeared to be the major factor affecting the dispersion of chalk to concentrations below detection limit (Balch et al., 2009).

**Carbonate Mineral Derivatives: Quicklime and Portlandite**

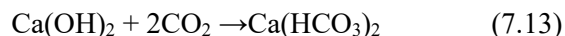
Given the poor solubility of  $\text{CaCO}_3$  in surface ocean seawater, Kheshgi (1995) investigated producing an alternative, quicklime (calcium  $\text{CaO}$ ). Although the addition of 1 mole of  $\text{CaO}$  to seawater removes 2 moles of  $\text{CO}_2$  (equation 7.8), the use of  $\text{CaO}$  is a less efficient CDR method because  $\text{CO}_2$  is released in the production of quicklime by the thermal breakdown of limestone (equation 7.10).



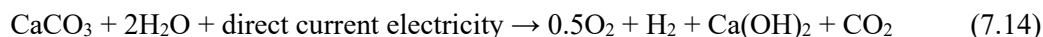
A by-product of  $\text{CaO}$  that is generated through slaker technology is portlandite (calcium hydroxide  $\text{Ca}(\text{OH})_2$ ; equation 7.12).



For average open-ocean pH, calcium hydroxide can react with  $\text{CO}_2$  to form calcium bicarbonate:



Similarly to  $\text{CaO}$ , while 2 moles of  $\text{CO}_2$  can be removed per mole of  $\text{Ca}(\text{OH})_2$ , there is only a net removal of 1 mole of  $\text{CO}_2$  because the generation of  $\text{Ca}(\text{OH})_2$  releases 1 mole of  $\text{CO}_2$  under acidic conditions and through electrolysis:



*Ocean Alkalinity Enhancement***7.3 EFFICACY****Dissolution Kinetics**

The dissolution kinetics of minerals have been studied through laboratory experimentation for decades. However, the two main approaches to the study of chemical weathering in the field (geochemical) and laboratory (individual mineral dissolution rates) rarely produce the same results (Brantley, 2008). There are also conflicting results regarding the effect of CO<sub>2</sub> and carbonate ions on dissolution rates (Wogelius and Walther, 1991; Golubev et al., 2005). Nonstoichiometry and incomplete dissolution have also been reported, perhaps due to dissolution of impurities, precipitation of secondary minerals, or preferential leaching of elements from the mineral surface (Brantley, 2008). These discrepancies between field and lab observations, and the large uncertainties regarding which factors govern mineral dissolution (White and Brantley, 1995) highlight the urgent need for field experimentation.

There are many choices of independent variables and expressions describing the dissolution rates of minerals as well as spatial and temporal variations in mineral properties and external influences such as diffusion and advection. Numerical simulations capable of handling this complexity would be required to address the observed variability. Ideally the dissolution kinetics of a mineral should reflect the underlying chemistry and physics of the reactions, although there are contrasting ideas explaining how solids dissolve such that there is no single rate equation that can be used to model natural and technological processes (Rimstidt et al., 2012). Along with temperature and pH, particle size and surface area are perhaps the most important factors governing dissolution rates (Rimstidt et al., 2012). A mineral surface is composed of sites with different surface properties that constitute the reactive (White and Peterson, 1990) or the effective surface area (Aagaard and Helgeson, 1982; Helgeson et al., 1984). However, most studies use instead the total surface area (also referred to as the BET [Brunauer–Emmett–Teller] surface area) or the geometric surface (Liittge and Arvidson, 2008), which consider all the surface sites uniformly reactive (Grandstaff, 1978; White and Peterson, 1990). However, aggregation could lead to overestimation of the available surface area (when BET values are applied).

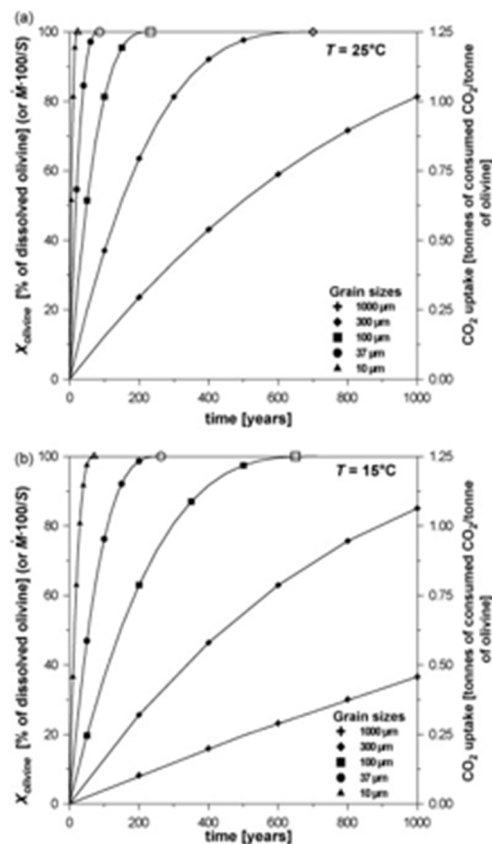
**Fate of Mineral Particles in the Surface Ocean**

A concern with the deployment of particles as one OAE approach (adding alkalized seawater following mineral dissolution is also an option) is the fate of the particles spread on the ocean surface. Possible scenarios that are likely to result in increased export of particles to depth include removal of mineral grains by grazers and conditions leading to particle aggregation during deployment of the pulverized mineral (Figure 7.1). Therefore, timing of mineral deployment is expected to be hugely important. For example, the amount and type of organic matter associated with biological processes, such as the presence of high concentrations of phytoplankton and their associated mucus, can impact particle aggregation and increase the size of aggregates (see Hamm, 2002) promoting export to depths below the mixed layer.

The effect of particle size on dissolution rates has been investigated with a focus on olivine (Figure 7.3). It appears that the most challenging aspect is the need to grind the mineral to ensure CO<sub>2</sub> removal in a timely manner and dissolution in the surface ocean. Calculations by Hangx and Spiers (2009) suggested that grained olivine between 2 and 6 mm is required to achieve significant steady-state CO<sub>2</sub> uptake rates within a few decades. Grain sizes around 1 μm appear to be appropriate to facilitate dissolution before sinking out of the surface mixed layer (Köhler et al., 2013). Interestingly, for particles smaller than 1 μm, Brownian motion appears to be the main mechanism driving aggregation (Köhler et al., 2013). Indeed a study by Bressac et al. (2012) using mesocosms where a Saharan dust deposition event was simulated revealed partial aggregation resulting in high sinking velocities, orders of magnitude greater than calculations based on modeled data (Köhler et al., 2013). Given the mineral characteristics of the dust—40 percent quartz, 30 percent calcite, and 25 percent clays (in addition to micro- and macro-

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nutrients), and given that the finest dust fraction is  $<20\ \mu\text{m}$ , this type of deposition event could be considered a natural analog for mineral deployments.



**FIGURE 7.3** Percentage of granular olivine dissolution ( $X_{\text{olivine}}$ ) (left y axis) and  $\text{CO}_2$  uptake per tonne of dissolved olivine (right y axis) as a function of time (see Hangx and Spiers [2009], for details). Open symbols indicate reaction times to reach steady-state reaction, at constant olivine supply rate. The amount of  $\text{CO}_2$  removed per tonne of olivine was calculated assuming reaction 2, which results in the formation of soluble Mg bicarbonate salts and  $\text{CO}_2$ :olivine uptake ratio of 1.25 t  $\text{CO}_2$  per tonne olivine. (a) Reaction time series at  $25^\circ\text{C}$ , assuming that the dissolution rate of olivine is  $1.58 \times 10^{-10}\ \text{mol}/\text{m}^2\cdot\text{s}$ . (b) Reaction progress at  $15^\circ\text{C}$ , with the olivine dissolution rate being  $5.19 \times 10^{-11}\ \text{mol}/\text{m}^2\cdot\text{s}$  (calculated using the dissolution rate at  $25^\circ\text{C}$  and an activation energy of 79.5 kJ/mol, following Wogelius and Walther (1992). SOURCE: Hangx and Spiers, 2009.

## 7.4 SCALABILITY

### Durability

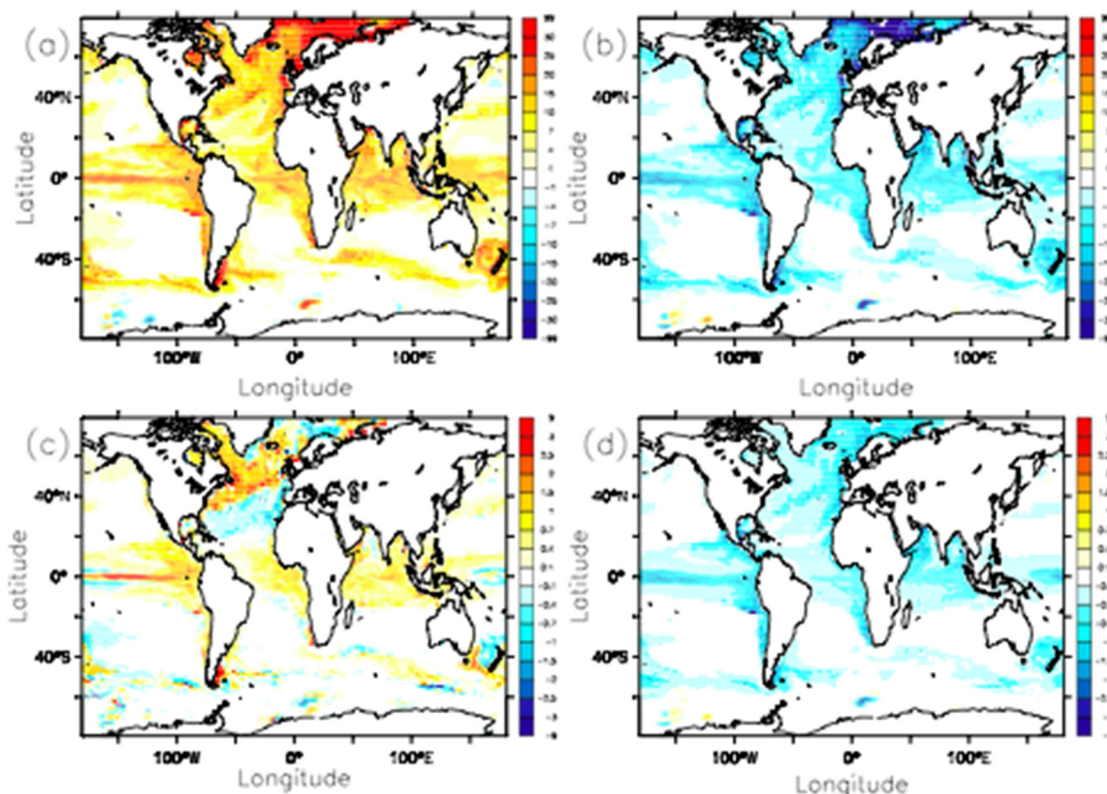
Like other ocean CDR approaches, OAE is only effective if  $\text{CO}_2$  can be “locked” away from the atmosphere for long time periods. The permanence of an ocean CDR approach has been defined as one that leads to sustained  $\text{CO}_2$  sequestration over centennial timescales. Although this has not been extended to OAE (see Siegel et al., 2021), OAE can be considered as permanent when the conversion of  $\text{CO}_2$  into other inorganic carbon molecules ( $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ ) remains stable for periods of time exceeding a century. The extent of permanence of OAE is critically dependent on the properties of the water column, including: (1) those that govern dissolution kinetics; (2) the abiotic (or biotic) precipitation of carbonate (an undesirable side effect because it leads to the release of  $\text{CO}_2$ ); (3) the amount and type of organic matter that leads to aggregation of mineral particles, for example, the adsorption of dissolved organic

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matter onto dust particles or the effect of colloidal-size particles and gels on particle aggregation (Alldredge and Silver, 1988; Engel, 2000; Armstrong et al., 2001; Francois et al., 2002; Klaas and Archer, 2002; van der Jagt et al., 2018); (4) the possible removal of particles by grazers (Banse, 1994); and (5) ocean physical processes such as advection and subduction (Itsweire et al., 1993), which dilute the local chemistry impacts from the site of deployment.

### Location and Frequency of Deployments

Critical issues determine the ideal frequency and location of deployments. In terms of the efficacy in removing carbon from the atmosphere, it has been suggested that only when deployments are conducted continuously is atmospheric  $\text{CO}_2$  successfully reduced, although these reductions are modest because atmospheric  $\text{CO}_2$  from human sources continues to increase (Keller et al., 2014). Locations for mineral deployment (see Figure 7.4) have been evaluated in the open ocean (Köhler et al., 2013) and coastal zones (Hangx and Spiers, 2009). The main challenge is that mineral particles must be ground to a very small size to avoid the rapid sinking of particles out of the euphotic zone before being dissolved, to ensure rapid  $\text{CO}_2$  uptake at the surface (Meysman and Montserrat, 2017). It has been suggested that  $\text{CaCO}_3$  powder could be added to the surface layer in regions where the depth of the boundary between supersaturated and unsaturated water (saturation horizon) is relatively shallow (250–500 meters) and where upwelling velocity is high (Harvey, 2008). The much deeper saturation horizons (depths where  $\Omega_{\text{cal}}$  and  $\Omega_{\text{arag}} = 1$ ) in the North Atlantic compared with those in the North Pacific and North Indian oceans (Jiang et al., 2015) could be important considerations when deciding deployments.



**FIGURE 7.4** Simulated anomalies ( $\text{g C/m}^2$  per year) from model runs representing scenarios when olivine is added with respect to a control without olivine (see Köhler et al., 2013). Values represent annual averages in 2009. (a) Diatom net primary production; (b) nondiatom net primary production; (c) export production of organic carbon at 87-meter depth. (d)  $\text{CaCO}_3$  export at 87-meter depth. SOURCE: Köhler et al., 2013 Licensed by Creative Commons CC BY 3.0.

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Decisions on the scale of deployments will be determined by a range of factors (see (Caserini et al., 2021), including

- accessibility of sources of sufficient mineral;
- need for substantial upscaling of the current magnitude of mining and production of derivatives (and the associated environmental and other effects);
- economics of rock mining, crushing, and transportation;
- accessibility and adaptation of existing ships;
- implementation of loading facilities in ports;
- international and national laws or regulations;
- restrictions that could limit mining, processing, transportation and/or discharge;
- carbon removal efficiency; and
- human elements, that is, persons' and governments' agreements to responsible intervention.

Simulation studies on the behavior of mineral particles following their release in the wake of a ship using different methodologies and fluid dynamic modeling approaches suggest that key parameters governing mineral dissolution in the upper layers of the water include particle radius and density, diffusion potential, volume discharge rate, vessel speed, waterline length, time after disposal, flow velocity at the injection point, diameter of the circular area of discharge, with other parameters such as geometry and porosity also expected to be important (Caserini et al., 2021).

The criteria for the choice of location of deployments remain to be determined. For coastal regions, ecosystems particularly susceptible to ocean acidification and upwelling zones could perhaps be good initial candidates for trials. For open-ocean deployments, in addition to new dedicated vessels, the use of existing vessels with modifications to transport and deploy mineral, when possible, would be financially, logistically, and energetically desirable. Long routes would be well suited for low discharge rates, and new designs would optimize mineral storage and deployment (Caserini et al., 2021). An important issue with mineral deployment is how to prevent loss of mineral to depth and the secondary precipitation of minerals (e.g.,  $\text{CaCO}_3$  or  $\text{Ca}(\text{OH})_2$  when deploying quicklime) (see Caserini et al., 2021).

If deployments were to be conducted on a large scale, atmospheric  $p\text{CO}_2$  removal might cause the release of  $\text{CO}_2$  from ocean regions that are not subject to addition of  $\text{CaCO}_3$ , consequently raising the pH and supersaturation in these regions (see Harvey, 2008). The addition of limestone powder in small particles would potentially increase albedo and thus induce a cooling effect while decreasing penetration of solar radiation into the mixed layer, reducing the strength of the biological carbon pump (Balch et al., 1996; Harvey, 2008).

An assessment of the potential for  $\text{Ca}(\text{OH})_2$  discharge at a global scale estimates between 1.7 Gt/yr (load at departure) and 4.0 Gt/yr (one or two intermediate reloads for bulk carriers and container ships, respectively) (Caserini et al., 2021) (Table 7.1). As an example, the global potential of  $\text{CO}_2$  removal from quicklime discharge by existing cargo and container ships while also carrying freight is 1.5-3.3 Gt  $\text{CO}_2$ /yr. However, there are significant uncertainties about the feasibility of using existing commercial vessels and what model would be applied to address the trade-offs to substitute a fraction of the profit-making transportation for mineral deployment. While additional infrastructure would be needed at ports to load vessels, and vessels would need to be adapted so that they could unload while steaming, a key limitation of using spare capacity in existing freight is that the locations for alkalinity deployments would be constrained to sea lanes. Alternatively, there is an argument for the use of a dedicated fleet of ships for mineral addition. The addition of a billion tonnes of mineral per year will likely require ~1,000 dedicated vessels (Harvey, 2008; Renforth et al., 2013; Caserini et al., 2021), a marginal, but substantial, increase on the 10,000 that are already operating. An increase in the fleet of vessels could cause environmental challenges including increase in ambient ocean noise levels (Kaplan and Solomon, 2016), potential transfer and establishment of nonindigenous species (Muirhead et al., 2015), and changes in concentrations and radiative forcing of short-lived atmospheric pollutants due to shipping emissions (Dalsøren et al., 2013).

*Ocean Alkalinity Enhancement***TABLE 7.1** Example of an Assessment of Potential Global Ca(OH)<sub>2</sub> Deployment from Bulk Carriers and Container Ships

		Bulk carriers		Container ships	
		Single load	Multiple load	Single load	Multiple load
Average tonnage	dwt		75000		45000
% dead weight cargo capacity (DWCC)	%		85%		85%
% DWCC usable for Ca(OH) <sub>2</sub>	%		15%		15%
% Tonnage used for transporting Ca(OH) <sub>2</sub>	%		13%		13%
Ca(OH) <sub>2</sub> load on board	t		9563		5738
Number of vessels per category	-		9286		4855
Distance traveled of the maritime route	km		6300		8900
Average cruising speed	km/h		21.4		27.4
Average at sea days per annum	d/year		181		218
Number of intermediate stops (with Ca(OH) <sub>2</sub> reload)	n°/year	0	1	0	2
Average distance traveled per typical sea-leg	km	6,300	3,150	8,900	2,967
Navigation duration of the route	d	12.3	6.1	13.5	4.5
Average discharge rate along the route	kg/s	9.0	18.0	4.9	14.7
Number of exploitable yearly travels per vessel	n°/year	15	30	16	48
Total discharged Ca(OH) <sub>2</sub> per vessel	Mt/year	0.14	0.29	0.09	0.28
Total discharged Ca(OH) <sub>2</sub> by vessel category	Gt/year	1.3	2.7	0.4	1.3

SOURCE: Caserini et al., 2020 Licensed by Creative Commons CC BY 4.0.

### Transportation

All OAE approaches require the extraction, processing, and transport of rock. If OAE deployments at a scale to contribute a meaningful quantity of U.S. removal requirements (e.g., 100–500 Mt CO<sub>2</sub>/yr), then dedicated rock extraction on the same order of magnitude (100–1,000 Mt/yr) would be required. The United States currently produces ~1.4 Gt/yr of crushed rock (USGS, 2021), 68 percent of which is limestone, shell, or dolomite, 7 percent is basic igneous rock, and the balance is made up of silica-rich igneous or sedimentary rock (granite or sandstone), metamorphic rock, or unidentified geology. Between 1990 and 2007, production capacity increased by nearly 800 Mt/yr to 1.8 Gt/yr (Figure 7.5). While annual fluctuations in production are likely driven by short-term variability in demand, a 10-year rolling average is possibly more representative of longer-term constraints for capacity increase. However, sustaining a 3 percent increase over 30 years would be sufficient to create an additional 2-Gt/yr extraction capacity.

The deployment of alkalinity would necessitate the creation of local and regional management and monitoring structures as well as significant investment in adaptation and coordination of existing mining, industrial processing, and transportation schemes. A recent analysis of transportation based on the International Maritime Organization for bulk carriers and container ships concluded that the maximum slaked lime potential discharge from all active vessels worldwide is between 1.7 and 4.0 Gt/yr (Caserini et al., 2021). Because some of these operations are presently powered by fossil fuels, measures such as minimizing transportation by conducting operations on a local scale when possible will need to be

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implemented to maximize the effectiveness of OAE. In addition to the effectiveness of atmospheric CO<sub>2</sub> removal, global deployments would require augmentation of the current fleet and a significant proportion of new dedicated ships, which would undoubtedly cause impacts due to enhanced maritime traffic, pollution, and noise. However, this would require the expansion of lime production (from ~360 Mt/yr to >500 Mt/yr by 2100) to a scale comparable to the global cement industry (4.5 Gt/yr), with technologies that prevent or reduce the emission of the process CO<sub>2</sub> (e.g., Hanak et al., 2017) such as electrochemical splitting of water, salt, or mineral powered by nonfossil electricity (e.g., House et al., 2007; Rau et al., 2018).

## 7.5 ENVIRONMENTAL AND SOCIAL IMPACTS

A requirement for OAE is the expansion of mining operations (see Figure 7.1, Part 1). It is estimated that the additional mining effort needed to remove at least 1 Gt of CO<sub>2</sub>/yr is equivalent to the global cement industry, which currently extracts ~7 Gt of rock per year (Renforth and Henderson, 2017). Adverse environmental impacts of mining include ground vibration from blasting, noise pollution, poor soil and air quality as a result of dust, low quality and quantity of surface water and groundwater, air and water pollution, both on and off the mine site, increase in truck traffic transporting mineral, sedimentation and erosion, and land subsidence. All these factors have direct impacts on wildlife habitat, forestland and recreational land, human habitat, physical, mental, and social wellness, food security, and cultural and aesthetic resources (Sengupta, 2021). However, it has been argued that materials produced from the iron and steel industry could play an important role in meeting our climate targets. Specifically, the use of industrial metal slag, rich in alkaline compounds and Ca and Mg ions, has the potential to enhance CO<sub>2</sub> capture (Gartner et al., 2020; Li et al., 2020; Chukwuma et al., 2021). The presence of mineral carbonate phases such as calcite, magnesite, ankerite, and kutnohorite in the material demonstrates carbonation reaction has occurred after slag formation and therefore there is still carbonation potential to be realized (Chukwuma et al., 2021).

Despite increasing efforts to minimize the negative impacts of mining on local communities, an expansion of the mining industry raises concerns not only about the environmental impact but also the local social landscape with implications for sustainability. Along with the promise of wealth and jobs, the expansion of mining can also bring negative social effects. Some examples include demographic changes resulting in a structural and functional transformation of the social environment including shifts in gender balance, increase in nonresident workforces, pressures on infrastructure, appropriation of land from the local communities, housing and services; social inequality, poor child development and education outcomes, pressures on families and relationships, drug and alcohol abuse, decline in community subsistence and lifestyles, and impacts on Indigenous communities (see Petrova and Marinova, 2013; Candeias et al., 2018; Sincovich et al., 2018). Significant impacts on workers' health include cancer, respiratory diseases, injuries, long-term exposure to chemical agents, and ergonomic issues (Candeias et al., 2018). In addition to mining, the release of mineral particles into seawater, particularly those smaller than 10 μm,<sup>3</sup> which can penetrate deep into the respiratory system, could be a concern for human health, and therefore deployment locations must be carefully selected (Daly and Zannetti, 2007).

The deployment of alkalinity as pulverized rock or alkaline seawater where mineral dissolution has previously been conducted has multiple environmental impacts (see Figure 7.1, Part 2). These impacts will be more pronounced at the point of deployment, and the magnitude of these impacts will be critically dependent on mixing regimes affecting the rate of dispersal of added mineral or alkalinized water. In addition to rising pH, the deployment of alkalinity could raise the saturation state ( $\Omega$ ) of CaCO<sub>3</sub> well above present-day levels near the injection site. Although saturation is strongly correlated with temperature, spontaneous precipitation of calcite or aragonite does not occur in seawater, even in the warmest tropical regions. Therefore, addition of alkalinity to cold waters should not lead to precipitation,

<sup>3</sup>See <https://www.epa.gov/pm-pollution/health-and-environmental-effects-particulate-matter-pm>; <https://www.epa.gov/pm-pollution/particulate-matter-pm-basics>.

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at least if levels are kept at or below the saturation state of the current warmest ocean waters (see Henderson et al., 2008).

Calcifying organisms are sensitive to changes in carbonate chemistry parameters including  $\Omega$ ,  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ . However, the impact of ocean alkalization (which increases  $\Omega$ , pH, and levels of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  and decreases  $\text{CO}_2$ ) is largely unknown because most of the literature has focused on environmental responses associated with ocean acidification (decreasing  $\Omega$ ,  $\text{CO}_3^{2-}$ , and pH and increasing  $\text{CO}_2$  and  $\text{HCO}_3^-$ ). Biological processes can alter expected responses to shifts in  $\Omega$  that can make interpretation of biotic responses challenging. One of these processes is the formation of organic films covering the mineral, a mechanism that has been described in mussels, coccolithophores and corals (Ries et al., 2009; Tunncliffe et al., 2009; Ho, 2013) and that appears to protect carbonate from dissolution. The biological effects of significant increases in both pH and carbonate and bicarbonate ion concentrations brought about by OAE methods remain unknown.

An increase in  $\Omega$  has the potential to increase abiotic or biologically mediated calcification at the ocean surface. While the precipitation of  $\text{CaCO}_3$  leads to the release of  $\text{CO}_2$ , an increase in  $\text{CaCO}_3$  has the potential to increase ballast (Klaas and Archer, 2002) of particulate organic carbon (made up of fixed  $\text{CO}_2$  *via* photosynthesis). Therefore, the hypothetical enhancement of calcification using some OAE protocols could have a positive or negative feedback on carbon removal, depending on the balance between the enhanced ballast feedback and the release of  $\text{CO}_2$  feedback as a result of  $\text{CaCO}_3$  precipitation (Riebesell et al 2009; Bach et al., 2019). These hypotheses need to be tested experimentally.

Many technical, environmental, logistical, social, and ethical questions remain unanswered. If OAE was deployed at large scale, for ocean pH to be maintained above 8.0, on the order of  $2\text{--}10 \times 10^{14}$  mol alkalinity/yr for cumulative emissions of 1,500–5,000 Pg C, respectively, would be required (Paquay and Zeebe, 2013). However, a research agenda should include driving models with realistic deployment scenarios. In the case of quicklime or slaked lime dissolution, the amount of carbon dioxide emitted from the mining, transformation of limestone into quicklime, and transport operations needs to be considered in the calculations. For example, just the transformation of limestone into quicklime releases  $\sim 1.4$  mol  $\text{CO}_2$  / mol limestone (Khesghi, 1995) including  $\sim 0.4$  mol resulting from the burning of coal during the mining operations of limestone plus 1 mol resulting from the transformation of limestone into quicklime (Khesghi, 1995). Therefore, producing large amounts of quicklime without carbon capture and storage would cause undesirable additional  $\text{CO}_2$  release (see Paquay and Zeebe, 2013). Some possible scenarios need to be considered; for example, it is possible that abiotic precipitation of  $\text{CaCO}_3$  takes place following addition of  $\text{CaO}$  and so this scenario would result in additional  $\text{CO}_2$  release. Nevertheless, regionally deployed OAE has the potential to help with recovery of ecosystems impacted by OA; for example, it could be effective in protecting coral reefs against OA (Feng et al., 2016), a major stressor to corals in addition to warming and eutrophication.

### **Biotic Impacts of Alkalinity Addition**

While the biological and ecological repercussions of OA have been extensively explored, the opposite process of alkalization and how it impacts marine life remains largely unknown, and thus there is an urgent need to generate empirical data on the impacts of OAE on marine biota. It is likely that the effects of alkalinity enhancement of terrestrial systems, for example, through agricultural liming, are already affecting the biota of some coastal and estuarine systems (see Guo et al., 2015; Müller et al., 2016), but these impacts remain unknown. It has been proposed that olivine dissolution will likely benefit silicifiers (diatoms) and possibly  $\text{N}_2$  fixers (cyanobacteria) and the release of additional Si, Fe, and Ni could increase productivity, promoting a “green ocean” (see Bach et al., 2019). There are, however, concerns about the potential negative impact of nickel and other metals leached during mineral dissolution on marine organisms and how micronutrient addition will affect the health and structure of marine communities. Indeed Ni toxicity could alter the success of marine organisms and their processes, although there are examples of Ni-limited cyanobacteria that could potentially benefit from Ni supply (Sakamoto and Bryant, 2001; Ho, 2013; Blewett and Wood, 2015b; Montserrat et al., 2017).



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In contrast with the green ocean, a “white ocean” has been proposed as the scenario where calcifiers would profit from the addition of  $\text{CaCO}_3$  derivatives (Bach et al., 2019). In reality, experimental work needs to address these hypotheses and evaluate the consequences of mineral dissolution products. At present, assessing feasibility is hindered due to the complexities of navigating the legal framework to obtain permits for conducting exploratory research in the form of small-scale field deployments in parallel with monitoring and verification. Social acceptance and costs are important considerations.

The release of metals to seawater and the effect on marine organisms is a serious concern. While the impurities in limestone are likely small and negligible in  $\text{CaCO}_3$  derivatives, the possibly toxic elements contained in some silicate rocks may alter the magnitude of primary production and the community structure of primary producers. An issue that has not yet been explored is the potential for bioaccumulation and biomagnification in the food chain, with potentially harmful impacts on food security. Another concern with adding powdered mineral on the ocean surface is that grazers (zooplankton, larvae of fish, echinoderms, etc.) might not discriminate between prey and mineral particles, with potentially damaging impacts. Ingestion of these particles could potentially enhance particle sinking via aggregation into feces, increasing sinking out of the euphotic zone and slowing dissolution (see Harvey, 2008).

Optical impacts of mineral addition are an important consideration when designing mineral deployments. For example, it is known that “white waters” caused by the  $\text{CaCO}_3$  plates produced during coccolithophore blooms can have important ecological consequences including decreased visibility, which affects visual foragers such as seabirds and fish (Baduini et al., 2001) making it difficult to see prey at the surface and possibly excluding some prey from these white waters (Baduini et al., 2001; Lovvorn et al., 2001; Eisner et al., 2005). In an experiment releasing uniform  $\text{CaCO}_3$  particles into the surface mixed layer, the optical signature for kilometer-sized surface patches of mineral particles was short-lived, largely due to horizontal eddy diffusion (Balch et al., 2009). Mesocosm experiments following the fate of Saharan dust (an analog of pulverized mineral addition to seawater) indicated rapid settling velocities, nonlinear export of particulate matter, and the formations of organic-mineral aggregates (Bressac et al., 2012). It is therefore expected that the optical signature associated with mineral deployment will be attenuated rapidly, within timescales of days (Balch et al., 2009).

Experimentation must address optimal particle size, dissolution kinetics in various water bodies, and impacts of trace elements and metals leached into seawater as the mineral dissolves. In the case of olivine, the addition of pulverized mineral in surface ocean waters (see Köhler et al., 2010, 2013) has two main potential issues—the slow dissolution kinetics and the leaching of metals that might have unique impacts on different marine organisms. It has been proposed that olivine grain sizes of  $\sim 10\ \mu\text{m}$  require on the order of 1–20 years (Hangx and Spiers, 2009; Schuiling and de Boer, 2011) while grain sizes on the order of  $1\ \mu\text{m}$  would sink slowly enough to guarantee a nearly complete dissolution within the mixed layer of the open ocean (Köhler et al., 2013), and the energy consumption for grinding might reduce the carbon sequestration efficiency by  $\sim 30$  percent.

For olivine, the biological and ecological repercussions of an increase in nickel from its naturally occurring trace concentrations in seawater ( $0.002\text{--}0.16\ \mu\text{mol/kg}$ ; see IPCS, 1991; Burton et al., 1994) need to be evaluated. Ni toxicity is a concern for some marine organisms and processes including spawning in mysid shrimps; DNA damage and metabolic and cytotoxic effects in the blue mussel *Mytilus edulis*; disruption of ionic balance in the green crab *Carcinus maenas* (Millward et al., 2012; Blewett and Wood, 2015a; Blewett et al., 2015). However, some cyanobacteria representatives might potentially benefit from Ni additions. For example, in the cyanobacterium *Synechococcus*, nitrogen assimilation can be limited by low Ni availability because urease appears to be limited by natural levels of nickel (Sakamoto and Bryant, 2001). In *Trichodesmium*, nickel appears to elevate superoxide dismutase (SOD) activities and nitrogen fixation rates, suggesting SOD protection of nitrogenase from reactive oxygen species inhibition of  $\text{N}_2$  fixation during photosynthesis (Ho, 2013).

Large-scale dispersion of mineral could also affect elemental ratios. Specifically,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  and other trace metals associated with minerals could affect biogeochemistry and organisms’ health. For example, increasing levels of Mg leaching from the mineral could result in increases in the Mg:Ca ratios

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that could affect the stability of carbonate. Indeed, calcite with a higher Mg content has been shown to be less stable in aqueous solutions (Bischoff et al., 1987) and high-Mg calcite is more susceptible to dissolution than aragonite. The amounts of silica, calcium, magnesium, iron, and nickel added alongside alkalinity strongly depend on the impurities of rocks used for OAE (Bach et al., 2019). Metal interference might also be possible; for example, high  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations may interfere with the uptake of nutrients by microorganisms and this is exemplified in the freshwater cyanobacterium *Microcystis aeruginosa*, in which Ca and Mg levels can influence Fe uptake (Fujii et al., 2015). Fe and Ni enrichment from olivine deployment could promote primary production by  $\text{N}_2$ -fixers until other nutrients (e.g., phosphorus) become limiting, leading to a more productive “green(er) ocean,” as depicted by Bach et al. (2019).

Corals have also been studied in relation to Fe availability and although responses to Fe enrichment appear to be strongly dependent on local environmental conditions, particularly the availability of other nutrients (Rädecker et al., 2017), field observations suggest a negative impact of Fe enrichment or Fe toxicity at high concentrations. For example, Fe leaching from shipwrecks has been connected to the abundance of invasive *Corallimorpharia* and benthic fleshy algae (Schroeder et al., 2008; Work et al., 2008; Kelly et al., 2014). Additionally, while modest increases in iron can promote growth, excess Fe concentrations were found to disrupt the coral–algal symbiosis through toxicity (Brown, 1989).

### **Impacts of Biota on Weathering**

In addition to the impacts of weathering on marine biota, organisms can accelerate mineral dissolution and act as catalysts for alkalization. The “benthic weathering engine” was described by Meysman and Montserrat (2017) as a mechanism of enhanced olivine weathering in marine sediments, fueled by microorganisms and invertebrate fauna in a low-pH environment. Indeed, the decomposition of organic matter by complex microbial consortia in the seabed releases  $\text{CO}_2$  and organic acids into the pore solution, resulting in acidification and thus promoting olivine weathering and the dissolution of carbonates, a process termed “metabolic dissolution” (Rao et al., 2012). In these environments, long, filamentous microbes called “cable bacteria” appear to be responsible for acidification (down to pH 5) of the top few centimeters of the sediment (Pfeffer et al., 2012), which promotes dissolution of acid-sensitive minerals (Riisgaard-Petersen et al., 2012; Meysman et al., 2015). In addition to microbes, macrofauna within the sediment can enhance olivine weathering through the process of bioturbation (Meysman et al., 2006). The transit of mineral particles through the gut of benthic fauna such as lugworms under high enzymatic activity and low pH, combined with mechanical abrasion during ingestion and digestion, appear to increase silicate mineral dissolution rates (Mayer et al., 1997; Needham et al., 2004; Worden et al., 2006). A perhaps less-studied process is the natural source of alkalinity via anaerobic degradation of organic matter. For example, the generation of alkalinity in mangrove sediments takes place via sulfate reduction,  $\text{CaCO}_3$  dissolution, denitrification, and ammonification (Krumins et al., 2013). At global scale, alkalinity production in sediments could make a contribution of as much as ~15 percent of the  $\text{CO}_2$  drawdown from the atmosphere in shelf and marginal seas (Thomas et al., 2009; Hu and Cai, 2011).

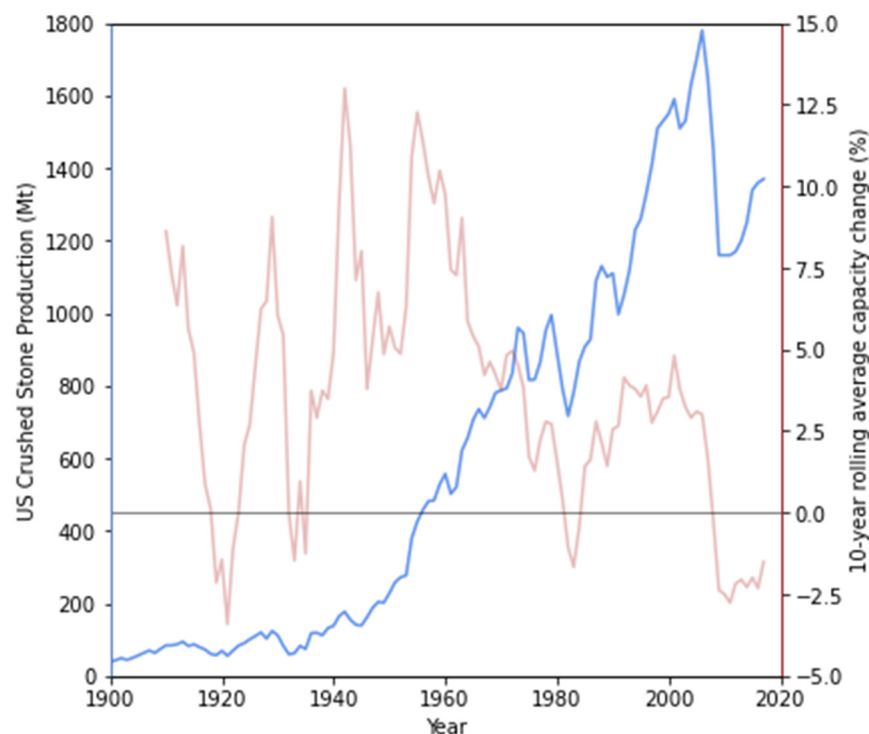
## **7.6 MONITORING AND VERIFICATION**

The monitoring of alterations in ocean conditions on the spatiotemporal scales required to constrain carbon uptake and ecosystem impacts remains a challenge. The main mechanisms to monitor ocean carbonate chemistry are through monthly or seasonal time-series stations at single locations (Bates et al., 2014), discrete measurements on recurrent cruise transects every decade (see Gruber et al., 2007; Talley et al., 2016), and underway measurements of  $p\text{CO}_2$  from research vessels and ships of opportunity (Bakker et al., 2016). Existing programs have been instrumental in providing data to quantify air–sea  $\text{CO}_2$  fluxes and the anthropogenic carbon inventories of the global ocean (Takahashi et al., 2009; Sabine and Tanhua, 2010; Bushinsky et al., 2019). There are, however, limitations for capturing trends and

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spatiotemporal dynamics with a degree of certainty because ship-based observations typically have poor seasonal resolution driven by logistical issues (remote locations and harsh weather conditions preventing operation at sea, disproportion of data associated with summer months, etc.) (Bushinsky et al., 2019). The development of sensors has addressed this issue, and examples include the commercially available SeaFET pH sensor using Honeywell Durafet technology (Martz et al., 2010; 2015), the recently developed ocean robot uncrewed surface vehicle that operates autonomously and provides hourly CO<sub>2</sub> flux estimates (Sutton et al., 2019), and the Moored Autonomous DIC (MADIC) system available for field deployments (Fassbender et al., 2015).

There is technological readiness to conduct all the measurements necessary to assess CDR potential. At least two of four parameters are required to fully describe the marine carbonate system (Millero, 2007). The choice of parameters (pH, partial pressure of CO<sub>2</sub>, DIC, and total alkalinity) depends on the specific process of interest. For example, anthropogenic carbon inventory determinations typically use DIC and total alkalinity while *p*CO<sub>2</sub> is required to study the direction of air–sea CO<sub>2</sub> fluxes and total alkalinity can be used to infer calcification and dissolution processes through the water column (Wanninkhof, 1992; Sabine et al., 2004). Protocols and best practice are already well established, and sensor technology is available in three out of the four parameters of the carbonate system with the exception of alkalinity sensors for which a suite and platform combination does not exist yet on a commercially available level. Current autonomous observational capabilities include surface moorings, fixed observatories, profiling floats, and emerging technologies including autonomous surface vehicles (gliders, autonomous underwater vehicles), which involves repackaging of systems rather than development of new sensors, and the use of wind and waves to power autonomous surface vehicles (see Bushinsky et al., 2019).



**FIGURE 7.5** Annual production of crushed stone in the United States (blue) and the 10-year rolling average change in production in the United States (red). SOURCE: USGS, mineral commodity summaries.

*Ocean Alkalinity Enhancement***7.7 VIABILITY AND BARRIERS****Co-benefits**

The main co-benefits of OAE are the potential mitigation of OA, which would have a positive impact on many organisms, particularly the CaCO<sub>3</sub>-producing community, and the potential for fertilization via the addition of metals such as iron. Assessing the impact of OAE deployments on calcification and the ecological fitness of calcifying organisms and other functional groups requires transitioning from laboratory experimentation and mesocosm-based trials to field deployments to determine the complexity of factors affecting the inorganic carbon chemistry. For example, the balance between ballasting of particulate organic carbon (enhanced by aggregation) and the contribution of calcification and its impact on CDR must be tested in the field under various seasonal and biological conditions (see Section 7.3). Similarly, the physical effect of particles (e.g., potential ingestion by grazers) and chemical impact of raised alkalinity on the physiology of organisms, which could alter important biogeochemical processes (e.g., calcification and silicification), must be explored in the field. For example, it has been suggested that a shift in phytoplankton functional group composition favoring diatoms could occur if silica-rich olivine is used to enhance alkalinity while coccolithophores might be promoted when carbonate-based minerals are used (Köhler et al., 2013; Bach et al., 2019). Additionally, specific regional sensitivities to OAE, for example, the Arctic Ocean and tropical oceans might become hot spots for biogeochemical changes following OAE (see González and Ilyina, 2016).

**Energy**

Proposals for OAE use a range of supply chains, technology options, and energy sources. All proposals involve the extraction, processing, transport, and dissolution of rocks or minerals and thus the energy costs of OAE include mining, transformation, grinding, transportation on land and at sea, monitoring and verification, and building of specialized vessels and pipes (see Figure 7.1). However, to date, a complete life-cycle analysis has not been conducted, and there are no empirical data for a scaled experiment or field trials with calculated energy budgets. This type of analysis is required and must be an element of OAE research schemes.

Limited information on energy consumption includes mineral extraction and grinding. Operations typically use diesel for on-site transport, and either on-site power generation when sites are small and remote (diesel generators, renewables) or power-grid integration. The energy demands to extract a rock and process it to centimeter to millimeter particle sizes is relatively small and routine practice (requiring ~5–20 kWh of electricity per ton CO<sub>2</sub> (Renforth, 2012). However, three times more energy is required to grind particles to diameters of ~10 μm (Hangx and Spiers, 2009). Freight energy requirements and associated emissions depend on the method of transport and distance traveled (Table 7.2). However, transport distances of 10's - 100's of km could still be feasible for OAE schemes (Renforth 2012, Moosdorf et al., 2014).

**TABLE 7.2** Freight Energy Demands and Associated Emissions from Extracted and Processed Minerals

<b>Transport Method</b>	<b>Gaseous CO<sub>2</sub> Emissions, t/km</b>	<b>Energy, MJ/(tonne/km)</b>	<b>Operating Expense, \$(t/km)</b>
Heavy goods vehicle by road	62	1.3	0.07
Rail freight	22	0.2	0.04–0.05
Inland waterways	31		
Large ship distribution	7	0.2	0.001

SOURCE: Adapted from Renforth (2012).

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Processes that facilitate accelerated mineral dissolution typically have the largest energy demand within a supply chain. All OAE approaches require the extraction and processing of minerals. While it is relatively inexpensive to extract and crush rock (tens of kilowatt hours per tonne for size reduction to millimeters), fine grinding requirements depend on mineral dissolution rate (Kelemen et al., 2020). For instance, EW may require on the order of 150–900 kWh/t to create sufficiently micrometer-size (10  $\mu\text{m}$ ) particles (Renforth, 2012). Ocean liming (the creation of  $\text{CaO}$  or  $\text{Ca(OH)}_2$  for addition to the ocean) requires  $\sim 5$  GJ/t of process heat and 150–300 kWh of electricity for the calcination of limestone, the distribution of lime into the ocean, and the geological storage of the produced gas (Kheshgi, 1995; Renforth et al., 2013). Electrochemical approaches may require thousands of kilowatt hours per tonne of  $\text{CO}_2$  (examined in greater detail in Chapter 8). Movement of materials by large ocean-going vessels is relatively less carbon intensive than other methods of transport (Table 7.2). Renforth et al. (2013) estimate that approximately 100 MJ/t of bunker fuel would be required for the distribution of lime into the ocean (which includes both onboard material handling systems and fuel for steaming) from a 300k-deadweight tonnage vessel.

From the range of OAE approaches, only ocean liming has received formalized technoeconomic assessment. Renforth et al. (2013) estimate the cost of ocean liming to be  $\sim \$120/\text{t CO}_2$  for oxy-fuel flash calcination of limestone, but this may be reduced to  $\sim \$70/\text{t CO}_2$  using other systems or dolomite as the mineral feedstock. Caserini et al. (2019) consider the potential integration of ocean liming with biomass energy and hydrogen production. The sale of hydrogen and greater carbon removal suggest costs could be as low as  $\$64/\text{t CO}_2$ . Preliminary calculations estimate that the operational costs of accelerated weathering of limestone may be only on the order of tens of dollars per tonne of  $\text{CO}_2$  (Langer et al., 2009), and that carbonate addition to upwelling regions may be on the same order of magnitude (Harvey, 2008). Costs associated with electrochemical approaches are considered in Chapter 8.

### Governance and Social Dimensions

The legal framework for ocean CDR is discussed in Chapter 2. Many of the international and domestic laws discussed in that chapter could apply to OAE.

With respect to the application of international law, researchers (e.g., Webb et al., 2021) have concluded that OAE would constitute “geoengineering” for the purposes of Decisions X/33, XI/20, and XIII/4, adopted by the parties to the Convention on Biological Diversity.<sup>4</sup> The decisions recommend that parties to the Convention and other governments avoid geoengineering activities that may affect biodiversity, except for “small scale scientific research studies . . . conducted in a controlled setting.”<sup>5</sup> The decisions are not legally binding, however. Additionally, researchers (e.g., Brent et al., 2019; Webb, 2020; Webb et al., 2021) have found that OAE may be considered a form of marine “pollution” under the United Nations Convention on the Law of the Sea and marine “dumping” under the London Convention and Protocol.

As discussed in Chapter 2, in 2013, the parties to the London Protocol adopted an amendment governing “marine geoengineering,” the definition of which is likely to encompass OAE.<sup>6</sup> The 2013 amendment establishes a framework under which parties may approve certain marine geoengineering activities.<sup>7</sup> However, at the time of writing, the framework applied only to activities relating to ocean

<sup>4</sup> Report of the Conference of the Parties to the Convention on Biological Diversity on the Work of its Tenth Meeting, Decision X/33 on Biodiversity and Climate Change, Oct. 29, 2010 (hereinafter Decision X/33); Report of the Conference of the Parties to the Convention on Biological Diversity on the Work of its Eleventh Meeting, Decision XI/20 on Climate-related Geoengineering, Dec. 5, 2012 (hereinafter Decision XI/20); Report of the Conference of the Parties to the Convention on Biological Diversity on the Work of its Thirteenth Meeting, Decision XIII/4, Dec. 10, 2016 (hereinafter “Decision XIII/4”).

<sup>5</sup> Para 8(w), Decision X/33; Para 1, Decision XI/20; Preamble, Decision XIII/4.

<sup>6</sup> Resolution LP.4(8), Amendment to the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972 to Regulate Marine Geoengineering, Oct. 18, 2013.

<sup>7</sup> Annex 4, Resolution LP.4(8).

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fertilization. Researchers (e.g., Brent et al., 2019; Webb et al., 2021) have noted that the framework could be expanded to apply to OAE in the future. However, unless and until that occurs, OAE activities will be subject to the general requirements of the London Convention and Protocol. Both instruments require marine dumping to be permitted by the country under whose jurisdiction it occurs and impose restrictions on when permits can be issued. Webb et al. (2021) concluded that OAE projects could likely be permitted by parties to the London Convention, but not by parties to the London Protocol.

The United States is a party to the London Convention and has implemented it domestically through the Marine Protection, Research, and Sanctuaries Act (MPRSA, 33 U.S.C. § 1401 et seq.). MPRSA applies to the “dumping” of “material” in the oceans (33 U.S.C. § 1411). The statutory definition of “dumping” has been interpreted as encompassing the discharge of ground rock for the purposes of OAE (e.g., Webb et al., 2021). Under MPRSA, OAE projects must be permitted by the Environmental Protection Agency (EPA) if the discharge occurs within the U.S. territorial sea, or if the rock is transported from the United States or on a U.S.-registered vessel (regardless of where the discharge occurs) (33 U.S.C. §§ 1411-1413). EPA must comply with various consultation and other procedural requirements before issuing permits (see Chapter 2).

Previous research (e.g., Webb et al., 2021; Webb, 2020) has examined other domestic laws that could apply to OAE, as well as related onshore activities, such as mining and rock grinding. The domestic laws applicable to onshore activities are not discussed here.

### **7.8 SUMMARY OF CDR POTENTIAL**

The criteria for assessing the potential for OAE as a feasible approach to ocean CDR, described in Sections 7.2–7.7, is summarized in Table 7.3.

### **7.9 RESEARCH AGENDA**

Field trials are urgently needed in both coastal and open-ocean waters to monitor mineral dissolution kinetics, the dynamics of the DIC system, biogeochemical and biological impacts, and carbon sequestration potential, and to assess technological readiness and determine environmental and societal impacts of OAE both in marine systems and on land.

Research consortia and philanthropic endeavors in coastal waters such as the nonprofit Project Vesta that proposes the EW of ground olivine on beaches to increase coastal carbon capture or the planning of pilot studies by the European Union-funded OceanNETs consortium, which includes offshore mesocosm experiments to assess the ecological impacts of OAE, are already under way. The location and characteristics of the offshore deployments remain open questions, although sites where upwelling velocities are high are likely desirable to prevent or delay export of mineral particles to depth. The importance of timing of deployment needs to be addressed in the field because seasonal properties of seawater, including those driven by biological events, alterations in community composition, and conditions leading to changes in dissolved organic matter could have major impacts on particle aggregation and export.

As knowledge of the chemistry and technology for deploying alkalinity matures, monitoring and verification plans need to be implemented to assess site- and temporal-specific dissolution kinetics, rates of alkalization, biological responses, the fate of particles and biogeochemical impacts through the water column, and the air–sea flux of CO<sub>2</sub> through observations using manipulations in mesocosms and the field. The necessary elements of research and development are highlighted in Table 7.5.

*A Research Strategy for Ocean-based Carbon Dioxide Removal and Sequestration***TABLE 7.3** CDR Potential of Ocean Alkalinity Enhancement

<p><b>Knowledge base</b> What is known about the system (low, mostly theoretical, few in situ experiments; medium, lab and some fieldwork, few CDR publications; high, multiple in situ studies, growing body of literature)</p>	<p><b>Low–Medium</b> Seawater–CO<sub>2</sub> system and alkalinity thermodynamics are well understood. Need for empirical data on alkalinity enhancement; currently, knowledge is based on modeling work. Uncertainty is high for carbon dioxide removal (CDR) efficacy and possible impacts.</p>
<p><b>Efficacy</b> What is the confidence level that this approach will remove atmospheric CO<sub>2</sub> and lead to net increase in ocean carbon storage (low, medium, high)</p>	<p><b>High Confidence</b> Need to conduct field deployments to assess CDR, alterations of ocean chemistry (carbon but also metals), how organic matter can impact aggregation, etc.</p>
<p><b>Durability</b> Will it remove CO<sub>2</sub> durably away from surface ocean and atmosphere (low, &lt;10 years; medium, &gt;10 years and &lt;100 years; high, &gt;100 years) and what is the confidence (low, medium, high)</p>	<p><b>Medium–High</b> &gt;100 years Processes for removing added alkalinity from seawater generally quite slow; durability not dependent simply on return time of waters with excess CO<sub>2</sub> to ocean surface.</p>
<p><b>Scalability</b> What is the potential scalability at some future date with global-scale implementation (low, &lt;0.1 Gt CO<sub>2</sub>/yr; medium, &gt;0.1 Gt CO<sub>2</sub>/yr and &lt;1.0 Gt CO<sub>2</sub>/yr; high, &gt;1.0 Gt CO<sub>2</sub>/yr), and what is the confidence level (low, medium, high)</p>	<p><b>Medium–High</b> Potential C removal &gt;0.1–1.0 Gt CO<sub>2</sub>/yr. (medium confidence) Potential for sequestering &gt;1 Gt CO<sub>2</sub>/yr if applied globally. High uncertainty coming from potential aggregation and export to depth of added minerals and unintended chemical impacts of alkalinity addition.</p>
<p><b>Environmental risk</b> Intended and unintended undesirable consequences at scale (unknown, low, medium, high) and what is the confidence level (low, medium, high)</p>	<p><b>Medium</b> (low confidence) Possible toxic effect of nickel and other leachates of olivine on biota, bio-optical impacts, removal of particles by grazers, unknown responses to increased alkalinity on functional diversity and community composition. Effects also from expanded mining activities (on land) on local pollution, CO<sub>2</sub> emissions.</p>
<p><b>Social considerations</b> Encompass use conflicts, governance-readiness, opportunities for livelihoods, etc.</p>	<p>Expansion of mining production, with public health and economic implications; general public’s potential for public acceptability and governance challenges (e.g., if perceived as “dumping”).</p>
<p><b>Co-benefits</b> How significant are the co-benefits as compared to the main goal of CDR and how confident is that assessment</p>	<p><b>Medium</b> (low confidence) Mitigation of ocean acidification; positive impact on fisheries.</p>
<p><b>Cost of scale-up</b> Estimated costs in dollars per metric ton CO<sub>2</sub> for future deployment at scale; does not include all of monitoring and verification costs needed for smaller deployments during R&amp;D phases Low, &lt;\$50/t CO<sub>2</sub>; medium, ~\$100/t CO<sub>2</sub>; high, &gt;&gt;\$150/t CO<sub>2</sub> and confidence in estimate (low, medium, high)</p>	<p><b>Medium–High</b> &gt;\$100–\$150/t CO<sub>2</sub> (low–medium confidence) Cost estimates range between tens of dollars and \$160/tCO<sub>2</sub>. Need for expansion of mining, transportation, and ocean transport fleet.</p>
<p><b>Cost and challenges of carbon accounting</b> Relative cost and scientific challenge associated with transparent and quantifiable carbon tracking (low, medium, high)</p>	<p><b>Low–Medium</b> Accounting more difficult for addition of minerals and non-equilibrated addition of alkalinity, than equilibrated addition.</p>
<p><b>Cost of environmental monitoring</b> Need to track impacts beyond carbon cycle on marine ecosystems (low, medium, high)</p>	<p><b>Medium</b> (medium–high confidence) All CDR will require monitoring for intended and unintended consequences both locally and downstream of CDR site, and these monitoring costs may be substantial fraction of overall costs during R&amp;D and demonstration-scale field projects.</p>
<p><b>Additional resources needed</b> Relative low, medium, high to primary costs of scale-up</p>	<p><b>Medium–High</b> Adaptation and likely expansion of existing fleet for deployment; infrastructure for storage at ports. Infrastructure support for expansion of mineral extraction, processing, transportation, and deployment.</p>

*Ocean Alkalinity Enhancement***TABLE 7.4** Costs and Energy Needs for Ocean Alkalinity Addition

OAE Method, Material	Cost (\$/t CO <sub>2</sub> )	Energy
Land, silicate rock	50-150	100–1,000 kWh/t
Coast, silicate rock	No data	~100–1,000 kWh/t
Ocean, silicate rock	No data	100–1,000 kWh/t
Ocean liming	70-130	5 GJ/t and 150-300 kWh
Accelerated weathering of limestone	10-40 (Opex)	No data
Ocean, carbonate addition to upwelling	20 (Opex)	~100 MJ/t

Specific elements of a research program include

- **Development of an empirical framework for OAE.** Laboratory, mesocosm, and field experimentation in close collaboration with the engineering field to assess the technical feasibility and readiness level of OAE approaches (including the development of pilot-scale facilities). These should include assessments of short- versus long-term deployments under contrasting oceanographic conditions including locations of varying upwelling velocities, different DIC system properties.
- **Assessment of the relationship between approach and environmental impact.** The environmental impact of OAE is closely related to the methods or technologies that promote alkalinity changes (e.g., the choice of rock or mineral and the mechanisms by which it is dissolved). An experimental program that considers the environmental response to OAE will be most effective if they were constrained by what might be practical.
- **Technology development and assessment.** Few of the methods for OAE have been developed beyond bench scale. As such, the costs and feasibility of the approaches remain speculative, which can be substantially improved with a research program designed to accelerate technology development and demonstration of pilot-scale facilities. This would have maximum impact if it were integrated with rigorous technoeconomic and life-cycle assessment.
- **Assessment of the relationship between point of addition and global impact.** All OAE approaches increase alkalinity at the point of addition, and mixing distributes that change across the surface, and, eventually, deep ocean. The impacts are likely to be largest around the point of addition, the magnitude of which will be controlled both by the rate of OAE and hydrodynamics. Research is needed to assess the dispersion or evolution of alkalinity, CO<sub>2</sub> gas exchange, and fate of dissolving particles at locations of OAE, and how these attenuate into regional and global waters.
- **Development of a strong monitoring program.** This would be focused on particulate and DIC at the surface and through the water column at the site of deployment and adjacent waters. This would require a parallel development of protocols for transparent and verifiable deployment, monitoring, and carbon accounting schemes.
- **Research on governance of OAE research.** Research into the legal framework of ocean CDR research and exploration of the legal framework relevant to obtaining permits to conduct field research.



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- **Development of strong educational programs.** This would be achieved through transparent data repository management efforts and engagement with schools and the public and private sectors.
- **Development of life-cycle analyses.** This would include costs such as expansion of mining, materials, transportation, environmental impact assessment, mineral deployment, and monitoring.
- **Development of strong collaborations.** This would include those with social scientists, economists, and governance experts to gain knowledge on public perception, acceptability, and costs.

**7.10 SUMMARY**

Approaches to increase ocean alkalinity have been proposed since the mid-1990s but remain at a relatively early stage of development. OAE attempts to mimic natural weathering processes by adding crushed minerals either directly to the ocean, to coastal environments, or to terrestrial environments. Given that the surface ocean is supersaturated with common carbonate minerals, they cannot be directly added to the ocean. To facilitate mineral dissolution, the reaction of carbonate minerals with elevated CO<sub>2</sub> has been suggested, initially for reducing fossil fuel emissions, but potentially for CDR by coupling with direct air capture or biomass energy carbon capture and storage. Others have proposed converting carbonate minerals into more reactive forms (e.g., lime or hydrated lime) for addition to the ocean. Finally, electrochemical approaches may be used to create basic and acidic solutions at each electrode, the former could be used for OAE while the latter would need to be neutralized through reaction with silicate minerals.

The two key mechanisms by which OAE could impact the environment are (i) elevated alkalinity that is “unequilibrated,” that is, high-pH, low-CO<sub>2</sub> concentrations that may be more acute around the point of addition; and (ii) the addition of other biologically active elements (iron or silica, as in ocean fertilization, or nickel, chromium, or other trace metals). Research is needed to assess the ecological response to OAE. Although much can still be learned from laboratory-based and “contained” (mesocosm) experiments, including exploring the impacts of OAE on the physiology and functionality of organisms and communities, implementation pathways to responsible deployment will require field trials. Such trials will be essential to assess how euphotic and benthic biogeochemical processes are affected, the response from complex communities, the indirect effects of OAE, and optimal environments and treatment methods. Coupling this research to a rigorous monitoring program will be essential in accounting for CDR and the environmental impact of the experiments, but would help scope the requirements of monitoring of scaled-up OAE.

The environmental impact of OAE would be closely related to the methods or technologies that promote alkalinity changes (e.g., the choice of rock or mineral and the mechanisms by which it is dissolved). An experimental program that considers the environmental response to OAE will be most effective if it were constrained by what might be practical. Research and development is required to explore and improve the technical feasibility and readiness level of OAE approaches (including the development of pilot-scale facilities). Research on social and governance considerations associated with contained and pilot-scale experiments and deployment (if any) is also required.

**TABLE 7.5** Research and Development Needs: Ocean Alkalinity Enhancement

#	Research Needs	Gap Filled	Environmental Impact of Research	Estimated Research Budget (\$M/yr)	Timeframe (years)
7.1	Research and development to explore and improve the technical feasibility and readiness level of OAE approaches (including the development of pilot-scale facilities)	Can we develop optimized approaches to enhance alkalinity in seawater?  What are the conditions leading to undesirable effects such as aggregation and reverse weathering?	Low impact of pilot facilities. Initially, most of the work will be lab and mesocosm based.	10	5
7.2	<b>Laboratory and mesocosm experiments to explore impacts on physiology and functionality of organisms and communities</b>	<b>What are the physiological effects of rising alkalinity on marine biota?</b>  <b>What are the effects of OAE on community structure?</b>	<b>Negligible impacts</b>	<b>10</b>	<b>5</b>
7.3	<b>Field experiments</b>	<b>What are the optimal sites to deploy alkalinity?</b> <b>How are biogeochemical processes affected in the euphotic zone as at depth?</b>  <b>How do complex communities respond to OAE?</b>  <b>What are conditions to avoid (e.g., possibly high dissolved organic matter) and those desirable (upwelling regions or estuaries?) to conduct deployments?</b>	<b>Modest impact for experiments conducted on a small spatial and temporal scale</b>	<b>15</b>	<b>5–10</b>
7.4	Research into the development of appropriate monitoring and accounting schemes, covering CDR potential and possible side effects.	Are ships of opportunity (coastal and open ocean) conducting measurements of the carbonate chemistry (through continuous systems) appropriate vehicles to detect change in alkalinity and carbonate chemistry? To what extent do they address CDR potential?  In the mid to long term (>5 years), what are the most appropriate locations and depths to deploy alkalinity sensors?	Modest impact because most of the research and technology supporting monitoring of the dissolved inorganic carbon system and biogeochemical impacts (e.g., calcification) are well established.	10	5–10

NOTE: Bold type identifies priorities for taking the next step to advance understanding of ocean alkalinity enhancement as an ocean CDR approach.