



# CO<sub>2</sub> Removal With Enhanced Weathering and Ocean Alkalinity Enhancement: Potential Risks and Co-benefits for Marine Pelagic Ecosystems

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Humankind will need to remove hundreds of gigatons of carbon dioxide (CO<sub>2</sub>) from the atmosphere by the end of the twenty-first century to keep global warming below 2°C within the constraints of the global carbon budget. However, so far it is unclear if and how this could be achieved. A widely recognized idea is to accelerate weathering reactions of minerals that consume CO<sub>2</sub> when they dissolve. Acceleration could be realized by pulverizing and distributing gigatons of these minerals onto land (termed “enhanced weathering (EW)”) or sea (termed “ocean alkalinity enhancement (OAE)”) thereby largely increasing their reactive surfaces. However, the desired consumption of atmospheric CO<sub>2</sub> during dissolution would inevitably be accompanied by a release of mineral dissolution products (alkalinity, Si, Ca, Mg, Fe, Ni, and maybe others). Here, we approximate their maximum additions to assess potential consequences for pelagic communities (mainly primary producers) and the biogeochemical fluxes they control. Based on this assessment, we tentatively qualify the potential to induce positive and/or negative side effects to be high for Fe, Ni, Si, intermediate for alkalinity, and low for Ca and Mg. However, perturbation potentials are always higher at perturbation hotspots and would be different for EW than for OAE. Furthermore, ecological/biogeochemical consequences of EW/OAE largely depend on the minerals used. We hypothesize that mainly calcifiers would profit in a scheme where CaCO<sub>3</sub> derivatives would be used due to beneficial changes in carbonate chemistry. Figuratively, this may turn the blue ocean into a white(r) ocean. When using silicates, the release of additional Si, Fe and Ni could benefit silicifiers and N<sub>2</sub>-fixers (cyanobacteria) and increase ocean productivity ultimately turning the blue ocean into a green(er) ocean. These considerations call for dedicated research to assess risks and co-benefits of mineral dissolution products on marine and other environments. Indeed, both EW and OAE could become important tools to realize CO<sub>2</sub> removal at the planetary scale but associated risks and/or co-benefits should be revealed before deciding on their implementation.

**Keywords:** plankton, risk assessment, iron, nickel, silicon, silicification, calcification

## FACING REALITY—THE NEED FOR NEGATIVE EMISSIONS TO MEET THE <2°C WARMING GOAL

Anthropogenic emissions of greenhouse gases increase the absorption of heat by the atmosphere thereby inducing global warming (Myhre et al., 2013). It is now widely accepted that anthropogenic warming needs to be limited to not more than 2°C to preserve the Holocene mode of operation of the climate system and thus to prevent intolerable risks for humankind (Schellnhuber et al., 2016). The 2015 Paris Agreement, signed by 194 parties and the European Union, adopted the scientific advice by the Intergovernmental Panel on Climate Change (IPCC) to keep global warming “well below 2°C,” and to “pursue efforts to limit the [average] temperature increase to 1.5°C” (United Nations Framework Convention on Climate Change, 2015). This goal can only be achieved when limiting near future CO<sub>2</sub> emissions to ~480–1,130 gigatons (Gt) (Le Quéré et al., 2016; Rogelj et al., 2016). Hence, when continuing at the current emission rate of ~37 Gt CO<sub>2</sub> per year, the 2°C emission target would be missed in ~13–31 years from now (Peters, 2016; Rogelj et al., 2016).

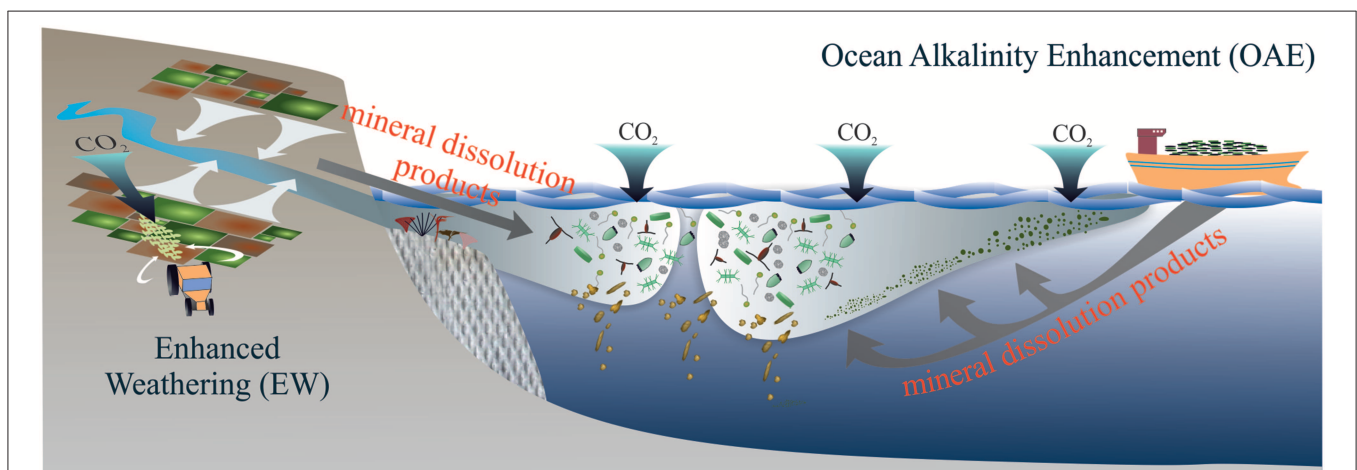
The remaining carbon budget to stay below 2°C calls for immediate and profound emission reductions roughly in the range of 1–10% year<sup>-1</sup> as anticipated in the techno-economic assessments of the RCP2.6 scenarios (Representative concentration pathways leading to ≤2.6 W/m<sup>2</sup> additional radiative forcing) (Rogelj et al., 2016; Rockström et al., 2017). What is widely unknown to the public, however, is that even the very optimistic emission trajectories summarized in RCP2.6 largely fail to remain within the carbon budget constraints for 2°C by decarbonization alone (Peters, 2016). In 108 out of the 116 RCP2.6 scenarios assessed in the last IPCC report, this is only achievable because of the large scale implementation of “negative emission technologies (NETs)” which remove CO<sub>2</sub> from the atmosphere and store it for geological timescales (Rau et al., 2012;

Anderson and Peters, 2016; Peters, 2016; Williamson, 2016; Minx et al., 2018). These NETs must be capable of removing something in the range of 600 Gt CO<sub>2</sub> from the atmosphere by the end of the twenty-first century to maintain a likely chance (i.e., >66%) to meet the <2°C goal (van Vuuren et al., 2011; Anderson and Peters, 2016; Fuss et al., 2016; Sanderson et al., 2016). Thus, the inability of societies to initiate dedicated mitigation now, will likely push us toward the future implementation of climate engineering where NETs will likely play a key role.

## COULD ENHANCED WEATHERING (EW) AND OCEAN ALKALINITY ENHANCEMENT (OAE) HELP TO SOLVE THE CLIMATE CRISIS?

Every NET has a range of economical and geospatial limitations. As such, a portfolio of approaches is needed to achieve carbon dioxide removal from the atmosphere (CDR) at the necessary scale (Nemet et al., 2018). Various NETs have been proposed so far but only a few have developed beyond the laboratory. There is yet little public funding, generally no established legal framework, and no social acceptance to ramp up any NET to the necessary scale (Oschlies and Klepper, 2017; Braun et al., 2018; Nemet et al., 2018). The public reservations are justified since NETs raise ethical concerns (Lin, 2013; Lawford-Smith and Currie, 2017; Shue, 2017; Lenzi, 2018) and may be associated with side effects for the Earth system (Keller et al., 2014; Fuss et al., 2018; Gattuso et al., 2018). However, since NETs will very likely become key tools for keeping global warming below 2°C it is vital to assess their associated environmental risks before their initiation (Oschlies and Klepper, 2017).

“Enhanced Weathering (EW)” and “Ocean Alkalinity Enhancement (OAE)” are two related NETs which are among the options to realize CDR (**Figure 1**). The idea is to accelerate natural rock weathering e.g., by spreading large amounts



**FIGURE 1 |** Schematic overview of EW and OAE. EW and OAE will bring mineral dissolution products into marine environments with so far largely unknown consequences for marine ecosystems and biogeochemical cycling therein. During EW, mineral dissolution products enter the ocean mostly via rivers so that perturbations first occur in estuarine and coastal regions. In the case of OAE, cargo ships could transport the minerals to coastal regions or further offshore and the distribution sites would be impacted most strongly.

of pulverized silicate and/or carbonate minerals onto warm and humid land areas (EW) or onto the sea surface (OAE). The increased exposure of these minerals enhances chemical weathering reactions whereby atmospheric CO<sub>2</sub> is consumed (**Box 1**) (Kheshgi, 1995; Schuiling and Krijgsman, 2006). Idealized Earth system model studies have shown that EW and OAE can mitigate climate change significantly when operated at a scale that is appropriate to the challenge (Caldeira and Rau, 2000; Köhler et al., 2010, 2013; Paquay and Zeebe, 2013; González and Ilyina, 2016; Hauck et al., 2016; Taylor et al., 2016; Feng et al., 2017; Lenton et al., 2018).

EW and OAE may be more amenable to implementation (Taylor et al., 2016). First, CDR through rock weathering is a natural process which consumes 1.1 Gt CO<sub>2</sub> year<sup>-1</sup> already today (Ciais et al., 2013). Second, neither EW nor OAE would require their own land, nutrients, or freshwater (Smith et al.,

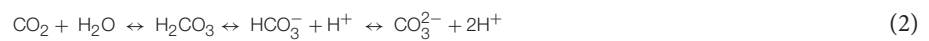
2016; although dust avoidance during EW may need freshwater, Taylor et al., 2016). They could be applied on open ocean regions or combined with agriculture with the additional benefit of enhancing crop yields and preventing soil erosion (Köhler et al., 2010; Beerling et al., 2018; Dietzen et al., 2018). Thus, in contrast to many other NETs, they are generally not competing with other Sustainable Development Goals like global food and water security but are potentially even beneficial for them (Beerling, 2017; Edwards et al., 2017; Heck et al., 2018). Third, EW/OAE-related alkalinity additions would buffer the CO<sub>2</sub>-induced decline in seawater pH (Köhler et al., 2010). Thus, EW/OAE would not only mitigate global warming (and its consequences such as sea level rise) by reducing atmospheric CO<sub>2</sub> but also specifically mitigate ocean acidification which is considered a major threat for marine ecosystems (Doney et al., 2009; Gattuso et al., 2015).

#### BOX 1 | CDR through alkalinity enhancement in aqueous media.

Total alkalinity (TA) is a complex chemical quantity composed of several ions and molecules (Zeebe and Wolf-Gladrow, 2001). TA is defined as the excess of proton acceptors over proton donors with respect to a certain zero level of protons (Dickson, 1981; Wolf-Gladrow et al., 2007). In terms of chemical concentrations this reads as:

$$TA = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{H}_3\text{SiO}_4^-] + [\text{NH}_3] + [\text{HS}^-] - [\text{H}^+] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] \quad (1)$$

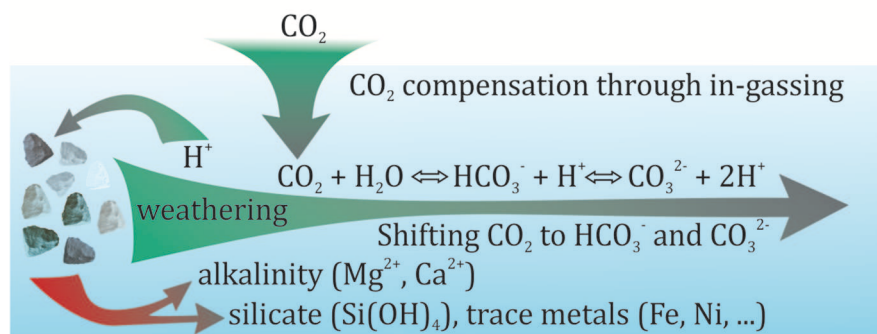
The dissolution of CO<sub>2</sub> in seawater and the subsequent reaction with H<sub>2</sub>O have no effect on TA because the formation of proton donors and acceptors is balanced.



A shift of the carbonate chemistry equilibrium (Equation 2) toward HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> would coincide with decreasing CO<sub>2</sub> concentration so that additional CO<sub>2</sub> from the environment could be absorbed and stored permanently. Such a shift toward HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> can be induced through the dissolution of minerals like olivine (Mg<sub>2</sub>SiO<sub>4</sub>) or quicklime (CaO). H<sup>+</sup> is consumed during the dissolution of these minerals and replaced by conservative ions with positive charges (in our cases Mg<sup>2+</sup> or Ca<sup>2+</sup>) (Pokrovsky and Schott, 2000; Wolf-Gladrow et al., 2007; Oelkers et al., 2018):



The positive charges from Mg<sup>2+</sup> and Ca<sup>2+</sup> must be balanced by negative ones due to the constraint of electroneutrality (Wolf-Gladrow et al., 2007). This ultimately forces the shift from CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> (**Figure 2**) and is measurable as an increase in TA which is the name-giving feature of “ocean alkalinity enhancement.”



**FIGURE 2 |** Graphical summary of CDR through chemical weathering in aqueous media (e.g., soil pore water or seawater). When EW/OAE-relevant minerals (e.g., quicklime or olivine) dissolve they consume protons which shifts the carbonate chemistry equilibrium away from CO<sub>2</sub> to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. Additional CO<sub>2</sub> can subsequently be absorbed by the aqueous media because the shift can cause CO<sub>2</sub> undersaturation relative to the surrounding atmosphere. For EW/OAE it is important that the dissolution occurs as long as the aqueous media is in contact with the atmosphere (e.g., in the surface mixed layer of the ocean) so that the under-saturated medium can be replenished with atmospheric CO<sub>2</sub>.

The minerals appropriate for EW/OAE comprise, for example, naturally occurring Mg-rich olivine-type silicates ( $\text{Mg}_2\text{SiO}_4$ ) (Schuiling and Krijgsman, 2006). These may absorb 1 Gt of  $\text{CO}_2$  for every 1–2 Gt of olivine-rich rocks when accounting for energy expenses due to mining, mineral grinding, and distribution (Moosdorf et al., 2014). Industrially reprocessed carbonates such as quicklime ( $\text{CaO}$ ) are another option (Kheshgi, 1995). To be effective, the energy-related and the chemical  $\text{CO}_2$  emissions during the endothermic calcination of  $\text{CaCO}_3$  in a kiln (i.e.,  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ ) need to be curtailed using carbon capture and storage (CCS) technologies where the generated  $\text{CO}_2$  is stored e.g., in underground reservoirs. For quicklime, a net removal of 1 Gt  $\text{CO}_2$  from the atmosphere would require  $\sim 1.8$  Gt  $\text{CaCO}_3$  source rock to produce  $\sim 0.8$  Gt  $\text{CO}_2$  for CCS and  $\sim 1.2$  Gt of  $\text{CaO}$  (Renforth et al., 2013). This estimation includes energy expenses from mining, mineral grinding, and distribution but note that the  $\text{CO}_2$  emission along the entire process chain could be reduced considerably when using renewable energies (Meier et al., 2006; Renforth et al., 2013).

The natural reserves of source rocks delivering quicklime, olivine, or other suitable minerals are large enough to sequester thousands of gigatons of  $\text{CO}_2$  (Hartmann et al., 2013; Taylor et al., 2016). The additional mining effort needed to remove several gigatons of  $\text{CO}_2$  per year roughly equals efforts of the global cement industry which currently extracts  $\sim 7$  Gt source materials per year (Renforth and Henderson, 2017). Although such amounts are large, they are consistent with the global construction aggregate industry which extracts  $\sim 50$  Gt year<sup>-1</sup> (Beerling et al., 2018). The range of technologies that have been proposed for increasing ocean alkalinity may pose significant engineering challenges. However, preliminary cost analyses suggest that they are within the range of other NETs [ $\$10$ – $\$500$  per ton of  $\text{CO}_2$  (Strefler et al., 2018; Pacala et al., 2019)]. Thus, if the world is serious about the  $<2^\circ\text{C}$  goal and anticipated carbon tax revenues are used to subsidize CDR, then EW/OAE could become economically viable options to realize negative emissions in the twenty-first century.

Under these prospects, it is essential that EW/OAE research expands from feasibility and cost studies to include assessments of risks and co-benefits (Oschlies and Klepper, 2017; Gattuso et al., 2018; Boyd and Vivian, 2019). While this is beginning for terrestrial environments (Beerling, 2017; Beerling et al., 2018), very little is known about impacts on marine systems. Here, several side effects have been conceived (Hartmann et al., 2013; Renforth and Henderson, 2017) but only in four cases were these specifically further investigated *in silico* (Köhler et al., 2013; Hauck et al., 2016) or *in vitro* (Cripps et al., 2013; Gore et al., 2018).

This paper aims to provide a comprehensive overview on potential risks and co-benefits associated with chemical EW/OAE-perturbations for pelagic environments. The overarching goal is to reveal key knowledge gaps thereby providing guidance for necessary future research.

## CHEMICAL PERTURBATIONS OF OCEAN ECOSYSTEMS THROUGH EW/OAE

In the case of EW, pulverized minerals would be distributed onto cropland and forests in warm and humid climates (Köhler et al., 2010; Taylor et al., 2016). The dissolution products originating from the chemical weathering reaction would be partially retained in soils and freshwater systems depending on their individual mobilities. However, a certain fraction would ultimately be discharged into the oceans and primarily affect coastal and estuarine systems (Figure 1; Laruelle et al., 2009; Dürr et al., 2011; Gaillardet et al., 2014). Indeed, anthropogenic alkalinity enhancement through agricultural liming and other activities are likely already occurring in various coastal and estuarine systems (Guo et al., 2015; Müller et al., 2016; Kapsenberg et al., 2017; Kaushal et al., 2018) but the impact of this on the organisms and ecosystems is unknown.

In the case of OAE, mineral dissolution products would be directly placed into the surface ocean and influence ocean biota in coastal and offshore regions without previous modification by the “terrestrial filter” (Figure 1). Logistically, minerals would most likely be added at discrete locations because an even distribution over entire ocean regions seems unfeasible (Köhler et al., 2013). This may lead to the formation of “hotspots” of impact, but this will depend on how minerals are added, the type of material added, and the attenuation/mixing in the surface ocean relative to dissolution rate of the mineral. Most likely, they would be (1) concentrated along ship tracks which disperse the material onto the sea surface (Köhler et al., 2013), (2) in the vicinity of on- and offshore platforms from where the dissolution products are released (Rau et al., 2013), or (3) on beaches or shallow shelf seas where minerals could dissolve on the seafloor and would still be within the mixed layer and therefore in contact with the atmosphere (Hangx and Spiers, 2009; Feng et al., 2017; Meysman and Montserrat, 2017). Accordingly, dissolution products from the weathering reaction will occur in gradients and it will be important to reveal how different ecosystems respond to high and low concentrations of mineral dissolution products.

Previous reviews have listed various suitable minerals for EW/OAE (Hartmann et al., 2013; Renforth and Henderson, 2017). The molecules or elements generated during chemical weathering of these minerals and sustained in solution thereafter comprise for major groups: I) Bicarbonate ( $\text{HCO}_3^-$ ) and carbonate ion ( $\text{CO}_3^{2-}$ ), hereafter summarized as “alkalinity”; II) Silicic acid ( $\text{Si}(\text{OH})_4$ ) hereafter termed silicate; III) Certain alkaline earth metals like calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ) but potentially also alkali metals like sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ); IV) a variety of “trace metals” associated with the minerals. Among these, iron ( $\text{Fe}^{2+}$ , or oxidized aqueous species), nickel ( $\text{Ni}^{2+}$ ) will be the major subject in this paper as these elements occur in high concentrations in basic and ultrabasic rocks (e.g., dunite), which are the most widely recognized source rocks for EW/OAE (Schuiling and Krijgsman, 2006; Hartmann et al., 2013). However, depending on the mineral selected, a wider variety of trace constituents should be considered in the future.



## RISKS AND CO-BENEFITS OF INCREASED ALKALINITY

### Perturbation

The desired effect of EW and OAE is to increase the alkalinity in aqueous media so that additional (ideally atmospheric)  $\text{CO}_2$  can be absorbed (**Figure 2; Box 1**). Idealized modeling studies suggest that EW/OAE could increase surface seawater alkalinity by about 100 to  $>2,000 \mu\text{mol kg}^{-1}$  by the year 2100 although the upper estimates are based on extreme, likely unrealistic, application scales (Köhler et al., 2010, 2013; Ilyina et al., 2013; Paquay and Zeebe, 2013; Keller et al., 2014; González and Ilyina, 2016; Taylor et al., 2016; Feng et al., 2017; Lenton et al., 2018). Alkalinity itself does not affect biology directly because it is a chemical concept, not an ion or molecule that could be sensed by organisms. Nevertheless, the increase in alkalinity substantially modifies pH and the concentrations of various ions and molecules of e.g., the carbonate system which can directly affect biological processes.

In EW applications, new alkalinity will enter the oceans mostly via rivers or streams. These watercourses are usually oversaturated with  $\text{CO}_2$  relative to the atmosphere and release globally about  $1.8 \text{ Gt C year}^{-1}$  mostly from remineralization of terrestrial biomass (Raymond et al., 2013). Hence, the additional alkalinity from EW would likely have exploited its  $\text{CO}_2$  uptake capacity before entering the oceans. In the case of OAE, alkalinity is generated in seawater. The perturbation of seawater carbonate chemistry depends on how much alkalinity is added per volume and/or how quickly this volume mixes with surrounding waters. It also critically depends on how fast the perturbed seawater equilibrates with the atmosphere. For example, alkalinity addition would consume  $\text{CO}_2$  from the surrounding seawater without immediate replenishment from the atmosphere when mineral dissolution occurs in a water body with slow air-sea gas exchange. In such a scenario carbonate chemistry perturbations are more severe than for fast air-sea gas exchange because high pH (i.e., low  $\text{H}^+$ ) excursions are not immediately mitigated by in-gassing  $\text{CO}_2$  (**Figure 3**). To generate negative emissions with OAE, it must be guaranteed that the generated  $\text{CO}_2$  deficit in seawater is compensated with atmospheric  $\text{CO}_2$ . Accordingly, carbonate chemistry perturbations will ultimately have to conform with the “air-equilibrated” scenario shown in **Figure 3**. Nevertheless, reaching this equilibrium may take several years depending on the oceanographic setting (Harvey, 2008; Feng et al., 2017). Thus, more extreme carbonate chemistry perturbations due to “non-equilibrated OAE” at perturbation hotspots may transiently occur (**Figure 3**) and these hotspots will also have a higher potential to affect marine biota.

### Current Understanding and Key Unknowns

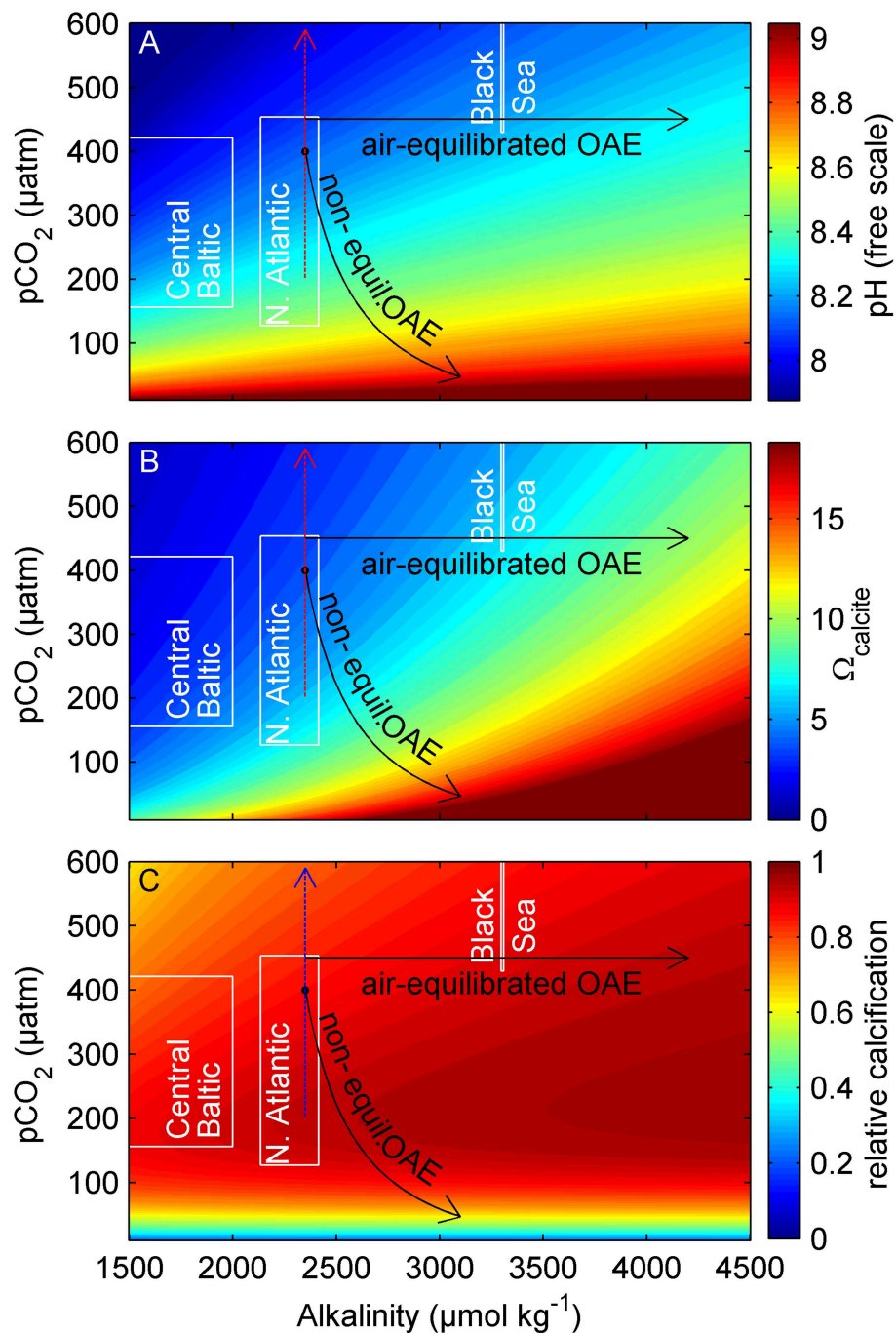
The strong shift in the carbonate system from  $\text{CO}_2$  to  $\text{HCO}_3^-/\text{CO}_3^{2-}$  associated with transient non-equilibrated OAE could potentially drive primary production into  $\text{CO}_2$  limitation (Riebesell et al., 1993). Phytoplankton, for example, can acclimate to  $\text{CO}_2$  limitation with carbon concentrating mechanisms (CCMs) which utilize  $\text{HCO}_3^-$  to support C-fixation (Giordano et al., 2005). However,  $\text{HCO}_3^-$  uptake cannot fully compensate

for limited  $\text{CO}_2$  since  $\text{HCO}_3^-$  must ultimately be converted to  $\text{CO}_2$  for C-fixation and can leak out of the cells before being incorporated in biomass (Rost et al., 2006). The threshold below which phytoplankton growth rates become notably affected by  $\text{CO}_2$  is genotype-specific and depends on growth conditions (e.g., light or temperature) but should generally be roughly below  $\sim 100 \mu\text{atm}$  (Riebesell et al., 1993; Goldman, 1999; Hansen, 2002; Bach et al., 2011; Sett et al., 2014). Thus, phytoplankton growth could be slowed to a variable degree along gradients of mineral dissolution hotspots. However, dilution with unperturbed water masses as well as  $\text{CO}_2$  in-gassing should quickly alleviate the problem so that new production supported by the available nutrients may shift in space and time but rather not with respect to its overall magnitude as it seems unlikely that the nutrients remain unutilized over the course of a seasonal cycle. Nevertheless, the pulses of low  $\text{CO}_2$ /high pH will affect species differentially as some will be more sensitive than others (Hansen, 2002; Pedersen and Hansen, 2003).

Perhaps the most fundamental outcome of more than two decades of ocean acidification research is that carbonate chemistry perturbations affect calcifying organisms disproportionately (Gattuso et al., 2015). Thus, it is meaningful to pay special attention to calcification when considering impacts of increased alkalinity on marine organisms and ecosystems. Ocean acidification (black arrow in **Figure 3**) is predicted to have adverse effects on calcifiers (Orr et al., 2005; Kroeker et al., 2010), mainly due to the increased proton ( $\text{H}^+$ ) concentration and decreased  $\text{CaCO}_3$  saturation state ( $\Omega$ ) (Jokiel, 2011; Bach, 2015; Cyronak et al., 2015; Waldbusser et al., 2015). EW and OAE have the opposite effect on carbonate chemistry conditions. Here,  $\text{H}^+$  decreases while  $\Omega$  increases which could significantly improve the conditions for calcification (**Figure 3**). The Black Sea is a suitable analog for a highly OAE perturbed marginal sea as it has a surface alkalinity of  $\sim 3,300 \mu\text{mol kg}^{-1}$  already today (**Figure 3**). The major planktonic processes in the Black Sea are similar to other oceans (Sorokin, 2002) but there is a remarkable particularity. The Black Sea harbors some of the most extensive blooms of calcifying phytoplankton (coccolithophores) and thick layers of calcareous ooze cover the sediments (Hay, 1988; Kopelevich et al., 2014). These blooms are likely promoted by the favorable carbonate chemistry conditions since coccolithophores are largely absent in the Baltic Sea—a lower alkalinity marginal sea (Müller et al., 2016) with in other respects comparable characteristics to the Black Sea (Tyrrell et al., 2008).

### Important Knowledge Gaps and Testable Hypotheses

We have argued in the previous section that transient shifts in carbonate chemistry conditions should have little impact on the overall productivity of marine ecosystems but could alter the species composition. The latter may be important because even though the perturbation is transient, it could induce knock on effects altering species composition and trophic interactions during the succession following the initial perturbation. Such a restructuring could have more severe biogeochemical consequences than initially anticipated. For



**FIGURE 3 |** Carbonate chemistry perturbation through EW/OAE. **(A)** Proton concentration, **(B)**  $\Omega$  of the  $\text{CaCO}_3$  mineral calcite, and **(C)** relative calcification rates of the coccolithophore *Gephyrocapsa oceanica* as a function of alkalinity and  $p\text{CO}_2$ . The arrows show the trajectories of ocean acidification (dotted), air-equilibrated OAE, and non-equilibrated OAE. Approximate carbonate chemistry conditions of the Baltic Sea, Black Sea, and North Atlantic (0–100 m depth) are shown in white boxes (data from Goyet et al., 1991; Key et al., 2004; Müller et al., 2016). Calculations were done with CO2SYS (Zeebe and Wolf-Gladrow, 2001) ( $T = 15^\circ \text{C}$ ,  $S = 35$ ,  $\text{H}^+$  on free scale,  $K_1$ ,  $K_2$  from Lueker et al., 2000). Calcification sensitivity of *G. oceanica* was determined in experiments and fitted to the coccolithophore calcification model proposed by Bach et al. (2015).

example, the phytoplankton spring bloom is typically dominated by large phytoplankton species (e.g., diatoms) but in the case of acute OAE perturbations the large species could be replaced by smaller ones which are morphologically better suited to deal with

low  $\text{CO}_2$  concentrations (Wolf-Gladrow and Riebesell, 1997; Flynn et al., 2012; Chrachri et al., 2018). Boyd and Newton (1995) compared organic carbon export to the deep ocean of the 1989 and 1990 North Atlantic spring blooms where a large diatom

species was dominant in 1989 and a smaller one in 1990. They found that, while primary production was similar in both years, particulate organic carbon export from the surface to 3,100 m depth was substantially lower in 1990 when the smaller species dominated (Boyd and Newton, 1995). Thus, it will be important to reveal if the transient but possibly pronounced carbonate chemistry perturbations associated with OAE have the potential to alter succession patterns and associated biogeochemical processes such as carbon export on larger scales.

EW/OAE will very likely have a much more sustained impact on calcifiers because the carbonate chemistry changes beneficial for calcification (i.e., increased  $\Omega$ ,  $\text{HCO}_3^-$ ; lower  $\text{H}^+$ ) will be permanent (Figure 3). An expected promotion of calcification through EW/OAE will occur at various scales. At first, low  $\text{H}^+$ /high  $\Omega$  conditions will be sensed at the physiological level and facilitated  $\text{CaCO}_3$  precipitation could allow the organisms to divert more energy into other metabolic processes and growth (Jokiel, 2011; Bach, 2015; Monteiro et al., 2016) (b). This may give calcifiers an energetic advantage and could increase their competitiveness relative to non-calcifiers. Indeed, a recent experiment with natural plankton communities demonstrated that differences in seawater pH can cause seemingly small differences in the growth rates of the dominant calcifier (in this case the coccolithophore *Emiliania huxleyi*) which were sufficient to induce order of magnitude differences in maximum population sizes among treatments (Riebesell et al., 2017). This not only had a considerable influence on the composition of the food web but also strongly altered biogeochemical fluxes such as carbon export or emissions of climate relevant trace gases (Bach et al., 2016; Webb et al., 2016; Riebesell et al., 2017). Accordingly, seemingly small effects of EW/OAE on organism physiology may be amplified in natural environments leading to ecological regime shifts toward calcifying species. Specifying the influence of EW/OAE on pelagic calcification will be important considering the biogeochemical relevance of this process as will be highlighted in the following paragraph.

About 1–2.6 Gt C are precipitated as  $\text{CaCO}_3$  by marine organisms every year (Lebrato et al., 2010). The vast majority of the  $\text{CaCO}_3$  is formed by coccolithophores, foraminifera, and pteropods (Sarmiento and Gruber, 2006; Lebrato et al., 2010). The formation of one mole of  $\text{CaCO}_3$  reduces alkalinity by 2 moles (Zeebe and Wolf-Gladrow, 2001) so that calcification counteracts the desired effect of EW and OAE. For example, net calcification in the surface ocean was increased by 10 % (in mol) through OAE, then 20 % more alkalinity would be consumed and the effectiveness of OAE would be strongly reduced. Furthermore, the EW/OAE-induced increase of  $\Omega$  could decrease  $\text{CaCO}_3$  dissolution in sinking aggregates which are  $\text{CaCO}_3$  under-saturated microenvironments in the surface ocean (Milliman et al., 1999). As a consequence, more alkalinity bound into sinking biogenic  $\text{CaCO}_3$ , would be exported to the deep ocean where its capacity to store atmospheric  $\text{CO}_2$  is not exploited. These relatively easily quantifiable negative feedbacks are complicated by the influence of pelagic calcification on the efficiency of the biological pump (Armstrong et al., 2002; Francois et al., 2002; Klaas and Archer, 2002). If EW/OAE stimulates calcification, then more  $\text{CaCO}_3$  ballast material

becomes available to accelerate sinking velocities of particulate organic carbon (Honjo et al., 2008; Bach et al., 2016). The accelerated sinking could amplify the efficiency of the biological carbon pump because organic carbon that is built with  $\text{CO}_2$  originating from the surface ocean would on average sink deeper into the ocean and lock the respired  $\text{CO}_2$  in the deep ocean for a longer time (Kwon et al., 2009). This amplified deep ocean  $\text{CO}_2$  sequestration of photosynthetically fixed carbon through the higher availability of ballast  $\text{CaCO}_3$  could allow  $\text{CO}_2$  to be taken up more efficiently by the oceans and therefore constitute a positive feedback on the CDR potential of EW/OAE. Thus, the hypothetical proliferation of calcification under EW/OAE applications could have a positive or negative feedback on EW/OAE efficacy, depending on if the “more ballast feedback mechanism” or the “less alkalinity feedback mechanism” become dominant [see (Riebesell et al., 2009) who discussed the influence of these two feedbacks in the context of ocean acidification]. An assessment of the “real” EW/OAE efficacy therefore needs to account for the response of calcifiers to EW/OAE and the biogeochemical feedbacks they drive.

## RISKS AND CO-BENEFITS OF INCREASED SILICATE CONCENTRATIONS

### Perturbation

EW and OAE can be realized with different minerals (Hartmann et al., 2013; Renforth and Henderson, 2017). Olivine-rich silicate rocks like dunite are considered as most effective because they occur naturally, are relatively fast dissolving, and do not require energy-intensive chemical processing before their dissolution (Schuling and Krijgsman, 2006; Renforth and Henderson, 2017). The flipside is that the desired generation of alkalinity coincides with the release of other chemicals such as dissolved silicate (DSi). Dissolving one mole of olivine leads to an increase in total alkalinity by 4 moles and in silicic acid ( $\text{H}_4\text{SiO}_4$ ) by one mole (Köhler et al., 2013; Box 1).

Estimating how much DSi enters pelagic ecosystems is difficult for EW but possible for OAE. The difficulty for EW comes from the unknown fraction of DSi that is retained in soils, as well as on land and in freshwater ecosystems. This retention will most likely be significant although a considerable amount will undoubtedly be discharged into coastal environments (Köhler et al., 2010; Dürr et al., 2011). OAE inputs are easier to assess because OAE only makes sense when all, or at least the vast majority, of the mineral added to the oceans dissolves in water layers which are in contact with the atmosphere within a few years after dissolution. Therefore, it can be assumed that most of the Si contained in silicates such as olivine would dissolve and enrich the DSi pool in the surface ocean. Assessments under more realistic constraints (e.g., accounting for mineral grinding and distribution) suggest that the maximum scale of mineral addition through OAE lies somewhere at around  $10 \text{ Gt year}^{-1}$  which is roughly  $70 \text{ Tmol DSi year}^{-1}$  if dunite was used (Box 2). Thus, OAE would be a source of DSi to the surface ocean that 5–14 fold higher than all natural sources combined (Box 2).



## Current Understanding

DSi is an essential nutrient for silicifying organisms and by far the most important silicifiers in the ocean are diatoms (Tréguer and De La Rocha, 2013). These are a group of globally distributed phytoplankton that utilize DSi to form a shell (frustule) made of biogenic silica (opal) (Sarhou et al., 2005). Diatoms were estimated to contribute ~25% to primary production on Earth (Nelson et al., 1995; Field et al., 1998). They usually initiate the seasonal phytoplankton succession and form blooms until they become nutrient-limited and other taxa with alternative nutrient acquisition strategies take over (Sommer et al., 2012).

DSi is often the nutrient that constrains diatom proliferation because it is highly deficient relative to other macronutrients throughout most subsurface water masses that supply nutrients to the euphotic zone through upwelling (Sarmiento et al., 2004). In fact it is the very “success” of diatoms throughout the Cenozoic that is thought to have driven the decrease in global ocean Si concentration (Conley et al., 2017). The deficiency in modern subsurface waters likely has two reasons. First, the opaline frustule dissolves relatively slowly so that DSi is remineralized on average at greater depths than other nutrients (Dugdale et al., 1995). Second, much of the subsurface water is formed by the subduction of Southern Ocean surface water (Sloyan and Rintoul, 2001). Before this water mass is subducted and spreads northwards, diatoms strip out and export DSi more than other nutrients thereby trapping DSi in the Southern Ocean (Sarmiento et al., 2004; Primeau et al., 2013; Holzer et al., 2014). These mechanisms explain why global diatom productivity in the present oceans is lower than it could be without prevailing shortage of DSi (Ragueneau et al., 2000; Sarmiento et al., 2004).

## Important Knowledge Gaps and Testable Hypotheses

Applications of silicate-based EW and OAE could relieve the present day DSi deficiency (Köhler et al., 2013). The DSi concentrations where diatom DSi uptake rates reach half of the theoretical maximum ( $K_{1/2}$ ) are species specific and range between 0.2 and 22  $\mu\text{mol kg}^{-1}$  (Sarhou et al., 2005). High DSi affinity (i.e., low  $K_{1/2}$ ) typically coincides with lower maximum uptake rates ( $V_{\text{max}}$ ). Accordingly, increased DSi in the surface ocean would favor diatoms with high  $V_{\text{max}}$  and  $K_{1/2}$  and therefore presumably fast-growing species (Sarhou et al., 2005). Furthermore, it could allow diatoms to reduce energy investments for DSi acquisition and enable them to construct thicker frustules (Martin-Jézéquel et al., 2000; Sarhou et al., 2005). Energy savings could accelerate diatom growth rates because available energy can be diverted into the acquisition of other nutrients while reinforced frustules would reduce grazing mortality (Hamm et al., 2003; Wilken et al., 2011; Friedrichs et al., 2013; Liu et al., 2016). Indeed, diatoms typically out-compete other phytoplankton when DSi is plentiful and other essential resources are sufficiently available (Armbrust, 2009). Thus, under silicate-based EW/OAE, diatoms could consume a larger fraction of the other limiting nutrients like N and P and ultimately become more dominant than they are already today. However, it will be important to assess if all diatoms profit equally from DSi enrichment due to the large range of DSi affinities among species (Sarhou et al., 2005). In theory, more heavily silicified diatom species should profit over proportionally from silicate-based EW/OAE as these have inherently higher DSi requirements to satisfy. Thus, it will be important to unravel if silicate-based

### BOX 2 | Additions of key elements in a global OAE scheme.

In this BOX we approximate how much Si, Ca, Mg, Fe, and Ni could be added to the surface ocean under an intense and immediately (i.e., 2020) initiated application of OAE. All approximations should therefore be seen as an upper threshold. Please note that we refrain from approximating element inputs via EW due to the unconstrained degree of element retention by the terrestrial filter. Our estimations are based on idealized scenarios calculated by Köhler et al. (2013), Keller et al. (2014), and Lenton et al. (2018) assuming an even addition of 10 Gt of  $\text{Mg}_2\text{SiO}_4$  (Köhler et al., 2013) or  $\text{Ca}(\text{OH})_2$  (Keller et al., 2014; Lenton et al., 2018) to the surface ocean excluding ice covered areas ( $\text{Ca}(\text{OH})_2$  “slaked lime” is  $\text{CaO} + \text{H}_2\text{O}$ ). For both minerals this results in a TA addition of around 250 Tmol  $\text{year}^{-1}$  because olivine adds double the amount of TA when dissolving but also has roughly double the molecular weight of  $\text{Ca}(\text{OH})_2$ . Lenton et al. (2018) simulated OAE for the twenty-first century also under the low emission scenario RCP2.6 and our estimation follows their scenario because they show that it only makes sense to implement OAE on a global scale when it is accompanied with rapid decarbonization.

The amounts of Si, Ca, Mg, Fe, and Ni added alongside TA strongly depend on the purities of minerals used for OAE. For our estimations we used elemental compositions of dunite provided by the Geochemistry of Rocks of the Oceans and Continents (GEOROCs) database (<http://georoc.mpch-mainz.gwdg.de/georoc/>). Values given in **Table 1** are means  $\pm$ SD of 609 Si, 604 Ca, 665 Mg, 496 Fe, and 145 Ni dunite samples all of which are globally distributed. For CaO, we used approximate compositions of  $\text{CaCO}_3$  precursors from America and central Europe (Gabe and Rodella, 1999; Galván-Ruiz et al., 2009; Šiler et al., 2018).

**Table 1** shows that the perturbation potential under an even distribution of minerals scales with element background concentrations in seawater. When considering a relatively even distribution we would consider the perturbation potentials to be high for Si, Fe Ni, intermediate for TA, and low for Ca and Mg. However, as mentioned in the main text, an even distribution of minerals over the entire surface ocean seems unfeasible due to logistic constraints (Köhler et al., 2013). Thus, even those elements marked with a lower potential under these idealized conditions may have significant influence on pelagic ecosystems at perturbation hotspots where they occur at high concentrations.

It is important to emphasize that all values given in **Table 1** should be seen as rough approximations. Large uncertainties are, for example, due to large variabilities in chemical source rock composition or uncertainties in estimates of natural inputs of TA and the other elements into the oceans. Furthermore, the added amounts do not account for bioavailability of elements. For example, Si in quicklime could be non-soluble quartz so that inferences on bioavailability must consider solubilities of individual phases. Likewise, Fe has generally a low solubility in seawater (Boyd and Ellwood, 2010) so that a very large fraction of the added Fe would presumably not become bioavailable. Nevertheless, in the particular case of Fe, the amounts that would be added in this 10 Gt dunite-based OAE scenario are so large relative to the surface seawater concentration that they could offset Fe limitation in large parts of the ocean even under the assumption that only 0.1% of dunite Fe becomes bioavailable (Hauck et al., 2016).

(Continued)



## BOX 2 | Continued

**TABLE 1** | Estimated additions of key components in an OAE scenario with 10 Gt rock year<sup>-1</sup> (see **BOX 2** for details).

Component	Residence time in the oceans <sup>a</sup> (years)	Dissolved surface ocean concentration <sup>b</sup> ( $\mu\text{mol kg}^{-1}$ )	Natural input of dissolved element into the oceans <sup>c</sup> (Tmol year <sup>-1</sup> )	Source material for OAE	Element content in source rocks (mol kg rock <sup>-1</sup> ) <sup>d</sup>	Amount added via OAE <sup>e</sup> (Tmol year <sup>-1</sup> )	N-fold the natural inputs	Amount added from 2020–2090 (Tmol)	Surface ocean concentration increase by 2090 <sup>f</sup> ( $\mu\text{mol kg}^{-1}$ )
TA	100,000	2,000–2,500	30			250	8	17,500	25–400
Si	10,000	0–80	5–14	Dunite	6.7 $\pm$ 0.6	67	5–14	4,692	
				Carbonate	0.70	7	0.5–1.4	490	
Ca	1,000,000	8,800–11,700		Dunite	0.3 $\pm$ 0.6	3.2		225	0.3–5
				Carbonate	15	150		10,500	15–240
Mg	11,600,000	45,500–60,600	6	Dunite	10 $\pm$ 2.4	101	16	7,045	10–160
				Carbonate	0.4	4	0.7	280	0.4–6
Fe	40	mostly <0.001		Dunite	1.4 $\pm$ 0.5	14		971	
				Carbonate	0.18	2		126	
Ni	4,000–10,000	0.002–0.012	1.5	Dunite	0.04 $\pm$ 0.01	0.4	0.3	30	
				Carbonate	0.00003	0.0003	~0.0002	0.02	

<sup>a</sup>Residence time for TA was estimated by dividing the oceanic inventory ( $\sim 3 \times 10^{18}$  mol) by riverine inputs (next column); Si from Tréguer and De La Rocha (2013); Ni from Gall et al. (2013); other values from Sarmiento and Gruber (2006).

<sup>b</sup>TA from Takahashi et al. (2014); Si from the World Ocean Atlas (<https://www.nodc.noaa.gov/OC5/indprod.html>); Ca and Mg from Zeebe and Wolf-Gladrow (2001) for a salinity range from 30 to 40 assuming conservative behavior; Fe from Schlitzer et al. (2018); Ni from Gall et al. (2013). Please note that the given ranges cover most of the surface ocean but deviations can occur regionally (e.g., Fe can be considerably higher in coastal regions or when affected by dust or hydrothermal plumes).

<sup>c</sup>TA from Amiotte Suchet et al. (2003) with only riverine alkalinity ( $\text{HCO}_3^-$ ) influx considered; Si from Tréguer and De La Rocha (2013); Mg from by Tipper et al. (2006); Ni from Gall et al. (2013). Please note that values for Ca and Fe are not provided due to large uncertainties (Jickells et al., 2005; Fantle and Tipper, 2014). For example, inputs of DFe are hard to quantify as it is difficult to constrain solubilities of particulate Fe sources (Jickells et al., 2005; Boyd and Ellwood, 2010).

<sup>d</sup>Please keep in mind that the element contents within source rocks for EW/OAE vary widely. Given the large globally distributed deposits of silicate and carbonate rocks, it may be possible to extract material to optimize the chemical composition or minimize the environmental impact. Such a procedure would require careful regulation and verification.

<sup>e</sup>The assumption is that 10 Gt of rock coincide with an addition of 250 Tmol TA year<sup>-1</sup>. The other elements are scaled to this mass with the molar contents per kg rock<sup>-1</sup> given in the previous column. Please note that the addition of 250 Tmol TA year<sup>-1</sup> for 10 Gt of rock is an (idealized) upper estimate based on the assumption that pure  $\text{Mg}_2\text{SiO}_4$  or  $\text{Ca}(\text{OH})_2$  dissolve. In reality annual TA additions through 10 Gt rock would likely be lower because such chemical purities will not be reached.

<sup>f</sup>Concentration increase for TA from Lenton et al. (2018) which vary regionally as indicated by the given range. The upper estimate is based on a scenario where TA was added evenly over tropical surface ocean. Please note that an even addition is probably infeasible so that higher concentrations would very likely occur in a more realistic scenario with localized additions. Concentration increases are also provided for Ca and Mg as these should, like TA, behave conservatively.

EW/OAE has the potential to shift diatom communities toward more heavily silicified species.

A particularly interesting aspect in the context of community shifts is the competition between calcifiers and silicifiers. We hypothesized above that calcifiers profit from alkalinity enhancement and would become more dominant under EW/OAE. However, a prerequisite for the success of calcifiers would be that growth of the usually more competitive silicifiers is kept in check by DSi limitation (Egge and Jacobsen, 1997; Tyrrell and Merico, 2004). Under silicate-based EW/OAE, this limitation is relieved so that the fertilization of calcifiers through alkalinity enhancement could be overcompensated by DSi fertilization on silicifiers. Humborg et al. (1997) provide an excellent case study where this effect may actually have been observed. The river Danube contributes ~70 % of the river inputs into the Black Sea but was dammed in the early 1970s. The damming reduced DSi inputs into the Black Sea and promoted coccolithophores at the expense of diatoms (Humborg et al., 1997). The reverse case (i.e., increase of DSi) would be true for silicate-based EW/OAE. Here, calcifiers may not be able to benefit from more favorable carbonate chemistry because silicifiers benefit at the same time. Addressing this is very important because the balance between calcification and silicification has tremendous influence on the efficiency of EW/OAE. For example, if DSi inputs reduce net calcification and the subsequent export of  $\text{CaCO}_3$  into the deep ocean by 10 % (in mol), then 20% more alkalinity remains in the surface ocean to absorb atmospheric  $\text{CO}_2$ . Such a reduction of marine alkalinity sink would enhance the  $\text{CO}_2$  uptake capacity of the oceans and therefore increase the effectiveness of EW/OAE. Indeed, paleo-oceanographic studies suggest that increased DSi leakage from the Southern Ocean during glacial periods may have led to a shift from calcification to silicification globally (Brzezinski et al., 2002). This could have reduced the marine alkalinity sink and enhanced the oceanic  $\text{CO}_2$  uptake capacity to such an extent that it can explain parts of the glacial-interglacial difference in atmospheric  $\text{pCO}_2$  (Matsumoto et al., 2002). It may therefore be an argument to use silicate minerals for EW/OAE as this may reduce the biotic alkalinity sink and thereby indirectly increase the EW/OAE efficacy.

A shift from calcification to silicification under silicate-based EW/OAE would also alter quality and quantity of ballast material in water column.  $\text{CaCO}_3$  has a higher density ( $2.7 \text{ g cm}^{-3}$ ) than BSi ( $2.1 \text{ g cm}^{-3}$ ) and is therefore considered to be more effectively accelerating the sinking of organic matter into the deep ocean (Klaas and Archer, 2002). However,  $\text{CaCO}_3$  ballast is currently considered to be only regionally important in the oceans whereas the influence of BSi ballast is thought to be more widespread (Wilson et al., 2012; Le Moigne et al., 2014; Tréguer et al., 2018). Accordingly, a further increase in diatom biomass and potential shifts toward more heavily silicified diatoms at elevated DSi inputs (see above) may amplify the ballast potential of BSi and therefore carbon export in silicate-based EW/OAE schemes (Köhler et al., 2013). Thus, we speculate that the proliferation of silicifiers, even if this comes at the expense of less pelagic calcifiers, could lead to a net increase of  $\text{CO}_2$  sequestration into the deep ocean and therefore constitute a positive feedback on

EW/OAE efficacy. If true, this could be another argument for silicate minerals.

## RISKS AND CO-BENEFITS OF INCREASED (EARTH) ALKALINE METAL CONCENTRATIONS

### Perturbation

It is expected that the most likely minerals to be used for EW/OAE are Ca or Mg oxides (e.g.,  $\text{CaO}$ ) and/or Ca or Mg silicates (e.g.,  $\text{Mg}_2\text{SiO}_4$ ). Ca and Mg are important ions for all organisms and in particular for calcifiers: Ca as a main ingredient and Mg as an inhibitor of precipitation which is excluded from the mineralisation space (Davis et al., 2000). Due to the high background concentrations of these alkali Earth metals in seawater, the relative change in their concentrations through addition to the surface ocean will be small (**Box 2**). However, it is likely that there will be considerable local perturbations through EW/OAE, and therefore Ca and Mg, at the input location for these schemes, on a regional scale. Biotic impacts through Ca or Mg may be pronounced at these perturbation hotspots before mixing through ocean currents disperses these chemicals to lower concentrations.

### Current Understanding

High intracellular calcium is incompatible with life. At high intracellular concentrations,  $\text{Ca}^{2+}$  causes aggregation of proteins and nucleic acids, affects the integrity of lipid membranes, and can precipitate with cytosolic phosphate removing a major nutrient from bioavailability within the cell (Case et al., 2007). All forms of life, from their origin, need an effective system for Ca homeostasis, which keeps intracellular  $\text{Ca}^{2+}$  at concentrations low enough to prevent apatite precipitation, at levels of  $\sim 0.1 \mu\text{M}$ , and  $\sim 10,000$ – $20,000$  times lower than that in seawater (Carafoli, 1987). Although maintenance of such a large  $\text{Ca}^{2+}$  concentration gradient can be used effectively for Ca signaling as a core component of cellular regulation, it comes at a metabolic cost. Thus, any perturbation of the environmental  $\text{Ca}^{2+}$  concentration could impose an additional metabolic cost to all forms of life from bacteria to the highest eukaryotes, meaning that marine food webs could be affected by high  $\text{Ca}^{2+}$  at perturbation hotspots.

Magnesium is the second most abundant cellular cation after potassium. In comparison to Ca, high intracellular concentrations of total and free magnesium ion ( $\text{Mg}^{2+}$ ) appear to be essential to regulate numerous cellular functions and enzymes, including ion channels, metabolic cycles, and signaling pathways up with intracellular concentrations ranging from 17–20 mmol  $\text{kg}^{-1}$ , just 2.5 times lower than ambient seawater (Romani, 2011). Understanding how cells regulate  $\text{Mg}^{2+}$  homeostasis remains incomplete but again must occur at some, but lesser than Ca, energetic cost to the cell (Romani, 2011).

### Important Knowledge Gaps and Testable Hypotheses

From a biomineralization perspective, it is possible that calcification will benefit from additional  $\text{Ca}^{2+}$  in a quicklime

OAE scheme (Stanley et al., 2005). The influence of Mg in an olivine scheme is more complicated. Mg is known to be a strong inhibitor of inorganic calcite precipitation through incorporation into the  $\text{CaCO}_3$  lattice (Davis et al., 2000). Mg incorporation raises the dissolution rate of the advancing crystal edge, which subsequently increases the mineral solubility, resulting in corresponding reduced net calcification. Aragonite is not inhibited by Mg incorporation into the  $\text{CaCO}_3$  lattice in the same way that calcite is. Incorporation of Mg into aragonite's crystal structure has been shown experimentally to have no effect on growth rate of aragonite crystals (Berner, 1975; Gutjahr et al., 1996). Changes in the concentration of Mg in seawater relative to Ca do appear to be reflected in the plankton fossil record. Here, high Mg/Ca ratios through low absolute Ca concentrations, as in the modern ocean, promoted aragonite, and high Mg-calcite mineralizers. Conversely, low Mg-calcite mineralizers such as the coccolithophores, were more prevalent during the Mesozoic, which was characterized by oceans with low Mg/Ca and high absolute  $\text{Ca}^{2+}$  concentrations (Stanley and Hardie, 1998; Ries, 2010). Therefore, studies in palaeoceanography may be useful to elucidate future changes we could expect from EW/OAE scenarios by acting as suitable analogs.

There is also the possibility that higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations may interfere with the uptake of nutrients by phytoplankton (and/or bacteria). For example, Ca and Mg have been shown to influence Fe uptake in the freshwater cyanobacteria *Microcystis aeruginosa* (Fujii et al., 2015). It is therefore possible that Ca and Mg have similar effects on marine phytoplankton which may have implications from primary production at EW/OAE perturbation hotspots.

Given that foraminifera mineralize first by the engulfing of seawater by a membrane, the low Mg/Ca of their calcite compared to inorganic predictions suggests an active role for pumping of Mg away from the region of mineralization (Segev and Erez, 2006). Two species of benthic foraminifera incorporate more Mg into shells as Mg/Ca increases, suggestive that control on the Mg content of the mineralizing space is not strictly regulated. The greatest increase in precipitation of  $\text{CaCO}_3$  was obtained at Mg/Ca of 1, and not at present-day seawater ratio (Mg/Ca = 5). Thus, it is possible that any decrease (increase) in the Mg/Ca ratio of the ocean will both increase (decrease) the degree of calcification of foraminifera, in addition to making the carbonate less (more) soluble by lowering its Mg/Ca ratio.

Pteropods are holoplanktonic gastropod molluscs which are the major producers of aragonite in the surface ocean today (Andersson et al., 2008). The response of pteropods to changing Mg/Ca is not well-constrained due to the difficulty of keeping pteropods alive in culture (Howes et al., 2014). The origination of the pteropods and rise in prevalence during high Mg/Ca in the Cenozoic may suggest that pteropods are favored by the emerging aragonite sea conditions (Burridge et al., 2017). Accordingly, they could be influenced oppositely to coccolithophores and foraminifera by Mg/Ca alterations associated with EW/OAE.

As a first step, it will be essential to constrain the impact of elevated Ca and/or Mg on the order of magnitude predicted in Table 1. To our knowledge, no work has specifically been completed on the response of plankton other than

coccolithophores or foraminifera to increased Mg, Ca or altered Mg/Ca. This work may also be important to complete for the major group of silicifiers, the diatoms, due to the competition between silicifiers and calcifiers mentioned before. If CaO were added to the ocean, thereby decreasing Mg/Ca, it is reasonable to hypothesize that coccolithophores as competitors of diatoms would be further strengthened and take a larger share of the available nutrient pool. There is huge opportunity for the utilization of palaeoceanographic studies to help with these predictions, due to the rich fossil and sediment record providing evidence of secular changes in Mg/Ca ratios over geological time showing that silicifiers have risen to open ocean dominance in high Mg/Ca oceans (Falkowski et al., 2004).

## RISKS AND CO-BENEFITS OF INCREASED TRACE METAL CONCENTRATIONS

### Perturbation

All minerals suitable for EW/OAE will contain elements considered as “trace metals” (Hartmann et al., 2013; Schlitzer et al., 2018). Trace metals occur at relatively low concentrations in seawater so that perturbations at the scale anticipated for EW/OAE are likely sufficient to have a fertilizing and/or toxic effect on organisms (Hartmann et al., 2013; Moore et al., 2013; Hauck et al., 2016). The diversity of trace metals added to the oceans via mineral dissolution would be large and highly dependent on the source mineral used for EW/OAE. For example, alkaline industrial residuals such as steel slags are considered to be useful for EW/OAE but they can contain trace metals such as Cr, Mo, Ni, Pb which could negatively influence the environment above critical threshold concentrations (Mayes et al., 2008; Renforth, 2019). Likewise, naturally occurring minerals like olivine or source  $\text{CaCO}_3$  for the production of CaO are associated with various elements, depending on their source region. It is beyond the scope of this paper to discuss the potential impacts of all trace elements contained in source material appropriately. We therefore focus on two particularly important ones—iron (Fe) and nickel (Ni). Fe is in focus because it is one of the key nutrients influencing pelagic ecosystems in the surface ocean (Moore et al., 2013; Tagliabue et al., 2017) and is abundant in minerals considered for EW/OAE (Hartmann et al., 2013). Ni is currently not considered as a key nutrient in the surface ocean (Moore et al., 2013) but its abundance in dunite, one of the major candidate rocks for EW/OAE, is very high so that highlighting this element is very reasonable (Meysman and Montserrat, 2017; Beerling et al., 2018).

Fe is rather immobile in soils (Gaillardet et al., 2014) so that Fe enrichment of rivers through EW should be relatively small. However, differences exist among rivers with those that contain large amounts of dissolved organic ligands (“blackwater rivers”) likely transporting more dissolved Fe to the oceans (Krachler et al., 2015; Vieira et al., submitted) which is an important aspect to consider when selecting EW application sites on land. Once riverine Fe reaches the ocean, much of it will be rapidly scavenged, for example by salt-induced flocculation or by settling particles so that Fe perturbations through EW

would be restricted mostly to coastal regions (Boyd and Ellwood, 2010) even though physical conditions at some estuaries (e.g., Congo) could transport material further offshore (Vieira et al., submitted). Ni is not as abundant as Fe in olivine but is more mobile in soils and more soluble in seawater (Gaillardet et al., 2014; Montserrat et al., 2017) so that Ni inputs through EW could be higher in coastal systems and potentially further off-shore. OAE short-circuits the terrestrial filter so that the trace metal contamination of the ocean realm would be significantly larger and directly depend on the dissolution rates of mineral powder and the solubilities of the dissolution products (Montserrat et al., 2017).

## Current Understanding (Fe)

Fe is an essential micronutrient needed as a co-factor in many enzymes (Tagliabue et al., 2017). The concentration of dissolved Fe (DFe) is mostly  $<1 \text{ nmol L}^{-1}$  in the surface ocean where productivity is in large parts Fe-limited (Moore et al., 2013; Schlitzer et al., 2018). Therefore, even a relatively small Fe addition of a few tons to Fe-limited surface ocean regions can induce a massive phytoplankton bloom visible from space (Boyd et al., 2007). The ideal olivine mineral for EW/OAE would be pure forsterite ( $\text{Mg}_2\text{SiO}_4$ ; **Box 1**) but in nature such purity rarely exists. Here, olivines typically occur as a mixture of forsterite and fayalite ( $\text{Fe}_2\text{SiO}_4$ ) (Taylor et al., 2016). A commonly found forsterite/fayalite mixing ratio is  $\sim 9:1$  and this rock type, termed “dunite,” exists in sufficiently large quantities to sequester maybe some hundreds of Gt  $\text{CO}_2$  from the atmosphere (Taylor et al., 2016). Fe enrichment scenarios tested with an Earth System model suggested that this iron fertilization of ocean primary production would increase OAE efficacy roughly by one third (Hauck et al., 2016). However, more recent thermodynamic modeling indicated that fayalite dissolution reduces alkalinity through secondary reactions (Griffioen, 2017), although this could not be confirmed in a dissolution experiment (Montserrat et al., 2017). Thus, the overall influence of Fe perturbations on the CDR potential of EW/OAE is very difficult to determine with our current level of understanding. Fe enrichment could, to a smaller extent, also occur under applications of artificially processed minerals. Quicklime for example is made by calcining natural  $\text{CaCO}_3$  rich source rocks with purities of  $<98\%$  typically achieved at industrial scale (Renforth and Kruger, 2013; Renforth et al., 2013). The majority of the remaining mass is composed of silicate and iron oxides. Therefore, Fe or Si addition when using calcined limestone will certainly be lower than from silicates such as dunite (**Box 2**).

## Important Knowledge Gaps and Testable Hypotheses (Fe)

Iron is often not the most limiting nutrient for phytoplankton in coastal environments as these usually receive DFe supply from sediment fluxes or terrestrial sources (Boyd and Ellwood, 2010). Increased DFe river discharge through EW may therefore have a limited effect on primary production near coasts. In the case of OAE the situation could be different. Counterintuitively, the addition of mineral particles could scavenge bioavailable DFe thereby reducing primary production. This may apply for mineral powder additions in DFe replete regions where DFe

scavenging (adsorption) by volcanic ash particles has been shown to outweigh the Fe release through dissolution thereby leading to a net removal of DFe (Rogan et al., 2016). However, when particles are added to a DFe deficient system the dissolution term outweighs the scavenging term leading to a net increase in DFe (Rogan et al., 2016). Thus, OAE applied in DFe-limited areas should enhance primary production unless the ecosystem is acutely co-limited by other nutrients such as nitrate. Indeed, DFe and N co-limitation is widespread, especially on the edges of sub-tropical gyres (Browning et al., 2017). OAE would strongly relieve DFe but not N limitation thereby favoring  $\text{N}_2$  fixing cyanobacteria (e.g., *Trichodesmium*) which are largely controlled by DFe availability in oligotrophic systems (Mills et al., 2004). It will therefore be essential to test if OAE could stimulate  $\text{N}_2$  fixation rates of cyanobacteria in these regions that may ultimately increase primary production and the CDR efficacy of OAE.

Altogether, the DFe related effects on primary production would most likely coincide with pronounced shifts in the composition of the plankton community. For example, a specific stimulation of cyanobacteria may initiate a reorganization of the energy flow along trophic pathways, ultimately affecting the marine food web in its entirety. Such indirect effects of EW/OAE may even be stronger than the first order chemical perturbation and therefore need to be taken into account (Strauss, 1991; Walsh, 2013). Ultimately, all the positive and negative side-effects that have been anticipated for ocean fertilization with iron (e.g., increased ocean productivity, deep-ocean hypoxia; Oschlies et al., 2010) would also have to be considered in the context of EW/OAE when minerals with considerable Fe content are used.

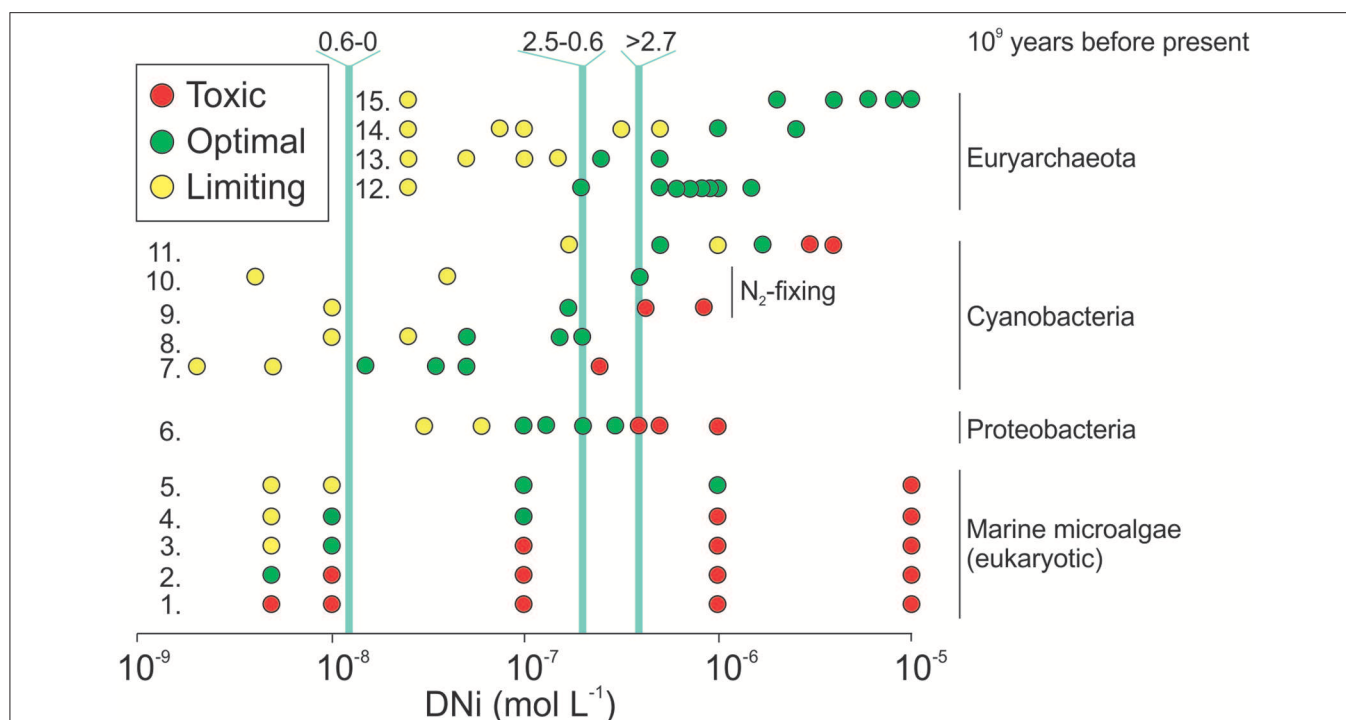
## Current Understanding (Ni)

Ni is rare in the Earth's crust but over-proportionally abundant in forsterite-rich olivine (Simkin and Smith, 1970). Ni is more mobile in soils than Fe especially at low pH and dissolves relatively quickly so that it is currently considered as the most important contaminant under silicate-based EW/OAE (Nieminen et al., 2007; Hartmann et al., 2013; Meysman and Montserrat, 2017; Montserrat et al., 2017; Beerling et al., 2018). It is an essential co-factor in variety of enzymes but Ni nutrient requirements and sensitivities to excess concentrations vary greatly among organisms (**Figure 4**). Eukaryotic microalgae have lower Ni requirements (mostly  $<2 \text{ nmol kg}^{-1}$ ) and are more sensitive to high concentrations than prokaryotes such as cyanobacteria (**Figure 4**). Ni has a higher solubility than Fe and occurs in the surface ocean mostly as  $\text{Ni}^{2+}$  in concentrations of about  $2\text{--}12 \text{ nmol kg}^{-1}$  so that bulk primary production is usually not limited by it (Konhauser et al., 2009; Gall et al., 2013; Moore et al., 2013). This also explains the general absence of a nutrient-like vertical concentration profile of Ni with the exception of the North Pacific (Glass and Dupont, 2017) where occasional Ni limitation of cyanobacteria communities have been observed (Dupont et al., 2010).

## Important Knowledge Gaps and Testable Hypotheses (Ni)

The influence of dissolved Ni (DNi) on pelagic systems has not been a particularly strong focus in Biological Oceanography so





**FIGURE 4 |** Effects of DNi on growth of (marine) microbes. Marine microalgae were grown in urea. The phyla of each microalgae is given in brackets behind each species name based on [www.AlgaeBase.org](http://www.AlgaeBase.org) (Guiry et al., 2014): 1. *Pavlova lutheri* (Haptophyta), *Chaetoceros gracilis* (Bacillariophyta "diatom"), *Olisthodiscus luteus* (Ochrophyta); 2. *Prymnesium parvum* (Haptophyta); 3. *Rhodomonas* sp. (Cryptophyta), *Achnanthes brevipes* (Bacillariophyta "diatom"), *Amphidinium carterae* (Miozoa "dinoflagellate"), *Skeletonema costatum* (Bacillariophyta "diatom"), *Hymenomonas elongata* (Haptophyta), *Porphyridium cruentum* (Rhodophyta); 4. *Thalassiosira* spp. (Bacillariophyta "diatom"); 5. *Cyclotella cryptica* (Bacillariophyta "diatom"); Proteobacteria: 6. *Cupriavidus necator*; Cyanobacteria: 7. *Synechococcus* spp.; 8. *Oscillatoria* sp.; 9. *Nostoc muscorum* (freshwater); 10. *Trichodesmium erythraeum*; 11. *Arthrospira maxima*; Euryarchaeota: 12. *Methanococcus voltae*; 13. *Methanococcoides methylutens*; 14. *Methanobacterium thermoautotrophicum*; 15. *Methanoxithrix soehngenii*; Light blue lines are reconstructed paleo seawater DNi concentrations in  $10^9$  years before present. The figure was adopted from Glass and Dupont (2017) who compiled the data from numerous references. Reproduced by permission of The Royal Society of Chemistry.

far but it may become important in the context of EW/OAE. Here, DNi could either function as nutrient or toxin with pronounced impacts on primary production and plankton community composition.

Recent dissolution experiments with olivine have shown that an increase of alkalinity of about  $100 \mu\text{mol L}^{-1}$  coincided with an increase of  $\sim 3 \mu\text{mol L}^{-1}$  in dissolved Ni (DNi) due to non-stoichiometric dissolution (Montserrat et al., 2017). These DNi concentrations are  $\sim 3$  orders of magnitude higher than ambient concentrations and would likely be harmful for many organisms (Figure 4). Thus, olivine-based EW/OAE could strongly affect marine plankton communities near perturbation hotspots. As for Fe, impacts of DNi will likely differ regionally and depend on the constitution and evolutionary history of plankton communities. For example, communities near estuaries may be adapted to higher DNi concentrations, especially when discharging rivers come from basaltic, olivine rich catchment areas (Nieminen et al., 2007). However, this should be the exception rather than the rule so that we would expect rather detrimental effects on biodiversity and productivity when too much DNi is released locally.

DNi is generally not considered to be an element that is bio-accumulated strongly by organisms (bio-accumulation

= enrichment within organism tissues) (Nieminen et al., 2007). Without bio-accumulation, there is also little potential for Ni bio-magnification along the food chain (i.e., Ni enrichment with increasing trophic level). However, as mentioned earlier, Ni is likely one of the most important trace metal contaminants under olivine-based EW/OAE but certainly not the only one. Other potential trace metals (e.g., Cr, Cu, or Cd) (Simkin and Smith, 1970; Beerling et al., 2018) may become bio-accumulated and bio-magnified, particularly in phytoplankton evolutionarily associated to the "red lineage" (Wilson et al., 2019). Furthermore, a suite of anthropogenic materials (e.g., slag from the production of steel, or mining residuals) could be used for EW (Renforth, 2019). These can contain a range of elemental compositions, and a material by material assessment is required for wider-scale impact. Thus, it may be possible that certain trace metals introduced into the environment via EW/OAE could bio-accumulate and bio-magnify which may cause health problems, particularly for end-members in the food chain like humans (Järup, 2003). It is therefore important to identify minerals associated with such risks and not use them for EW/OAE. Indeed, trace metal toxicity may become a key decisive factor for the acceptability of EW/OAE

applications and strongly influence the choice of rocks that could ultimately be used.

The toxicity-related hypothesis outlined above refers to EW/OAE scenarios where very high DNi concentrations occur. However, after dilution of the perturbation signal in the oceans through space and time DNi may dilute from harmful to fertilizing concentrations (**Figure 4**). Ni is an essential co-factor for enzymes involved in urea cycling and utilization (Nieminen et al., 2007; Glass and Dupont, 2017) and has been shown to limit growth of cyanobacteria- and picoeukaryota-dominated phytoplankton communities (Dupont et al., 2010). Therefore, EW/OAE-related DNi inputs could stimulate primary production in certain oligotrophic settings. Indeed, the growth rate of the predominant  $N_2$ -fixer *Trichodesmium* has been shown to profit strongly from DNi amendments (Ho, 2013) such that ecological regime shifts toward more cyanobacteria in subtropical gyres would be a plausible consequence of olivine-based EW/OAE. If true, moderate increases of DNi may under certain circumstances locally enhance marine productivity and therefore EW/OAE efficacy through a stimulation of  $N_2$ -fixation.

## SYNTHESIZING THE INFLUENCE OF DIFFERENT PERTURBATION SCHEMES IN A COMMON FRAMEWORK

In the sections above we highlighted potential risks and co-benefits associated with individual mineral dissolution products. In the following we try to synthesize the various factors in a common framework to establish potential scenarios under sustained EW/OAE.

EW and OAE at the scale needed for relevant CDR could shift the present day ecological/biogeochemical equilibrium (“blue ocean”) into a new steady state depending on the applied source mineral (**Figure 5A**). Quicklime or other industrially reprocessed minerals should contain relatively fewer contaminants (**Box 2**) so that EW/OAE would mostly constitute an increase of alkalinity and  $Ca^{2+}$ . Here, calcifiers should profit from the favorable carbonate chemistry while silicifiers and  $N_2$ -fixers are affected to a minor extent (perhaps slightly negatively because calcifiers acquire more of the available nutrients). In such a scenario, the blue ocean could turn into the “white(r) ocean” where calcifiers become more important (**Figure 5B**).

When natural minerals such as olivine are used then the desired alkalinity increase coincides with a substantial DSi and trace metal enrichment (**Box 2**). In this scenario, global primary production would likely increase mostly due to Fe fertilization in Fe-limited open ocean regions (Köhler et al., 2013; Hauck et al., 2016). Silicifiers could profit from the additional DSi and strengthen their global dominance. Coccolithophores could be out-competed by silicifiers.  $N_2$ -fixers could profit from Fe and Ni enrichment and reinforce primary production further until other nutrients (e.g., P) become limiting. This transformation under olivine-based EW/OAE could result in a more productive “green(er) ocean” (**Figure 5C**).

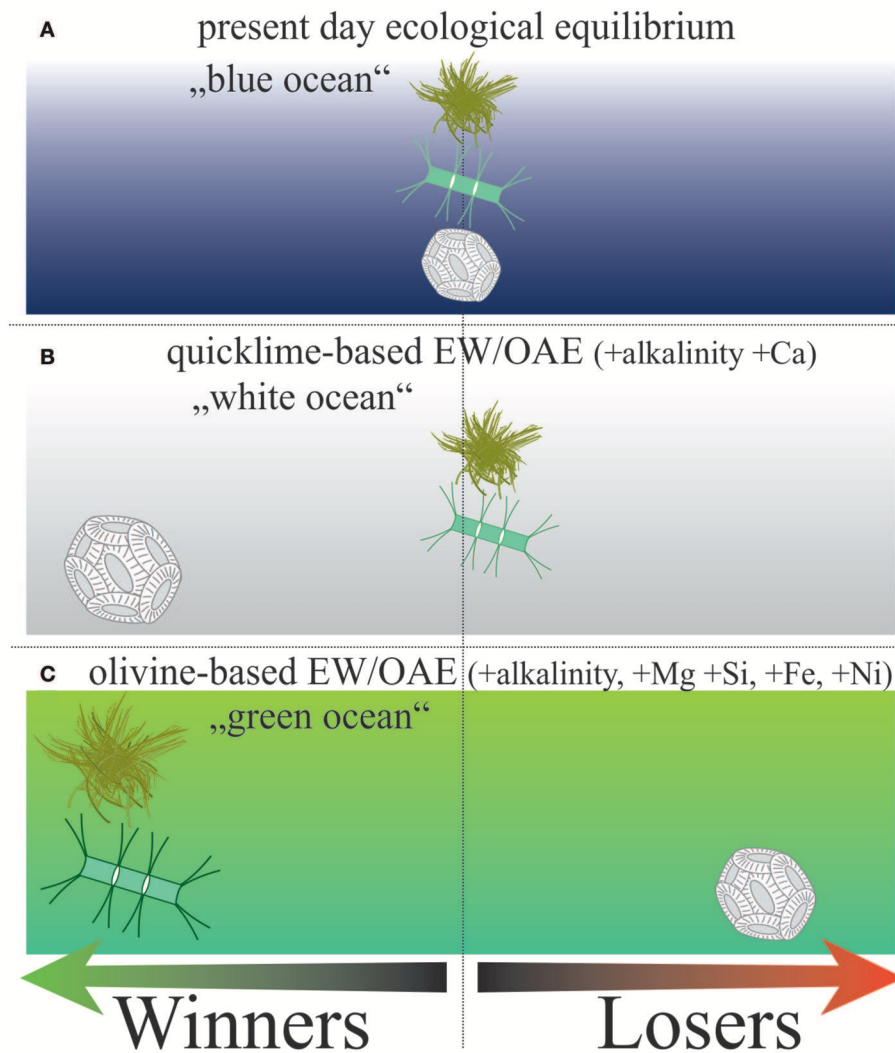
If ecological shifts toward a white(r) or green(er) ocean were shown to be realistic consequences of different EW/OAE schemes, they may influence: 1) if humankind is willing to accept changes of the affected ocean environments including their associated risks and co-benefits; 2) the choice of minerals to be used and amounts to be added in order to find the right balance between CDR efficacy and acceptability of EW/OAE.

## OUTLOOK

The risks and co-benefits discussed in this paper are based upon the presently available information on the most prominent dissolution products of the most widely considered source minerals (quicklime and silicate minerals such as olivine). Future research might reveal other minerals to be more suitable for EW/OAE and these minerals may be associated with other risks and co-benefits. Furthermore, the timing of mineral additions may become an important factor to consider in OAE schemes since side-effects may play out differently when additions occur in different seasons. Finally, we acknowledge that there are most certainly other risks/co-benefits that have been neglected in our discussion and the list will only become more complete once the hands-on research on this topic gained momentum.

Testing the “white or green ocean hypothesis” will require a broad and mechanistic understanding how dissolution products affect species and, more importantly, entire ecosystems. It needs the full scale of experimental approaches, including physiological studies, mesocosms, and modeling. Importantly, lessons learned from previous research efforts suggest that *in situ* surveys should be initiated early in a developing field to cover the ecological complexity of natural plankton communities (Riebesell and Gattuso, 2015). This could be realized by studying natural analogs such the Black Sea as an example for a high alkalinity marginal sea. Likewise, sites of intense natural weathering of basaltic rocks along volcanic islands may provide insights on more regional impacts (Hartmann et al., 2009). Studies of marine paleo-environments may also improve our understanding of EW/OAE, since there are episodes in the geological past where seawater chemistry had similarities to what could be expected under EW/OAE in the future [e.g., higher DNi (Glass and Dupont, 2017) or higher alkalinity (Tyrrell and Zeebe, 2004)].

Ultimately, it will be important to plan and eventually execute (sub-) mesoscale *in situ* OAE experiments since only experiments at the scale envisioned for OAE perturbations can provide a more comprehensive picture of ecosystem-wide impacts (Carpenter, 1996). Indeed, previous mesoscale iron enrichment studies have provided insights on the efficacy and potential side-effects of this NET that would probably not been revealed with conventional methodology (Boyd and Bressac, 2016). However, comprehensive risk assessments for environment including ethical considerations in an open public discourse would have to be made to assess whether such experimentation would be morally acceptable (Lawford-Smith and Currie, 2017; Oschlies and Klepper, 2017; Pidgeon and Spence, 2017; GESAMP, 2019).



**FIGURE 5 |** The “white or green ocean hypothesis.” This schematic drawing synthesizes the potential changes in the present day ecological equilibrium **(A)** under either quicklime-based **(B)** or olivine-based EW/OAE **(C)**. 🌱 = cyanobacteria; 🌀 = coccolithophores; 🌿 = diatoms.

Concerning legal aspects, there is currently some unclarity with respect to the governance for NETs (Boyd and Vivian, 2019). OAE may fall into either national regulation if activities were limited to the inland waters, or the global “London Convention (LC)/ London Protocol (LP),” treaties that regulate marine pollution from the dumping of wastes or other matter at sea [The International Maritime Organization (IMO) listed 87 members to the LC and 51 members to the LP where the latter was agreed to further modernize the LC and eventually replace it (July, 2019; [www.imo.org](http://www.imo.org))]. The LC/LP sets high hurdles on legitimate scientific research involving additions of minerals to the open oceans (e.g., ocean iron fertilization and potentially also open ocean alkalinity enhancement) but does not prohibit it (GESAMP, 2019). EW is not within the scope of the LC/LP because land-based sources of dissolution products would not be considered within their definition of “dumping” materials in the oceans. The assessment of risks and co-benefits of EW/OAE

should therefore be paralleled by the development of a precise regulatory framework that is informed by the independent scientific community (Oschlies and Klepper, 2017; Gattuso et al., 2018; Boyd and Vivian, 2019).

Assessing EW/OAE impacts on ocean ecosystem is a new and understudied research branch in Biological Oceanography but the methodology and the scientific expertise is already largely established. For example, the widespread interest in the marine carbon cycle and ocean acidification has catalyzed the proliferation of global networks of stationary or robotic carbonate chemistry observation platforms which could be used to assess the success of OAE to store CO<sub>2</sub> in seawater (e.g., <http://www.goa-on.org> or <http://biogeochemical-argo.org>). This constitutes an invaluable basis since only certified long-term storage (ideally >>1,000 years) can be used for carbon management. Furthermore, biology-centered ocean acidification research formed a well-trained research community that can

easily design and perform experiments to investigate EW/OAE-related carbonate chemistry impacts on marine biota. Marine Si cycling and trace metal ecotoxicology are equally established research fields and the available knowledge of highly skilled scientists will become invaluable to determine risks and co-benefits of EW/OAE for the oceans. The key challenge is to bring together expertise from already established fields in Biological Oceanography in order to make the necessary progress within the limited timeframe given by the remaining carbon budget to stay below 2°C.

## DATA AVAILABILITY STATEMENT

Publicly available datasets were analyzed in this study. All references where the data is available is given in the corresponding text passages.

## AUTHOR CONTRIBUTIONS

LB conceptualized the research, compiled information in Table 1, composed the figures, and drafted the

manuscript except for section risks and co-benefits of increased (Earth) alkaline metal concentrations. SG and RR drafted risks and co-benefits of increased (Earth) alkaline metal concentrations. All authors revised and improved the manuscript.

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