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Geochemical Negative Emissions Technologies: Part I. Review

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Over the previous two decades, a diverse array of geochemical negative emissions technologies (NETs) have been proposed, which use alkaline minerals for removing and permanently storing atmospheric carbon dioxide (CO₂). Geochemical NETs include CO₂ mineralization (methods which react alkaline minerals with CO₂, producing solid carbonate minerals), enhanced weathering (dispersing alkaline minerals in the environment for CO₂ drawdown) and ocean alkalinity enhancement (manipulation of ocean chemistry to remove CO₂ from air as dissolved inorganic carbon). CO₂ mineralization approaches include *in situ* (CO₂ reacts with alkaline minerals in the Earth's subsurface), surficial (high surface area alkaline minerals found at the Earth's surface are reacted with air or CO₂-bearing fluids), and *ex situ* (high surface area alkaline minerals are transported to sites of concentrated CO₂ production). Geochemical NETS may also include an approach to direct air capture (DAC) that harnesses surficial mineralization reactions to remove CO₂ from air, and produce concentrated CO₂. Overall, these technologies are at an early stage of development with just a few subjected to field trials. In Part I of this work we have reviewed the current state of geochemical NETs, highlighting key features (mineral resources; processes; kinetics; storage durability; synergies with other NETs such as DAC, risks; limitations; co-benefits, environmental impacts and life-cycle assessment). The role of organisms and biological mechanisms in enhancing geochemical NETs is also explored. In Part II, a roadmap is presented to help catalyze the research, development, and deployment of geochemical NETs at the gigaton scale over the coming decades.

Keywords: carbon dioxide removal (CDR), mineral carbonation, enhanced weathering in soils, coastal enhanced weathering, biomineralization, ocean liming, climate change

HIGHLIGHTS

- Geochemical NETs (*in situ*, *ex situ* and surficial carbon mineralization, enhanced weathering, ocean alkalinity enhancement, etc.) are extensively reviewed.
- The potential role of biotechnology in geochemical NETs is given special focus.
- The Review (Part I) is accompanied by a Roadmap (Part II) to help catalyze development of geochemical NETs at scale in the coming decades.

INTRODUCTION

To meet the 2°C climate target set out in the Paris Agreement, the atmospheric concentration of CO₂-equivalent (CO₂eq) should not exceed 450 ppm (or 430 ppm for the 1.5°C target) (Spier, 2020). To achieve this, a drastic decrease in anthropogenic emissions is required, which can be achieved through the expansion of renewable energy generation and lower emissions from land-use and land-use-change. The International Energy Agency (IEA) estimates that carbon capture and storage (CCS), i.e., capturing and storing CO₂ before it is released to the atmosphere, may prevent upwards of 6 Gt CO₂ yr.⁻¹ by 2050 (Haszeldine et al., 2018). In addition, negative emissions technologies (NETs) may also need to remove 10 Gt CO₂ yr.⁻¹ by 2050, and 20 Gt CO₂ yr.⁻¹ by the end of the century (National Academies of Sciences, Engineering, and Medicine, 2019). These targets necessitate technologies capable of capturing, removing, and storing CO₂ at a large scale.

Carbon can be stored as organic materials, e.g., terrestrial vegetation, ocean biomass, and biochar, or as pure CO₂ deep underground in sedimentary rocks. However, the permanence of these storage media vary greatly, creating uncertainty and legacy issues for industry, policymakers, and regulators (Lackner, 2003). On the other hand, carbon can be permanently stored in the form of the carbonate anion (CO₃²⁻) in solid minerals, e.g., calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃), or in the form of dissolved bicarbonate (HCO₃⁻) in ocean water. These forms of storage can be achieved by three main groups of technologies, commonly referred to as CO₂ mineralization, enhanced weathering, and ocean alkalinity enhancement, collectively referred to here as “geochemical NETs.”

Most geochemical NETs involve enhancing the reactions of alkaline minerals with CO₂ (and H₂O), mimicking natural chemical weathering reactions of silicate rocks at the Earth's surface, which removes ~1.1 Gt CO₂ yr.⁻¹ from the atmosphere, primarily stored as ocean bicarbonate (Strefler et al., 2018). The goal of geochemical NETs is to add considerably to this natural removal rate as a tool to combat climate change. In the last two decades, and particularly during the past few years, research on geochemical NETs has grown considerably, with many novel approaches being explored. Several companies and projects have been recently established. Though some are already operating at the kiloton (kt) scale, as a group they are, by and large,

at an early stage of their development, with just a few at the pilot scale.

In Part I of this work, geochemical NETs are reviewed and their potential impacts and limitations discussed. In Part II, a set of projects and interventions that warrant prioritization are presented in the form of a roadmap with the aim of catalyzing the development and deployment of geochemical NETs at the scale necessary to achieve significant carbon removal.

OVERVIEW OF GEOCHEMICAL NETs

A geochemical NET is any technology which involves the use of substantial amounts of alkaline minerals in its flowsheet and involves enhancing the reaction of CO₂ and mineral alkalinity for the purpose of safely removing and storing CO₂ from the atmosphere as stable carbonate minerals, or dissolved ocean bicarbonate. At a fundamental level, most geochemical NETs are simply an acid-base neutralization of the form given in Equation (1).

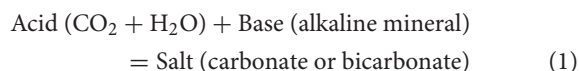
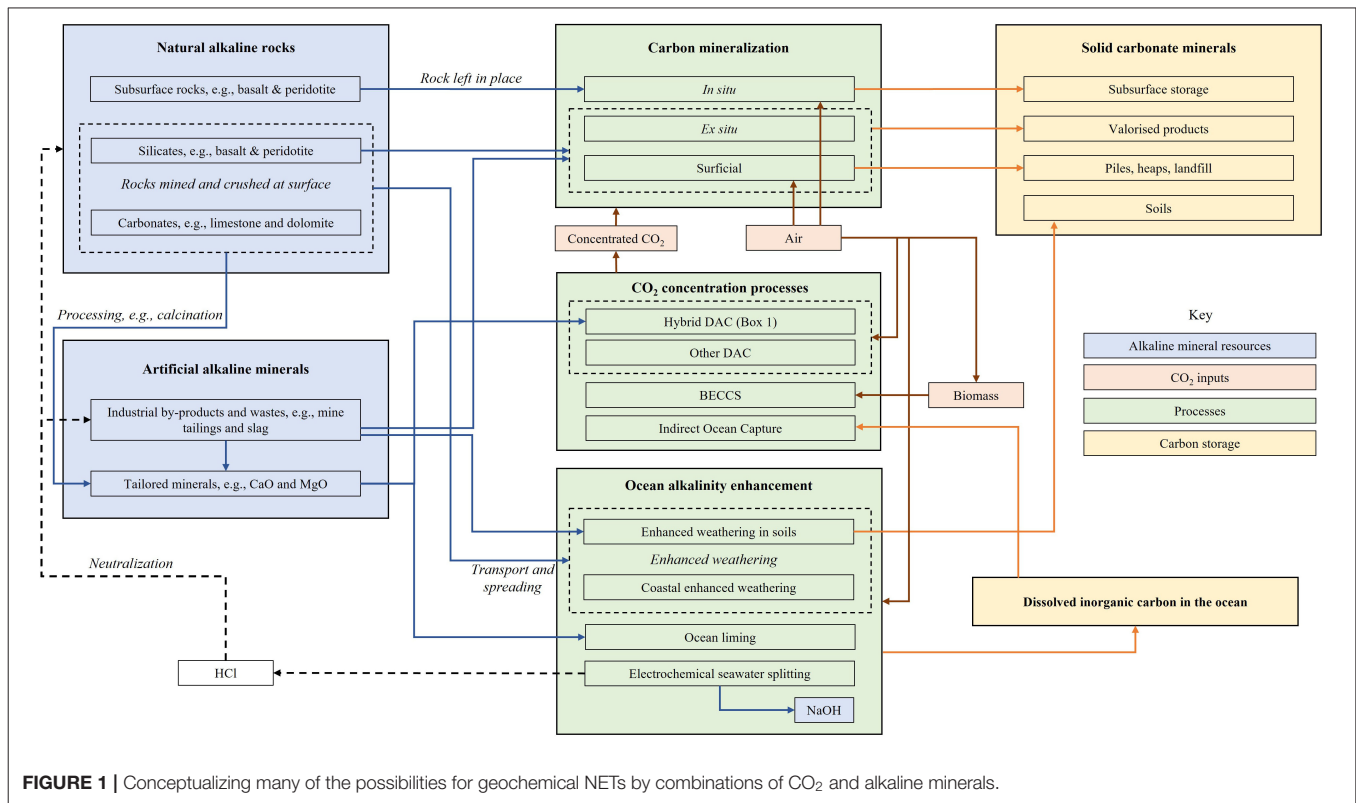


Figure 1 conceptualizes how sources of CO₂ and mineral alkalinity can be combined, giving rise to various geochemical NETs. In order for such a technology to be carbon negative, it must remove significantly more CO₂ than it emits from its life-cycle (Fajardy and Mac Dowell, 2017). Therefore, CO₂ must be removed directly or indirectly from the atmosphere, typically using renewable energy or bioenergy, rather than fossil fuel energy.

In order to create solid carbonate minerals, CO₂ (and H₂O) must react with alkaline minerals (**Table 1**). Alkaline minerals are simply any natural or artificial mineral that is rich in alkaline earth metals (second column of the periodic table), particularly magnesium (Mg) or calcium (Ca), since these are far more abundant than strontium or barium, etc. (which also form stable carbonate minerals). Common Ca- and Mg-rich minerals are given in section the Common Alkaline Minerals. These minerals are found in natural igneous, metamorphic, and sedimentary rocks (section Naturally Occurring Alkaline Rocks) as well as in industrial by-products and wastes such as mine tailings, cement kiln dusts, fly ash, slag, desalination brines, etc., or minerals tailored for purpose (section Artificial Alkaline Minerals—Industrial By-Products and Wastes, and Tailored Minerals and **Table 2**). Abundant silicate minerals rich in alkali metals (first column of the periodic table), in particular sodium and potassium, may be able to contribute in some geochemical NETs, but their carbonates are too soluble for long-term carbon sequestration. While other elements may also form carbonate minerals (e.g., cadmium, cobalt, copper, iron, lead, manganese, nickel, uranium, zinc) their abundance, stability, or toxicity limit their large-scale reaction with CO₂.

Most of the reactions between CO₂, H₂O and mineral alkalinity (section Reaction Chemistry) are thermodynamically



favorable, as indicated by their negative Gibbs free energies. The result of these reactions is either a solid carbonate mineral (section Carbonate Products and Other Secondary Minerals), or dissolved ocean bicarbonate. However, owing to kinetic limitations, the reaction between rock outcrops containing natural alkaline minerals and CO₂ at ambient conditions occurs on geological timescales. Therefore, the main goal of geochemical NETs is to considerably enhance the rate of these reactions to a timescale relevant to climate change mitigation by manipulating the kinetics (section Kinetics).

Those geochemical NETs which predominantly produce solid carbonate minerals (section CO₂ Mineralization), can be divided conceptually into *in situ*, *ex situ* and surficial CO₂ mineralization. *In situ* approaches typically involve circulation of CO₂-rich fluids through alkaline rocks, e.g., basalt or peridotite, in the Earth's subsurface (Matter and Kelemen, 2009). *Ex situ* approaches typically involve reacting high concentration CO₂ with finely ground natural alkaline minerals or artificial alkaline by-products/wastes in engineered reactors. These reactions typically go to completion within minutes using high temperatures, pressures, concentrated CO₂ and/or other reagents such as acids (Sanna and Maroto-valer, 2016). On the other hand, surficial approaches typically involve reaction of air, or CO₂-bearing fluids/gases, with ground minerals at the Earth's surface, occurring more slowly than *ex situ* reactions. Examples include reactions of natural minerals in controlled environments like greenhouses (Myers and Nakagaki, 2020), or in heaps or piles

of artificial wastes such as slags (Stolaroff et al., 2005) or mine tailings (Wilson et al., 2006, 2009). In both *ex situ* and surficial CO₂ mineralization, the carbonate products may be valorized (sold or utilized), whereas in *in situ* approaches the mineralized CO₂ is safely and permanently stored underground. Surficial approaches may also be harnessed for the purpose of cost-effective direct air capture (DAC) (**Box 1**).

Other geochemical NETs involve the dispersing of alkaline minerals for the purpose of enhanced weathering in large open spaces, exploiting certain environmental conditions. Where the reactive medium is soil, this is referred to as enhanced weathering in soil, or terrestrial enhanced weathering (section Enhanced Weathering in Soils) (Schuiling and Krijgsman, 2006). Where the weathering takes place at beaches and coastal shelves, the method is referred to as coastal enhanced weathering (Montserrat et al., 2017). Coastal enhanced weathering is one approach for ocean alkalinity enhancement (OAE), which is any process that involves increasing alkalinity in the oceans, resulting in atmospheric CO₂ removal. Other methods for OAE include ocean liming (Caserini et al., 2021), and a range of electrochemical processes (House et al., 2007; Davies, 2015; Mustafa et al., 2020). The role of alkaline minerals in ocean-based NETs is discussed in the section Ocean Alkalinity Enhancement. Key features of the different geochemical NETs are summarized in **Table 3**. Finally, biological mechanisms that influence geochemical reactions or transport ions may potentially be integrated into many of the above-mentioned

TABLE 1 | Mg-, Ca-, Na-, silicate, oxide, hydroxide, aluminate, carbonate, etc., minerals typically encountered in geochemical NETs, with their Gibbs free energies (ΔG_f) and enthalpies (ΔH_f) of formation (Robie and Hemingway, 1995), and in some cases their Gibbs free energies (ΔG_r) of reaction with H₂O and CO₂ at 1 atm and 25°C [calculated using data from Robie and Hemingway (1995)].

Mineral	Formula	Molar mass (g mol ⁻¹)	ΔG_f (kJ mol ⁻¹)	ΔH_f (kJ mol ⁻¹)	Reaction	ΔG_r (kJ mol ⁻¹)	ΔH_r (kJ mol ⁻¹)
Carbonation – aqueous							
Calcite	CaCO ₃	100.09	-1128.5	-1207.4	CaCO ₃ + CO ₂ + H ₂ O → Ca ²⁺ + 2HCO ₃ ⁻	22.8	-35.9
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	277.11	-4034.0	-4361.7	Mg ₃ Si ₂ O ₅ (OH) ₄ + 6CO ₂ + 5H ₂ O → 3Mg ²⁺ + 6HCO ₃ ⁻ + 2H ₄ SiO ₄	24.7	-308.4
Dolomite	CaMg(CO ₃) ₂	184.41	-2161.3	-2324.5	CaMg(CO ₃) ₂ + 2CO ₂ + 2H ₂ O → Mg ²⁺ + Ca ²⁺ + 4HCO ₃ ⁻	48.6	-86.2
Hydromagnesite	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	546.54	-5864.16	-6514.9	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O + 6CO ₂ → 5Mg ²⁺ + 10HCO ₃ ⁻	27.9	-357.6
Ikaite	CaCO ₃ ·6H ₂ O	208.21	-2540.9	-2954.1	CaCO ₃ ·6H ₂ O + CO ₂ → Ca ²⁺ + 2HCO ₃ ⁻ + 5H ₂ O	12.6	-4.0
Magnesite	MgCO ₃	84.32	-1029.5	-1113.3	MgCO ₃ + CO ₂ + H ₂ O → Mg ²⁺ + 2HCO ₃ ⁻	22.5	-54.1
Monohydrocalcite	CaCO ₃ ·H ₂ O	118.11	-1361.6	-1498.3	CaCO ₃ ·H ₂ O + CO ₂ → Ca ²⁺ + 2HCO ₃ ⁻	18.8	-30.8
Nesquehonite	MgCO ₃ ·3H ₂ O	138.38	-1723.8	-1977.26	MgCO ₃ ·3H ₂ O + CO ₂ → Mg ²⁺ + 2HCO ₃ ⁻ + 2H ₂ O	5.4	-47.5
Sodium carbonate	Na ₂ CO ₃	105.99	-1045.3	-1129.2	Na ₂ CO ₃ + CO ₂ + H ₂ O → 2Na ⁺ + 2HCO ₃ ⁻	-29.9	-51.9
Thermonatrite	NaHCO ₃	124.01	-851.2	-949.0	Na ₂ CO ₃ ·H ₂ O + CO ₂ → 2Na ⁺ + 2HCO ₃ ⁻	-26.2	-37.2
Anorthite	CaAl ₂ Si ₂ O ₈	278.22	-4007.9	-4229.1	CaAl ₂ Si ₂ O ₈ + 2CO ₂ + 3H ₂ O → Ca ²⁺ + 2HCO ₃ ⁻ + Al ₂ Si ₂ O ₅ (OH) ₄	-36.8	-169.2
Diopside	MgCaSi ₂ O ₆	216.57	-3036.6	-3210.7	MgCaSi ₂ O ₆ + 4CO ₂ + 6H ₂ O → Ca ²⁺ + Mg ²⁺ + 4HCO ₃ ⁻ + 2H ₄ SiO ₄	25.4	-189.8
Forsterite	Mg ₂ SiO ₄	140.71	-2053.6	-2173.0	Mg ₂ SiO ₄ + 4CO ₂ + 4H ₂ O → 2Mg ²⁺ + 4HCO ₃ ⁻ + H ₄ SiO ₄	-25.3	-263.2
Jennite	Ca ₉ Si ₆ O ₁₈ (OH) ₆ ·8H ₂ O	927.32	-13644.4	-272.0	Ca ₉ Si ₆ O ₁₈ (OH) ₆ ·8H ₂ O + 18CO ₂ + 10H ₂ O → 9Ca ²⁺ + 18HCO ₃ ⁻ + 6H ₄ SiO ₄	-457.5	-1145.9
Larnite	Ca ₂ SiO ₄	172.25	-2191.2	-823.0	Ca ₂ SiO ₄ + 4CO ₂ + 4H ₂ O → 2Ca ²⁺ + 4HCO ₃ ⁻ + H ₄ SiO ₄	-85.1	-282.0
Rankinite	Ca ₃ Si ₂ O ₇	288.42	-3748.1	-1293.1	Ca ₃ Si ₂ O ₇ + 6CO ₂ + 7H ₂ O → 3Ca ²⁺ + 6HCO ₃ ⁻ + 2H ₄ SiO ₄	-83.2	-386.2
Tobermorite	Ca ₉ Si ₆ O ₁₂ (OH) ₁₀ ·5H ₂ O	588.94	-10466.4	-824.6	Ca ₉ Si ₆ O ₁₂ (OH) ₁₀ ·5H ₂ O + 10CO ₂ + 7H ₂ O → 5Ca ²⁺ + 10HCO ₃ ⁻ + 6H ₄ SiO ₄	-513.0	-941.4
Wollastonite	CaSiO ₃	116.17	-1549.9	-1635.2	CaSiO ₃ + 2CO ₂ + 3H ₂ O → Ca ²⁺ + 2HCO ₃ ⁻ + H ₄ SiO ₄	-5.1	-103.0
Brucite	Mg(OH) ₂	58.33	-833.5	-924.5	Mg(OH) ₂ + 2CO ₂ → Mg ²⁺ + 2HCO ₃ ⁻	-26.2	-135.2
Lime	CaO	56.08	-603.1	-635.1	CaO + 2CO ₂ + H ₂ O → Ca ²⁺ + 2HCO ₃ ⁻	-118.3	-214.7
Periclase	MgO	40.31	-569.2	-601.5	MgO + 2CO ₂ + H ₂ O → Mg ²⁺ + 2HCO ₃ ⁻	-63.5	-172.4
Portlandite	Ca(OH) ₂	74.1	-898.4	-986.1	Ca(OH) ₂ + 2CO ₂ → Ca ²⁺ + 2HCO ₃ ⁻	-60.1	-149.5
CAH10	CaAl ₂ O ₄ ·10H ₂ O	488.14	-4622.3	-	CaAl ₂ O ₄ ·10H ₂ O + 2CO ₂ → Ca ²⁺ + 2HCO ₃ ⁻ + 2Al(OH) ₃ + 6H ₂ O	-68.5	-
C2AH8	Ca ₂ Al ₂ O ₅ ·8H ₂ O	478.2	-4812.8	-	Ca ₂ Al ₂ O ₅ ·8H ₂ O + 4CO ₂ → 2Ca ²⁺ + 4HCO ₃ ⁻ + 2Al(OH) ₃ + 3H ₂ O	-125.3	-
C3AH6	Ca ₃ Al ₂ (OH) ₁₂	378.32	-5019.3	-	Ca ₃ Al ₂ (OH) ₁₂ + 6CO ₂ → 3Ca ²⁺ + 6HCO ₃ ⁻ + 2Al(OH) ₃	-165.8	-
C4AH13	Ca ₄ Al ₂ O ₇ ·13H ₂ O	755.41	-7327.5	-	Ca ₄ Al ₂ O ₇ ·13H ₂ O + 8CO ₂ → 4Ca ²⁺ + 8HCO ₃ ⁻ + 2Al(OH) ₃ + 6H ₂ O	-238.8	-

(Continued)

TABLE 1 | Continued

Mineral	Formula	Molar mass (g mol ⁻¹)	ΔG _r (kJ mol ⁻¹)	ΔH _r (kJ mol ⁻¹)	Reaction	ΔG _r (kJ mol ⁻¹)	ΔH _r (kJ mol ⁻¹)
C2FH8	Ca ₂ Fe ₂ O ₅ ·8H ₂ O	416.01	-3919.0	-	Ca ₂ Fe ₂ O ₅ ·8H ₂ O + 4CO ₂ → 2Ca ²⁺ + 4HCO ₃ ⁻ + Fe ₂ O ₃ + 6H ₂ O	-163.2	-
C3FH6	Ca ₃ Fe ₂ O ₆ ·6H ₂ O	436.05	-4125.5	-	Ca ₃ Fe ₂ O ₆ ·6H ₂ O + 6CO ₂ → 3Ca ²⁺ + 6HCO ₃ ⁻ + Fe ₂ O ₃ + 3H ₂ O	-203.8	-
C4FH13	Ca ₄ Fe ₂ O ₇ ·13H ₂ O	618.27	-6433.7	-	Ca ₄ Fe ₂ O ₇ ·13H ₂ O + 8CO ₂ → 4Ca ²⁺ + 8HCO ₃ ⁻ + Fe ₂ O ₃ + 9H ₂ O	-276.7	-
Tricarboaluminate	Ca ₆ Al ₂ (CO ₃) ₃ (OH) ₁₂ ·26H ₂ O	1147.11	-14536.0	-	Ca ₆ Al ₂ (CO ₃) ₃ (OH) ₁₂ ·26H ₂ O + 9CO ₂ → 6Ca ²⁺ + 12HCO ₃ ⁻ + 2Al(OH) ₃ + 23H ₂ O	-131.0	-
Carbonation – solid							
Anorthite	CaAl ₂ Si ₂ O ₈	278.22	-4007.9	-4229.1	CaAl ₂ Si ₂ O ₈ + CO ₂ + 2H ₂ O → CaCO ₃ + Al ₂ Si ₂ O ₅ (OH) ₄	-59.5	-133.3
Diopside	MgCaSi ₂ O ₆	216.57	-3036.6	-3210.7	MgCaSi ₂ O ₆ + 2CO ₂ + 4H ₂ O → CaCO ₃ + MgCO ₃ + 2H ₄ SiO ₄	-19.9	-99.8
Forsterite	Mg ₂ SiO ₄	140.71	-2053.6	-2173.0	Mg ₂ SiO ₄ + 2CO ₂ + 2H ₂ O → 2MgCO ₃ + H ₄ SiO ₄	-70.3	-155
Gehlenite	Ca ₂ Al ₂ SiO ₇	274.21	-3808.7	-4007.6	Ca ₂ Al ₂ SiO ₇ + 2CO ₂ + 5H ₂ O → 2CaCO ₃ + 2Al(OH) ₃ + H ₂ SiO ₄	-111.6	-237.4
Jennite	Ca ₃ Si ₆ O ₁₈ (OH) ₆ ·8H ₂ O	927.32	-13644.4	-272.0	Ca ₃ Si ₆ O ₁₈ (OH) ₆ ·8H ₂ O + 9CO ₂ + H ₂ O → 9CaCO ₃ + 6H ₄ SiO ₄	-662.4	-822.8
Larnite	Ca ₂ SiO ₄	172.25	-2191.2	-823.0	Ca ₂ SiO ₄ + 2CO ₂ + 2H ₂ O → 2CaCO ₃ + H ₄ SiO ₄	-130.7	-210.2
Lime	CaO	56.08	-603.1	-635.1	CaO + CO ₂ → CaCO ₃	-141.0	-178.8
Merwinite	MgCa ₃ Si ₂ O ₈	328.71	-4339.4	-4566.8	MgCa ₃ Si ₂ O ₈ + 4CO ₂ + 4H ₂ O → 3CaCO ₃ + MgCO ₃ + 2H ₄ SiO ₄	-205.3	-371.5
Rankinite	Ca ₃ Si ₂ O ₇	288.42	-3748.1	-1293.1	Ca ₃ Si ₂ O ₇ + 3CO ₂ + 4H ₂ O → 3CaCO ₃ + 2H ₄ SiO ₄	-151.5	-386.2
Tobermorite	Ca ₃ Si ₆ O ₁₂ (OH) ₁₀ ·5H ₂ O	588.94	-10466.4	-824.6	Ca ₃ Si ₆ O ₁₂ (OH) ₁₀ ·5H ₂ O + 5CO ₂ + 2H ₂ O → 5CaCO ₃ + 6H ₄ SiO ₄	-626.8	-761.9
Wollastonite	CaSiO ₃	116.17	-1549.9	-1635.2	CaSiO ₃ + CO ₂ + 2H ₂ O → CaCO ₃ + H ₄ SiO ₄	-27.8	-67.1
Brucite	Mg(OH) ₂	58.33	-833.5	-924.5	Mg(OH) ₂ + CO ₂ → MgCO ₃ + H ₂ O	-48.7	-81.1
Portlandite	Ca(OH) ₂	74.1	-898.4	-986.1	Ca(OH) ₂ + CO ₂ → CaCO ₃ + H ₂ O	-82.8	-113.6
Periclase	MgO	40.31	-569.2	-601.5	MgO + CO ₂ → MgCO ₃	-75.9	-118.3
	Amorphous silica precipitation*						
	H ₄ SiO ₄ → SiO ₂ + 2H ₂ O					-22.7	-22.3

*The enthalpy and free energy for precipitation of SiO₂ from H₄SiO₄ is given (last row) to enable calculation of the free energy and enthalpy of carbonation reactions where SiO₂ is the product.

TABLE 2 | Current production values for some common artificial minerals used in geochemical NETs, with estimated production values and NET potentials by 2050.

	Current annual production levels (Gt of material)	2050 forecast production (Gt of material)	2050 NET potential (Gt CO ₂ yr. ⁻¹)	References
Ash	0.6–1	17–29	0.07–0.14	Renforth, 2019
Cement—uptake into cement and construction and demolition wastes	1.4–5.8	40–170	1.4–2.0	Renforth, 2019
Mine tailings	9–17		1.1–4.5	Bullock et al., 2021
Red mud	0.12	3.5	<0.1	Renforth, 2019
Slag (BOF, BFS)	0.17–0.5	5–15	0.3–0.5	Renforth, 2019
Desalination brines (dry NaOH)	0.12	0.06	0.2	Gao et al., 2017; Jones et al., 2019; Ihsanullah et al., 2021
Lime (CaO)	0.43	0.9–1.6*	Unknown, but potentially on the order of 0.5–5***	Renforth, 2019
Magnesia (MgO)	0.14	0.5**		José et al., 2020

*Forecast production lower estimate from Renforth (2019), upper estimate assuming additional 10% yr.⁻¹ growth.

**Upper estimate assuming additional 10% yr.⁻¹ growth.

***Lower estimates assuming once through capacity (e.g., ocean liming) on production forecast. Higher estimates for proposals that consider looping Ca or Mg (McQueen et al., 2020) with subsequent geological storage.

BOX 1 | Harnessing surficial mineralization processes for direct air capture.

Direct Air Capture (DAC) requires the removal of CO₂ from the air to produce a concentrated source of CO₂. This concentrated CO₂ can then either be utilized or permanently stored. Surficial mineralization processes have been proposed that fit this definition. For example calcium oxide (Hanak et al., 2017; Hanak and Manovic, 2018) or magnesium oxide (McQueen et al., 2020) looping systems. Calcium looping is a pre- or post-combustion CO₂ capture technology which uses high temperatures. Carbonation is usually performed at around 650°C to form calcium carbonate (CaCO₃). The carbonates, while still hot, are then fed into the next part of the system where they are calcined above 900°C. The calcination step regenerates the lime and produces a more concentrated source of CO₂ which is suitable for CCS (Martínez et al., 2018). Hybrid surficial DAC works similarly, except that CaO or MgO is carbonated under ambient conditions in air, at potentially unlimited scale. The carbonation step in air has slower reaction kinetics than calcium looping processes and is thought to be dependent on a relative humidity above 55% (Erans et al., 2020; Samari et al., 2020). For further details on these and other DAC systems see (Sanz-Pérez et al., 2016; Okesola et al., 2018; McQueen et al., 2021a).

methods to improve efficiency (section Application of Biotechnology to Geochemical NETs).

ALKALINE MINERAL RESOURCES

Common Alkaline Minerals

A mineral is an inorganic solid with distinctive chemical and physical properties, composition, and atomic structure, whereas rocks are an assemblage of minerals. In geochemical NETs, the alkalinity for the neutralization reaction (Equation 1) is usually supplied by abundant Ca- and Mg-rich silicate (or aluminosilicate) minerals, and in some cases the oxides, hydroxides or carbonates of calcium and magnesium (see

Table 1). Potential material resources for magnesium-bearing minerals are much larger than that of calcium owing to their natural availability, while on the other hand, markets for magnesium-based products are much smaller than that of calcium-based products. Minerals rich in other cations such as Na, K, Fe are also considered in some approaches (Kheshgi, 1995; Palandri and Kharaka, 2005; Campbell, 2019).

Naturally Occurring Alkaline Rocks

Alkaline minerals are found in alkaline rocks, including: (i) igneous rocks, such as basalt and peridotite (McGrail et al., 2006; Kelemen and Matter, 2008; Matter and Kelemen, 2009; Clark, 2019; Kelemen et al., 2020), (ii) metamorphic rocks, such as serpentinites (Okamoto et al., 2006; Power et al., 2013b; Bide et al., 2014; Dichicco et al., 2015), and (iii) sedimentary rocks such as limestone and dolomite (Rau and Caldeira, 1999; Rau et al., 2007; Rau, 2011). There are two main types of igneous and metamorphic alkaline rock considered for geochemical NETs: (i) mafic rocks such as basalt, and (ii) ultramafic rocks such as peridotite and serpentinite. Mafic and ultramafic rocks are chemically and physically distinct. For example, mafic rocks typically contain 15–28% MgO, 1–15% CaO, and 46–54% SiO₂ (among other minor components), whereas ultramafic rocks typically contain 35–46% MgO, 5–15% CaO, and 42–48% SiO₂ (Sen, 2014). Depending on the particular geochemical NET, some rock types might be more suitable than others, e.g., olivine may be more promising than basalt in enhanced weathering approaches. For *in situ* mineralization, both mafic (e.g., basalt) and ultramafic (e.g., peridotite and serpentinite) formations with suitable properties, such as high porosities and permeabilities, will allow for cost-effective storage. Together, mafic and ultramafic rocks represent over 90 teratonnes (Tt) of resources, sufficient to store the equivalent of 700-years worth

TABLE 3 | Qualitative comparison of geochemical NET processes.

	CO ₂ mineralization				Enhanced weathering and ocean alkalinity enhancement		
	<i>In situ</i>	<i>Ex situ</i>	Surficial	Enhanced weathering in soils	Enhanced weathering at coasts	Ocean liming	Electrochemical seawater splitting
Where?	Subsurface	Reactors	Heaps, piles, ponds, greenhouses	Forest and agricultural soils	Beaches and coastal shelves	Oceans	Coastal zones and oceans
CO ₂ source	Suited for industrial flue gases, but also air/DAC	Industry (potentially also DAC)	Air/DAC/industry	Air	Air	Air	Air
If concentrated CO ₂ is used, is it retained?	Yes, minor losses	Yes	Potential losses	N/A	N/A	N/A	N/A
CO ₂ transport?	Some approaches	No	Some approaches	N/A	N/A	N/A	N/A
Mineral transport?	Rocks in place	Rocks transported to CO ₂ sources	Minimal transport, some spreading	Transport and spreading	Transport and spreading	Transport and spreading	Rocks transported to electrochemical reactor
Carbon products	Carbonate minerals	Carbonate minerals	Carbonate minerals	Carbonate minerals, ocean (b)carbonate	Ocean (b)carbonate	Ocean (b)carbonate	Ocean (b)carbonate
Can carbon products be utilized?	No	Yes	Yes	No	No	No	No
Temperature and pressure	Rock formation dependent (depth)	Likely non-ambient	Ambient	Ambient	Ambient	Non-ambient (calcination)	N/A
Enhancements	CO ₂ concentration, reaction driven cracking, H ₂ O/CO ₂ ratio, additives	Grinding, mixing, agitation, sonication, acids, salts, additives, pre-treatments, CO ₂ concentration, solid-liquid ratio, humidity	Grinding, mixing, agitation, sonication, dispersing minerals, sparging, CO ₂ concentration, solid-liquid ratio, humidity	Comminution. Physical, chemical and biological location-dependent weathering	Comminution. Physical, chemical, and biological location-dependent weathering	Calcination to produce highly reactive CaO	Electricity
CO ₂ removal rate	Days to years	Minutes	Weeks to months	Years	Years	Weeks	Weeks
Potential removal scale	Gt CO ₂ yr. ⁻¹	Mt CO ₂ yr. ⁻¹	Mt CO ₂ yr. ⁻¹	Mt-Gt CO ₂ yr. ⁻¹	Mt-Gt CO ₂ yr. ⁻¹	Mt-Gt CO ₂ yr. ⁻¹	Mt CO ₂ yr. ⁻¹
Emissions reduction (ER) or NET	ER or NET	ER or NET	ER or NET	NET	NET	NET	NET
Monitoring and verification	Potentially straightforward	Straightforward	Potentially straightforward	Difficult	Difficult	Difficult	Difficult

of global CO₂ emissions (Bide et al., 2014). For *ex situ* and surficial mineralization, as well as for enhanced weathering, near-surface deposits of mafic and ultramafic alkaline rocks could be mined, crushed, and ground to create high surface areas to facilitate a reasonable rate of reaction with CO₂. In this regard, the available rock resources that could be used for geochemical NETs at the Earth's surface are plentiful, since the estimates for global sand, gravel, and stone reserves amount to more than 190 Tt (Sverdrup et al., 2017). If only a small part of this industry were to be redirected toward production of crushed alkaline rocks for surface geochemical NETs, then many Gt CO₂ yr⁻¹ would be achieved in the near future. The reason is that a robust and expanding industry is already in place, i.e., the construction aggregates industry, which annually extracts and processes 50 billion tons (Gt) of rocks (range 47–59 Gt) (Sverdrup et al., 2017). Finally, it may be possible to use natural carbonate rocks for enhanced weathering and remove CO₂ from air in the form of bicarbonate (Kirchner et al., 2020).

Artificial Alkaline Minerals—Industrial By-Products and Wastes, and Tailored Minerals

In addition to naturally occurring mineral resources, some geochemical NETs can also exploit abundant artificial mineral resources (Table 2). These are typically wastes or by-products of industrial processes, landscaping, or quarrying (Dijkstra et al., 2019). On a global scale, it is estimated that 7 Gt of these alkaline mineral by-products/wastes are produced annually, with a combined potential to capture and store CO₂ away from the atmosphere at 2.9–8.5 Gt yr⁻¹ by 2100 (Renforth, 2019). More specifically, these materials include: (i) iron and steelmaking slags (blast furnace, basic oxide, electric arc furnace, ladle furnace, and argon oxygen decarburization slags) (Mayes et al., 2018; Pullin et al., 2019; Reddy et al., 2019; Luo and He, 2021); (ii) cement wastes (cement and concrete wastes, construction and demolition wastes, cement kiln/bypass dust, recycled calcium sulfates, and blended hydraulic slag cement) (Huntzinger et al., 2009a; Medas et al., 2017; Pedraza et al., 2021); (iii) ashes and relevant residues [bottom ash from furnaces and incinerators (municipal solid waste incinerator bottom ash, fly ash, boiler ash, coal slag, oil shale ash), air pollution control residues (cyclone dust, cloth bag dust), and fuel combustion ashes (coal fly ash, lignite fly ash, oil shale, biomass ashes)] (Alba et al., 2001; Baciocchi et al., 2006; Sun et al., 2008; Zhang et al., 2008; Montes-Hernandez et al., 2009; Prigiobbe et al., 2009; Lombardi et al., 2016; Brück et al., 2018; Liu et al., 2018; Ji et al., 2019; Vassilev et al., 2021); (iv) mine and mineral processing wastes (asbestos tailings, nickel tailings, diamond tailings, and red mud) (Wilson et al., 2010, 2014; Power et al., 2014, 2020; Gras et al., 2017; Mervine et al., 2018); (v) alkaline paper mill wastes (lime kiln residues, green liquor dreg, paper sludge) (Pérez-López et al., 2008; Sun et al., 2013; Li and Sun, 2014; Spínola et al., 2021); and (vi) reject brines from desalination (Mustafa et al., 2020). The latter can be employed by electrochemical approaches that aim at removing acidity (HCl) from seawater and return alkalinity (NaOH). Currently, more than 95 million m³ of desalinated water is produced daily on a

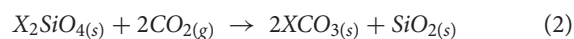
global scale, which is responsible for generating more than 141 million m³ of brine each day that is typically discharged into the oceans, often negatively affecting the receiving ecosystems (Jones et al., 2019). This number is on the rise, since recent estimates suggest that by 2030 the global desalination capacity will be more than 200 million m³ day⁻¹ (Ihsanullah et al., 2021), while this number could be more than tripled by 2050 since the total global desalination population is projected to increase by 3.2-fold in 2050 compared to the present (Gao et al., 2017). These very large volumes of reject brines (waste) present certain advantages for OAE, since their mean salinity is twice that of seawater (Ihsanullah et al., 2021), suggesting that if they were used for OAE, CO₂ removal at the Mt yr⁻¹ scale at least could be achieved in the nearterm.

Regarding the solid alkaline waste materials, these are generally low-cost (Huijgen et al., 2005) and often deposited in heaps or buried at the shallow subsurface, implying that these are more accessible and more readily available than natural minerals. Furthermore, most legacy deposits may be only partially weathered, suggesting their great potential for CO₂ removal. For example, 40–140 years after deposition, a slag deposit in Consett, England, which is estimated to be over 30 Mt, has only reached ~3% of its CO₂ sequestration potential (Pullin et al., 2019). Artificial alkaline minerals also tend to have higher reactivities than natural minerals, due to their activation by various industrial pre-treatments (e.g., grinding and heat treatment), which often create high surface areas and higher crystal disorder (La Plante et al., 2021a). However, compared to natural alkaline rocks, they are less abundant and may contain more labile toxic metals, possibly making their use problematic in large-scale geochemical NETs.

Therefore, rather than using wastes and by-products of existing industrial processes, artificial alkaline minerals, tailored for the purpose of negative emissions, could be more promising. For example, the carbonates of calcium and magnesium can be calcined, the CO₂ generated by their decomposition could be captured and stored, while the resulting high-reactivity oxides (CaO and MgO) could be used in different NETs such as power generation using an integrated solid-oxide fuel cell (Hanak et al., 2017), metal oxide looping DAC (see Box 1) (McQueen et al., 2020), or ocean liming applications (Renforth and Kruger, 2013; Renforth et al., 2013). Substances other than CaO and MgO have also been investigated for hybrid DAC systems, such as sodium and potassium oxides, and related compounds (Nikulshina et al., 2008; Campbell, 2019).

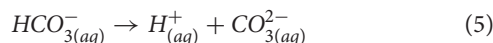
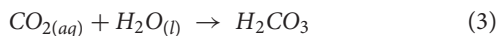
REACTION CHEMISTRY

Reactions of alkaline minerals with CO₂ can occur as gas-solid systems (e.g., Equation 2).

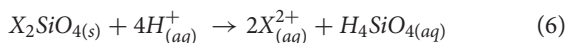


Where X is Mg or Ca. Humidity is usually required to catalyze these reactions. See section Gas-Solid Kinetics for discussion on the kinetics of gas-solid reactions.

Alternatively, and more commonly, reactions of alkaline silicate minerals with CO₂ occur in the aqueous phase. First, CO₂ dissolves in water forming carbonic acid (H₂CO₃), which releases acidity, H⁺, into solution:



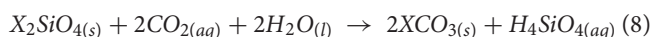
Alkaline mineral surfaces then react with H⁺:



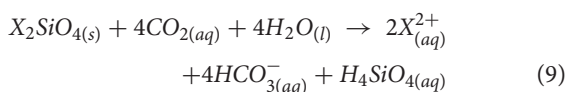
Over time, carbonate minerals may precipitate:



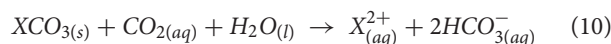
Overall the reaction is:



Theoretically, 1 mol of CO₂ is removed for every 1 mol of alkaline metal. Similar reactions can occur for a wide array of alkaline silicate minerals (**Table 1**). In some geochemical NETs, such as coastal enhanced weathering, the goal is to remove carbon and store it as dissolved ocean bicarbonate, rather than minerals:

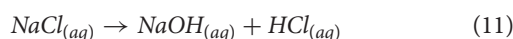


In this case, 2 mol of CO₂ are theoretically removed for every 1 mol of alkaline metal (example reactions are given in **Table 1**). The residence time of bicarbonate is tens to hundreds of thousands of years in the ocean and thus it can be considered a stable store of carbon since abiotic mineral carbonate formation is kinetically inhibited by the ocean's chemistry (Renforth and Henderson, 2017). Alkaline carbonates can also be used to remove CO₂:

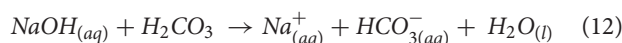


In this instance, 1 mol of CO₂ is theoretically removed for every 1 mol of alkaline metal, assuming the carbon is stored as ocean bicarbonate.

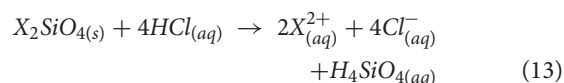
Some geochemical NETs do not react alkaline minerals with CO₂ or H₂CO₃ directly, but instead react alkaline minerals with other acids, which are by-products or wastes of other NETs. For example, electrochemical seawater dialysis may produce HCl (House et al., 2007; Davies, 2015):



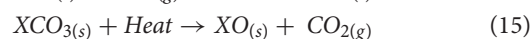
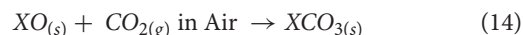
Where NaOH is used for ocean alkalinity enhancement and CO₂ removal:



And where HCl is disposed of by reaction with alkaline minerals.



Furthermore, some geochemical NETs capture CO₂ from air and produce concentrated CO₂ gas in a looping process (McQueen et al., 2020):

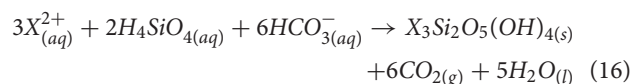


The concentrated CO₂ stream can then be used or safely stored geologically. This process may be possible with minerals other than Ca- and Mg- oxides.

CARBONATE PRODUCTS AND OTHER SECONDARY MINERALS

Solid products of geochemical NETs primarily include carbonate minerals such as calcite (CaCO₃), magnesite (MgCO₃), dolomite (CaMg(CO₃)₂), and various hydrated magnesium carbonates (Mg₅(CO₃)₄(OH)₂·nH₂O). These are stable enough to be stored for long time periods. Other carbonate minerals such as siderite (FeCO₃), dawsonite (NaAl(CO₃)(OH)₂), and ankerite (Ca(Fe,Mg,Mn)(CO₃)₂) can act as stores of carbon, but may only be stable in subsurface environments (Hellevang et al., 2005; Snæbjörnsdóttir et al., 2014; Yu et al., 2020).

Besides carbonates, other products of mineral carbonation and weathering include silica, iron oxides, and clays. These secondary minerals, including the carbonate products, can occlude reactive surfaces, halting further reaction (Béarat et al., 2006; Andreani et al., 2009; Maher et al., 2009; Saldi et al., 2013; Sissmann et al., 2014). The role of clay mineral formation *via* “reverse weathering” (Equation 16) is a subject of ongoing debate within several geochemical NETs, as these reactions may inhibit their CO₂ sequestration efficiencies (Montserrat et al., 2017; Oelkers et al., 2018; Renforth and Campbell, 2021).



Where X is a cation such as Mg²⁺ or Ca²⁺. Successful geochemical NETs will likely include approaches for avoiding or minimizing the extent and impact of secondary minerals.

KINETICS

The field of kinetics involves the study of reaction rates, and provides the basis for reactor design and system optimization. Although conversion of alkaline minerals into carbonates is thermodynamically favored in the presence of CO₂, the reactions are kinetically inhibited. To become an effective tool for climate change mitigation, conversion rates must be enhanced considerably. **Table 3** summarizes some common enhancements. In geochemical NETs, there are many competing effects, and

trade-offs will be required. For example, maintaining a low pH can significantly increase the dissolution rate of silicate minerals but will limit the formation of carbonate minerals, while elevated temperatures favor mineral dissolution and carbonate precipitation, they also lead to lower CO₂ solubility. These competing effects are particularly relevant to direct carbonation. Separating dissolution and precipitation allows each process to be optimized independently (indirect carbonation). See section *Ex situ* for more details on direct vs. indirect approaches. Generally speaking, most geochemical NETs are CO₂-mineral-water systems that can be divided into gas-solid (section Gas-Solid Kinetics), or aqueous (section Aqueous Phase Kinetics). In the latter, three main processes occur: (i) mineral dissolution (section Mineral Dissolution); (ii) CO₂ dissolution and hydration (section CO₂ Dissolution and Hydration); and (iii) precipitation of carbonate minerals (section Carbonate Precipitation). Biological influences on kinetics are discussed separately in the section Application of Biotechnology to Geochemical NETs.

Gas-Solid Kinetics

Gas-solid kinetics are relevant to *ex situ* (Bacocchi et al., 2009) and surficial (Myers and Nakagaki, 2020) CO₂ mineralization, as well as DAC (McQueen et al., 2020). These systems operate with gaseous (humidity), rather than liquid water, thus avoiding significant leaching of potentially toxic metals (El-Naas et al., 2015). The reaction of spherical particles of natural and artificial alkaline minerals with CO₂ is usually limited by ion diffusion through a growing product layer, a process often described by a shrinking core model such as in Equation (17) (Yagi and Kunii, 1955).

$$t = \frac{\rho_{solid} r^2}{6DC_{gas}} \left[1 - 3 \left(\frac{r-d}{r} \right)^2 + 2 \left(\frac{r-d}{r} \right)^3 \right] \quad (17)$$

where t is time (s), ρ_{solid} is the molar density of Ca or Mg in the solid phase (mole m⁻³ of mineral), r is the particle radius (m), d is the thickness of the product layer (m), C_{gas} is the CO₂ concentration in the gas phase (moles m⁻³ of gas), and D is the carbonate ion diffusivity through the product layer (m² s⁻¹). The ion diffusivity has an Arrhenius temperature dependence, thus increasing temperature increases carbonation rate (Li, 2020). According to Equation (17), using pure CO₂ rather than ambient air increases the reaction rate by 3 orders of magnitude whereas grinding from 10 mm to 10 μm increases mineralization rates by 6 orders of magnitude. Values of D for relevant minerals can vary across 7 orders of magnitude depending on the mineral composition and structure (Myers et al., 2019). Other kinetic enhancements are possible for gas-solid processes. For example, in fluidized bed processes, the use of a nanosilica additive increased the gas-solids contact efficiency and carbonation rates of Ca(OH)₂ (Pontiga et al., 2013), while attrition has been shown to prevent the build-up of passivating product layers, improving CO₂ uptake by CaO (Chen et al., 2012).

Humidity also plays a crucial role in gas-solid approaches. For example, the rate and extent of reaction between portlandite (Ca(OH)₂) and CO_{2(g)} (60–90°C) was found to increase

significantly with increasing humidity, proposed to be due to the rate limiting step of dissolution of Ca(OH)₂ in adsorbed surface water (Shih et al., 1999). For brucite (Mg(OH)₂), dehydroxylation/rehydroxylation processes have been shown to induce morphological changes, including translamellar cracking and delamination, that can serve to enhance carbonation reactivity *via* disruption of the passivating product layer (McKelvy et al., 2001; Fagerlund et al., 2012). Humidity is found to have similar mechanistic effects on gas-solid carbonation of natural silicate minerals such as wollastonite (CaSiO₃) (Longo et al., 2015) and chrysotile (Mg₃Si₂O₅(OH)₄) (Larachi et al., 2010, 2012), mine tailings (Veetil and Hitch, 2020), and industrial alkaline by-products/wastes such as air pollution control residue (Bacocchi et al., 2006), fly ash (Liu et al., 2018) and calcium silicate hydrates found in hydrated portland cement (Steiner et al., 2020).

Aqueous Phase Kinetics Mineral Dissolution

Mineral dissolution is the degradation of a solid mineral in aqueous media, with the subsequent release of soluble species such as Mg²⁺/Ca²⁺ and H₄SiO₄ (e.g., Equation 6). The rate of carbon sequestration in geochemical NETs is often limited by the mineral dissolution rate. Mineral dissolution can be described by the rate law:

$$Rate = SA.k_0.e^{-E_A/RT} \cdot \prod_i a_i^{n_i} f(\Delta G) \quad (18)$$

where SA is the reactive surface area, k_0 is the standard rate constant, E_A/RT is apparent activation energy divided by the gas constant, R , and temperature, T , a_i is the activity of aqueous species i to the power of n , and $f(\Delta G)$ is a function of the Gibbs free energy change (see Lasaga, 1998; Black et al., 2015 for more detail).

As implied in Equation (18), the rate of dissolution is directly proportional to the reactive surface area (Brantley and Mellott, 2000). For earth-surface geochemical NETs that make use of rocks, crushing and milling is needed to increase reactive surface areas (Haug et al., 2010; Moosdorf et al., 2014; Rigopoulos et al., 2016). For subsurface mineralization, high vesicularity basalts provide large reactive surface areas (Galeczka et al., 2014; Xiong et al., 2018). Temperature also plays an important role in mineral dissolution, since the rate constant in Equation (18) greatly depends on temperature and even small increases in the temperature will largely increase mineral dissolution rates. As a result, in *ex situ* approaches mineral dissolution rates are often enhanced through temperature increase (Gerdemann et al., 2007). For *in situ* approaches, greater depths are prioritized, since the naturally warmer underground temperatures will greatly enhance carbonation rates, by up to 76 times compared to ambient surface rocks (Paukert et al., 2012). Indeed, fully carbonated peridotites (listevenites) give a good indication of the enormous potential of carbonation of ultramafic rocks at high temperatures (Falk and Kelemen, 2015). Finally, for enhanced weathering at the Earth's surface, warm tropical regions are typically prioritized, since in these areas mineral dissolution rates are greatly accelerated (Kohler et al., 2010).

The composition of the aqueous phase also plays an important role. For example, the dissolution rates of minerals such as forsterite and apatite increase linearly with decreasing pH (Brantley, 2008). However, others may show a non-linear dependence, for instance albite has a parabola-shaped dependence, having a minimum at pH ~ 5 (Gislason et al., 2014). In some geochemical NETs, carbonic acid provides the acidity needed to enhance dissolution (see Equation 3) (O'Connor et al., 2000; Kanakiya et al., 2017) while in others, organic and inorganic acids will provide acidity (van Hees et al., 2000; Kakizawa et al., 2001; Teir et al., 2007a,b). Organic acids can also catalyze silicate dissolution by acting as chelators, which complex and solubilize cations in the mineral crystal framework (Drever and Stillings, 1997; Lazo et al., 2017; Oelkers et al., 2018). Inorganic ligands, such as sulfate and phosphate (Pokrovsky et al., 2005) may also enhance mineral dissolution.

Dissolution rates are also dependent on the solids' composition. In silicate minerals, the dissolution rate is controlled by breaking of the shortest and strongest (usually the Si–O) bonds. Thus, minerals with a low degree of silica polymerization (e.g., olivine) dissolve at faster rates than minerals with higher degrees (e.g., quartz) (Goldich, 1938). For this reason, artificially tailored minerals such as MgO and CaO exhibit much faster dissolution rates than silicates, making them good candidates for OAE (Kheshgi, 1995; Renforth and Henderson, 2017). Furthermore, calcium-rich minerals dissolve faster than their magnesium-rich counterparts, owing to the comparatively weaker Ca–O bond (Brantley, 2008). The presence of transition metals and their potential for reduction–oxidation (redox) reactions, particularly Fe and Mn, can have a substantial impact on dissolution rates, e.g., Fe(III)–O bond is stronger than Fe(II)–O bond, suggesting that reductive conditions could increase mineral dissolution rates (Brantley, 2008). Silicates tend to dissolve non-stoichiometrically, i.e., the ratio of release rates for the various species is not equal to the stoichiometry of the starting mineral, often because their most soluble elements, e.g., Na, K, Ca, Mg, are released preferentially (Brantley, 2008). Such incongruent dissolution may lead to the formation of a silica-rich outer layer on the particle surfaces, inhibiting further dissolution (Béarat et al., 2006; Andreani et al., 2009; Maher et al., 2009; Saldi et al., 2013; Sissmann et al., 2014). Surfaces can also be passivated by precipitating secondary minerals which limit diffusion of reactants and products (King et al., 2010). Agitation and sonication have been employed to reduce the impact of surface passivation (Santos and Van Gerven, 2011). Organisms can also prevent secondary mineral precipitation by secreting organic chelators (Liermann et al., 2000; Buss et al., 2007; Torres et al., 2019).

Figure 2 shows the CO₂ removal potential *via* enhanced weathering (mineral dissolution) for the most relevant alkaline minerals contained within various types of mine tailings over a 50-year period (Bullock et al., 2022). The removal potential is determined according to weathering (Equation 6) *via* a shrinking core model under two conditions: “unimproved” (pH of 6–8, and common grain sizes for these materials, e.g., 75 μm for platinum group metal (PGM) tailings) and “improved” (pH of 3–4, and grain sizes of 10 μm for all

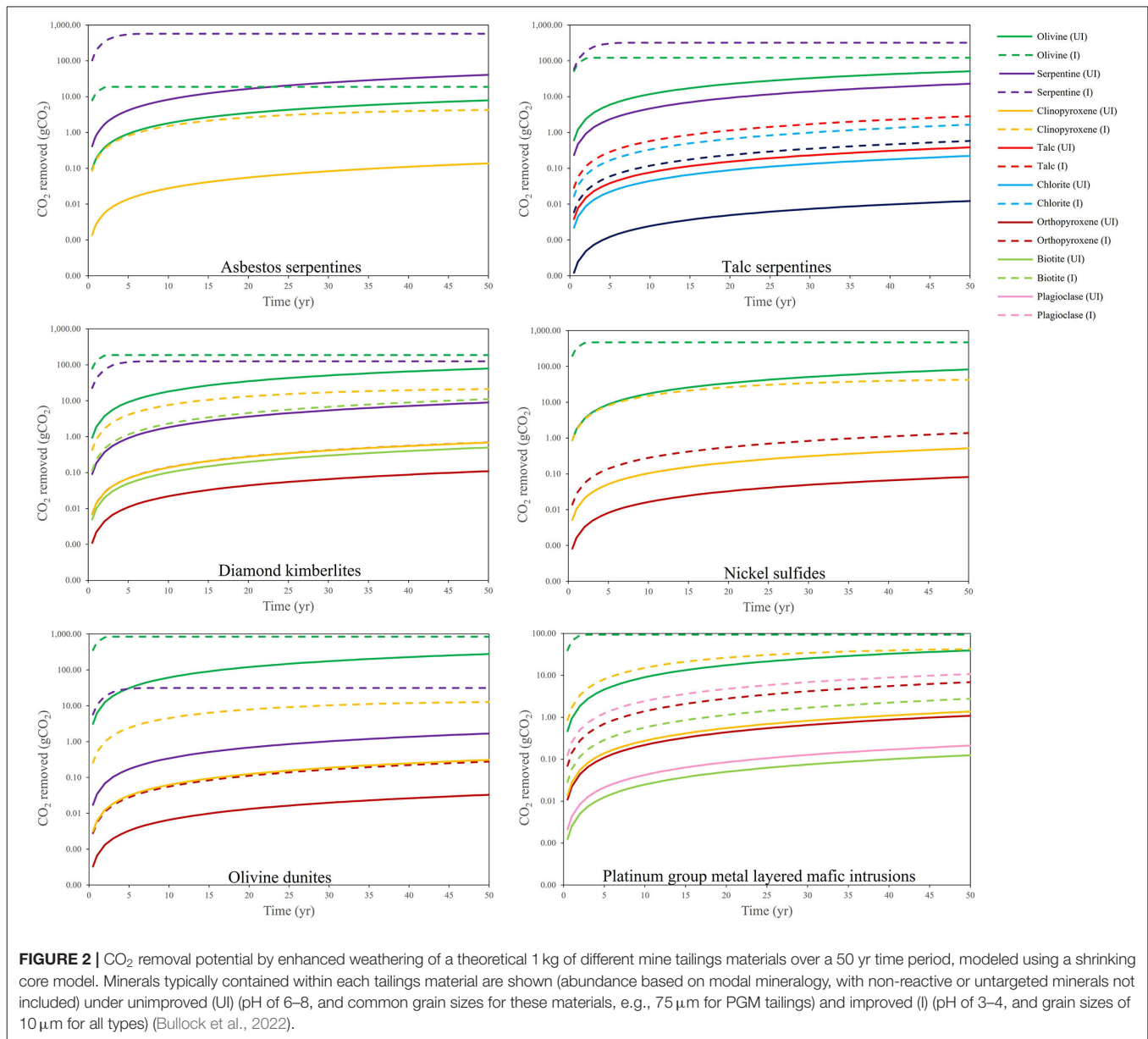
types). Tailings containing high abundances of olivine, serpentine and clinopyroxene show the highest CO₂ removal potential due to their favorable kinetics. The rates of CO₂ removal are estimated to become substantially augmented using improved conditions. Specifically, Bullock et al. (2022) estimate that the average annual global CO₂ removal potential of tailings weathered over 2030–2100 to be ~ 93 (unimproved conditions) to 465 (improved conditions) Mt CO₂ yr⁻¹. These data clearly demonstrate the enormous impact that enhancing the reaction kinetics can have on the CO₂ removal potential of alkaline materials.

CO₂ Dissolution and Hydration

In low and neutral pH aqueous solutions CO₂ will react with water and form carbonic acid, H₂CO₃, with deprotonation to form bicarbonate, HCO₃⁻, and carbonate, CO₃²⁻ (Equations 3–5) (Knoche, 1980). As the pH increases, the equilibrium shifts further to the right, increasing the concentrations of HCO₃⁻ and CO₃²⁻. At higher pH values (>8) the CO₂ reaction mechanism changes, with HCO₃⁻ forming directly *via* the much faster reaction (Morel and Hering, 1993):



This behavior is the essence behind many geochemical NETs which use dissolved mineral alkalinity as the driving force for CO₂ capture and sequestration. However, in some geochemical NETs, mineral dissolution is not the limiting factor, but rather they are constrained by the CO₂ availability, particularly where atmospheric air is the CO₂-bearing gas (Power et al., 2013b; Gras et al., 2017). According to Henry's Law, doubling the CO₂ partial pressure approximately doubles the CO₂ solubility (Henry and Banks, 1803). Increasing CO₂ partial pressure can be achieved by increasing the total pressure or by increasing the gas phase CO₂ concentration (O'Connor et al., 2000, 2001). In some geochemical NETs, CO₂ is artificially pre-concentrated by DAC or bioenergy with carbon capture and storage (BECCS) (Kelemen et al., 2020). Others exploit the Earth's natural mechanisms for pre-concentrating CO₂. For example, in enhanced weathering in soils, the weathering rate of the applied alkaline minerals is accelerated due to elevated concentrations of CO₂ in the soil pores, which traces back to microbial/plant respiration (Robbins, 1986), while some ocean NETs may take advantage of the higher carbon concentration by volume of seawater compared to air (de Lannoy et al., 2018). Furthermore, diffusion of CO₂ into the aqueous phase can be artificially accelerated through bubbling (Legendre and Zevenhoven, 2017; Abe et al., 2021), stirring (Gadikota, 2020), spraying solution in scrubbing towers (Gunnarsson et al., 2018), spraying fluids rich in mineral dissolution products (Stolaroff et al., 2005), sparging (Kelemen et al., 2020), or by using thin films of alkaline solution trickled over high surface area packing materials (Keith et al., 2018). The rate of hydration of CO₂ into carbonic acid can be catalyzed by the enzyme carbonic anhydrase (CA) (Lindskog, 1997) (section The Influence of Organisms and Biological Mechanisms on the Chemical Reactions Underlying Geochemical NETs). In coastal enhanced weathering, the CO₂ concentration from surface to

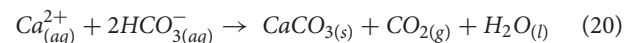


seabed is constantly resupplied since the shallow, high-energy coasts enable rapid sea-air mixing and equilibration. Other factors might also influence CO₂ dissolution rates. For example, CO₂ solubility in aqueous solutions decreases with increasing temperature, as related *via* the temperature dependence of Henry’s coefficient (Carroll et al., 1991), and also with increasing salinity due to the “salting out effect” (Setschenow, 1889; Yasunishi and Yoshida, 1979).

Carbonate Precipitation

Most geochemical NETs require production of dry solid carbonate minerals, and in some of these approaches carbonate precipitation is the rate-limiting step. For example, in OAE, precipitation of carbonate minerals reduces the efficiency of the

overall sequestration by release of CO₂:



In general, precipitation occurs when the aqueous medium is oversaturated with respect to the mineral that precipitates, i.e., the ionic activity product is higher than the equilibrium constant; whereas dissolution occurs when the aqueous medium is undersaturated with respect to these minerals (Brantley, 2008). For calcium carbonate precipitation (Equation 7), the stoichiometric solubility product, K_{sp}^* , is defined by:

$$K_{sp}^* = [Ca^{2+}]_{sat} \times [CO_3^{2-}]_{sat} \quad (21)$$

where $[Ca^{2+}]_{sat}$ and $[CO_3^{2-}]_{sat}$ are the equilibrium concentrations of each species in a solution saturated with $CaCO_3$ (at a specific temperature, pressure, and salinity). The saturation state, Ω , is then defined as:

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp}^* \quad (22)$$

where $[Ca^{2+}]$ and $[CO_3^{2-}]$ are the concentrations of each species in solution. If $\Omega = 1$, the solution is at equilibrium with the mineral phase. If $\Omega < 1$, the aqueous phase is undersaturated, and calcium carbonate is expected to dissolve, whereas if $\Omega > 1$ then the aqueous phase is oversaturated, and calcium carbonate is expected to precipitate. However, even when saturated, carbonate minerals may not always precipitate. For example, the presence of $Mg_{(aq)}^{2+}$ is known to inhibit calcium carbonate formation (Morse et al., 2007). Similarly, organic and inorganic ligands present in the aqueous phase can inhibit calcium carbonate formation *via* complexation and adsorption (Morse et al., 2007), although some enhance the precipitation rates by accelerating desolvation kinetics (Schott et al., 2009). The rate of carbonate precipitation increases with increasing pH, owing to the shift of aqueous equilibrium toward CO_3^{2-} (Ruiz-Agudo et al., 2011). Higher temperatures and pressures result in greater precipitation of calcium carbonate and (hydrated) magnesium carbonates (Zeebe and Wolf-Gladrow, 2001; Hänchen et al., 2008). In turbulent conditions, eddy formation increases the diffusion rates of species enhancing carbonate precipitation (Dreybrodt et al., 1997). Precipitation of $CaCO_3$ is ~ 4 orders of magnitude faster than precipitation of $MgCO_3$, as Ca^{2+} is much larger than Mg^{2+} and the water molecules in its coordination sphere are held more loosely, enabling faster exchange with carbonate (Schott et al., 2009). Notably, microorganisms have been observed to catalyze the nucleation of $MgCO_3$ (McCutcheon et al., 2019). Microorganisms can catalyze nucleation of carbonate precipitation by concentrating cations near the surfaces of cell walls or extracellular polymeric substances (Dupraz et al., 2009).

PROCESSES

Processes for geochemical NETs that produce solid carbonate minerals *via* CO_2 mineralization include *in situ*, *ex situ* and surficial approaches. Processes which increase the ocean's storage capacity of dissolved inorganic carbon (DIC) are termed OAE and include coastal enhanced weathering, electrochemical seawater splitting, and ocean liming. Enhanced weathering in soils produces both carbonate minerals (carbonation) and also lead to ocean alkalization since cations from rock dissolution will remain dissolved in water and eventually be transferred to the oceans (Renforth, 2012; Lefebvre et al., 2019). **Table 3** summarizes some of the defining features of each of these processes. Furthermore, geochemical NETs which use alkaline minerals in their flowsheets but which do not necessarily result in carbon storage are introduced in **Box 1**. Note that descriptions of geochemical NETs, e.g., CO_2 mineralization, enhanced weathering, OAE, etc., in other sources may vary from the ones in this review, and that their defining features may overlap in one or more ways.

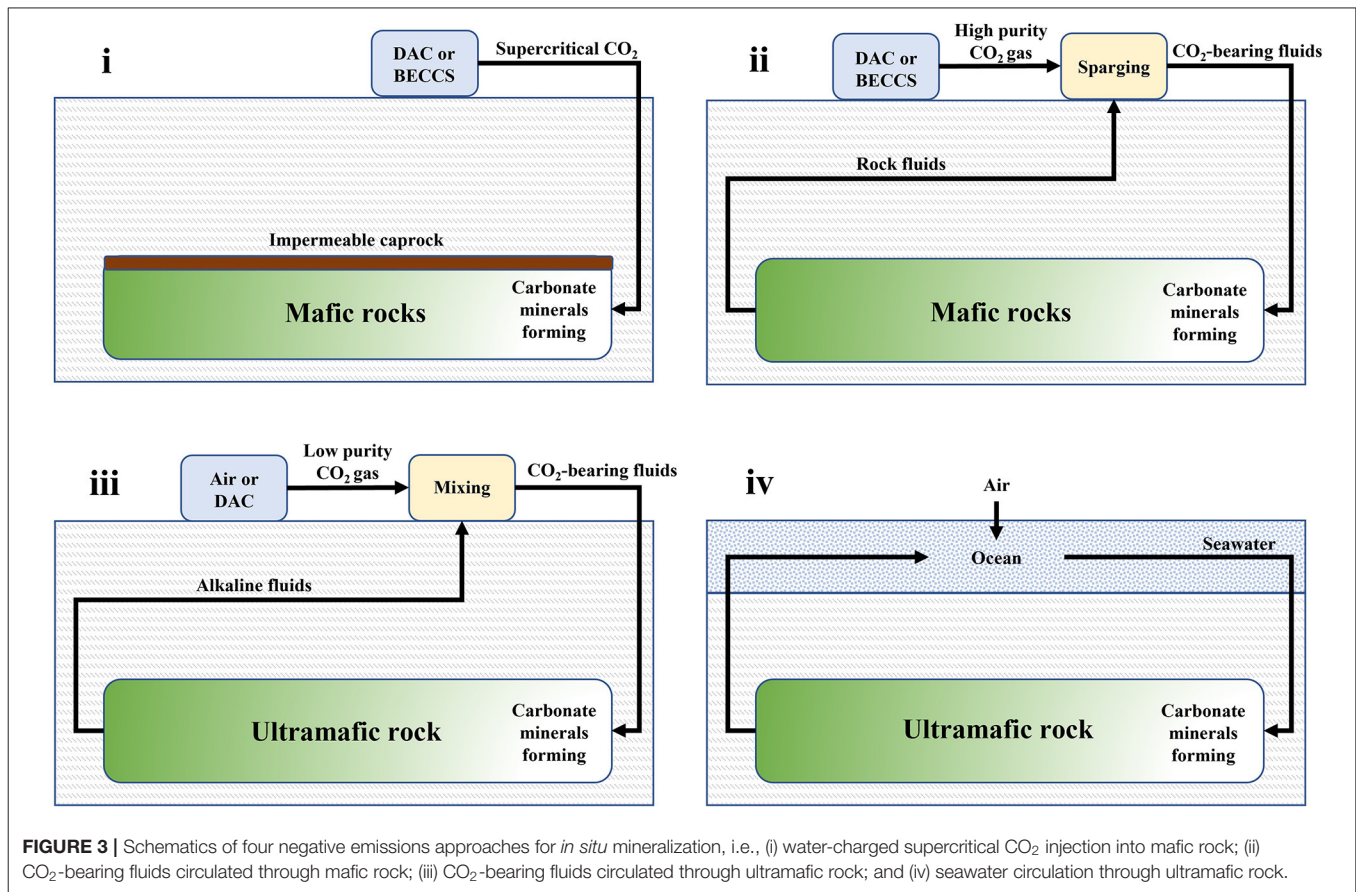
CO_2 Mineralization

In situ

In CCS, CO_2 is typically injected as a pure supercritical fluid into geological formations, such as deep sedimentary formations, salt mines, depleted oil fields, or unmineable coal seams, where it becomes trapped in rock pores and structural spaces, with minimal CO_2 mineralization. An impermeable caprock is needed in order to limit leakage and long-term monitoring is required (Zhang and Song, 2014). In *in situ* mineralization, the focus is on mineral storage, rather than pore and structural storage. This is achieved by injecting supercritical CO_2 , or CO_2 -rich fluids, into alkaline geological rock formations. Once injected, the CO_2 creates a low pH zone within the rock, enhancing dissolution of the surrounding silicate minerals and causing Mg^{2+} and Ca^{2+} to be released (Equation 6). As mineral dissolution increases, the pH begins to increase, which in turn induces the precipitation of stable carbonate minerals (Equation 7). With mineralization there is less need for long-term monitoring of the storage efficacy compared to traditional forms of CCS, particularly when CO_2 is pre-dissolved prior to injection. However, pre-dissolution incurs additional cost and complexity compared to injection of pure supercritical CO_2 (Blondes et al., 2019).

As mentioned above, there are two main types of alkaline rock formation suitable for *in situ* mineralization: (i) mafic rocks such as basalt, and (ii) ultramafic rocks such as peridotite and serpentinite. Due to their higher alkalinity, ultramafic rocks have greater potential for CO_2 mineralization per cubic volume of rock, while their exothermic reaction with CO_2 releases larger amounts of heat which is beneficial for the mineralization reaction kinetics (National Academies of Sciences, Engineering, and Medicine, 2019). However, ultramafic rocks are usually found at greater depths, are less porous and permeable, and have a wider range of crystal size than mafic rocks (Kelemen and Matter, 2008). For both, capacity is large (section Naturally Occurring Alkaline Rocks), and these rocks are widely geographically distributed (Pilorgé et al., 2021). For example, extensive reserves of onshore flood basalts exist in the US, India, and Russia. However, most of the potential lies offshore, as the majority of the seafloor is composed of basalt. Although most peridotite is deeply buried, near-surface deposits can be found in locations such as Oman, United Arab Emirates, the Mediterranean, the Pacific Islands and New Zealand.

There are four main approaches to negative emissions *via in situ* mineralization which are based on the rock types and engineering methods employed, with two of them being already demonstrated at the kt CO_2 yr^{-1} removal scale (**Figure 3**). In the first (i) approach, CO_2 is injected into porous mafic rock formations, e.g., basalt, as a supercritical fluid. An impermeable caprock is needed to minimize CO_2 leakages. If the rocks are not already water-saturated, then some water can be co-injected alongside the supercritical CO_2 to facilitate mineralization. This has been successfully demonstrated in 2013 by the Wallula project, whereby 977 tons of water-saturated supercritical CO_2 from the industry were injected into a permeable Columbia River basalt at a depth of 900 m over a 3-week period (McGrail et al., 2011, 2014, 2017a,b; Spane et al., 2012; White et al., 2020; Holliman



et al., 2021). Although CO₂ mineralization was observed in sidewall core samples, evidence suggests that much of the CO₂ remains structurally trapped (White et al., 2020; Holliman et al., 2021).

In the second (ii) approach, an impermeable caprock is not present and thus pre-dissolution of CO₂ in reservoir fluids or seawater is required, prior to injection into porous basalt. Recirculation of the CO₂-carrier fluids helps maintain a constant rock formation pressure, reducing the chance of seismic activity, as well as enabling monitoring of the extent of mineralization *via* tracers such as ¹⁴C rich CO₂ or Ca isotopes (Matter et al., 2016; Snæbjörnsdóttir et al., 2017; Gíslason et al., 2018; von Strandmann et al., 2019; Clark et al., 2020). This approach was adopted at a geothermal energy plant in Hellisheiði, Iceland (Carbfix project). Specifically, CO₂ (and H₂S) emitted by the process were pre-dissolved by sparging in water and then co-injected with geothermal brine into highly-fractured basalt at depths of 300–1000 m (Matter et al., 2009; Gíslason et al., 2010; Gutknecht et al., 2018). Each ton of CO₂ required ~25 tons of water. To date, more than 70,000 tons of CO₂ have been injected with an estimated 60% successfully mineralized (Clark et al., 2020). In 2021, the world's first DAC-mineralization plant (Project Orca) went live as a collaboration between CarbFix and the company Climeworks, with the goal to annually remove 4 kt CO₂. Modeling studies indicate that basalt carbonation may be limited by alkalinity constraints and lead to the existence of

unreacted free-phase CO₂ (Tutolo et al., 2021). However, recent field-scale three-dimensional transport models of the CarbFix injection site indicate mineralization rates remain high even after many years of injection and that 300 Mt CO₂ can be stored using just 10% of the rock pore space (Ratouis et al., 2022). The role that secondary minerals, e.g., clays and zeolites, play in the reactivity of CO₂ with basalt is yet to be fully understood. Furthermore, the evolution of dissolution and precipitation fronts and their effect on rock permeability and fluid flow during the injection period is another phenomenon with great uncertainty (Lisabeth et al., 2017; Peuble et al., 2018).

In the third (iii) approach, alkaline geological fluids are extracted from ultramafic rock formations, such as peridotite, and allowed to absorb CO₂ from air in surface ponds creating DIC. The fluids are then recirculated through the rock where DIC reacts and forms carbonate minerals. This speculative approach is based on natural terrestrial alkaline springs and their associated surface travertine deposits (Kelemen and Matter, 2008; Kelemen et al., 2011; Power et al., 2013b). However, the circulation of fluids with such low concentrations of dissolved carbon could be prohibitively expensive. Therefore, it has been suggested that this approach can be scaled cost effectively by combination with DAC that produces low purity (3–5 wt.) CO₂ (Kelemen et al., 2020). Although the process seems promising, challenges remain. For example, as the fluid pathways become filled with product carbonate minerals the permeability of the rock formation would

reduce, inhibiting CO₂ transport to unreacted rock further from the injection well and causing the system to become self-limiting. On the other hand, volume expansion during carbonation can create enough force to fracture the host rock, maintaining permeability. Such “reaction-driven cracking” could increase permeability, thus enhancing the efficiency of *in situ* mineralization in peridotite (Kelemen and Hirth, 2012; Kelemen et al., 2013; Sohn, 2013; Evans et al., 2020). Overall, the balance between clogging and cracking during *in situ* mineralization in peridotite remains a key uncertainty.

In the fourth (iv) and final approach, seawater is circulated through ultramafic rocks near the oceans (Kelemen and Matter, 2008). Although largely speculative, some natural analogs exist which indicate potential feasibility (Grozeva et al., 2017; Kelemen, 2017; Picazo et al., 2020). This approach simultaneously increases alkalinity of the ocean, while removing DIC in seawater by reaction with peridotite, thus creating a double driving force for CO₂ drawdown from the air into the ocean *via* manipulation of the Revelle factor (Eggleston et al., 2010). Thermal gradients between the rock and seawater could drive natural circulation.

DAC with *in situ* mineralization is energy intensive and can require significant heat for regenerating capture sorbents, in addition to significant power input for CO₂/air sparging and fluid pumping. In both the CarbFix and Orca projects, the heat and power needs are met by geothermal energy (Marieni et al., 2018; Adams et al., 2020). Geothermal fluids typically have temperatures of 70–250°C (Zarrouk and Moon, 2014) enabling integration with DAC systems whose synthetic sorbents (usually amine-based polymers) are regenerated in a similar range. Tectonically active areas such as the Western United States, Alaska, Hawaii, British Columbia, Indonesia, the Philippines, Italy, Turkey, New Zealand, Japan, Iceland, Kenya, Mexico, El Salvador, and Central America (Zarrouk and Moon, 2014) could provide low-cost opportunities for geothermal powered DAC and mineralization. As new geothermal technologies develop, such opportunities could expand elsewhere (Olasolo et al., 2016). Alternatively, the CO₂ and power requirement for *in situ* mineralization could be simultaneously provided by bioenergy (Turner et al., 2018), which has the advantage of lower levelized cost of CO₂ capture than DAC. However, pipelines would be needed for transportation of CO₂, and issues with biodiversity, land requirements, sustainability, and scalability could arise (Burns and Nicholson, 2017; Smith et al., 2019).

In situ mineralization may have fewer adverse environmental and human health effects than surface-based geochemical NETs, since materials are mostly contained beneath the Earth's surface where they have little direct impact on ecosystems and biodiversity, and typically use less land and fresh water than other NETs (National Academies of Sciences, Engineering, and Medicine, 2019). Wastewater could be co-injected with CO₂ for dual benefit (Phan et al., 2018). *In situ* mineralization could have other potential co-benefits, such as enabling the transition of workers from fossil fuel industries into the clean energy sector where near-identical skills are required. Reaction-driven cracking could be applied to *in situ* mining of metals and uranium (Kelemen et al., 2020). On the other hand, there

are potential risks with the injection of CO₂ and fluids for geological storage, including: (i) production and leakage of methane (CH₄) and hydrogen sulfide (H₂S) to the atmosphere by CO₂-reducing bacteria (Guyot et al., 2011); (ii) groundwater acidification (Li et al., 2018); (iii) heavy metal mobilization, which could contaminate local water supply (de Orte et al., 2014); and (iv) increasing seismicity (Blondes et al., 2019). The latter presented certain key challenges, which were identified during the initial stages of the CarbFix project where several (micro)seismic events were initially observed (Hjörleifsdóttir et al., 2021). Improved engineering methods, i.e., constant recirculation of the fluids, reduced seismic occurrences, while engagement with local residents aided public acceptance of the project. Partnership with Climeworks, as well as the addition of a geothermal lagoon for bathing also aided in improving public acceptance (Aradóttir and Hjálmarsson, 2018).

Ex situ

Ex situ routes were the first approaches for CO₂ mineralization to be investigated for the purpose of climate change mitigation (Lackner et al., 1995), particularly focusing on reducing point source emissions. *Ex situ* mineralization involves reacting high surface area alkaline minerals with CO₂-rich gases, mainly in engineered reactors (Gerdemann et al., 2007). *Ex situ* approaches using crushed natural rocks rich in minerals such as olivine (Kwon et al., 2011), serpentine (Park and Fan, 2004; Wang and Maroto-Valer, 2011b; Nduagu et al., 2012), and wollastonite (Huijgen et al., 2006; Daval et al., 2009; Xu et al., 2019) have been investigated, but industrial alkaline wastes and by-products, such as mine tailings (Bodénan et al., 2014) or iron and steel slags (Yadav and Mehra, 2017), are likely better suited to *ex situ* processes owing to greater reactivity than their natural counterparts, as discussed in the section Artificial Alkaline Minerals—Industrial by-Products and Wastes, and Tailored Minerals. High temperatures and pressures (Domingo et al., 2006), high CO₂ partial pressures (Li et al., 2019), additives (Krevor and Lackner, 2009), and mechanical (Fabian et al., 2010; Li and Hitch, 2018), or heat activation (Farhang et al., 2019) could be used to capture and store CO₂ within timeframes relevant to industrial processes. Although *ex situ* processes are likely best integrated with readily available sources of concentrated CO₂ from industry, integration with DAC may also be possible. For example, OCO Technology, which makes carbonate construction materials, is now working with London-based Mission Zero Technologies, to use CO₂ sourced by air capture (OCO Technology, 2021).

Ex situ processes can be broadly categorized as either “direct” or “indirect.” Direct CO₂ mineralization occurs in one step, as a gas-solid (Kwon et al., 2011; Liu et al., 2018) or as a gas-liquid-solid process (Benhelal et al., 2019; Li et al., 2019). Indirect CO₂ mineralization methods use multiple steps which overall result in the dissolution of a silicate mineral and the creation of a carbonate mineral. First Mg and/or Ca is extracted from the mineral feedstocks, followed by reaction with CO₂. This is usually achieved by a pH swing approach using reagents, e.g., hydrochloric acid (Lackner et al., 1995; Ferruffino et al., 2018),

acetic acid (Kakizawa et al., 2001), ammonium salts (Wang and Maroto-Valer, 2011a; Highfield et al., 2012), ammonia and brine (based on solvay process) (Huang et al., 2001) or molten salt ($\text{MgCl}_2 \cdot n\text{H}_2\text{O}$) (Wendt et al., 1998), where the acidic reagents aid in mineral dissolution and the alkali reagents aid in carbonate precipitation. Reagents should be recycled as part of the process. Direct processes have the advantage of greater simplicity, whereas indirect approaches have the advantage of faster throughput and the production of high purity carbonate minerals (Zevenhoven et al., 2011). Direct mineralization requires pure CO_2 for reaction (necessitating integration with either DAC or BECCS), whereas some indirect processes produce reactive alkaline hydroxides that may be suitable for direct reaction with atmospheric CO_2 .

Ex situ approaches can also produce useful carbonated products (Fernández Bertos et al., 2004; Hills et al., 2020; Qiu, 2020). Other valuable side products such as hydrogen could enable *ex situ* processes to become more economical (Kularatne et al., 2018). However, life cycle assessments (LCAs) frequently show that not all *ex situ* approaches result in negative emissions (Ncongwane et al., 2018; Thonemann et al., 2022). Further information on different *ex situ* processes can be found elsewhere (Sanna et al., 2014; Veetil and Hitch, 2020; Yadav and Mehra, 2021).

Surficial

Surficial CO_2 mineralization is any process by which low purity CO_2 (either from the air, or low CO_2 concentration gases and liquids) is reacted with alkaline materials in piles, fields, pools, or large indoor spaces such as greenhouses. Surficial processes generally require less intensive reaction conditions than *ex situ* processes, with carbon removal occurring over weeks to months, rather than minutes. Surficial approaches allow minerals to be carbonated near to their site of production, thus reducing mineral transportation costs. Like *ex situ* approaches, surficial approaches enable the sale of the carbonated minerals, for example, as aggregates for the building and construction sector (Huntzinger et al., 2009a,b; Liu et al., 2021).

Surficial mineralization of crushed alkaline materials was investigated by Myers and Nakagaki (2020) who proposed a gas-solid method whereby finely crushed materials are spread thinly in vertical tiers in a greenhouse. Solar panels drive fans which continuously supply fresh air over the layers of material and trays of water provide the necessary humidity. This approach suggested the use of a variety of alkaline materials from natural mafic and ultramafic rocks to anthropogenic materials such as slag and lime. Other surficial approaches have investigated carbonation of existing mafic and ultramafic mine tailings (Wilson et al., 2006; Power et al., 2010, 2014, 2020; Mervine et al., 2018; Kelemen et al., 2020) and industrial wastes such as slag (Stolaroff et al., 2005). Artificial materials are usually favored due to their greater reactivity than natural minerals. In general, most industrial wastes and by-products (Table 2) present promising opportunities for surficial mineralization due to their wide availability and relatively low cost (Renforth, 2019).

CO_2 availability is often the limiting factor in ambient weathering of mine tailings and other industrial alkaline wastes

(Wilson et al., 2009; Pullin et al., 2019). Therefore, increasing the CO_2 supply in surficial processes using DAC to provide low purity CO_2 could lower overall costs compared to air (Kelemen et al., 2020). While higher purity CO_2 could theoretically be used, significant losses would occur for systems which are not closed. The availability of humidity in the air could also be a limiting in some cases, with some studies quoting a minimum requirement of 55–60% relative humidity required for the reaction to take place (Erans et al., 2020; Samari et al., 2020).

Surficial mineralization of anthropogenic waste materials may serve a dual purpose of waste management (*via* a reduction in liability associated with hazardous materials) in addition to CO_2 removal. This may be achievable at greater scale and lower cost than *ex situ* approaches. For example, the building and construction industry is thought to be accountable for 40% of solid waste worldwide (Shan et al., 2017). Stockpiles of steel slag produce highly alkaline leachates ($\text{pH} > 10$) (Yi et al., 2012) that can lead to environmental issues surrounding potential heavy metal mobilization and local pollution (Mayes et al., 2008). Carbonation reduces the pH of these wastes, and reduces the mobility of toxic metals. Similarly, carbonation destroys the hazardous asbestiform aspect of some mine tailings (Bobicki et al., 2012). Likewise, 70 million tons of highly alkaline red mud, a waste product of alumina production, are generated annually. Disposal of this waste is challenging due to aluminum toxicity and leaching of alkalinity into groundwater supplies (Bobicki et al., 2012). Carbonation mitigates these effects (Renforth, 2012) and enables the products to be used as a soil amendment, a reagent for removal of nitrogen and phosphorus from wastewater, a fertilizer additive, brick manufacture, plastic filler, and cement production (Bonenfant et al., 2008).

Most of the work conducted on mineralization processes has focused on *ex situ* approaches where high conversion can be reached rapidly (Sanna et al., 2014). Alternative surficial approaches are emerging which can potentially combine the scalability of enhanced weathering with the ability to produce useful carbonate products, or to remediate hazardous industrial mineral wastes. However, the kinetics of ambient mineralization are poorly understood, and more work is needed.

Enhanced Weathering in Soils

Enhanced weathering in soils aims to accelerate the natural process of weathering through the spreading of crushed Mg- and Ca-rich silicate rocks in agricultural, urban, and forest soils (Renforth, 2012; Hartmann et al., 2013; Beerling et al., 2020; Haque et al., 2020b). Carbonate rocks, such as limestone or dolomite, could also be used for enhanced weathering in soils, however, (i) they are unlikely to achieve the same spatial flux of alkalinity (Renforth and Campbell, 2021); (ii) they have a lower CO_2 sequestration potential; and (iii) they deliver fewer co-benefits than silicate rocks (Beerling et al., 2018). Through enhanced weathering in soils, atmospheric CO_2 is drawn down into the soil, dissolved into porewaters and transformed into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) anions. The result of this process includes carbon stored as carbonate minerals in soils, or dissolved bicarbonates and carbonates draining into

surface waters and eventually transported to the ocean where they contribute to ocean alkalinity (Renforth and Campbell, 2021). Depending on the type of mineral used, enhanced weathering in soils has the potential to remove between 0.3 and 1.25 tons of atmospheric CO₂ per ton of mineral dissolved (Renforth, 2012; Moosdorf et al., 2014; Haque et al., 2019), although the maximum scalable potential when using rocks is <1. Cost estimates for enhanced weathering in soils vary by country ranging from US\$55–190 per ton of CO₂ removed, with estimates for China, India, Indonesia or Brazil at the lower end, and USA, Canada and European countries at the higher end of the cost range (Beerling et al., 2020).

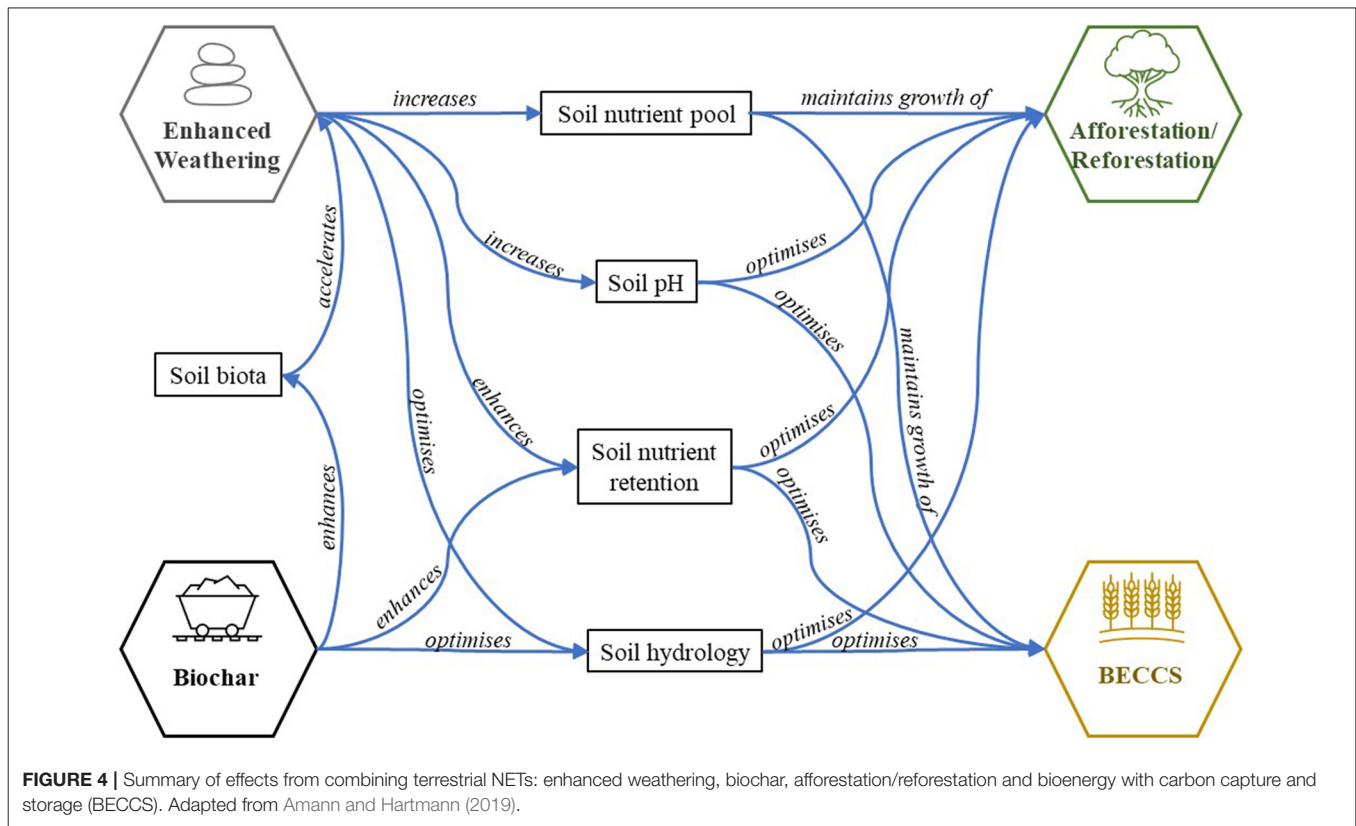
The weathering rate of silicate minerals depends on several abiotic and biotic factors. Specifically, it increases with increasing surface area (Strefler et al., 2018), while higher pH, lower temperature, and precipitation rates, along with varying soil CO₂ partial pressure can negatively affect the weathering rates (Verbruggen et al., 2021). Biogeochemical and biomechanical activity can also affect weathering rates in soils (Vicca et al., 2022). Plants may enhance silicate mineral weathering in soils through their roots and associated mycorrhizal fungi, *via* diverse mechanisms such as the release of organic acids (Taylor et al., 2009; Thorley et al., 2015; Verbruggen et al., 2021) and secretion of acids or stimulation of acid-generating nitrification by nitrogen-fixing plants (Bolan et al., 1991; Epihov et al., 2017; Perakis and Pett-Ridge, 2019). Invertebrates in soil also contribute to weathering, both chemically, through the action of gut microbiota, and mechanically by bioperturbation (Van Groenigen et al., 2019; Vicca et al., 2022).

Besides capturing CO₂, enhanced weathering in soils also presents potential associated benefits. For example, soil pH is increased by alkalinity fluxes, eroded soils are replenished in the long-term with macro (e.g., Mg, Ca, K, P, and S) and micronutrients (e.g., B, Mo, Cu, Fe, Mn, Zn, and Ni) (Leonardos et al., 1987; Hartmann et al., 2013; Anda et al., 2015), while plant resilience to biotic and abiotic stress improves (Beerling et al., 2018). Particularly in agricultural land, enhanced weathering in soils could help revert agricultural soil erosion, act as a liming agent, and help reduce the use of fertilizers and pesticides (Kantola et al., 2017; Beerling et al., 2018, 2020; Haque et al., 2020b). As croplands cover 10% of the Earth's land surface (Monfreda et al., 2008), there is potential for large-scale application. Additionally, the equipment currently used in farming (e.g., lime spreaders) can be easily adapted to spread ground rocks on agricultural lands. Forested areas also provide opportunity for enhanced weathering in soils. The associated benefits of applying silicate rock dust on soils could promote plant growth and survival rate, through replenishing soil nutrients (Leonardos et al., 1987; Hartmann et al., 2013; Anda et al., 2015) and through increasing plant resilience to external stresses (Beerling et al., 2018). Moreover, mycorrhizal fungi associated with plant roots are one of the main drivers of silicate rock weathering in soils (Taylor et al., 2009; Thorley et al., 2015; Verbruggen et al., 2021). Urban and brownfield soils also present certain advantages for soil enhanced weathering (Manning and Renforth, 2013). In urban soils, enhanced weathering can be integrated in the landscape design to create carbon sinks, such

as “carbon capture gardens,” while brownfields have the potential to develop value by removing CO₂ as part of their remediation process (Manning and Renforth, 2013).

Alongside its many potential co-benefits, enhanced weathering in soils also has several drawbacks and risks, associated with comminution (which is the most energy demanding step of the process) (Renforth, 2012), transportation (as the distance from quarry to field increases, the CO₂eq emissions increase and by extension the CO₂ sequestration potential declines) (Lefebvre et al., 2019), and pollutants embedded into the mineral matrix being released in the environment through weathering (Haque et al., 2020a). For example, depending on the chemical composition of the parent material, the weathering of silicate minerals such as olivine might release heavy metals including chromium (Cr), nickel (Ni), or other elements [e.g., silicon (Si)], affecting the receiving ecosystems. Particularly in croplands, if these elements are present in concentrations higher than recommended by soil quality guidelines, they could be incorporated in the food chain, acting as pollutants and also affecting human and environmental health (ten Berge et al., 2012; Haque et al., 2020a). Plants with metal-accumulating mechanisms have been proposed as a strategy for preventing contamination of soils and water with toxic metals during enhanced weathering (Suhroff, 2022). There are also concerns about the effect of alkalinity addition to freshwater ecosystems, which have been shown to be sensitive to pH changes (Morgan, 1987; Wyatt and Stevenson, 2010; Pulido et al., 2012). Furthermore, the mining of natural rocks can have an ecological impact on wildlife, and/or require deforestation (Edwards et al., 2017). To reduce the need for mining and lower the overall cost, silicate-rich non-hazardous by-products or wastes from industrial processes, such as iron and steel slag (Das et al., 2019) or cement kiln dust (Beerling et al., 2020), can be used. Nevertheless, long-term comprehensive field studies across different climates and soil types are required to assess the suitability of spreading industrial alkaline wastes or by-products in soils (Beerling et al., 2020).

Finally, enhanced weathering in soils could be combined with other NETs, such as afforestation or reforestation, or with the feedstock crops used in BECCS and biochar. A combination of different approaches implemented together has a greater potential of achieving the CO₂ removal capacity that is needed (Minx et al., 2018) and reducing operational costs (Beerling et al., 2018). Additionally, combining enhanced weathering in soils with afforestation or reforestation and biochar could also lead to synergies, both through negating one another's potential negative impacts, and through increasing the carbon capture uptake (Amann and Hartmann, 2019). **Figure 4** shows the synergistic effects of combining enhanced weathering in soils, BECCS, afforestation/reforestation, and biochar. One proposed co-deployment scenario is the combination of enhanced weathering and biochar onto land used to grow crops for BECCS. In this scenario, the crushed rocks would act as a source of micro- and macronutrients (Leonardos et al., 1987; Hartmann et al., 2013; Anda et al., 2015), while biochar would increase nutrient release (Atkinson et al., 2010) and crop productivity (Jeffery et al., 2011; Kantola et al., 2017).



Ocean Alkalinity Enhancement

Seawater covers the majority of the Earth's surface (Shiklomanov, 1993) and is a large natural reservoir of carbon. Specifically, DIC in ocean water, which is dissolved CO_2 gas and bicarbonate and carbonate ions, is 140 times higher, by volume, than gaseous carbon in the atmosphere (de Lannoy et al., 2018). An equilibrium between atmospheric CO_2 and surface ocean waters exists, described by the Revelle factor, which accounts for $\sim 25\%$ of anthropogenic (surplus) CO_2 emissions already absorbed (Watson et al., 2020). The main mechanism for CO_2 mineralization in the oceans is its dissolution in seawater, since when CO_2 reacts with water (H_2O) it forms carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and acidity (H_3O^+), the latter mainly neutralized by carbonate ions (CO_3^{2-}) forming again bicarbonate, but also contributing to acidification (Egleston et al., 2010). As a result, the oceans are annually sequestering ~ 0.5 Gt CO_2 from the atmosphere (Renforth and Henderson, 2017). However, the capacity of the oceans for CO_2 uptake is not infinite and cannot cope with the increasing anthropogenic CO_2 emissions. Furthermore, CO_2 is acidic and therefore its uptake by surface ocean waters comes at the expense of their natural alkalinity, i.e., their mean pH has dropped by ~ 0.1 units over the past two centuries from an initial average of ~ 8.2 (Caldeira et al., 2005), and is projected to further decline by ~ 0.3 by 2100 (Figuerola et al., 2021). Note that pH scale is logarithmic and therefore the ~ 0.1 drop corresponds to around a 26% reduction of the surface ocean waters' mean alkalinity.

Research has previously explored injection of CO_2 into the deep ocean (Caldeira et al., 2005), however, the possibility of storing neutralized CO_2 as increased alkalinity is gaining increasing attention (Renforth and Henderson, 2017), along with the removal of DIC from seawater. Specifically, two main ocean-based NETs include: (i) removing carbon (DIC) from seawater, similar to DAC, using electrochemical processes (de Lannoy et al., 2018; Eisaman et al., 2018; La Plante et al., 2021a); and (ii) artificially increasing ocean alkalinity for enhancing seawater's carbon sequestration capacity (Renforth and Henderson, 2017), a process popularly known as ocean alkalinity enhancement (OAE) (Bach et al., 2019; Gagern et al., 2019). For the first pathway, given that the majority of carbon in seawater is in the form of carbonate and bicarbonate ions, CO_2 extraction processes must "swing" alkalinity to extract as much DIC as possible. DIC-depleted seawater will then return to the oceans, where atmospheric CO_2 will be taken up to maintain the air-ocean equilibrium. Therefore, ocean water can be used for both carbon capture and/or storage. Other CO_2 storage pathways exist, however these are not long-term DIC storage, but rather "ephemeral" storage up to 1,000 years of pure phase CO_2 , such as dry ice torpedoes where CO_2 is released from the sea surface with the goal being to penetrate the sea floor (Herzog and Drake, 1996), and intentional storage of CO_2 in deep ocean, as solid CO_2 hydrate, possibly in depths higher than 3,000 m, where CO_2 is denser than seawater and long-term storage is promoted (Caldeira et al., 2005). However, these storage pathways have been associated with environmental impacts on deep ocean ecosystems (Caldeira et al., 2005), while,

even in the deep ocean solid CO₂ hydrate will slowly decompose (GHG, 2004).

Electrochemical processes aim at controlling seawater's pH and trigger the removal of DIC (Sharifian et al., 2021). In the context of geochemical NETs, an acid (HCl) and an alkali (NaOH) are first produced, by seawater/brine electrolysis or electrodialysis, which can be used for two different distinct processes, i.e., the “acid” and the “base” process, respectively. In the acid process, HCl is used to acidify (to pH ~4) degassed (O₂ and N₂ have been removed) seawater, thus converting DIC to CO₂ gas, which is then captured (e.g., using hollow fiber membrane contactors). In the base process NaOH is directly added to seawater to raise the pH (>9) and precipitate carbonates in the form of CaCO₃ (de Lannoy et al., 2018). Subsequently, the natural alkalinity is restored in the decarbonized seawater of both processes, which is then returned to the ocean to recapture CO₂ and store it as bicarbonate (Eisaman et al., 2018). It could be possible to directly release the elevated-pH seawater from the base process to the ocean, since this will lead to additional atmospheric CO₂ uptake due to ocean alkalinity enhancement. Even though only the base process comprises a direct mineralization pathway (CaCO₃ is the final product), the gaseous CO₂ acid process can also be used to produce carbonate minerals. Single-step carbon sequestration and storage is similar to the base process since carbonate minerals are electrochemically (flow-through membraneless electrolysis) formed from DIC and divalent cations (Ca and Mg) that are naturally contained in seawater, however, in this case, without the need of fine-pore membranes but rather coarse-mesh electrodes (La Plante et al., 2021b). The main challenge in electrochemical processes pertains to high electricity and raw material (mainly electrodes or membranes) inputs (Sharifian et al., 2021), which raise costs and possibly environmental impacts.

In OAE alkaline materials, such as natural or artificial minerals and industrial waste/by-products (Renforth, 2019), are used to increase the oceans' alkalinity, thereby adding to its natural capacity as a carbon sink, i.e., CO₂ is permanently (>10,000 years) stored as aqueous bicarbonate ions (Renforth and Henderson, 2017). Three main methods for addition of alkaline materials to the ocean have been proposed: (i) coastal enhanced weathering (Meysman and Montserrat, 2017; Renforth and Campbell, 2021), whereby crushed or pulverized silicate minerals are spread onto beaches and coastal shelves and waves and currents promote their dissolution and the release of alkalinity into the ocean; (ii) ocean liming, whereby lime is spread on the open ocean for artificial alkalinity enhancement (Paquay and Zeebe, 2013; Renforth et al., 2013); and (iii) electrochemical approaches, which do not aim to remove DIC from seawater, but produce alkaline agents that can be used for OAE (House et al., 2009). Wastes from different industrial processes could also be used for OAE at scale (Renforth, 2019). However, alkaline wastes can be enriched with harmful pollutants, such as trace (heavy) metals (Gomes et al., 2016), and therefore, more likely, might find limited application for OAE, at least in the near future.

For silicate minerals to be quickly dissolved in the upper ocean, pulverization (<1 μm) is required (Meysman and Montserrat, 2017), which is energy intensive and not practical

(Hangx and Spiers, 2009). On the other hand, it can take up to thousands of years for olivine sand to fully dissolve in coastal environments (Hangx and Spiers, 2009), but high-energy shallow marine environments (coastal shelves and beaches) can greatly accelerate olivine dissolution (Schuiling and de Boer, 2011). Specifically, natural forces acting on the coastal environments, such as waves and currents, can be used to enhance the dissolution rates of silicate minerals (Montserrat et al., 2017). Among the industrially mined silicate minerals, olivine has been found promising for coastal enhanced weathering, since it is abundant and readily available (olivine mines can be found across the world), while its dissolution rate is significantly higher (three orders of magnitude) compared to ordinary quartz (Meysman and Montserrat, 2017). Similar to enhanced weathering in soils, coastal enhanced weathering can capture 0.28 g C per g olivine dissolved in ocean water (Köhler et al., 2013). On the other hand, olivine also contains various nutrients (mainly silicic acid and iron) that improve phytoplankton growth (fertilization), leading to a maximum carbon capture capacity of up to 0.57 g C per g of olivine spread (Hauck et al., 2016). Nonetheless, among others, silicic acid can alter marine biology, shifting phytoplankton species composition toward silicifiers such as diatoms (Köhler et al., 2013), while phytoplankton fertilization cannot be considered as a direct mineralization pathway. Silicifier growth can also turn the color of seawater to greener shades (Bach et al., 2019). Overall, coastal enhanced weathering appears promising, however, many open questions exist, including non-stoichiometric dissolution, pore-water saturation in the seabed, possible secondary reactions, and the exact ecosystem and feedback effects of large-scale olivine dissolution (Montserrat et al., 2017).

The surface ocean waters are supersaturated with respect to calcite (CaCO₃), i.e., limestone, and therefore its “activation,” typically through calcination prior to its spreading for OAE, has been proposed (Khesghi, 1995). As such, ocean liming is typically achieved using artificial alkaline minerals such as calcium oxide (CaO) or more likely calcium hydroxide (Ca(OH)₂) (Caserini et al., 2021), which will rapidly dissolve and release alkalinity in seawater (Justnes et al., 2020). Specifically, limestone is mined, crushed, washed, milled, and then calcined, before being transported and dispersed into surface ocean waters for alkalinity enhancement. It has been reported that 1.4–1.7 tons of limestone can uptake 1 ton of CO₂ from the atmosphere (Renforth et al., 2013). Since (bi)carbonate ions are added to seawater, ocean liming can benefit calcifiers such as corals (Comeau et al., 2013; Feng et al., 2016), coccolithophores, foraminiferans, and pteropods (Figuerola et al., 2021) which are threatened by ocean acidification (Doney et al., 2020). The rapid growth of calcifiers such as coccolithophores can give a bluer or whiter shade to the ocean color (Bach et al., 2019). Ocean liming faces several engineering challenges (Renforth et al., 2013), particularly in capturing and storing the carbon emissions from limestone decomposition (Paquay and Zeebe, 2013) and ocean spreading (Caserini et al., 2021), along with uncertainties pertaining to the responses of marine organisms to large-scale lime addition (Paquay and Zeebe, 2013; Das and Mangwani, 2015). Furthermore, ocean liming appears to

allow calcifiers to outcompete silicifiers, while coastal enhanced weathering allows for the opposite (Moore, 2021). This implies that these NETs can be used in tandem to maximize the uptake of atmospheric CO₂ and maintain the balance between different marine (micro)organisms.

Finally, it is possible to use electrochemistry to remove acidity, in the form of HCl, from seawater or from brines [e.g., from the desalination industry (Mustafa et al., 2020)] and store or neutralize this acidity (e.g., using silicate minerals) and return alkalinity (NaOH is produced along with HCl while excess alkalinity can also be produced from the dissolution of silicate minerals) to the oceans (House et al., 2007; Davies, 2015). Electrolysis or electrodialysis can be used to split seawater/brines and generate acidity and alkalinity; however, the proposed processes are typically energy intensive, with values in the range of 3–18 GJ per t of CO₂ removed from the atmosphere (Renforth and Henderson, 2017). Brines with high salt concentrations can be used to improve the process efficiency in acid (HCl) and alkali (NaOH) production; however, it is unlikely that the existing brines, primarily from the desalination industry, are sufficient for scaling up this process to the gigaton range. Therefore, it is more likely that electrochemical processes for OAE will be used complementary to coastal enhanced weathering and ocean liming, at least until the technology matures and becomes more energy efficient.

Application of Biotechnology to Geochemical NETs

Organisms are known to control many of the key reactions underlying geochemical NETs (Table 4), and microbial weathering strongly influences geologic cycling (Finlay et al., 2020; Samuels et al., 2020). The organisms, biomolecules and metabolisms underlying biogeochemical activity provide a diversity of mechanisms that can be integrated into geochemical NETs. Further, they can potentially be enhanced through protein engineering, directed evolution, metabolic engineering or other synthetic biology methods. Examples of naturally-existing mechanisms, applications of biotechnology to geochemical NETs to date, and future perspectives are discussed in the following three subsections.

The Influence of Organisms and Biological Mechanisms on the Chemical Reactions Underlying Geochemical NETs

Many bacteria and fungi promote dissolution of alkaline minerals by altering the chemical microenvironment at the mineral surface, in some cases for liberation of essential nutrients (Rogers and Bennett, 2004). Mechanisms include acidification *via* secretion of protons and weak organic acids, generation of carbonic acid as a byproduct of respiration, production of strong acids by chemolithotrophs, and production of polymeric and small molecule organic acids that act as chelators that catalyze mineral dissolution (Barker et al., 1997; Drever and Stillings, 1997; Nordstrom and Southam, 1997; Bennett et al., 2001; Lazo et al., 2017; Pokharel et al., 2019; Gerrits et al., 2021). Fungi can also increase the surface area of rocks by exerting mechanical forces that induce cracking (Bechinger

et al., 1999). Lichen (a mutualism between a fungus and a cyanobacterium) are particularly active in silicate mineral weathering, through penetration of hyphae and thalli, secretion of organic acids, and provision of dissolved carbonate and acidification through respiration (Chen et al., 2000). Rates of secretion of weathering agents by fungi and bacteria are reported to vary by mineral substrate and nutrient availability (Bennett et al., 2001; Schmalenberger et al., 2015), indicating that weathering can occur by mechanisms that are actively regulated by organisms. Organisms can also facilitate alkaline mineral dissolution by inhibiting the formation of passivating iron oxide layers; one such mechanism is secretion of small-molecule chelators known as siderophores (Liermann et al., 2000; Buss et al., 2007; Ahmed and Holmström, 2014; Torres et al., 2019). There has been some disagreement over the extent to which microbes and organic acid chelators catalyze mineral dissolution, and the range of minerals on which they act (Pokrovsky et al., 2009, 2021; Oelkers et al., 2015), indicating the need for further discourse and research to obtain clarity on the contexts in which microbial weathering occurs. Microbial biofilms have also been observed to reduce mineral dissolution rates in some contexts by inhibiting the exchange of ions with the bulk solution (Ullman et al., 1996; Lüttge and Conrad, 2004). Plant roots can also secrete organic acids that act as catalytic chelators (Ryan et al., 2001), and also support fungal and bacterial communities with weathering activity (Kang et al., 2017; Ribeiro et al., 2020; Verbruggen et al., 2021), which together contribute to weathering within the rhizosphere.

Microbially-mediated precipitation of carbonates is also widespread (Zhu and Dittrich, 2016; Görden et al., 2020), and its mechanisms are more thoroughly characterized than those of silicate dissolution. Many organisms promote carbonate precipitation by generating alkalinity or increasing ionic saturation state through metabolic activity. Photosynthetic organisms, which are thought to have influenced the majority of calcium carbonate formation through Earth's history (Altermann et al., 2006; Riding, 2006), promote carbonate precipitation by increasing pH through conversion of HCO₃⁻ to CO₂ and OH⁻, after which CO₂ is assimilated into biomass and OH⁻ is released (Power et al., 2007; Kamennaya et al., 2012). Ureolytic bacteria increase pH by producing NH₄⁺, OH⁻ and CO₃²⁻ through hydrolysis of urea (Zhu and Dittrich, 2016). Microbial degradation of amino acids as an energy source, called ammonification, also produces NH₄⁺, OH⁻ and CO₃²⁻ (González-Muñoz et al., 2010). Anaerobic oxidation of organic matter *via* reduction of nitrates by denitrifying bacteria, or reduction of sulfates by sulfate-reducing bacteria, produces alkalinity *via* consumption of protons and thereby also favors carbonate precipitation (Baumgartner et al., 2006; Martin et al., 2013). Oxalotrophic bacteria also promote carbonate precipitation by liberating both CO₃²⁻ and Ca²⁺, along with CO₂, through metabolism of solid calcium oxalate, which is abundant in many soils (Cromack et al., 1977; Braissant et al., 2002). Aerobic oxidation of organic matter by heterotrophs can also promote carbonate precipitation by producing CO₂, when CO₂ is limiting (Dupraz et al., 2009; Sánchez-Román et al., 2011).

TABLE 4 | Influence of biological agents on reactions or ions underlying geochemical NETs.

Type	Biological agent	Effects	Process
Organisms	Silicate-weathering microbes (e.g., <i>Knufia petricola</i>)	Acceleration of silicate dissolution, e.g., 7x increase in olivine dissolution by <i>Knufia petricola</i> in benchtop experiment (Pokharel et al., 2019).	Microbes can acidify the mineral surface microenvironment by secreting organic acids or by respiration; secrete small-molecule or polymeric organic acids/chelators that catalyze silicate dissolution; or prevent surface passivation by chelation of iron (Lazo et al., 2017; Torres et al., 2019).
	Strong acid-generating microbes (e.g., <i>Acidithiobacillus</i>)	Acceleration of silicate dissolution, e.g., 39 and 84% of Mg liberated from chrysotile mine tailings in stoichiometric and excess sulphuric acid conditions, in benchtop experiment (McCutcheon et al., 2015)	Chemolithotrophs can produce strong acids through metabolism of minerals, such as production of sulphuric acid by <i>Acidithiobacillus sp.</i> through metabolism of metal sulfides, which readily dissolve alkaline minerals (Nordstrom and Southam, 1997; Power et al., 2010; Schippers et al., 2014).
	Carbonate-precipitating microbes (e.g., cyanobacteria)	Promotion of carbonate precipitation, e.g., 18x increase in carbonate formation from serpentine mine tailings, with cyanobacteria-dominated microbial consortium (McCutcheon et al., 2016).	Phototrophs, ureolytic bacteria, and other microbes can increase pH and generate (bi)carbonate ions through metabolic activity; various microbes, and particularly cyanobacteria, secrete EPS that nucleate carbonate precipitation; and heterotrophs can supply CO ₂ by oxidizing organic carbon or metabolizing cation-saturated EPS (Dupraz et al., 2009; Zhu and Dittrich, 2016).
	Silica-forming microbes (e.g., diatoms)	Sequestration of waste silicic acid, the buildup of which may inhibit mineral carbonation, e.g., diatoms sequestered 87% of silicon in microbial carbonation experiments with synthetic alkaline wastewater (McCutcheon et al., 2019).	Diatoms and siliceous sponges form silica shells or skeletons (Sumper and Kröger, 2004; Müller et al., 2013a). Photosynthetic diatoms are found naturally growing in alkaline mine wastewater.
Enzymes and proteins	Carbonic anhydrase (CA)	Alleviates CO ₂ hydration kinetics as a rate-limiting factor	CAs are metalloenzymes that catalyze equilibration between dissolved CO ₂ and carbonic acid (Mesbahuddin et al., 2021). Some CAs can also inhibit or nucleate carbonate precipitation depending on ionic conditions (Miyamoto et al., 2005; Rodriguez-Navarro et al., 2019).
	Silicateins and silaffins	Sequestration of waste silicic acid, the buildup of which may inhibit mineral carbonation.	Catalysis of polymerization of silica from silicic acid (Sumper and Kröger, 2004; Müller et al., 2013a).
	Calcareous shell matrix proteins	Various functions, including nucleation and inhibition of carbonate precipitation, mineralization templating, CA activity, concentrating ions.	A complex matrix of proteins and other biomolecules coordinates the formation, morphology and nanoscale structure of shells in mollusks and corals (Falini et al., 2015; Marin, 2020).
	Ion transporters	Manipulation of ion concentrations in microenvironments, including Ca ²⁺ , Mg ²⁺ , H ⁺ , HCO ₃ ⁻ , and H ₄ SiO ₄	Passive or active (ATP-dependent) transport of ions to manipulate intra- or extracellular concentrations, to provide input ions for photosynthesis, calcareous shell formation, siliceous shell formation, or other purposes (Martin-Jezequel et al., 2000; Dominguez, 2004; Maguire, 2006; Buch-Pedersen et al., 2009; Reinfelder, 2011; Knight et al., 2016).
Non-enzymatic biocatalysts	Extracellular polymeric substances (EPS)	Promotion of carbonate precipitation; catalysis or inhibition of silicate dissolution	Negatively charged EPS adsorbs and concentrates cations, which nucleate carbonate precipitation, and digestion of EPS by heterotrophs liberates bound cations and produces CO ₂ to raise the saturation state (Dupraz et al., 2009). Some EPS can catalyze silicate dissolution by concentrating protons or chelating cations, and others may inhibit silicate dissolution by adsorbing to mineral surfaces (Welch et al., 1999).
	Organic acids and chelators	Catalysis of silicate dissolution, e.g., 10–100-fold acceleration of forsterite dissolution by oxalic and phthalic acids (Oelkers et al., 2018).	Organic acids, which frequently also act as chelators, provide acidity and/or complex and solubilize cations within the mineral crystal framework in a pH-dependent manner (Lazo et al., 2017; Oelkers et al., 2018).
	Siderophores	Inhibition of the formation of passivating iron oxide.	Siderophores are a large class of microbial and plant chelators that bind diverse cations, particularly Fe ions, at high affinity and promote their uptake from the environment (Ahmed and Holmström, 2014).

Carbonate precipitation can also be influenced through biophysical mechanisms. Some extracellular materials secreted by microbes, broadly termed extracellular polymeric substances

(EPS), contain a diversity of negatively charged or chelating chemical moieties that bind cations, and are observed to either inhibit or promote carbonate precipitation in different

contexts. Under conditions of low saturation of bound cations, EPS can inhibit carbonate precipitation by depleting the microenvironment of cations, while under conditions of high saturation, EPS can promote carbonate precipitation by enriching the microenvironment with cations (Dupraz et al., 2009). Degradation of EPS by heterotrophs, which liberates bound cations and (bi)carbonates, can also induce carbonate precipitation (Dupraz et al., 2009). The surfaces of microbial cells themselves, which often bear negatively charged functional groups, can also promote carbonate precipitation by attracting cations (Dupraz et al., 2009). High EPS production in combination with alkalinity generation make cyanobacteria particularly effective at nucleating and precipitating carbonates (De Philippis et al., 2001; Decho et al., 2005; Braissant et al., 2009).

Notably, biological precipitation of magnesite (MgCO_3) has been observed at room temperature (McCutcheon et al., 2019; Zhang et al., 2020), despite being inhibited at temperatures below 80°C in abiotic conditions due to the high energy of dehydration of aqueous Mg^{2+} (Saldi et al., 2009). The proposed mechanism for magnesite precipitation at ambient temperature is dehydration by the negatively charged EPS and cell surfaces (Power et al., 2017). Magnesite precipitation is preferable compared to hydrated magnesium carbonates, since it contains a higher stoichiometric fraction of carbon.

Enzymes and peptides are also known to catalyze reactions relevant to geochemical NETs, including hydration of CO_2 and carbonate precipitation. Of these, CO_2 hydration is the best studied and presently the most tractable to engineering. Carbonic anhydrases (CAs) are metalloenzymes that catalyze equilibration between dissolved CO_2 and carbonic acid (Lindskog, 1997). They are among the most efficient enzymes known in nature, with their rates often being diffusion-limited. They exist as ≥ 8 evolutionarily distinct families of CA genes across all domains of life (Mesbahuddin et al., 2021), with diverse enzymatic parameters. CAs are involved in diverse processes, including biomineralization of calcium carbonates (Bertucci et al., 2013; Müller et al., 2013b; Karakostis et al., 2016; Sharker et al., 2021). CAs commonly have additional activity, including inhibition or promotion of carbonate precipitation (Miyamoto et al., 2005). A recent study found that bovine CA directly influences carbonate precipitation mechanisms in multiple ways: it interacts with growing calcium carbonate crystals, thereby modifying their growth and morphology; it can also inhibit precipitation under conditions of low CO_2 , possibly by stabilizing pre-nucleation ion complexes; and it can undergo conformational changes and oligomerization under high pH or high CO_3^{2-} and Ca^{2+} concentrations, abrogating anhydrase activity and instead templating nucleation of calcium carbonate (Rodríguez-Navarro et al., 2019). It has been suggested that the above mechanisms of CA are involved in the controlled growth of calcareous structures like shells (Rodríguez-Navarro et al., 2019). Carbonic anhydrase has also been demonstrated to catalyze the dissolution of calcite, possibly by catalyzing the transfer of protons into the mineral lattice during protonation of CO_3^{2-} (Dong et al., 2020).

Multicellular and unicellular organisms also demonstrate exquisite control over carbonate precipitation using combinations of the aforementioned mechanisms during

the formation of shells and intracellular carbonate inclusions. Intracellular formation of carbonates in bacteria has been observed, including in environments that are undersaturated with respect to carbonate mineral phases, suggesting that active mechanisms control the ion transport and mineral precipitation, though the precise mechanisms of control are as-yet unclear (Görge et al., 2020). Shells in coccolithophores, mollusks, corals and reptilian and avian eggs are typically $>95\%$ CaCO_3 by mass, with the remaining organic matter consisting of diverse proteins and polysaccharides functioning to scaffold, nucleate, or remodel calcium carbonate, including intracrystalline proteins (Falini et al., 2015; Taylor et al., 2017; Marin, 2020; Gautron et al., 2021). While the specific biomolecular functions of most shell organic components are unclear, many functions have been identified, including proteins that promote or inhibit calcium carbonate nucleation, as well as CAs (Evans, 2019; Marin, 2020). Interestingly, coccolithophores produce individual calcium carbonate particles known as coccoliths intracellularly within specialized vesicles, after which the particles are secreted onto the cell surface to form a shell (Taylor et al., 2017).

Other enzyme families, especially enriched in ocean-dwelling siliceous organisms, facilitate silica polymerization. Silicateins are enzymes found in sponges that catalyze polymerization of amorphous silica (Müller et al., 2013a), and silaffins are highly post-translationally modified peptides found in diatoms that do the same (Sumper and Kröger, 2004; Lechner and Becker, 2015). Silicase is an enzyme reported to catalyze the dissolution of amorphous silica (Schröer et al., 2003), though we are unaware of other published work in which silicase activity is documented reproduction of the original results should be pursued to inspire confidence in their robustness.

Further, active biological transport mechanisms exist for concentrating or depleting Ca^{2+} , Mg^{2+} , H^+ , HCO_3^- , and H_4SiO_4 within microenvironments (Martin-Jezequel et al., 2000; Dominguez, 2004; Maguire, 2006; Buch-Pedersen et al., 2009; Reinfelder, 2011; Knight et al., 2016). For example, carboxysomes are cyanobacterial organelles within which bicarbonate is actively concentrated and then converted to CO_2 by CA, thereby providing high levels of CO_2 to the photosynthetic enzyme RuBisCO (Price et al., 2008).

Some research has investigated the influence of supercritical CO_2 on microbes, with potential relevance to the use, or passive influence, of microbes on subsurface CO_2 mineralization for storage. While supercritical CO_2 generally inhibits microbial growth (Yu and Chen, 2019), multiple studies have found organisms with only mildly inhibited growth under supercritical CO_2 and have investigated its effects on community structure and geochemistry (Peet et al., 2015; Santillan et al., 2015; Jin and Kirk, 2016; Freedman et al., 2017, 2018; Ham et al., 2017; Li et al., 2017; Boock et al., 2019).

Collectively, the organisms and biological mechanisms discussed in this section constitute a starting point for the integration of biology into alkaline mineral NETs.

Biologically-Enhanced Geochemical NETs

Biotechnology research has explored applied methods for geochemical NETs to a limited degree. Pioneering examples

to date have focused primarily on enhanced dissolution and carbonation of mine tailings (Power et al., 2010; McCutcheon et al., 2014) at laboratory scale.

Sulfur-oxidizing bacteria have been proposed for use in dissolution of alkaline minerals by catalyzing the production of sulphuric acid from sulfides, e.g., sulphidic mine tailings (Power et al., 2010). Similar approaches are used for biomining of copper and other metals (Schipper et al., 2014). Laboratory optimization experiments found that such an approach liberated 39% of Mg from chrysotile mine tailings while maintaining leachate pH suitable for carbonate precipitation, and up to 84% of Mg in acidic leachate (McCutcheon et al., 2015). The cost of transporting acid-generating feedstocks, which are consumed stoichiometrically as silicates dissolve, may be strongly influenced by relative geographic location of tailings and feedstocks (Power et al., 2014). Combination of this approach with microbially-mediated carbonate precipitation has been proposed for carbon sequestration in ultramafic mine tailings or other *ex situ* applications (Power et al., 2014).

Cyanobacteria have been proposed as catalysts for precipitation of carbonates in alkaline mineral NETs (Jansson and Northen, 2010). In laboratory experiments, a cyanobacteria-dominated consortium sourced from an alkaline tailings lake was inoculated into columns of acid-leached chrysotile tailings and caused precipitation of a crust of magnesium carbonates containing ~18-fold more carbon than abiotic controls (McCutcheon et al., 2016). Large-scale bioreactor experiments simulating an artificial alkaline wetland with inoculation of a microbial consortium confirmed cyanobacteria-mediated formation of a magnesium carbonate crust, but found that depletion of essential nutrients, including phosphate, in the reaction medium limited microbial growth and EPS production in the majority of the bioreactor, drastically reducing mineral precipitation (McCutcheon et al., 2014). Increased nutrient delivery in a follow-up experiment resulted in biofilm growth that outpaced carbonate precipitation (McCutcheon et al., 2019); these studies indicate that nutrient distribution is an important consideration in scaled deployment. The latter study also found that diatom growth successfully sequestered ~87% of the silicon in the bioreactor, providing a sink for silicon waste produced during alkaline mineral dissolution. A microbial carbonation experiment on site at a tailings pile failed to produce a cemented carbonate-chrysotile crust; the authors hypothesized that accessibility of water and CO₂, as well as effects of weather, limited microbial growth and carbonate precipitation (McCutcheon et al., 2017). Failure of the latter experiment illustrates the need for increased application-focused research and lends support to the notion that microbial carbonation of tailings may benefit from more controlled environments like bioreactors as compared with open tailings piles.

Oxidation of waste organics to CO₂ in the presence of alkaline minerals has been proposed as a mechanism for promoting carbonation in contexts where CO₂ accessibility is limiting; such an approach sequesters carbon that was fixed into organics, preventing its decay and the subsequent return to the atmosphere (Mitchell et al., 2010; Power et al., 2011, 2014). Heterotrophic bacteria have been shown to promote carbonate precipitation

via oxidation of organic matter in laboratory experiments with phototrophic and heterotrophic consortia in mine tailings (Power et al., 2011) and ureolytic microbes in synthetic brine (Mitchell et al., 2010).

These early investigations into microbially-enhanced carbon sequestration in mine tailings illustrate promise for more scaled deployment. Carbon sequestration potential using microbes in mine tailings has been variously estimated at 123 t ha⁻¹ yr⁻¹ (McCutcheon et al., 2016) to 222–238 t ha⁻¹ yr⁻¹ (McCutcheon et al., 2019) based on rates found in laboratory experiments, or 175 Mt yr⁻¹ globally if carbonation is taken to completion, which could also be economically viable (Power et al., 2014). Applications using minerals mined for the purpose of weathering would increase this potential drastically. However, field trials and pilot tests, as well as integration and optimization of the combined use of phototrophs, heterotrophs, enzymes and biostimulants will be required to determine the true benefits and costs these approaches can bring to carbon removal and sequestration.

Some authors have proposed the biomass produced during phototroph-mediated carbonate precipitation could be used for production of fuels or other commodity chemicals (Ramanan et al., 2010; Power et al., 2011), providing a second source of economic utility. The biomass could also be fed to heterotrophs, producing carbonic acid and other organic acids that would dissolve alkaline minerals and further precipitate carbonate.

CA has been investigated for applications in carbon capture, utilization and storage (CCUS), primarily in point source CO₂ scrubbers (Alvizo et al., 2014; Bose and Satyanarayana, 2017; Giri et al., 2020; Mesbahuddin et al., 2021). Some research has investigated the use of CA in geochemical NETs. Bovine CA has been shown to efficiently promote carbonation of alkaline minerals by alleviating the hydration of CO₂ as a kinetic barrier, with 240 and 360% increased sequestration rates of carbon in brucite under non-optimized conditions with sparging of 10% CO₂ (Power et al., 2016) or ambient air (Power et al., 2013a), respectively. *E. coli* expressing recombinant CA were also shown to facilitate carbonate precipitation (Kim et al., 2012; Tan et al., 2018). The native CA activity in unicellular algae was found to facilitate carbonate precipitation during sparging of 10% CO₂ in alkaline media while producing algal biomass. These experiments warrant further research into deployment of CA in geochemical NETs.

Ureolytic (Mitchell et al., 2010) and denitrifying (Martin et al., 2013) bacteria have also been explored for their potential to mediate carbonate precipitation for carbon sequestration. However, the utility of these alkalinity-generating heterotrophs is limited by the requirement that the carbon should be delivered as a reduced carbon feedstock (urea in the case of ureolytic), since they only produce enough alkalinity to mineralize the carbonate their metabolism produces (Mitchell et al., 2010). However, they may be useful for sealing pores *via* carbonate precipitation to form caprock for subsurface storage of supercritical CO₂ (Cunningham et al., 2009).

While most engineered biomineralization research has been conducted under ambient pressures, a few studies have been performed at higher pressures more relevant to subsurface

mineralization; however these studies were performed using ureolytic and denitrifying bacteria for the purpose of caprock formation (Martin et al., 2013; Mitchell et al., 2013). Organisms have been found growing as deep as 2.8 km in the subsurface, so the challenge of growth under high pressure is not insurmountable (Chivian et al., 2008; Glombitza et al., 2016).

In addition to sequestering carbon, biomineralization of alkaline minerals can provide a means for bioremediation of toxic metals or other pollutants by locking them within solid carbonate (Gadd, 2010; Zhu and Dittrich, 2016; Krajewska, 2018; Jain and Arnepalli, 2019; Ehrlich et al., 2021). Microbially-mediated carbonation of mine tailings may serve the dual purpose of sequestering carbon and remediating mine sites (McCutcheon et al., 2016).

It has also been proposed that alkaline minerals could be integrated into industrial microbial wastewater treatment and biogas production systems, where they would both neutralize acidity and sequester CO₂ (Lu et al., 2018), with laboratory work showing promising results. In the methods proposed, microbes are not used for direct interaction with the minerals, but rather the minerals are integrated into existing microbial digestion or microbial electrosynthesis processes.

Toward Further Integration of Biology Into Geochemical NETs

Despite these exciting examples, we posit that the possibility-space of biologically-enhanced geochemical NETs is drastically under-explored given the broad ability of biological mechanisms to influence the key reactions. Organisms or biomolecules could be incorporated into the abiotic geochemical NETs described in the previous sections to improve reaction kinetics or prevent inhibitory passivation.

In environments where the dissolution rate of CO₂ is limiting, CAs could be deployed in solution, immobilized on surfaces or within water-permeable beads (Xu et al., 2021), or produced by organisms engineered to secrete or display it (Zhu et al., 2022). CAs could also be used to catalyze the dissolution of calcite, generating alkalinity (Subhas et al., 2017). Silicase enzymes, if developed, could be useful for promoting the dissolution of alkaline minerals that contain polymerized silica, extending fast dissolution beyond the typically-favored orthosilicates (i.e., extend enhanced weathering beyond olivines to include pyroxenes, feldspars, etc.). Silicas could also help to dissolve passivation layers of amorphous silica.

Microbes could also be co-injected alongside aqueous or supercritical carbon dioxide to facilitate *in situ* mineralization. Microbes and enzymes could be particularly useful in reactor-based mineral weathering environments, where conditions can be more precisely controlled.

Microbes could also be applied alongside minerals that are distributed for terrestrial or coastal enhanced weathering efforts (Ribeiro et al., 2020). Given that environmental microbes generally function in communities, emerging methods for modification of microbial communities (Lawson et al., 2019) could be developed for use in many of the applications proposed above (e.g., in soil). If non-native or engineered microbes were used, the impact of uncontained release on indigenous ecosystems would need to be carefully considered, though

challenges to stable establishment of non-native microbial communities is more likely to be encountered than unwanted proliferation (Albright et al., 2022).

Given the ability of organisms to alter chemical microenvironments, they may be useful in contexts where different conditions are desired at the mineral surface compared to the bulk solution; for example, acidic conditions could be generated at a mineral surface to enhance dissolution kinetics while more basic conditions are maintained in the bulk to favor carbonate precipitation, or catalysts could be secreted at the mineral surface to avoid costs of chemically altering the bulk. In general, the microbes or biomolecules used could be native or non-native, and unmodified or engineered. Engineered organisms may provide superior performance, as they could be optimized both for the unnatural chemical and physical environments created by geochemical NETs and for their specific roles in technologies; for example, catalysts discovered using molecular engineering methods could be produced metabolically by engineered organisms.

Biological approaches may also enable tuning of the characteristics of the output materials of geochemical NETs for improved utility; for example, carbonate or silica particles could be produced biologically for use as cement additives that may reduce emissions from cement production, or sequester carbon in concrete, while improving concrete performance (Müller et al., 2013a; Gadikota et al., 2015; Show et al., 2015; Singh et al., 2015; Iravani and Varma, 2019). Diatoms could also be used for low-cost production of silica particles, potentially with surface functionalization or enzymatic display, for use in concrete or other applications (Sardo et al., 2021).

Deployment of microbes or enzymes in the context of geochemical NETs may require tolerance of extreme conditions of pH, ionic strength, temperature, and/or pressure. Enzymes may need to be engineered for stability and/or isolated from extremophilic organisms (Packer and Liu, 2015; Mamo and Mattiasson, 2016; Ma et al., 2019; Ren et al., 2019; Yin et al., 2019); such work is already underway for carbonic anhydrase (Mesbahuddin et al., 2021). Deployed organisms, whether engineered or unmodified, will also need to tolerate those conditions; in the case of engineered organisms, this will require the development of synthetic biology methods for organisms that are presently non-standard (Wannier et al., 2020; Filsinger et al., 2021).

Many of the biogeochemical mechanisms discussed in this section have not received much attention from molecular biotechnology. Development of high-throughput platforms for their study and engineering will benefit both their application to NETs and the study of their underlying biology. For example, platforms for highly multiplexed screening, selection, or directed evolution of variants of enzymes or organisms that dissolve silicates or precipitate carbonates would be useful both for discovering natural mechanisms and for engineering. Such platforms are ubiquitous in well-developed medical domains of molecular biotechnology (Packer and Liu, 2015; Zeymer and Hilvert, 2018; Zeng et al., 2020; Madhavan et al., 2021).

Risks of environmental biocontamination should be considered before deployment of organisms in uncontained environments, such as mine tailings ponds or the subsurface.

While engineering organisms for environmental deployment is a new frontier, we note that it is not without precedent, as there are many such research efforts underway (Coleman and Goold, 2019; Jaiswal and Shukla, 2020; Janssen and Stucki, 2020; Rylott and Bruce, 2020; Zhou et al., 2022), including field trials (Carvalho et al., 2015). Advances in biocontainment may provide options for restricting the spread of engineered microbes outside the intended environment (Lee et al., 2018).

Given the apparent potential for biotechnology to contribute to geochemical NETs, we encourage the research and funding communities to more thoroughly investigate possibilities, including designs for possible NETs incorporating biological mechanisms and applied engineering of specific mechanisms, as well as the underlying biogeochemical science. Design and techno-economic considerations should be examined, accounting for the constraints biotechnology could alleviate and introduce, for example, reductions in capital and operating expenditures resulting from improved kinetics and extent of reaction, as well as methods and costs for delivering feedstocks to stimulate organism growth. The diversity of organisms and biomolecules that manipulate key reactions, as well their chemical mechanisms and metabolic and genomic underpinnings, should be more comprehensively examined. New research tools should be developed that will benefit both the fundamental biology and engineering of relevant mechanisms. Although biotechnology applications for geochemical NETs are currently under-developed, they may prove to play an important role with continued dedicated efforts. Possible applications range in complexity, with some accessible today while others will require years or decades of concomitant advances in basic biology, biotechnology, and NETs engineering. The latter group may assist in driving down costs to enable the crucial scaling of NETs by mid-century.

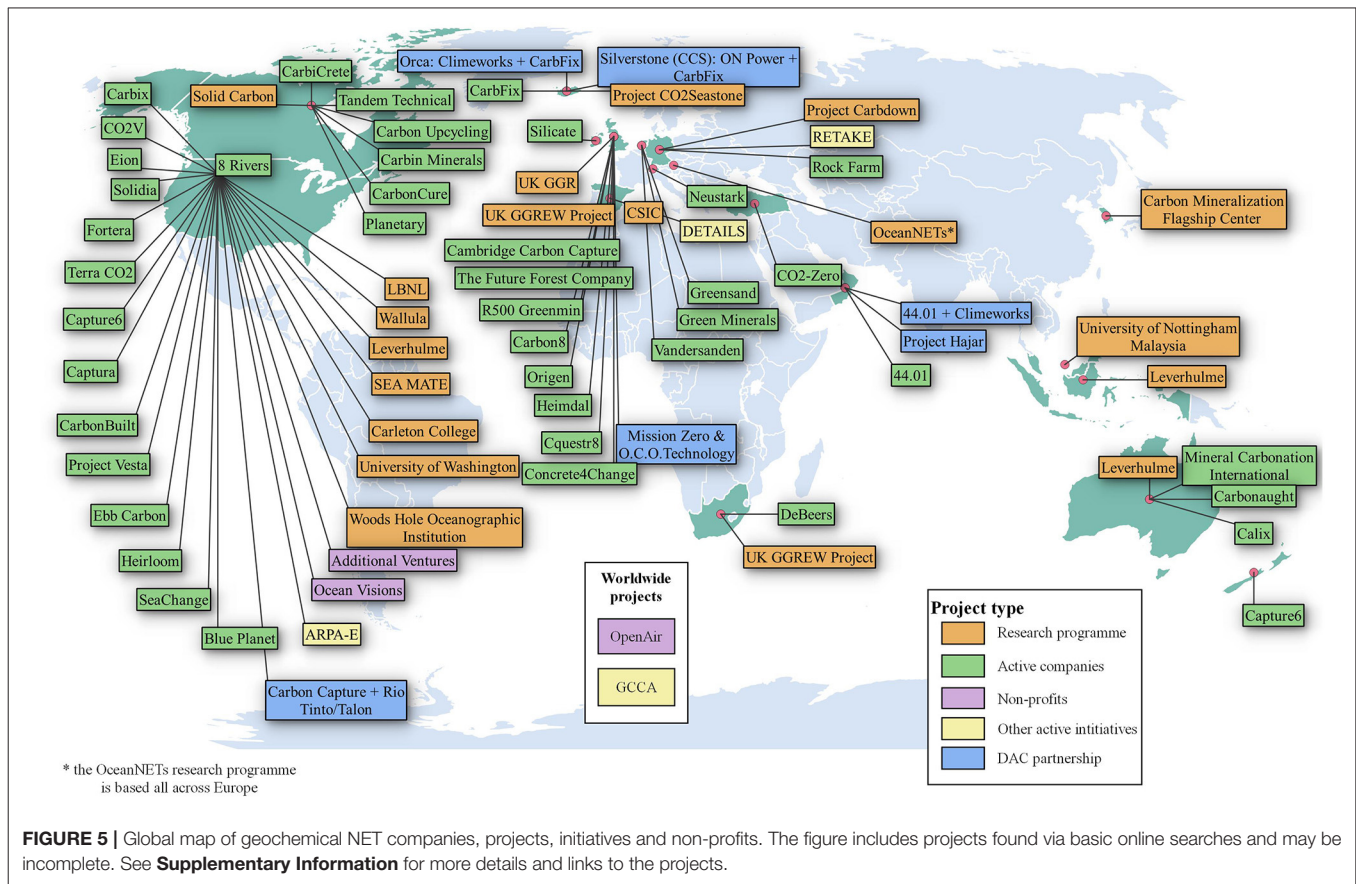
LIFE CYCLE ASSESSMENT ON GEOCHEMICAL NETs

Research has mainly focused on techno-economic aspects of different geochemical NETs, and NETs in general. However, this is not the case for other important aspects such as their social perspective, including social acceptance, and their environmental perspective, the latter typically examined using the life cycle assessment (LCA) methodology. Specifically, even though (geochemical) NETs aim at removing CO₂, they could also be responsible for emitting GHGs and other pollutants throughout their life cycle (Cooper et al., 2022). Therefore, LCA can play an important role in both identifying such emissions and minimizing them, and also in comparing, from the environmental perspective, different NETs to identify the most promising solution under the local conditions. The reason is that the environmental performance of NETs depends not only on the technology but also on local conditions and spatial restrictions. For example, Lefebvre et al. (2019) found that transportation (distance from quarry to field) was a key limitation to enhanced weathering in soils, whereas Deutz and Bardow (2021) studied the environmental sustainability of the DAC plants in Hinwil and Hellisheiði, operated by Climeworks, and noted that the LCA

results are very sensitive to the energy sources. Furthermore, when comparing different NETs, a wide range of environmental impacts should be considered (McQueen et al., 2021b) as well as other aspects of each technology. For example, Cooper et al. (2022) compared the effectiveness in carbon sequestration of afforestation/reforestation, enhanced weathering, DAC, and BECCS and noted that even though the first had the lowest environmental impact it exhibited very low carbon removal rates, whereas BECCS had a lower impact on climate change and toxicity compared to enhanced weathering and DAC, but a much higher impact on land use.

However, more research is required on LCA, since many challenges pertaining to different functional units, system boundaries, the climate change-energy nexus, and the timing of GHG emissions and removals make the direct comparison of different NETs difficult (Goglio et al., 2020). Furthermore, when system expansion has been used in LCA, avoided emissions, due to substitution of certain processes, have been misinterpreted as negative emissions, i.e., as carbon removal from the atmosphere, and therefore there is a need to distinguish between avoided and negative emissions, along with consistency in system boundaries and functional units (Terlouw et al., 2021). For example, when 27 LCA studies on NETs were reviewed by Tanzer and Ramírez (2019), 41% (11 studies) labeled avoided emissions as negative emissions, while it was also noted that system boundary choices also play an important role on the perceived emission balance of a NET. For this reason, guidelines for LCA studies on NETs have been proposed (Müller et al., 2020), while detailed life cycle inventory (LCI) data for different spatial extents, power systems, and chemical processes pertaining to NETs are also required (Cruz et al., 2021). The importance of the system boundary, allocation/system expansion, data availability and accuracy, parameter uncertainty, permanence of CO₂ removal, and the need for common guidelines in LCAs for NETs has been also highlighted (McQueen et al., 2021b). In this regard, the integration of LCA with techno-economic analysis (TEA) can decrease NETs uncertainty and improve technology readiness levels (TRL) (Li and Wright, 2020).

Finally, apart from capturing and permanently storing CO₂, (geochemical) NETs can also be associated with a wide range of positive but also negative environmental impacts, which have yet to be fully identified and therefore are not typically included in the system boundary of LCA studies. For example, ocean acidification greatly impacts marine ecosystems and reliant human communities (Doney et al., 2020), particularly affecting tropical coral ecosystems (Comeau et al., 2013; Feng et al., 2016). However, these positive effects of alkalinity addition, along with possible negative ones such as changes in the primary productivity, respiration, and photophysiology of living organisms in alkalized seawater (Gore et al., 2019) or freshwater (Mant et al., 2013) have yet to be fully identified and quantified and therefore cannot be captured in LCA studies that examined ocean alkalinity enhancement NETs. This is also the case for terrestrial NETs. For example, although the potential co-benefits of dispersive enhanced weathering approaches are numerous, these are difficult to quantify and use as inputs in LCA studies, since their potentially irreversible effects may not become apparent until years after application, at which



point the socio-technical systems may already be entrenched [see Collingridge dilemma (Collingridge, 1979)]. Therefore, there is a need for more research on the biological responses of different NETs, as to identify and quantify both the negative and positive effects and then use this data as inputs in LCA studies dealing with NETs. By doing so, more robust and reliable LCA results will be obtained which could also play an instrumental role in improving the social acceptability of NETs. Specifically, public acceptability can be a potential constraint on the research and deployment of NETs (Bertram and Merk, 2020) and particularly of the ocean-based NETs, which might face a greater public acceptability challenge than their terrestrial counterparts (Cox et al., 2021). To this end, apart from the environmental perspective, the social and economic perspectives should also be considered, thus examining the overall life cycle sustainability of each NET and effectively communicating the results to improve public perceptions and acceptability.

THE CURRENT STATE OF GEOCHEMICAL NETs

The recent Innovation for Cool Earth Forum (ICEF) Roadmap underlined that geochemical NETs have the lowest ratio of policy coverage to potential impact compared to other NET approaches. Most policy frameworks [e.g., 45Q, CA LCFS, EU CTS (Low Carbon Fuel Standard; EU Emissions Trading

System (EU ETS); Internal Revenue Service, 2021)] have criteria that unintentionally exclude geochemical NETs. International agreements prohibit commercial NETs that involve the release of alkaline feedstock into the ocean. However, some government agencies such as the Advanced Research Projects Agency-Energy (ARPA-E) in the US are exploring the potential contribution of alkaline mineral-based technologies to negative emissions, enhanced metal recovery, and the decarbonization of industry and mining (ARPA-E, 2021).

While geochemical NETs remain a niche industry, the emergence of recent projects, such as those that offer carbon removal credits or sequester carbon within concrete, suggest that the industry is expanding. New companies are involved in piloting projects, some partnering with DAC companies that provide input CO₂, e.g., the *in situ* mineralization projects underway in Iceland and Oman. Early but increasing exploration by large organizations in agriculture, mining, and concrete includes diamond miner DeBeers, who is experimenting in-house with mineralizing kimberlite (DeBeers group, 2019), Rio Tinto, who recently invested in a CarbonCapture DAC+mineralization project (Hiar, 2021), and The Global Cement and Concrete Association (80% of global production), whose 2021 roadmap calls for industrial-scale carbon capture at calcination sites (GCCA, 2021).

A list of companies and projects currently known to the authors is shown geographically in the map given in **Figure 5**. This map illustrates the range of projects underway today,

but underlines that we are far from having a large-scale, high-functioning geochemical NETs industry, as many of these projects are in their infancy and have yet to deploy geochemical NETs or remove substantial amounts of CO₂.

FINAL REMARKS

In this review, the body of knowledge on geochemical NETs was distilled and comprehensively discussed, focusing on terrestrial, subterranean, and ocean-based geochemical NETs. Over the last two decades, an enormous amount of work has been published relating to geochemical NETs, suggesting the large strides that have been made in this regard. It appears that these technologies have great potential for carbon removal and storage, owing to the vast resource of low cost natural and artificial alkaline minerals, their thermodynamically favorable reactions with CO₂, and the long-term stability of the carbon-bearing products they form. However, the field of geochemical NETs remains, by and large, nascent with few fully-fledged technologies being available. To avoid the worst effects of climate change the introduction of geochemical NETs at scale (Gt CO₂ yr.⁻¹) is required as soon as possible. To achieve this, proactive, deliberate, and strategic initiatives are necessary for accelerating technology maturity along with substantially improving the public acceptance of these technologies, which is required for their large-scale introduction. For this reason, in Part II of this work, a roadmap, which is accessible and actionable to both specialist and non-specialist actors, is put forth with the goal of catalyzing the implementation of gigaton-scale removal on the timeframes that the Intergovernmental Panel on Climate Change (IPCC) and other key organizations suggest that is needed from as soon as 2025.

AUTHOR CONTRIBUTIONS

All authors contributed to the drafting and revision of the manuscript, and read and approved the final submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fclim.2022.879133/full#supplementary-material>

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NOMENCLATURE

Carbonic anhydrase (CA): Enzyme that catalyzes equilibration between dissolved CO₂ and carbonic acid.

CO₂ mineralization: also referred to as mineral carbonation, a process by which CO₂ becomes a solid mineral, namely carbonate. The term carbon mineralization is also widely used in the field and should not be confused with conversion of organic carbon into CO₂.

Direct air capture (DAC): an engineered process of capturing carbon dioxide directly from ambient air and generating a concentrated stream of CO₂ for sequestration or utilization.

Dissolved inorganic carbon (DIC): $\text{HCO}_3^-_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})} + \text{CO}_{2(\text{aq})}$

Enhanced weathering: a method whereby crushed alkaline minerals, typically Mg- and Ca-rich silicates, are spread in the environment where they undergo physical, chemical and biological weathering, thus removing CO₂ from the atmosphere and storing it as carbonate minerals and ocean bicarbonate. Two main types of enhanced weathering exist—coastal enhanced weathering and enhanced weathering in soils. Over longer time frames, these are also methods of ocean alkalinity enhancement.

Extracellular polymeric substances (EPS): A broad term for biological polymers secreted by microbes. Depending on specific properties, EPS can influence ion concentrations in microenvironments, nucleate carbonate precipitation, and catalyze mineral dissolution.

Ex situ mineralization: High surface area alkaline minerals are reacted with CO₂-rich gases in engineered reactors, enhanced by elevated temperature and pressure, or using reagents. Mineral

reactants are usually transported to a site of CO₂ production. Carbonate mineral products may be utilized.

Geochemical NETs: Any negative emissions technology which involves substantial amounts of alkali or alkaline minerals in its flowsheet.

Indirect ocean capture (IOC): Technologies which remove dissolved inorganic carbon from the ocean, and thus CO₂ from the atmosphere, *via* air-ocean gas exchange due to the pH sensitivity of the ocean's carbonate buffer system.

In situ mineralization: CO₂-bearing fluids or wet supercritical CO₂ are injected into suitable rock formations beneath the Earth's surface where the CO₂ is mineralized.

Negative emissions technologies (NETs): Any technology which removes CO₂ from the air, directly or indirectly, for the purpose of climate change mitigation. Also known as carbon dioxide removal (CDR) technologies.

Ocean alkalinity enhancement (OAE): Technologies that increase the alkalinity of seawater to enhance the ocean's natural carbon sink.

Ocean liming: Spreading soluble alkaline minerals in the ocean to increase ocean alkalinity.

Surficial mineralization: Air, or low purity CO₂-bearing gases or fluids, are reacted with high surface area natural alkaline rocks, mine tailings or other alkaline industrial wastes, in large piles, heaps, or in controlled spaces such as greenhouses, forming carbonate minerals. Surficial processes, like enhanced weathering, occur more slowly than *ex situ* processes but unlike enhanced weathering, minerals are not transported or spread in the environment.