

Review

# Alkaline Mineral Soil Amendment: A Climate Change ‘Stabilization Wedge’?

Fatima Haque, Yi Wai Chiang  and Rafael M. Santos \* 

School of Engineering, University of Guelph, 50 Stone Road East, Guelph, ON N1G 2W1, Canada; fhaque@uoguelph.ca (F.H.); chiange@uoguelph.ca (Y.W.C.)

\* Correspondence: santosr@uoguelph.ca; Tel.: +1-519-824-4120 (ext. 52902)

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**Abstract:** Extreme climate change due to heat-trapping gases, especially carbon dioxide, necessitates its mitigation. In this context, the carbon dioxide sequestration technology of enhanced weathering has for years been investigated, with a possible implementation strategy via alkaline mineral soil amendment being more recently proposed. Candidate materials for enhanced weathering include calcium and magnesium silicates, most notably those belonging to the olivine, pyroxene and serpentine groups of minerals, given their reactivity with CO<sub>2</sub> and global availability. When these finely crushed silicate rocks are applied to the soil, the alkaline earth metal cations released during mineral weathering gradually react with carbonate anions and results in the formation of pedogenic carbonates, which, over time, and under the right conditions, can accumulate in the soil. This review paper critically reviews the available literature on alkaline mineral soil amendments and its potential to sequester enough CO<sub>2</sub> to be considered a climate change ‘stabilization wedge’. Firstly, evidence of how agricultural soil can serve as a carbon sink is discussed, based on the observed accumulation of inorganic carbon in alkaline mineral-amended soils. Secondly, the impact of alkaline minerals on agricultural soil and crops, and the factors determining the rate of the weathering process are assessed. Lastly, the CO<sub>2</sub> sequestration potential via alkaline mineral soil amendment is quantified according to an idealized shrinking core model, which shows that it has the potential to serve as a climate change stabilization wedge.

**Keywords:** carbon sequestration; climate change mitigation; alkaline minerals; enhanced weathering; soil amendment; stabilization wedge

## 1. Introduction

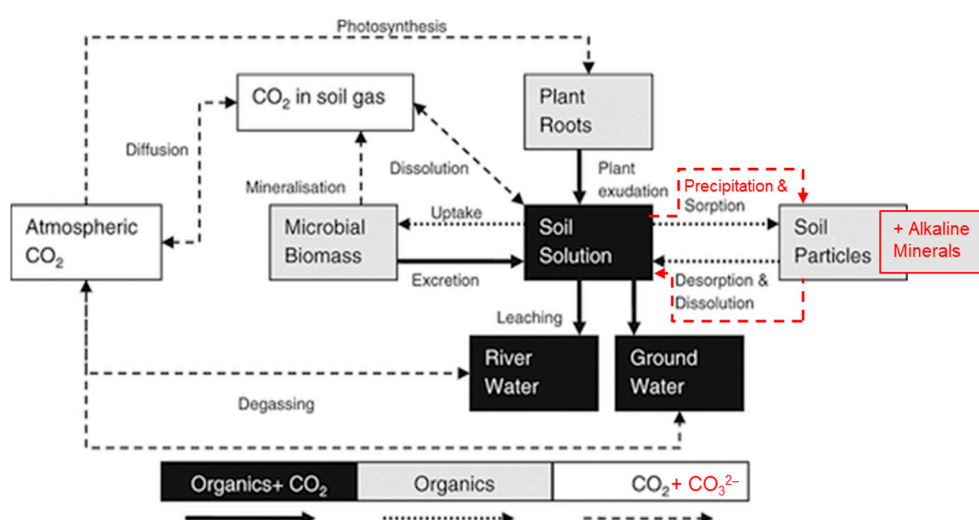
Atmospheric carbon dioxide (CO<sub>2</sub>) concentration, and that of other greenhouse gases (GHGs), has increased over more than a century as a consequence of anthropogenic activities. The simultaneously recorded rise in global surface temperatures, originally noted by [1], and the recently more frequent occurrence of extreme weather events [2], can be fundamentally linked to the reduced transmissivity of the atmosphere to infrared radiation as a result of the accumulation of GHGs [3]. There is a global commitment to reduce GHG emissions and institute global-scale carbon capture and storage (CCS), as exemplified by the Mission Innovation initiative launched at the United Nations Climate Change Conference 2015 [4]. As there is no single CCS solution for all emissions sources, and no single GHG source that can sufficiently cut emissions to curb climate change, Pacala and Socolow [5] have proposed the concept of ‘stabilization wedges’. In that CCS model, a stabilization wedge is an individual mitigation approach, sized to achieve 3.67 Gt CO<sub>2</sub> (eq) year<sup>−1</sup> in emissions reduction by the year 2054. When applied simultaneously, the conceived wedges would be capable of mitigating the emission of 642 Gt of CO<sub>2</sub> (eq) by that year. In this context, this review paper looks at soil inorganic carbon

accumulation, due to alkaline mineral amendment to soils, as a potential climate change stabilization wedge that could be added the CCS model of Pacala and Socolow [5].

Natural soil plays a functional role in the global carbon cycle as it offers a reservoir for approximately 2500 Gt of carbon (C), which is well in excess of the atmospheric reservoir (800 Gt C) [6,7]. Pedogenic processes in soils regulate atmospheric  $\text{CO}_2$  by two major natural pathways: via photosynthesis and the organic matter cycle, and by weathering of alkaline minerals. The first affects the soil organic carbon (SOC) pool, while the latter affects the soil inorganic carbon (SIC) pool. While there have been numerous studies on increasing the capacity of the SOC pool [8,9], less attention has been given to the SIC pool, in particular to methods capable of building up the SIC pool by the application of alkaline minerals to soils.

Given that the capacity of accessible reserves of alkaline minerals for  $\text{CO}_2$  sequestration surpasses the amount of carbon contained in fossil fuel reserves [10], the application of some of these minerals to soils could become an important climate stabilization wedge. Candidate materials for enhanced weathering are calcium and magnesium silicates, including olivine group ( $(\text{Mg,Fe})_2\text{SiO}_4$ ) minerals, such as forsterite ( $\text{Mg}_2\text{SiO}_4$ ) and fayalite ( $\text{Fe}_2\text{SiO}_4$ ), pyroxene group ( $(\text{Ca,Na,Fe}^{\text{II}},\text{Mg})(\text{Cr,Al,Fe}^{\text{III}},\text{Mg,Mn,Ti,V})\text{Si}_2\text{O}_6$ ) minerals, such as wollastonite ( $\text{CaSiO}_3$ ) and enstatite ( $\text{MgSiO}_3$ ), and serpentine group minerals ( $(\text{Mg,Fe}^{\text{II}})_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) [11]. Global reserves of peridotite (olivine and pyroxenes) and serpentine are estimated to be sufficient to sequester all carbon that may be emitted from the presently recognized reserves of coal, oil and natural gas [12,13].

The amendment of alkaline minerals to soil leads to a process that can be referred to as enhanced chemical weathering [14]. When finely crushed/milled calcium- or magnesium-rich silicate rock powder is applied to the soil, the alkaline earth metal cations released during the mineral weathering gradually react with carbonate anions dissolved in soil pore water, which in turn originate from the atmosphere or from soil microbial processes [15]. The result is the formation of carbonate and bicarbonate salts that either precipitate and accumulate in the soil (as SIC) or that flow into with the groundwater, eventually entering an aquifer and accumulating in the ocean. Figure 1 illustrates how this inorganic pathway of  $\text{CO}_2$  in soil, as a result of alkaline mineral soil amendment, fits into the well-known organic carbon cycle in soil. The long-term fate of the sequestered  $\text{CO}_2$  depends on the solubility of the carbonates at the soil pH, but either mechanism (SIC accumulation or bicarbonate transport to the ocean) that results from enhanced chemical weathering may provide an effective means to reduce atmospheric  $\text{CO}_2$  concentration [14].



**Figure 1.** Adapting the broad conceptualization of organic carbon and inorganic  $\text{CO}_2$  dynamics in the environment to include (in red) alkaline mineral amendments and resulting carbonate precipitation/dissolution pathways for  $\text{CO}_3^{2-}$ . Adapted from Hartmann et al. [14] with permission from John Wiley and Sons (4580401336716).

Alkaline minerals can be added to the agricultural soil for pH correction/control, a process referred to as liming due to the traditional use of limestone and other calcium carbonate-based materials, or blended with peat, compost and fertilizers [16]. For example, assuming that enough wollastonite ( $\text{CaSiO}_3$ ) would be applied over several years to a crop field that a 1 mm-equivalent layer of wollastonite would be deposited, 29 tonnes of wollastonite would be deposited per hectare ( $100 \text{ m} \times 100 \text{ m}$ ), which could stoichiometrically sequester 11 tonnes  $\text{CO}_2\text{-ha}^{-1}$ . If Ontario's (Canada) agricultural land area (12.7 million acres) were to be covered by this 1 mm-equivalent layer of wollastonite, the  $\text{CO}_2$  storage capacity would be up to 57 megatonnes.

This review paper critically reviews the available literature on alkaline mineral soil amendments and their potential to sequester  $\text{CO}_2$  via enhanced weathering. Firstly, evidence of how agricultural soil can serve as a carbon sequestration tool is provided. Secondly, the impact of alkaline minerals on agricultural soil and crops, and the factors limiting the weathering process are assessed. Lastly, the  $\text{CO}_2$  sequestration potential via mineral soil amendment is quantified according to an idealized shrinking core model.

## 2. Carbon in Agricultural Soil

Carbon in agricultural soils is chemically classified as either soil organic carbon (SOC) or soil inorganic carbon (SIC). Globally, the naturally occurring SOC and SIC pools are estimated to be 1500 Gt C and 950 Gt C, respectively [7]. The SOC includes humus, decomposed plant and animal residues, charcoal and microorganisms. The SIC pool includes primary and secondary carbonates, such as calcite ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) [17], and can be classified into lithogenic and pedogenic carbonates. Lithogenic carbonates are the primary carbonates that refer to the detrital particle derived from the carbonate bedrock (especially limestone) that are formed in marine environments. Pedogenic carbonates refer to the secondary carbonates formed in the soil and is further classified as calcitic pedogenic carbonates (formed by calcite remobilization) and silicatic pedogenic carbonates (formed by silicate weathering). Calcitic pedogenic carbonates are derived from pre-existing carbonates; hence, it does not result in net carbon sequestration. On the other hand, carbonation of alkaline earth elements derived from silicate minerals results in net positive sequestration through the formation of silicatic pedogenic carbonates [18].

The global SOC pool can be augmented in soils through local or regional best management practices (BMPs) applied to croplands, forested lands or grasslands, to optimize natural organic processes towards stabilization of organic compounds in the soil, as discussed in Section 2.1. Increasing the global SIC pool, on the other hand, necessitates greater human influence, by means of the addition of mined or industrially processed minerals (including virgin, waste and residual materials) to the soil for enhanced weathering, as discussed in Section 2.2, or the application of biochar [19].

### 2.1. Soil Carbon Sequestration as SOC

Improved agronomic practices, including crop rotation, use of improved crop varieties and use of cover crops, increase the input of residual organic carbon into the soil, which leads to increased SOC stored content. BMPs, and their net  $\text{CO}_2$  sequestration potential, are summarized in Table 1. The buildup of SOC takes many years, and the efficiency of the BMPs summarized in Table 1 depends on the soil type, soil saturation and drainage practices and climatic conditions [20]. Hence, agricultural soils act as both net sources as well as sinks for GHGs, including atmospheric  $\text{CO}_2$ .

**Table 1.** Techniques to enhance soil organic carbon (SOC) storage in agricultural soils [18,20–30].

Practice	Example	CCS (t CO <sub>2</sub> ha <sup>-1</sup> year <sup>-1</sup> )	Acceptance <sup>a</sup>	Agreement <sup>b</sup>	Net GHG Emission (t CO <sub>2</sub> ha <sup>-1</sup> year <sup>-1</sup> )	Effect
Cropland Management	Reduced tillage	0.41	H	M	0.44	Reduced decomposition and weed control.
	Crop rotation	0.59	H	H	0.69	Reduced reliance on N inputs.
	Eliminate summer fallow	0.17	H	-	-	Reduces SOM decay.
	Nutrient management	0.27	M	H	0.48	Control on N <sub>2</sub> O release.
	Water management	1.14	L	L	1.14	Improves aeration.
	Increased productivity (e.g., fertilization, irrigation)	0.30	M	M	-	Stimulate N <sub>2</sub> O emission.
Grassland management	Grazing intensity improvement	0.45	L	L	0.46	Influence crop growth.
Land restoration	Restore permanent grass or woodland	2.57	L	H	3.72	Improves soil fertility
Organic soil management	Use organic residues (manure, biosolids, crop residues)	1.83	M	H	2.17	High density C source
	Organic soil restoration	55.0	M	H	51.8	
Bioenergy	Energy crop plantation	0.42	M	H	0.44	CO <sub>2</sub> neutral sources

<sup>a</sup> 'Acceptance' denotes the likelihood of acceptance by farmers. <sup>b</sup> 'Agreement' denotes the relative degree of agreement in the literature. H = high, M = medium, and L = low. CCS: carbon capture and storage; GHGs: greenhouse gases.

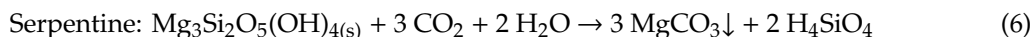
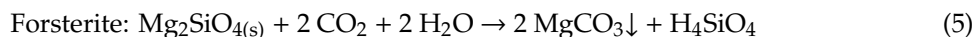
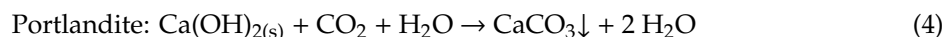
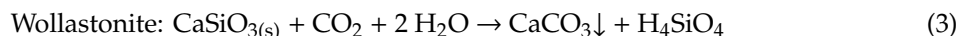
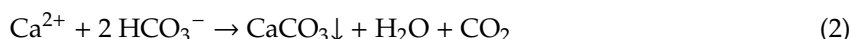
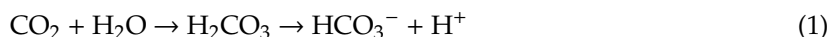
Another modern technique to store C as well as reduce N<sub>2</sub>O emissions includes the use of biochar as a soil amendment [31]. Biochar is porous with high carbon content and surface area, produced by pyrolysis of plant or waste feedstock [32]. Biochar contains stable forms of carbon, which are recalcitrant to degradation, hence mitigating CH<sub>4</sub> or CO<sub>2</sub> loss [33]. Thus, biochar can store carbon in the soil for as long as 1000 years [34,35] and thus contribute towards the reduction of anthropogenic CO<sub>2</sub> emissions. Additionally, biochar can minimize the use of N fertilizers, and indirectly contribute towards mitigating overall GHG emissions [36].

A series of studies from Syracuse University over the last decade has shown that the application of calcium silicate (wollastonite) can also help in increasing soil organic matter (SOM) in forested soil, as well as contributing to nutrient management by increasing exchangeable calcium, thereby improving the pH of the nutrient-depleted, acidic forest soil [37–39]. Wollastonite is used as a liming agent for the forest soil to improve the soil fertility, but these studies have not looked at inorganic carbon sequestration potential of this silicate mineral.

## 2.2. Soil Carbon Sequestration as SIC via Enhanced Weathering

The term ‘enhanced weathering’ refers to exposing milled minerals to the atmosphere, whereby the large specific surface area of fine powders aids in the rate of the weathering reactions, versus naturally occurring rocks that slowly weather [15]. Long-term atmospheric CO<sub>2</sub> sequestration in agricultural soils can be made possible through weathering of Ca silicates and Mg silicates, because the released Ca<sup>2+</sup> and Mg<sup>2+</sup> are precipitated as soil inorganic carbonates [40]. Formation of pedogenic carbonates offers a sink for carbon that is effectively permanent, and the amount of SIC presently held within soils has been estimated to be 720–950 Gt C [7,41]. These values can be augmented by addition of a variety of calcium and magnesium silicates, including wollastonite (CaSiO<sub>3</sub>), enstatite (MgSiO<sub>3</sub>), forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), fayalite (Fe<sub>2</sub>SiO<sub>4</sub>), olivine ((Mg,Fe)SiO<sub>4</sub>), diopside (MgCaSi<sub>2</sub>O<sub>6</sub>) and serpentine ((Mg,Fe)<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) [11].

In enhanced weathering, firstly, CO<sub>2</sub> reacts with H<sub>2</sub>O to form bicarbonate (HCO<sub>3</sub><sup>−</sup>) and a proton (H<sup>+</sup>) (Equation (1)). Secondly, the metal ion from the mineral is liberated by the proton and ultimately reacts with the bicarbonate to precipitate as a carbonate (Equation (2)). Equations (3)–(6) represent some examples of mineral weathering [42–44]. Calcite solubility, and hence the transport of Ca<sup>2+</sup> and HCO<sub>3</sub><sup>−</sup>/CO<sub>3</sub><sup>2−</sup>, depends on the soil solution chemistry. Therefore, either in the longer term (as a result of soil porewater dilution by rainwater) or in the shorter term (as a result of intensive irrigation in some crops), CaCO<sub>3</sub> may be dissolved and instead of remaining in the soil profile, the ions (Ca<sup>2+</sup>, CO<sub>3</sub><sup>2−</sup>) may leach into the groundwater, and eventually into the oceans, where under more alkaline conditions they are again precipitated as calcium carbonates (Equation (7)) [45].



### 3. Alkaline Minerals as Soil Amendment

#### 3.1. Soil Inorganic Carbon Accumulation

This section summarizes recent studies focusing on using alkaline minerals for the purpose of inorganic carbon accumulation in soils. The significance of the reported results demonstrates that enhanced weathering has the potential to rapidly and substantially remove atmospheric CO<sub>2</sub>.

Renforth et al. [16], Renforth and Manning [46] and Washbourne et al. [42] studied carbon sequestration in urban soils used for construction projects, and reported SIC accumulation due to enhanced weathering of alkaline minerals. Washbourne et al. [42] studied the changes in SIC concentration in an urban soil at the city of Newcastle upon Tyne, UK, and reported that the prepared soil (composed of material derived from demolition, including fines from the on-site production of crushed concrete secondary aggregates) has a potential to sequester 85 t of CO<sub>2</sub>·ha<sup>-1</sup> annually, or an increase in SIC content of 23 t of C·ha<sup>-1</sup>·year<sup>-1</sup>, based on the measurement of inorganic carbon content over an 18-month period. The atmospheric origin of the newly formed pedogenic calcite was confirmed using <sup>14</sup>C dating, and the extent of carbonation was found to extend more than 1 m below the surface [42].

Manning et al. [47] studied the effect of adding finely ground basaltic quarry fines (basalt and dolerite), in combination with compost, to soils meant for land restoration projects, on the SIC accumulation as well as on plant growth. The basalt used contained 14.8 wt% of combined CaO and MgO content, and the dolerite similarly contained 15.5 wt% of these alkaline oxides. Food industry waste compost (pH 5.89) and anaerobic digester compost (pH 9.01) were used for the blend. The basalt-compost blend supported the growth of a wide range of vegetation tested (21 in total, including mustard, woolly thistle, white clover) with an annual SIC accumulation rate of 36.7 t of CO<sub>2</sub>·ha<sup>-1</sup>, to a depth of 1 m [47].

Haque et al. [48] studied the co-benefits of wollastonite weathering in agricultural soil, to grow green beans and corn. Wollastonite mineral, containing 55% SiO<sub>2</sub>, 26% CaO, and 9% MgO as major alkaline oxides, was added to sandy loam soil (pH 4.94) to reach a pH of 7.23. Geochemical modelling, using Visual Minteq v3.1 was used to confirm that at a pH of 7.23, which was obtained by mixing 1 kg of wollastonite with 8 kg of soil, the saturation index becomes positive, which is required for the precipitation of solid carbonate phases, especially calcite (CaCO<sub>3</sub>) in the case of wollastonite. It was reported that wollastonite-amended soil cultivated with beans showed a higher soil inorganic carbon accumulation of 0.606 ± 0.086 wt% over a period of 8 weeks, thus sequestering carbon dioxide at a rate of 24.3 t of CO<sub>2</sub>·ha<sup>-1</sup>·month<sup>-1</sup>, to a depth of 6 inches [48].

Amann et al. [49] applied dunite (predominantly olivine) to agricultural soils to quantify the impact on dissolved inorganic carbon (DIC) in the presence of crop plants. The alkaline mineral, dunite, contained 40% SiO<sub>2</sub> and 45% MgO as major alkaline oxides. The DIC concentration in the soil solution increased after a year, and a CO<sub>2</sub> consumption rate of 0.68 t of CO<sub>2</sub>·ha<sup>-1</sup>·year<sup>-1</sup>, to a depth of 15 cm was reported [49].

These studies conclude that the alkaline mineral soil amendment has the potential to accumulate inorganic carbon in the soil and to act as a climate change ‘stabilization wedge’.

#### 3.2. Other Effects of Alkaline Mineral Soil Amendment

Using alkaline minerals as a soil amendment not only contributes towards soil inorganic carbon accumulation (and thus CO<sub>2</sub> sequestration), but also amends soil chemical properties potentially resulting in improved soil fertility. Some agricultural soils are characterized by low calcium (Ca) and high aluminum (Al) content; as a result, plant root growth will be impaired, and water and nutrients uptake by plants will be affected. Van Straaten [50] has evaluated the effect of multi-nutrient silicate rock fertilizers on nutrient cycling and biochemical processes at the root surfaces, finding that it has the potential to supply the soils with macronutrients (N, P, K) and micronutrients (especially Ca and Mg) [50].



Table 2 analyzes the application of olivine and basalt as alkaline mineral amendments in terms of the increase in exchangeable basic cations in the soil. ten Berge et al. [44] reported that soil pH increased from 4.89 (control) to 5.96 at the highest olivine dose (204 tonne·ha<sup>-1</sup>), and Mg<sup>2+</sup> and K<sup>+</sup> bio-available amount increased with increasing olivine dosage, which is responsible for increasing the soil pH, thus improving the soil nutrient profile [44]. As the basic cation content continues to increase at higher mineral application rate, following plant uptake, cation supplementation should be effective to sustain soil fertility for a considerable time period. Furthermore, Gillman et al. [51] examined the soil chemical effects of applying finely ground basalt dust to seven types of highly weathered soil in Queensland and reported that the concentration of exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup> increased in the soil, thus ameliorating the acidic soil. Hence, alkaline mineral soil amendment results in base-saturation which promotes a soil microbe balance, thus aiding in better plant growth [51].

**Table 2.** The effect of alkaline mineral amendment on the exchangeable basic cation content of the amended soil.

Treatment	pH	Increase in Mg <sup>2+</sup> (%)	Increase in K <sup>+</sup> (%)	Reference
KIES 1	4.9	15.7	27.6	[44]
KIES 2	5.04	30.6	55.2	
OLIV 1	4.99	68.9	20.9	
OLIV 2	5.1	132.8	16.0	
OLIV 3	5.34	257.6	54.0	
OLIV 4	5.96	691.2	130.7	
Soil Treated with Basalt (25 t/ha)	Increase in Ca <sup>2+</sup> (%)	Increase in Mg <sup>2+</sup> (%)	Increase in K <sup>+</sup> (%)	Reference
Haplorthox on basalt	6.8	32.4	109.1	[51]
Haplorthox on basalt fan	44.2	128.0	140.0	
Tropudult	39.0	215.4	266.7	
Haplorthox on metamorphic rock	88.5	200.0	63.6	
Dystropept on basalt alluvium	11.2	53.5	90.9	
Dystropept on granite alluvium	16.6	133.3	50.0	
Haplorthod	110.8	335.7	171.4	

'KIES 1 and KIES 2' denotes the fertilizer kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O) treatment at dosage 0.15 and 0.3 g·(kg soil)<sup>-1</sup>, respectively. 'OLIV 1' to 'OLIV 4' denotes treatment with olivine at a dosage of 1630, 8150, 40,700, and 204,000 kg·ha<sup>-1</sup>, respectively.

Excessive use of alkaline minerals as soil amendment can be associated with some possible negative effects. The release of metals contained in the mineral composition during the weathering (e.g., Ni, Mn, Cr) may pose an environmental risk. For example, the dissolution of olivine is associated with Ni releases and plant uptake [44]. On the other hand, some of these same metals act as micronutrients required by plants. Therefore, their presence can be beneficial, as long as their soil concentration does not exceed toxic levels [52]. At soil conditions, Ni is more susceptible to leaching as compared to Mn or Cr; hence, this necessitates the study of possible side effects of the release of Ni from alkaline mineral soil amendments [53].

The release of Ni from olivine into the food chain and the wider environment could set limits to permissible olivine doses. ten Berge et al. [44] reported a range of 0.09–1.383 mg/kg of Ni while growing ryegrass (*Lolium perenne* L.) in olivine treated soil [44], which is very low compared to the toxicity threshold of 10 mg/kg of Ni [54]. Grasses grown over basaltic fines accumulated 2.17 mg/kg as bioavailable Ni [55], whereas those grown on serpentine-derived soils accumulated higher levels of Ni (11.1–39.3 mg/kg) [56]. Fernández et al. [57] reported Ni content of 12–34 mg/kg in the foliage of various crops grown over serpentine-derived soils, with highest values for sugar beet (*Beta vulgaris* L.). These levels can result in high Ni accumulation in kidney tissue of grazing cattle [56].

To assess the severity of Ni release, the geoaccumulation index (*I<sub>geo</sub>*), introduced by Müller [58] and widely employed in trace metal studies [59], can be used. It compares the measured concentration

of a metal in the soil to a soil quality guideline value, and indicates an uncontaminated soil when  $I_{geo} < 0$ . It is thus a means of indicating the environmental risk associated with metal release. The  $I_{geo}$  for the amended soils was computed as part of this review using the Equation (8):

$$I_{geo} = \log_2 \left( \frac{C_n}{1.5 SQGE} \right) \quad (8)$$

where  $C_n$  is the measured concentration of every trace metal found in the agricultural soil (mg/kg) and  $SQGE$  is the soil quality guideline value (for the environmental health) of the metals found in the soil (mg/kg) [60].

Based on soil quality guideline of environmental health, the threshold for agricultural soil for Ni is 45 mg/kg. Using the data available from the work of ten Berge et al. [44],  $I_{geo}$  value can be estimated for Ni release due to the different dosage of olivine (Table 3) [44]. The  $I_{geo}$  values for all these treatments are less than zero ( $I_{geo} < 0$ ), hence implying that the amended soils were not contaminated in that study.

**Table 3.** Geoaccumulation index analysis of data from ten Berge et al. [44].

Treatment	Ni (mg/kg)	$I_{geo}$ Ni
OLIV 1	0.00013	−18.99
OLIV 2	0.00026	−17.99
OLIV 3	0.00056	−16.78
OLIV 4	0.00138	−15.57

Long-term application of alkaline minerals to agricultural soils could lead to a gradual increase in  $I_{geo}$  value. In the long-term, one way of managing the released metal concentration is by controlling the rate of mineral application, which can be estimated using Equation (9). For example, in the case of olivine (containing ~3 g Ni/kg of olivine, [16]) and assuming a soil density of 1.3 tonne·m<sup>−3</sup>, and an accumulation depth of 50 cm, the maximum application capacity for olivine in such soil would be 98 tonne·ha<sup>−1</sup>.

$$\text{Rate of application} = \frac{(\text{Threshold value for metal}) \times (\text{Soil density}) \times (\text{Accumulation depth})}{\text{Total concentration of metal in the mineral}} \quad (9)$$

#### 4. Factors Controlling Mineral Weathering

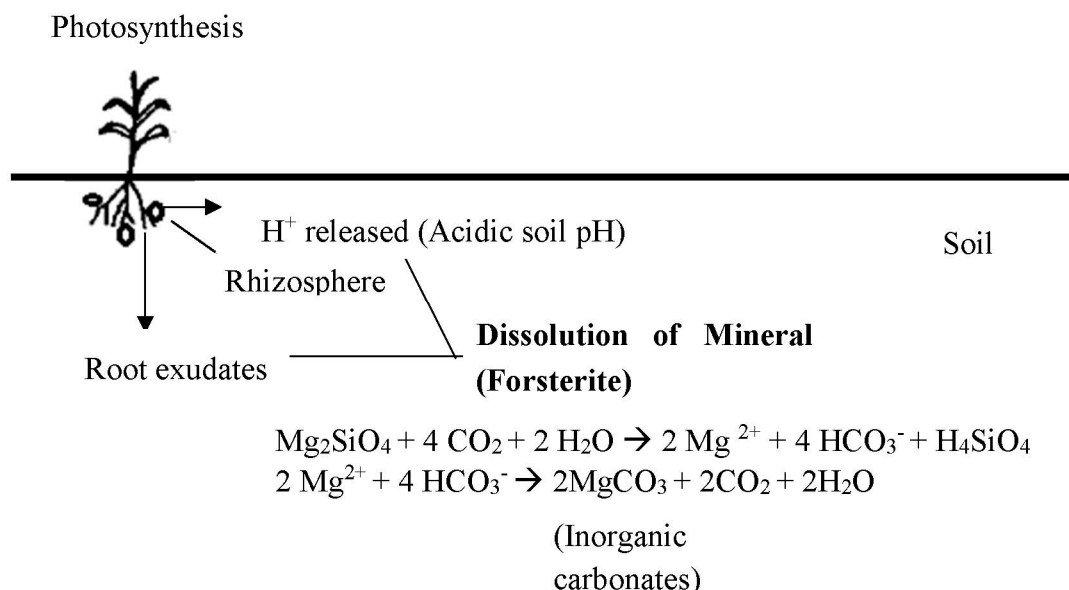
There are several factors to be considered to ensure that an alkaline mineral soil amendment can serve the purpose of a climate change stabilization wedge. That is, to remove CO<sub>2</sub> from the atmosphere at a sufficiently rapid rate.

##### 4.1. Role of Plants and Microbes

Organic acids released by plants play an important role in the soil weathering processes. Several organics anions (citrate, oxalate, malate), released as root exudates, and phytosiderophores or secretions from mycorrhizal symbionts (lichen acid, uronic acid, peptides, and amino acids), have been reported to directly affect the dissolution of minerals in soil [61–64]. Nezaf et al. [65] reported that mineral dissolution rate in soil, on the same forested land, varies considerably as a function of vegetation cover.

Microbial activity also has been found to induce weathering of olivine, basalt and feldspars [61,66]. Haque et al. [48] investigated the role of a leguminous crop (green beans, *Phaseolus vulgaris* L.) in enhanced weathering of wollastonite-amended soil. They reported that *Rhizobiaceae* bacteria, associated with legumes' root nodules and aiding in nitrogen fixation, release protons into the soil that stimulate the dissolution of alkaline minerals (as illustrated in Figure 2) [48].





**Figure 2.** Role of plants and microbes in enhanced weathering (Adapted from Haque et al., 2019, [48]).

#### 4.2. Dissolution Rate

Dissolution rate is measured on the basis of Ca, Mg and Si. The release of Ca and Mg from the silicate minerals in soil depends on many parameters, such as the dissolution rate, temperature, soil pH and the specific surface area of mineral grains. Table 4 summarizes dissolution rates of different classes of alkaline minerals, such as anorthite (a plagioclase feldspar), wollastonite (a calcium silicate), diopside (a pyroxene) and tremolite (an amphibole). The alkaline minerals with greater logarithmic rate value, i.e., the ones with higher dissolution rate, at soil pH conditions (5.1–7.7) are the favourable alkaline minerals to serve the purpose of CO<sub>2</sub> sequestration via enhanced weathering. Wollastonite (inosilicate) has a dissolution rate higher than forsterite (orthosilicates belonging to olivine group), but the availability and location of the alkaline mineral are also important to determine its feasibility as a mineral soil amendment. Olivine, a major constituent of dunite rock, is mined in a number of countries including Spain, Italy, Norway, Sweden, Austria, Greece, Cyprus and Turkey, and it costs in the order of a few tens of US\$ per ton in the Rotterdam harbour [67]. The world reserves of wollastonite are estimated to exceed 100 million tonnes with large reserves in China, Finland, India, Mexico, Spain, Canada and the U.S [68]. The world reserve of the various alkaline minerals is provided by the U.S. Geological Survey in the Mineral Commodity Summaries report [68].

**Table 4.** Dissolution rate at 25 °C for different classes of alkaline minerals at neutral and acidic pH (compiled from Palandri and Kharaka [69]).

Class	Mineral	log $W_r$ (moles/m <sup>2</sup> s) pH 5.1–7.7	log $W_r$ (moles/m <sup>2</sup> s) pH 2.0–4.0
Feldspars	Albite	−12.56	−10.16
	Oligoclase	−11.84	−6.97
	Andesine	−11.47	−8.88
	Labradorite	−10.91	−7.87
	K-feldspar	−12.41	−10.06
Feldspathoids	Nepheline	−8.56	−2.73
	Leucite	−9.2	−6

Table 4. Cont.

Class	Mineral	log $W_r$ (moles/m <sup>2</sup> s) pH 5.1–7.7	log $W_r$ (moles/m <sup>2</sup> s) pH 2.0–4.0
Orthosilicates	Forsterite	−10.64	−6.85
	Fayalite	−12.8	−4.8
	Almandine	−10.7	−5.2
	Grossular	−10.7	−5.1
	Andradite	−10.7	−5.2
	Staurolite	−12.22	−6.9
	Zoisite	−11.2	−7.5
	Kyanite	−17.44	−10.17
	Epidote	−11.99	−10.6
Cyclosilicate	Cordierite	−11.2	−3.8
	Tourmaline	−11.2	−6.5
Inosilicates	Augite	−11.97	−6.82
	Bronzite	−11.7	−8.3
	Diopside	−11.11	−6.36
	Enstatite	−12.72	−9.02
	Wollastonite	−8.88	−5.37
Amphibole	Anthophyllite	−14.24	−11.94
	Glaucophane	−10.1	−5.6
	Tremolite	−10.6	−8.4
Phyllosilicates	Biotite	−12.55	−9.84
	Glauconite	−9.1	−4.8

## 5. Modeling Enhanced Weathering

It is challenging to predict the weathering rate of a mineral in an amended soil. As mentioned earlier, it depends on a number of parameters: specific surface area (SA), temperature (T) and pH, which can be expressed by Equation (10) [25]:

$$W_r = SA \cdot k \cdot e^{\frac{E}{RT}} \cdot a_{H^+} \cdot (1 - \Omega). \quad (10)$$

where  $a_{H^+}$  is related to pH,  $E$  is the activation energy,  $k$  is the dissolution rate constant and  $\Omega$  is the mineral saturation (Q/K) [70].

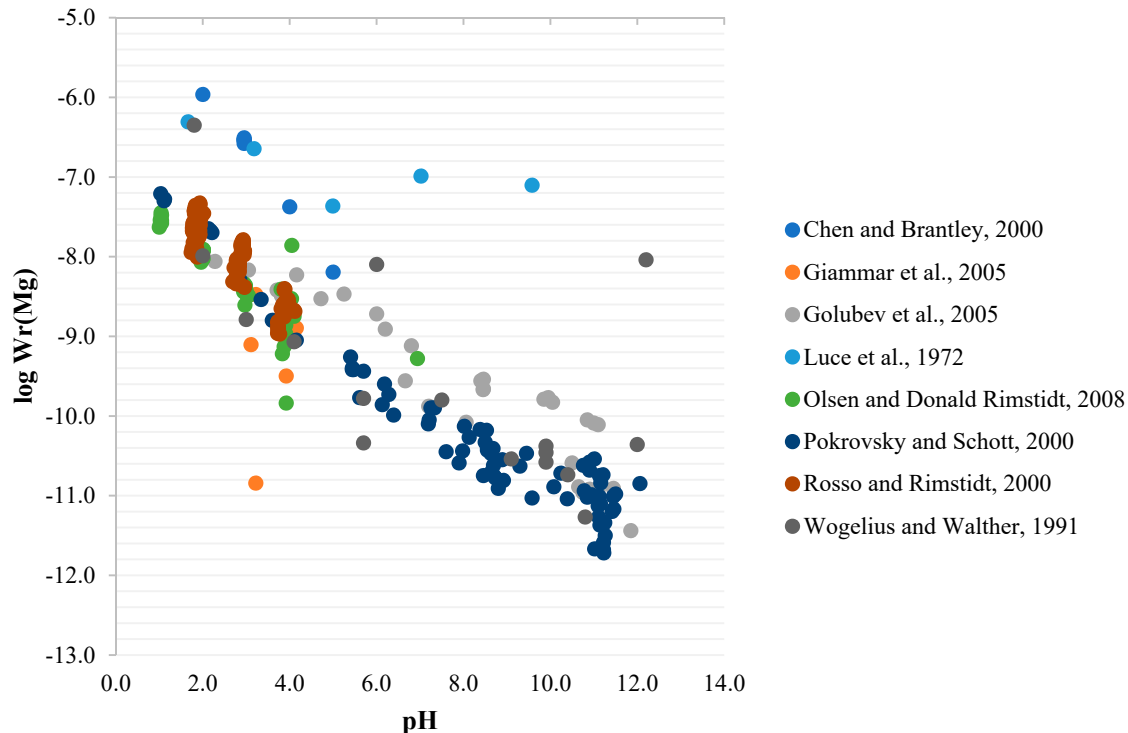
However, applying this relationship to investigate weathering on a field scale is challenging. The proportion of active SA of the mineral may change with time. The hydraulics and biogeochemistry of the soils are complex, which depends on intermittent rainfall and evapotranspiration, which changes the soil pore water saturation level  $\Omega$ .  $a_{H^+}$  depends on the soil pH, which fluctuates due to the mineral application as well as soil organic matter decomposition and root exudations [61,69]. The dissolution rate constant ( $k$ ) changes if there is the formation of secondary minerals or surface adsorption of cations on existing minerals. A reaction-limiting silica-rich secondary or passivating layer can form as alkaline minerals weather, hence slowing the dissolution reaction. Such layer formation is a complex process that can be associated with incongruent dissolution and silica deposition on the reaction surfaces [71].

In the next section, a shrinking core model is presented as an alternate means to predict enhanced weathering rates, with olivine taken as the case study mineral, due to the large availability of dissolution rate data.

### A Shrinking Core Model for Enhanced Weathering Estimation

This section analyses the concept of enhanced weathering of olivine in soil applications, with the aim of demonstrating quantitatively whether it can contribute significantly to CO<sub>2</sub> sequestration. Figure 3 demonstrates the available data dissolution rate ( $W_r$ ) (mole/m<sup>2</sup>s) of olivine group minerals in

solutions with controlled pH at 25 °C [72,73]. From this data, a dissolution rate of  $1.63 \times 10^{-9}$  mol/m<sup>2</sup>s can be estimated at a soil pH value of pH 4.5. The partial pressure of CO<sub>2</sub> in the soil varies between 2–10 kPa, and at these pressures, the pH of soil porewater in equilibrium with the soil gas may be as low as 4.5 [51]. This pH value is used in this analysis to estimate the weathering rate at the most favourable conditions for silicate dissolution.



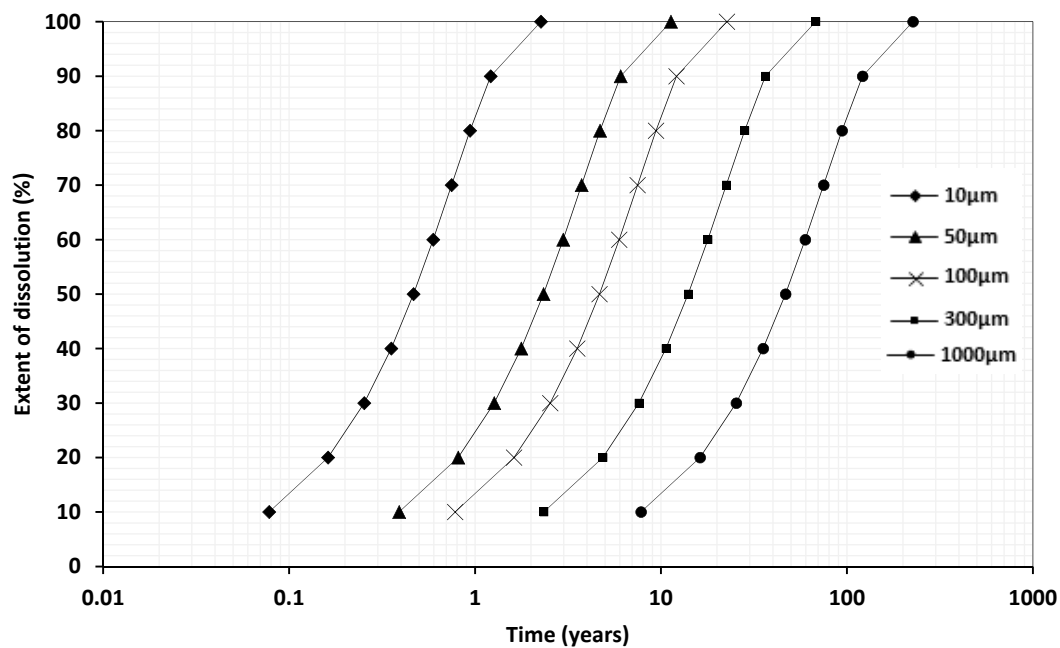
**Figure 3.** Variation in dissolution rate ( $W_r$ ) of olivine group minerals as a function of pH [63,72,74–80].

Weathering rate of minerals can be used to assess the CO<sub>2</sub> sequestration potential of alkaline mineral soil amendment. The basic forsterite weathering equation (Figure 2) shows that 1 tonne of pure forsterite can fix 1.25 tonnes of CO<sub>2</sub>. For a given extent of forsterite dissolution ( $X$ ), initial particle diameter ( $D_o$ , m) can be related to dissolution rate ( $W_r$ , moles (mineral)·m<sup>-2</sup>·s<sup>-1</sup>) through the shrinking core model (Equation (11)) [70,81]:

$$X(t) = \frac{D_o^3 - (D_o - 2 \cdot W_r \cdot V_m \cdot t)^3}{D_o^3} \quad (11)$$

where  $V_m$  is the molar volume of the material (m<sup>3</sup>·mole<sup>-1</sup>),  $43.02 \cdot 10^{-6}$  m<sup>3</sup>·mole<sup>-1</sup> for olivine [43],  $t$  is the dissolution time (s) and the shrinking core model assumes that all mineral grains are spherical particles.

Figure 4 shows the progress of forsterite dissolution versus time, calculated using the shrinking core model equation for a range of initial particle sizes at a pH of 4.5. The corresponding time taken to dissolve 25%, 50% and 100% of forsterite at 25 °C are listed in Table 5. It can be concluded that a particle size of <50 µm is needed to accelerate the dissolution rate of forsterite to levels that can contribute significantly to CO<sub>2</sub> sequestration within a 10-year period. This result is in consensus with Hangx and Spiers' [43] prediction that terrestrial (i.e., soil) spreading of crushed olivine is more promising than coastal spreading (as seen in Table 5), given the more acidic soil pH.



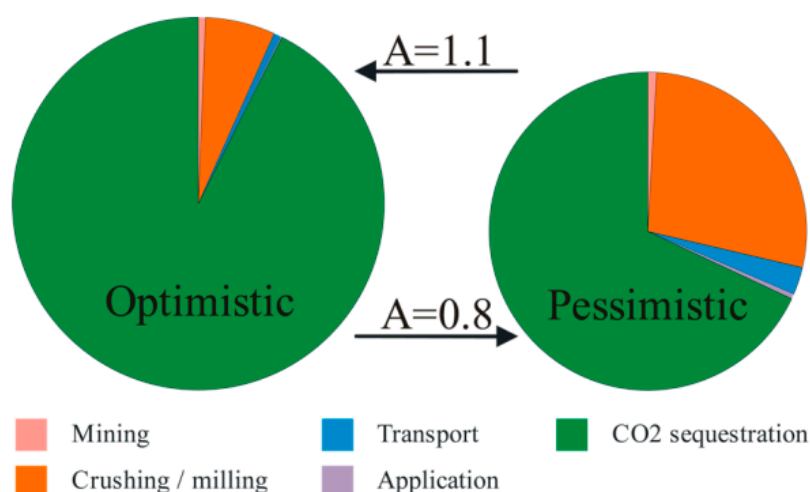
**Figure 4.** Extent of forsterite dissolution as a function of time for various initial particle sizes, at a pH of 4.5.

**Table 5.** Reaction time and CO<sub>2</sub> uptake for various grain sizes of olivine at soil pH 4.5.

	X (vol %) Mineral Dissolution					
	25%		50%		100%	
	CO <sub>2</sub> Sequestered (tonne CO <sub>2</sub> /tonne mineral)					
Grain Size (μm)	Time (years) at pH 4.5 <sup>a</sup>	Time (years) at pH 8.2 <sup>b</sup>	Time (years) at pH 4.5 <sup>a</sup>	Time (years) at pH 8.2 <sup>b</sup>	Time (years) at pH 4.5 <sup>a</sup>	Time (years) at pH 8.2 <sup>b</sup>
10	0.21	2	0.47	5	2.3	23
50	1.0	-	2.3	-	11	-
100	2.1	21	4.7	48	23	233
300	6.2	64	14	144	68	700
1000	21	213	47	481	226	2333

<sup>a</sup> denotes the data computed in this study. <sup>b</sup> denotes the data collected from Hangx and Spiers [43].

Moosdorf et al. [15] provided detailed budgeting on the net CO<sub>2</sub> removal via terrestrial enhanced weathering. Net CO<sub>2</sub> budget of enhanced weathering was calculated as a difference between the potential CO<sub>2</sub> sequestration (based on the silicate rock properties) and the CO<sub>2</sub> emissions due to mining, comminution, transport and application. It was reported that the choice of source rocks and mineral comminution technique (crushing, milling, grinding) are the main factors dominating CO<sub>2</sub> sequestration potential of enhanced weathering process (Figure 5). After accounting for all possible emissions, Moosdorf et al. [15] reported that 0.5–1.0 tonne CO<sub>2</sub> can be sequestered per tonne of silicate rock.



**Figure 5.** CO<sub>2</sub> budgets per tonne of alkaline mineral according to the optimistic scenario and pessimistic scenario. The areas (A) of the pies represent the potential maximum CO<sub>2</sub> sequestration of each scenario. Reprinted (adapted) with permission from Moosdorf et al. [15]. Copyright (2019) American Chemical Society.

## 6. Conclusions

This review paper has critically analyzed the data available in the literature to understand if alkaline mineral soil amendment can serve as a climate change ‘stabilization wedge’. Agricultural soil offers a vast sink to sequester atmospheric CO<sub>2</sub>, as global land area covered by crop fields, and the rate of application of soil amendments is compatible with the amount of alkaline minerals that must be spread and exposed to CO<sub>2</sub>/HCO<sub>3</sub><sup>−</sup>/CO<sub>3</sub><sup>2−</sup> to enable enhanced weathering to make a meaningful impact on climate change mitigation. Studies to date show that weathering of alkaline minerals added to soils (agricultural, forested and urban) can result in soil carbon sequestration in the form of inorganic carbonates. In addition to contributing towards the accumulation of soil inorganic carbon, alkaline minerals have been shown to be able to improve soil fertility and nutrient profile by amending the soil pH (in cases of acidic soils) and providing plant-available inorganic nutrients such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup> and H<sub>4</sub>SiO<sub>4</sub>. In this way, alkaline soils have the potential to replace, even if partially, traditional soil amendments such as limestone and industrial fertilizers, contributing to the avoidance of CO<sub>2</sub> emissions from the manufacturing and application of these materials.

While experimental studies are certainly needed to validate the CO<sub>2</sub> sequestration mechanism of enhanced weathering, especially in the complex geochemical system in soils, modeling can be very helpful to predict the rate of weathering under different conditions, and thus help estimate the true potential of alkaline mineral soil amendment to act as a climate change stabilization wedge. Modeling enhanced weathering is challenging, as the complexity of soil geochemistry cannot be exactly simulated, nor is it fully understood, and there is still limited data on the dissolution kinetics of silicate minerals. We used a shrinking core model to elucidate at least one important aspect of alkaline soil mineral amendment, which is the required particle size for weathering to reach completion within a reasonable time period. In the case of olivine, the suggested particle size and time period arrived at by our model were, respectively, 50 µm and 10 years.

What exactly constitutes a reasonable time period is still uncertain, but should take in account factors such as land lease contract lengths and requirements of carbon credit programs (e.g., the Nori Carbon Removal Marketplace [82]) for CO<sub>2</sub> sequestration verification. It is also encouraging that some silicates are more reactive to weathering than olivine under soil conditions, most notably wollastonite. The implementation of an alkaline soil amendment program with such mineral could be the first step to raising awareness about this climate change mitigation strategy and collecting field-scale long-term data on CO<sub>2</sub> sequestration, before other minerals become widely used for the same purpose,

even if slower in achieving the goal. There is an active field-scale research looking at the ambient sequestration of CO<sub>2</sub> into mining tailings: Clinton Creek asbestos mine in the Yukon (Canada), Diavik diamond mine in the Northwest Territories (Canada), and Mount Keith nickel mine in Western Australia [83]. This field-scale research will be helpful to understand how the rate and extent of carbon mineralization is affected at distinct climatic and hydrological conditions. Conducting rigorous and long-term experimental work, at bench- and field-scales, will help academics, farmers and government institutions to understand the long-term effects of weathered silicate minerals in the soil, in terms of soil geochemistry, soil microbiology and crop health, and to more accurately predict the net CO<sub>2</sub> sequestration of alkaline mineral soil amendment.

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