Chapter 13

Geochemical drivers of enhanced rock weathering in soils

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1.1 Introduction

Despite climate change acting as one of the greatest challenges facing humanity in the 21st century, international initiatives have not yet been able to curb the emissions of carbon dioxide (CO_2) from anthropogenic activities and their impacts on global temperatures [1,2]. Alongside the necessary future technological and socio-economic changes needed to reduce CO_2 emissions, the use of carbon dioxide removal (CDR) technologies appears now essential to limit global warming below 2°C above preindustrial levels [3–7].

Among all CDR technologies, enhanced rock weathering has been attracting increasing attention as a potentially decisive and scalable mitigation solution [8–11]. It aims at accelerating one of the most powerful regulating feedbacks of Earth's climate [12–15], by increasing the specific surface area of highly reactive igneous rocks through grinding, in order to accelerate their chemical weathering. Three types of enhanced rock weathering are currently the subject of active research, each corresponding to the type of environment in which the rock powder is eventually applied: oceanic, coastal, and terrestrial enhanced weathering. This chapter will concentrate on terrestrial enhanced rock weathering (ERW) which has been the focus of most laboratory, field, and modelling research efforts and for which we have the greatest hindsight.

Terrestrial ERW describes the process of applying silicate rock powders to soils – mainly agricultural ones. When silicate minerals react with carbonic acid in the soil solution, ERW sequesters CO_2 directly in the form of alkalinity (esp. bicarbonate ions; see the example of wollastonite weathering in Eq. 1). Calcium carbonate may subsequently precipitate from the bicarbonate and dissolved calcium ions (Eq. 2), resulting in 50% of the initially sequestered CO_2

being degassed and 50% being locked in a solid mineral form. After transport in rivers, the mean residence time of dissolved inorganic carbon in the global oceans is at least 1000 years and can be considered to be much longer if calcite removes it from solution as a precipitate [18]. ERW is thus an almost permanent carbon sink on a human timescale.

$$\mathrm{CaSiO_3} + +3\mathrm{H_2O} + 2\mathrm{CO_2} \leftrightarrow \mathrm{H_4SiO_4} + \mathrm{Ca^{2+}} + 2\mathrm{HCO_3}^- \tag{1}$$

$$\mathrm{Ca^{2+}} + 2\mathrm{HCO_3}^- \leftrightarrow \mathrm{CaCO_3} + 3\mathrm{H_2O} + \mathrm{CO_2} \tag{2}$$

Currently, mafic rocks such as basalts are considered ideal candidates for ERW due to their high reactivity, high base metal contents, and relatively low heavy metal concentrations [8,16] (albeit with important questions regarding potential heavy metal accumulation in the long run [17]). Basalt's natural weathering sequesters 0.2 Gt CO_2.yr^{-1} [19] and the additional sequestration potential associated with ERW is often estimated between 0.2 and 4 Gt CO_2.yr^{-1} [4,8,10,20,21]. To put those values in perspective, this order of magnitude of mitigation would compensate 1% to 21% of the current annual atmospheric CO_2 rise [22] and could significantly contribute to the 1 Gt CO_2eq yr^{-1} reduction target expected from agriculture by 2030 in the fight against climate change [23].

On top of sequestering CO_2 in the form of alkalinity, ERW is also promoted for its additional climate, food safety and soil cobenefits, namely its potential to (1) decrease emissions of other potent greenhouse gases such as nitrous oxide [24,25] and methane [26]; (2) counter soil acidification and therefore increase nutrient availability and limit the bioavailability of toxic elements [27]; (3) release key nutrients for crop production such as phosphorous, potassium, and calcium [27]; and (4) sequester CO_2 in the form of additional organic matter in soils and biomass that would result from greater plant productivity, thereby boosting other land-based CDR technologies (e.g., afforestation and reforestation, agricultural land management practices) [28,29].

But before being deployed worldwide, several potentially limiting environmental, technical, and socio-economic factors need to be considered [8,9,30–33]. In addition to some well documented aspects (summarized in Table 1.1), we believe that geochemical considerations regarding the weathering rates of silicate minerals deserve further attention. This chapter reviews fundamental weathering principles and experimental findings to provide a geochemical perspective on ERW under a range of soil conditions. This chapter will only deal with soil geochemistry. For information on the role of soil organisms and biological processes in ERW, we refer to the excellent review by Vicca et al. [34].

Table 1.1 Potentially limiting factors affecting ERW large-scale development, listed for each operational step.

MINING	GRINDING	TRANSPORT	SPREADING
• Rock composition (toxic trace metal content, presence of asbestos) • Environmental impact of increasing mining operations • Legal and social resistance to mining • Mining energy requirements, costs, and carbon footprint	• Infrastructure and machinery for optimal grain size • Health hazards related to dust exposure • Grinding energy requirements, costs, and carbon footprint • Packaging costs	• Import/export infrastructure • Transport energy requirements, costs, and carbon footprint • Transport obstacles (remote mines, inaccessibility of some fields, etc.) • Transport and storage conditions	• Farming equipment (high load spreaders, dust suppression equipment) • Spreading energy requirements, costs, and carbon footprint • Social resistance against widespread geoengineering • Health hazard related to dust exposure • Environmental regulation

1.2 Fundamental geochemical considerations

Without artificial *enhancement*, it is estimated that silicate minerals will naturally weather and remove the current excess atmospheric CO_2 emissions within timescales of approximately 270 kyr [35,36]. The ambition for ERW is to decrease this time horizon by several orders of magnitudes by optimizing the weathering system. These optimization strategies include (1) amending soils with highly reactive silicate materials; (2) using powders with very small grain sizes and high surface areas; and (3) deploying the amendments strategically in soils with pH, moisture, and temperature conditions compatible with the maintenance of high weathering rates. This section reviews the factors which are likely to influence ERW efficiency.

1.2.1 Influence of mineralogy

The drawdown of atmospheric CO_2 using silicate powders is strongly controlled by mineralogy [37,38]. Despite the generally vast CDR capacity of ERW feedstocks [39,40], variations in mineralogical composition will influence both the total amount of CO_2 which can be removed, and the removal rate under Earth's surface conditions [41,42]. Basalt, the main candidate for terrestrial ERW, is a category of rock that varies from roughly 100% glass to 100% crystalline and includes a wide variety of minerals. The content of non-hydrolytic species (so called, base cations) in minerals or glass predicts the total CO_2 removal potential of the ERW feedstock. In basalt, the most abundant base cations are usually magnesium and calcium, with lesser amounts of sodium and potassium. Hydrolytic species such as iron and aluminum are not believed to contribute to CO_2 removal during chemical weathering, as any alkalinity generated during the acid hydrolysis of their silicate form should be consumed during precipitation of secondary oxides (see for example, Eq. 3 and 4 summarizing fayalite weathering in surface conditions). Consequently, basalts with high Ca, Mg and/or alkali content should have the highest CO_2 removal potential.

$$\mathrm{Fe_2SiO_4 + 2H_20 + 4CO_2 \leftrightarrow SiO_2 + 2Fe^{2+} + 4HCO_3{}^-} \tag{3}$$

$$\mathrm{2Fe^{2+} + 4HCO_3{}^- + \tfrac{1}{2}O_2 \leftrightarrow Fe_2O_3 + 2H_20 + 4CO_2} \tag{4}$$

Kinetic considerations are in all likelihood, much more important than stoichiometry for determining CO_2 removal during ERW. At constant pH, the weathering kinetics of basalt's major base cation-containing minerals vary by more than 4 orders of magnitude between fast-dissolving Mg-olivine and Ca-plagioclase, and the slow-dissolving and much less abundant K-feldspar minerals (Figure 1.1).

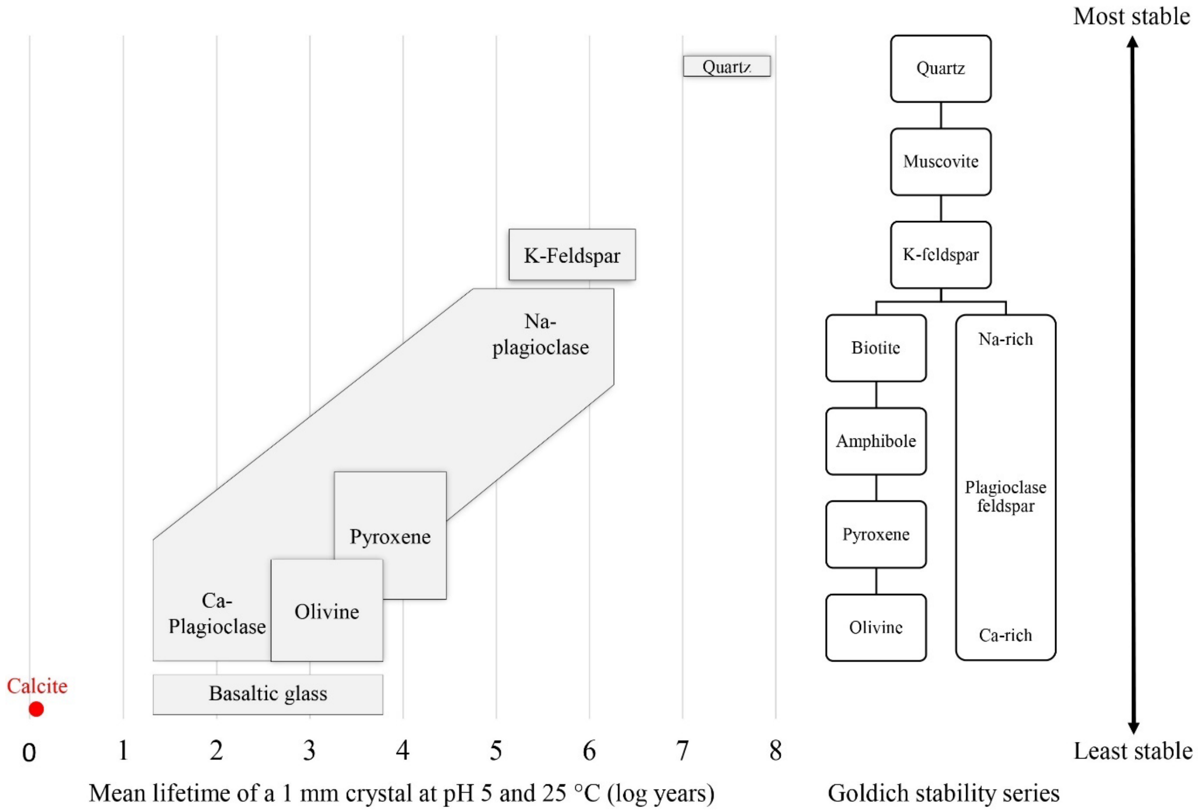

Figure 1.1 Goldich stability series (right) and mean lifetime of several key basaltic minerals (left) with box area proportional to mineral abundance in basalt. ERW being often presented as a potential alternative to agricultural liming, calcite was also represented (red circle) (Modified from Lasaga et al. 1994; Kump et al. 2000; and Wilson 2004).

When accessory minerals are included, this variation can be even higher. Although much of this heterogeneity was initially overlooked in some studies, recent work now points toward the need to focus only on the most reactive basalts for successful ERW. Lewis et al. found for instance that basalts display up to a 6-fold difference in CDR potentials 15 years after application, mainly due to the compositional variations in olivine and augite [42], two of the most common and fastest-weathering minerals in basalts. Another major source of significant kinetic variability is the amount of amorphous phase (glass) in each basalt. Basaltic glasses can weather even faster than olivine depending upon pH and composition [43] and can therefore lead to wide weathering differences, at least during the initial stage of ERW [44].

1.2.2 Influence of grain size

The effect of grain size on ERW kinetics may be more complex than initially expected. The underlying rationale for ERW includes grinding silicate rocks to increase their specific surface area (SSA) and thereby their reactivity. When evaluating the negative relationship between grain size and SSA, laboratory measurements generally show that a grain diameter of 100 μm is the approximate threshold below which the SSA of many silicate minerals increases rapidly with decreasing grain size [45]. Incubation experiments [17,46] as well as modelling studies [8,47] generally outline the positive impact of finer particles on mineral dissolution kinetics. Some calculations have even suggested that grain sizes < 10 microns would be required for successful ERW operations [48]; yet the use of very fine grain sizes would pose a number of challenges and risks.

Firstly, grinding basalt to a very fine particle size requires substantial additional energy input. Increasing the fineness of grind from 100 μm to 10 μm increases on average the energy and the associated CO_2 emissions by an order of magnitude [47,49], with a significant impact on the net CDR efficiency of basalts. Rinder et al. calculated for instance that, for a fineness of grind of 10 μm, comminution alone would emit 45.0 kg $CO_2.t^{-1}$ (or 15% of the intrinsic CDR potential of basalts) [48]. This level of emission was calculated for a country with a balanced energy mix (Austria) and would go beyond 100 kg $CO2.t^{-1}$ for countries with the most carbon-intensive energy mixes (e.g., South Africa, India, Poland, or Indonesia). In addition, finer particles, especially of silicate composition, can create severe human health hazards for those handling the materials [31]. Finally, the literature has put forward concerns regarding the impacts of fine particles addition on soil physical properties, namely, soil water and air movement [29,50].

Fine rock particles could indeed clog the soil porosity, as sometimes measured during liming operations. Liming consists in applying various forms of calcium- and/or magnesium-based materials to soil to increase its pH. Although generally considered beneficial for soil structure [51], liming has sometimes been associated with a detrimental change in pore size distribution and connectivity. The addition of calcium oxides and hydroxides (CaO or $Ca(OH)_2$) at rates varying between 1 and $5t.ha^{-1}$ occasionally led for instance to a decrease in macroporosity in clay-rich soils [52,53]. If ERW triggered a similar decrease in porosity, this could prevent the solution from being regularly flushed (a condition needed to maintain high weathering rates, as detailed in section 1.5) and could also impede gas diffusion. It should be noted that CO_2 diffuses 10'000 times faster in air than in water [54], so that any reduction of the soil macroporosity (usually air-filled at field capacity) could constitute a potential drawback for CO_2 availability during weathering reactions.

Similarly, any limitation in oxygen associated with a lower air-filled porosity would impede soil respiration, thereby decreasing CO_2 and carbonic acid production.

Despite these risks, there is currently no field-scale evidence regarding a potential detrimental effect of ERW on soil structure, deep percolation and gas diffusion. In a recent ERW soil column experiment, the highest weathering rates of the olivine-rich rock dunite were observed in columns with coarser grains [55] . The authors suggested that this could be due to the impact of improved water movement and gas exchange. If such results were confirmed, the use of at least a fraction of coarser grains might be warranted under appropriate conditions. This could alleviate the ERW carbon footprint associated with grinding while ensuring a limited impact on soil structural and hydrological properties.

1.2.3 Influence of temperature

The relationship between silicate weathering rates and temperature has long been explored both in the laboratory and in catchments with silicate lithologies [56,57]. Weathering rates tend to increase exponentially with temperature, provided that the supply of fresh weatherable minerals and of water are not limiting [58–61]. In a recent ERW mesocosm experiment, the weathering rate of olivine at 4°C was for instance two orders of magnitude lower than at 19°C [62].

However, the complexity of the soil environment makes the temperature dependency of weathering uncertain under open field conditions. For instance, the increase in biological activity and soil respiration could on one hand further increase weathering rates at higher temperatures; while on the other hand, a higher evapotranspiration could cause a soil moisture deficit which would impair weathering reactions. Additionally, it is indeed known that CO_2 solubility decreases with increasing temperature. Between the common soil temperatures of 10°C and 25°C for temperate and tropical climates respectively, CO_2 solubility declines by a factor of two. Thus, while warm (tropical) environments probably offer the best possibility for high weathering kinetics, the balance between various geochemical and biophysical processes may allow for ERW operations in temperate climates to still yield competitive CDR rates.

1.2.4 Influence of pH

Perhaps the most important geochemical control on ERW rate is pH. The weathering rates of silicate minerals either decrease with increasing pH or follow a U-shaped curve, with minimal rates at circumneutral conditions (Figure 1.2). Although different laboratories have shown different pH dependence rates for several of the important basaltic minerals [63,64], rates always increase at acidic ($pH < 6$) pH conditions and can sometimes also increase at alkaline pH ($pH > 9$) conditions. For example, the dissolution rate of anorthite (the Ca-rich end member of plagioclase feldspar) is on average 2 orders of magnitude lower at pH 7 than at pH 3 and 10 [65]. At low pH, weathering reactions favor the dislocation of metal cations by protons while, in highly alkaline conditions, the detachment of negatively-charged silica oxyanions controls the dissolution process [66]. Soils with pH greater than 9-10 are, however, very uncommon in natural systems and even more in agricultural settings. The subsequent section will therefore only focus on ERW under acidic to mildly alkaline ($pH < 9$) conditions.

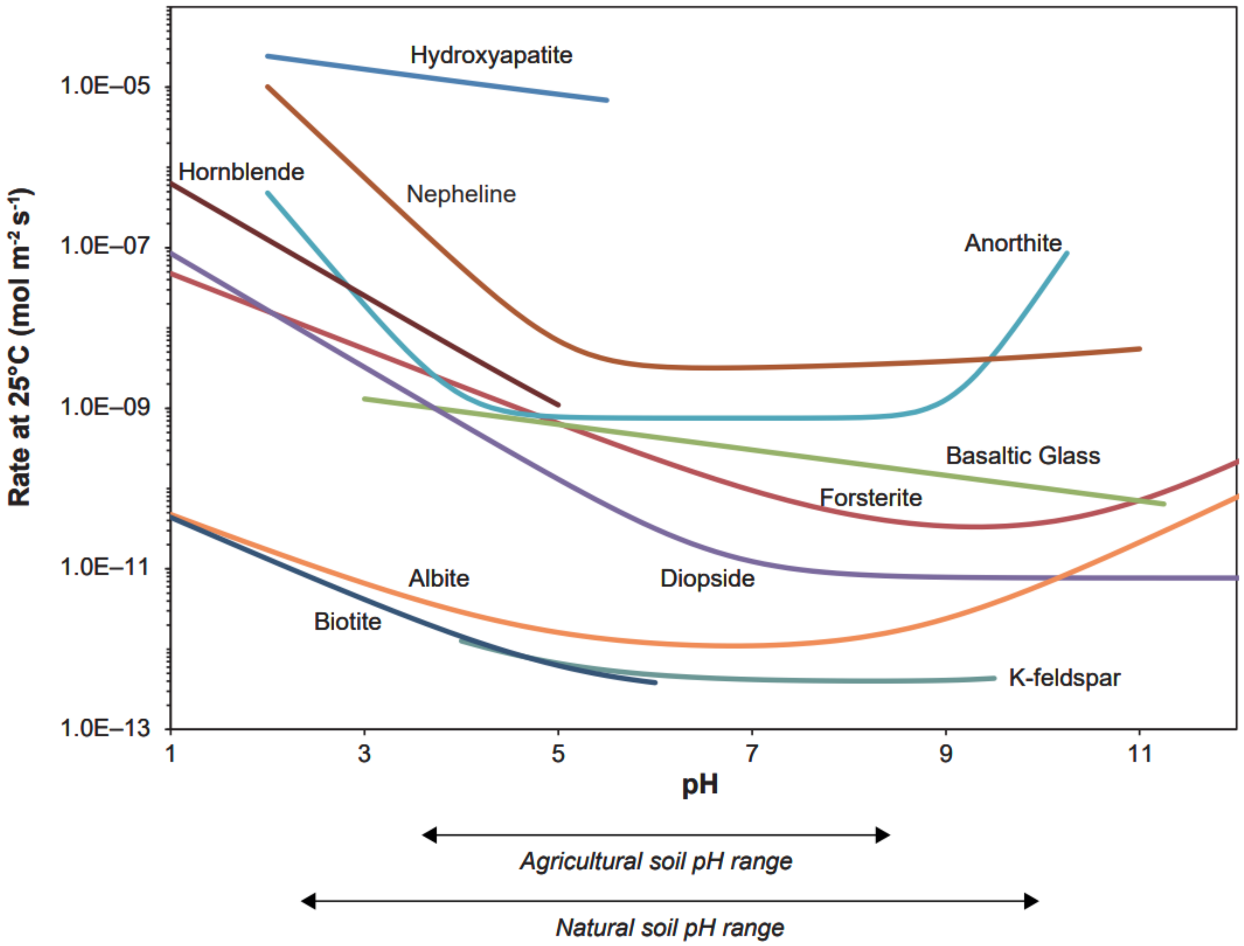

Figure 1.2 Weathering rate of several silicate minerals as a function of pH. (Figure modified from Zhang et al. 2017 *[67]* based on weathering rates from Palandri &Karaka 2004 *[43]*)

Here it should be noted that the chemical weathering of silicates does not automatically consume CO_2. In strict geochemical terms, ERW is based on an acid hydrolysis, where protons are consumed as they dislodge metal cations from the silicate crystal structure (Eq. 5). Over geological timescales, it is well established that the type of acid participating in this hydrolysis regulates the CO_2 drawdown. While silicate weathering by carbonic acid consumes CO_2 (as depicted in Eq. 1), weathering by sulfuric acid produced during the oxidation of sulfides does not [68].

In agricultural soils, the protons available for the acid hydrolysis of silicates can be generated by a variety of different processes [69,70]. The most prevalent are listed below (Table 1.2):

1. CO_2 dissolution in rain (from atmospheric CO_2) and in the soil solution (from aerobic respiration) forming carbonic acid (Eq. 6)
2. Oxidation and dissolution of sulfur and nitrogen oxides in atmospheric water leading to the formation of sulfuric and nitric acids, respectively (Eq. 7-10)
3. Oxidation of sulfides contained (in traces) in basalts creating sulfuric acid (Eq. 11)
4. Oxidation of elemental sulfur from fertilizers leading to the formation of sulfuric acid (Eq. 12)
5. Oxidation of ammonium contained in ammonium-based fertilizers or resulting from the mineralization of organic compounds, resulting in proton release (Eq. 13)

Table 1.2. List of some acid-base reactions directly or indirectly impacting ERW

Process	Chemical reaction	Equation
Silicate acid hydrolysis (example of wollastonite)	$CaSiO_3 + H_2O + 2H^+ \leftrightarrow Ca^{2+} + H_4SiO_4$	(5)
Carbonate equilibrium	$CO_{2\,(g)} + H_2O \leftrightarrow H_2CO_3{}^* \leftrightarrow HCO_3{}^- + H^+$	(6)
Sulfuric acid atmospheric formation and dissociation	$2SO_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2SO_{3\,(g)}$	(7)
	$SO_{3\,(g)} + H_2O \leftrightarrow H_2SO_4 \leftrightarrow SO_4{}^{2-} + 2H^+$	(8)
Nitric acid atmospheric formation and dissociation	$2NO_{(g)} + O_{2\,(g)} \leftrightarrow 2NO_{2\,(g)}$	(9)
	$2NO_{2\,(g)} + H_2O \leftrightarrow HNO_3 + HNO_2 \leftrightarrow NO_3{}^- + NO_2{}^- + 2H^+$	(10)
Sulfide oxidation (example of pyrite)	$FeS_2 + H_2O + \frac{7}{2}O_{2\,(g)} \leftrightarrow FeSO_4 + H_2SO_4$	(11)
Elemental sulfur oxidation	$2S + 3O_{2\,(g)} + 2H_2O \leftrightarrow 2H_2SO_4 \leftrightarrow 4SO_4{}^{2-} + 4H^+$	(12)
Ammonium oxidation to nitrate (abridged nitrification reaction)	$NH_4{}^+ + 2O_{2\,(g)} \leftrightarrow NO_3{}^- + H_2O + 2H^+$	(13)

If the acid hydrolysis of silicates is driven by carbonic acid, then proton consumption *de facto* sequesters CO_2 as a bicarbonate ion (Eq. 1). On top of this, carbonic acid being a weak acid, this proton consumption will shift the carbonate equilibria to the right (Eq. 6) thereby favoring further CO_2 dissolution and carbonic acid replenishment. However, if the acid hydrolysis is driven by sources of acidity other than carbonic acid, then silicate weathering does not result in any direct CO_2 consumption. At best, proton consumption could mitigate the acidification of the soil solution and of the downstream reservoirs (rivers, lakes, oceans), thus preserving the alkalinity-associated carbon storage and preventing CO_2 from degassing with acidifying conditions as seen in most headwater streams [59].

The activity of carbonic acid in soils is influenced by soil pH and CO_2 partial pressure (pCO_2) for the most common soil temperatures [71]. At ambient conditions, the pKa of carbonic acid is 6.4 meaning that carbonic acid is half dissociated (Eq. 6) at pH 6.4 and that its ability to act as a proton donor decreases dramatically as the pH decreases below this threshold (e.g., at pH 4.5, only 1.4% of H_2CO_3 is dissociated in $HCO_3^- + H^+$). Although carbonic acid concentration increases with pCO_2, it is estimated that carbonic acid donates on average less than 25% of all protons involved in silicate weathering for a pH below 5.2 despite the elevated pCO_2 levels measured in soils (often between 10 to 100 times atmospheric pCO_2) [72]. At these pH values, the majority of silicate weathering is therefore driven by non-carbonic acids and will not result in CO_2 sequestration. Although weathering rates increase as pH decreases, the optimal soil pH range for ERW operations may therefore be at moderate acidic conditions where slower weathering rates would be compensated by a higher CO_2 sequestration [72]. Field trials are now required to identify ERW's "pH Goldilocks zone(s)".

1.2.5 Influence of saturation conditions

ERW efficiency relies fundamentally on a dissolution reaction (Eq. 5), meaning that all the factors affecting solubility and solute concentration during weathering will logically impact ERW outcomes. As silicate minerals dissolve and in the absence of flushing or secondary precipitation, the concentration of reaction products in the bulk solution increases, thereby slowing down weathering rates. This situation is especially important given that many soil solutions are already considered close to thermodynamic saturation with respect to primary silicate minerals [64]. This aspect has long been underestimated in laboratory experiments which have often worked with solutions far from thermodynamic saturation. This situation has led to the so- called "field-lab discrepancy" with lab-based weathering rates being 1-4 orders of magnitude higher than field-derived rates [73].

In this respect, soil texture and structure play a determining role. A high clay content (> 40-50 %) as well as compacted soil features (e.g., soil crusting on the surface, plow pan, overall compaction, etc.) are factors that are known to limit soil macroporosity and permeability [74], which in turn prevents the adequate drainage of the soil solution. Conversely, extremely coarse sandy soils have a limited ability to retain water, which restrains the time of contact between minerals and the soil solution [75]. Optimizing ERW kinetics will therefore consist in not only selecting basalts that are highly reactive, grinding them to suitable grain sizes, but also in choosing terrains with the climatic and hydrological conditions that ensure both optimal supply of water for mineral dissolution and enough soil drainage to leach solutes.

1.2.6 Influence of secondary precipitation

Fast consumption of CO_2 is usually observed during the initial stages of silicate weathering due to the rapid dissolution of loosely bonded ions and highly reactive phases and surfaces [37,41]. After that, mineral weathering rates can slow down because these reactive components are exhausted, solutes build up in solution, or grain surfaces are passivated by secondary phases [73,76,77]. Secondary amorphous phases (especially silica-rich surface layers) as well as oxide, clay and carbonate precipitations are indeed commonly observed following fresh silicate amendments [58,73,76–78]. Although the first signs of precipitation have been observed within days, their effects on weathering rates are disputed [79,80]. Some studies did not measure any impact on weathering rates at all, or even measured higher rates following secondary precipitation, attributing these results to the maintenance of far-from-equilibrium conditions [81–84]. Secondary phase precipitation is indeed one of the main mechanisms which can remove ions from solutions, thus keeping them undersaturated or far-from-equilibrium (i.e., very dilute) with respect to the mineral phases they are dissolving. Several other studies conducted in laboratory, watersheds or soils measured however a significant weathering rate reduction that was usually explained by the coating, or *passivation*, of silicate mineral surfaces reducing the surface area in contact with reactive fluid [85–88]. Surface passivation mechanically slows down the release of cations from the silicate mineral lattice into the solution and thereby slows the whole reaction [89,90]. The current understanding is that the impact of surface passivation on weathering rates depends on 1) the extent of passivation (some secondary precipitates remain very localized while other coat the entire surface [91]) and 2) on the crystallographic structure similarities between the dissolving and precipitating phase favoring dense nucleation and epitaxial growth [80,92,93].

At the scale of the soil column, secondary precipitations could accumulate to the point where gas diffusion and water movement would be hindered by a hardpan. In the ERW context, the most probable type would be an accumulation of secondary carbonates resulting from an excess in bicarbonate ion. The cations and bicarbonate anions produced from the silicate weathering reaction can indeed accumulate in the soil profile to the point that the soil solution reaches supersaturation. In arid and semi-arid climates marked with seasonal precipitation deficits, this situation can lead to the quantitative precipitation and accumulation of secondary carbonates known as pedogenic carbonates. These precipitations take different forms ranging from coatings to nodules and even cemented carbonate layers known as *caliche* or *calcrete* [94]. Such formations are common in basaltic environments (e.g., in the Deccan Plateau in India [95,96] and in Hawaii [97]) and in areas having received important calcium-rich dust deposits [98,99]. The regular and heavy applications of fresh basaltic material during ERW operations raise the risk of similar precipitations with detrimental effects on basalt weathering dynamics (similar to the impact of clogging detailed in section 1.2) and soil fertility as a whole (shallower root exploration and anchorage, lower resilience towards drought, lower water infiltration rates, etc.). Whether this could happen within years or decades due to ERW remains, however, an open question. In nature, calcrete formation is a slow process requiring between 10^3 and 10^5 years depending on environmental conditions [94]. On the other side, the magnitude at which fresh highly reactive material is being applied in ERW operations is one to three orders of magnitude higher than aeolian deposits for instance [100]. The extent to which these secondary precipitations could have a detrimental effect on soil structural and hydraulic properties is therefore another research avenue that needs to be explored.

1.2.7 Synthesis of geochemical factors influencing ERW

Given all these considerations, not all basalts and soils offer optimal ERW conditions (Table 1.3). In addition to regional parameters such as temperature and precipitation, careful site and rock selection including parameters such as rock grain size, mineralogy and pH will be likely to play an equally decisive role to maximize ERW overall efficiency.

Table 1.3. Fundamental rock and soil geochemical parameters affecting ERW efficiency.

	Conditions…	**… impeding ERW**	**… favoring ERW**
Basalt properties	Mineralogy	Slower-reacting minerals (e.g., K-felspar and Na-plagioclase)	Fast-reacting minerals (e.g., olivine, Ca-plagioclase)
	Amorphous phases (glass)	Low content	High content
	Elemental composition	Low base cation content (Ca^{2+}, Mg^{2+}, K^+ and Na^+)	High base cation and high Fe and Al contents
	Grainsize	Coarse (> 100 µm)	Mainly fine (< 50-60 µm)
Soil properties	Soil pH	Circumneutral or slightly alkaline	Acidic soil conditions
	Temperature	Low temperatures	Year-round warm temperature
	Moisture regime	Arid to semi-arid	Humid to sub-humid
	Texture	Heavy-clay or sandy soils	Intermediate (loamy soils)
	Structure	Compacted, disconnected	Optimal porosity and connectivity
	Water-holding capacity	Very poor (decreasing mineral exposure to water) or excessive (causing soil saturation)	Moderate between retention and regular flushing

1.3 What do ERW experiments teach us and where from here?

Exploring the fundamental geochemical factors affecting silicate weathering rates in a medium as complex as soil suggests that ERW operations will display highly contrasting results depending on regional and local conditions (Figure 1.3). While past ERW experiments confirm the importance of the geochemical principles detailed above, their experimental design did not include certain parameters that now must be systematically included to enable a comprehensive evaluation of ERW efficiency.

1.3.1 Lessons from ERW experiments

The first lab and field trials in the 19th century focused on silicate rocks as alternatives to fertilizers [101–104] with overall encouraging yield results [102–111], despite some exceptions [115–117]. At the time, these contrasting results were principally attributed to the varying crop abilities to extract nutrients, rather than to geochemical factors such as grain size or mineralogy [114,118–120]. Interestingly, the increasing attention towards ERW since the late 1990s has led to the "rediscovery" of the fertilizing capabilities of rock powder, yielding generally comparable favorable results [8,121–130].

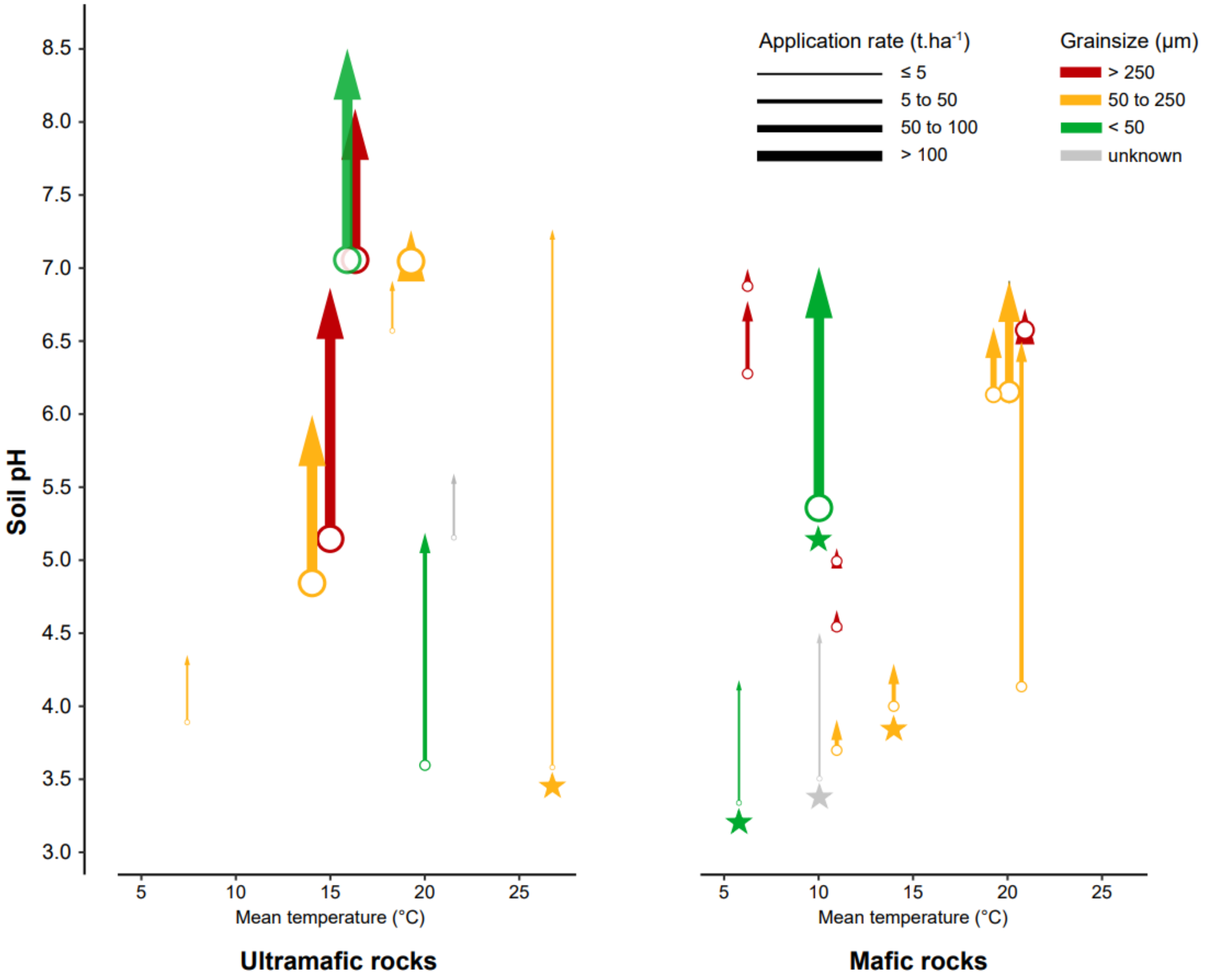

Figure 1.3 Changes observed in soil pH during ERW mesocosm and field experiments using either ultramafic or mafic rocks over a median duration of 12 months. Each arrow represents one ERW experiment for which the rock powder (p80 grainsize (µm)), the initial rock powder application rate (ton.ha^{-1}) and mean temperature (°C) over the course of the experiment are indicated. Field experiments are indicated (star shape) at the bottom of each arrow (Source: derived from the following experimental results [27,46,55,122,124,126–128,136–143,148–150]).

Following these early experiments, studies in the 20th century explored the wider potential of silicate minerals to enhance soil chemical attributes like pH, cation exchange capacity, and base cation concentrations. Overall, significant increases in pH as well as in nutrient concentrations (calcium, magnesium, potassium, phosphorous and silicon) were observed [46,131–143].

Changes in pH were especially informative. The pH increase in pore fluids that results from proton consumption during silicate weathering – provided that the rock powder contains no carbonate – is indeed a blunt yet instructive way to compare overall weathering efficiency. When comparing ERW experiments from the pH change perspective (Figure 1.3), the following trends are observed:

1. *ERW efficiency should not be taken for granted* : pH changes ranged from very large to nil even when using highly reactive minerals in a warm climate.

2. *Ultramafic rocks tend to be more reactive than mafic rocks*: as a trend, changes in pH tend to be more important in equivalent conditions or even at colder temperatures.
3. *Rock powders with a fine grain size (<50 µm) are more reactive*: no matter the rock category, experiments using finer particles systematically outperformed experiments with coarser grain sizes in similar conditions.
4. *When using coarser-grained minerals, only massive rock powder application rates (> 100 $t.ha^{-1}$) lead to detectable effects*: rock powder with coarse grain sizes tends to lead to non-significant changes at low to moderate application doses (below 50 $t.ha^{-1}$) while triggering significant increases at higher doses.
5. *Temperature plays a determining role*: the rise in pH, although not systematic, tends to increase with temperature and could be especially influential when grainsizes between 50 and 250 µm are chosen.

1.3.2 Designing future ERW experiments

The trends described above remain fragile given the field-lab discrepancy. Many experiments so far relied on chemical reactors to investigate the dissolution of one mineral at a time, including each of the three important reactive minerals for ERW, namely olivine, plagioclase, and pyroxene [43,144]. Experiments were also used to dissolve powdered crystalline or glassy basalt rock in continuously stirred or column reactors with and without organic molecules [145–147]. To date, however, no one has successfully used these laboratory-scale measurements to predict rates *a priori* for natural systems. This is because such predictions would require knowledge of a large amount of rock, soil and environmental data that is difficult or maybe even impossible to quantify, given the variability of natural systems. Furthermore, so many processes are coupled in natural systems, so that predictive capability is hampered where parameterized models are not available.

Nevertheless, improvement in our understanding of ERW kinetics is still possible. As seen earlier, the impact of rock powder on crop yields has been successfully determined using field experiments, with a reasonably robust consensus emerging regarding the fertilizing capabilities of rock powder. When transposed to the ERW context, these studies however often lack one or several key parameters to calculate and analyze weathering kinetics (e.g. rock powder specific surface area).

One research avenue toward a better understanding of basalt weathering would therefore be the use of appropriately designed experiments. To do so, we suggest that future field experiments systematically record a series of parameters regarding the experimental context, the feedstock as well as the soil and leachate properties (summarized in Table 1.4). Climatic variables should evidently be recorded, given the first-order control that they exert on chemical weathering rates. Agricultural practices significantly influence soil physical and chemical properties (e.g., via soil cultivation practices, pesticide, and fertilization inputs) and should also be accounted for. The feedstock's properties (grainsize, mineralogy, glass content, etc.) as well as the soil properties (pH, texture, etc.) are known to affect weathering rates (as seen in Section 1) and should therefore equally be included. Finally, several chemical parameters should be monitored during the experiment both in the soil and in the soil solution (leachate) to trace the kinetics, benefits, and potentially adverse effects of ERW [130,151–153]. By consistently incorporating these parameters, future research will contribute to improving our fundamental understanding of ERW dynamics and of its overall efficiency and potential at a larger scale.

1.3.3 **Table 1.4.** Suggested parameters that future field experiments should include to better understand basalt weathering in the ERW context

Categories	Parameters
Climatic context	▪ Climate classification ▪ Mean temperature and temperature range ▪ Rainfall and/or irrigation frequency and rates ▪ Rainfall and/or irrigation water properties (pH, EC, composition)
Agricultural context (if applicable)	▪ Land use (forest, pasture, cropland) ▪ Farming system (conventional, organic) ▪ Current crop type and crop rotation ▪ Soil cultivation regime (tillage method, frequency, and depth) ▪ Pesticide use (product, dose, elemental composition) ▪ Fertilizer and amendment use (type, dose, composition)
Feedstock characteristics	▪ Grainsize distribution ▪ Specific surface area ▪ Mineralogy composition and glass content ▪ Elemental composition (major, minor, and trace elements) ▪ Application method (top-dressed or incorporated, depth if applicable) and rate
Initial soil properties	▪ Soil category / classification ▪ Soil moisture regime and drainage class ▪ Grainsize distribution and textural class ▪ Bulk density ▪ Soil pH ▪ Cation exchange capacity and exchangeable ion contents ▪ Total or pseudo-total elemental composition (major, minor, and trace elements) ▪ Organic carbon and nitrogen content ▪ Inorganic carbon content
Leachate parameters to monitor during ERW experiment	*High frequency (several times per year)* ▪ Leachate pH ▪ Dissolved inorganic and organic carbon (DIC-DOC) ▪ Electrical conductivity ▪ Major, minor, and trace element concentrations
Soil parameters to monitor during ERW experiment	*High frequency (several times per year)* ▪ Soil pH ▪ Whenever possible, greenhouse gas fluxes (CO_2, CH_4 and N_2O)
	Low frequency (every 1 to 5 years) ▪ Organic carbon and nitrogen content ▪ Cation exchange capacity and exchangeable ion contents ▪ Total or pseudo-total elemental composition (major, minor and trace elements)

1.4 Conclusion

Fundamental geochemical considerations together with the emerging ERW experimental results suggest that the efficiency of ERW as a CDR technology is likely to be subject to very large variation, and that the current state of knowledge is not sufficient to develop robust predictive capabilities. The heterogeneous mineralogy and reactivity of basalt as well as the regional and local pedoclimatic parameters heavily influence its weathering and in turn its ability to sequester CO_2. ERW efficiency should therefore not be taken for granted but should, rather, be pursued based on a careful rock and soil geochemical selection.

On top of this, understanding ERW is not only a geochemical challenge. Its efficiency and large-scale deployment will depend on broad scientific and technological cooperation. If ERW is to become one day a significant CDR technology, future research programs will need to bring together the fields of geochemistry, engineering, life cycle-analysis, biology, soil physics, hydrology, agronomy as well as social sciences such as economy, law, and sociology.

The importance of lifting constraints and closing research gaps is not only an issue for future ERW operations. As time to combat climate change runs out, CDR funds need to be allocated based on solid science to insure their overall efficiency as well as the credibility of the scientific community in the long run.

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