Perspective
Nutrient-doped synthetic silicates for enhanced weathering, remineralization and fertilization on agricultural lands of global cold regions – A perspective on the research ahead

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SUMMARY
There is now a dire demand for negative emissions technologies (which sequester CO₂ from the atmosphere) that can be rapidly deployed, are scalable, and are demonstrably safe and effective. Enhanced weathering of silicate minerals has demonstrated a significant potential for CO₂ capture and sequestration by the formation of pedogenic carbonates in soils, subsoils, and sediments. This technique has also been shown to deliver fruitful results in terms of improving soil health, and in turn plant health, through remineralization. The silicate minerals that possess the highest weathering rates (e.g., wollastonite), are relatively rare in nature, whereas the abundant ones (e.g., anorthite and forsterite) have a slower pace of weathering, especially in colder and drier climates such as found in the extensive agricultural lands of Western Canada and the Western United States. Herein, we offer a perspective on the opportunities for computational studies targeting atomic-scale interaction of CO₂ with silicates and synthesis of fast-weathering silicates (such as larnite and bredigite), whose composition can be tuned to also support soil fertilization and remineralization, and whose production must be integrated with green and carbon-neutral technologies to ensure net-negative life cycle emissions.

BACKGROUND AND MOTIVATION

With no single carbon capture and sequestration solution able to limit the global temperature rise to 1.5–2°C by 2100, additional negative emissions technologies, for carbon drawdown, are required to complement the current mitigation approaches. Enhanced rock weathering (ERW) is one negative emissions technology that, applied globally, could remove gigatonnes of CO₂ per year from the atmosphere.1,2 In ERW, CO₂ removal occurs through the exposure of certain silicate minerals to the atmosphere, soil pore water, and oceanic waters, whereby CO₂ is transiently captured as soluble bicarbonates and permanently trapped as thermodynamically stable carbonates.1,2 ERW applications were originally proposed for agricultural and forestlands and coastal areas, where water, air, and (micro)biological activities could work together to weather minerals and transport sequestered CO₂ to long-term carbon sinks.3 The inorganic carbon capacity of soils is enhanced by amending them with calcium- or magnesium-rich silicate rocks,4,5 which leads to enhanced weathering and in turn accelerates CO₂ sequestration via mineral carbonation (Figure 1). Soil inorganic carbon produced by ERW near the soil surface gradually migrates to the subsoil, becoming part of the natural pedogenic carbonate pool.6 Farms provide an excellent setting for large-scale ERW through mineral soil amendments,1 because of the available infrastructure and experience with spreading comminuted mineral amendments (e.g., liming and phosphate rock), and the typically suitable soil properties and local climate: sufficient soil acidity and rainfall are key drivers of silicate weathering.

Recent ERW research has focused on tropical and temperate regions of the world owing to the relatively slow weathering rates of the most abundant silicates (basalt and olivine) in the colder and dryer regions of the world, wherein soils also tend to be more basic because of slower weathering of pre-existing soil carbonates.8 For example, Canada possesses extensive agricultural lands, but the conditions of much of it, especially in the Prairies, for ERW of basalt and olivine are not suitable, because it may take centuries to capture any notable CO₂ from the environment. In a recent investigation by Strandmann et al.,1 the
dissolution of olivine added to soil at 4°C was reported to be orders of magnitude slower than under optimal conditions for ERW. Another recent investigation by Bertagni et al.\textsuperscript{10} plotted the global mineral dissolution rates, as shown in Figure 2. According to this plot, major portions of the world, such as much of Western Canada and the Western United States, among several other countries, will not be able to gain benefit from the ERW technique, owing to climatic limitations. Of Canada’s 62,195,226 hectares of farming land, 39% is in the province of Saskatchewan, and 32% is in the province of Alberta.\textsuperscript{11} The agricultural lands in these two provinces have substantially colder and drier climates, and consequently more alkaline soils\textsuperscript{12} than those in the provinces of Ontario and Quebec. Similarly in the US, the northern plains (North Dakota, South Dakota, Nebraska, and Kansas) account for the largest share of cropland at 39.2 million hectares.\textsuperscript{13} The colder climates with lower rainfall rates and higher pH of soil make it difficult to weather naturally occurring silicate minerals. This research gap needs to be addressed to tap the ERW potential more broadly to tackle climate change.

Although wollastonite (CaSiO\textsubscript{3}) has been demonstrated to weather relatively fast (in the order of a crop season) in suitable agricultural soil,\textsuperscript{7} the present challenge is that such reactive naturally occurring silicates are less abundant, and global stocks in the order of hundreds of megatonnes\textsuperscript{14} would rapidly deplete once ERW scales up. Moreover, to maximize net-negative emissions, silicates should be available near point-of-use; yet, these scarce silicates are located in sparse ore reserves. For example, the currently commercialized wollastonite reserves in Canada are located in Ontario and Quebec, thus far from Alberta or Saskatchewan. The transport of minerals has been shown to be the largest factor affecting net-carbon sequestration potential.\textsuperscript{15} This perspective introduces the idea of synthetic silicates and their potential use in ERW in colder, dryer, and remote locations. The idea is that synthetic minerals can be made to be significantly more reactive than their natural counterparts,\textsuperscript{16} and their composition can be tailored to provide additional agronomic benefits.\textsuperscript{17,18} Also, the silicate production process can potentially be integrated with other technologies (geological sequestration and cement production),\textsuperscript{19,20} to minimize the overall environmental footprint.

Renforth\textsuperscript{21} recently presented the idea of synthesizing ikaite (CaCO\textsubscript{3}·6H\textsubscript{2}O) as a fast-weathering mineral that can be used in cold seawater for CO\textsubscript{2} capture. The synthesis of this mineral is not novel, as it is based on established geochemical processes, however, its production (which includes pumping/compressing/cooling operations) can be achieved in a CO\textsubscript{2}-negative manner if very low-carbon footprint electricity is used. Likewise, the methodology and conditions for the synthesis of silicate minerals, via solid-state sintering, are well established,\textsuperscript{16} but there is substantial research scope in tuning their composition of mineralogical properties for ERW in colder regions. In addition, new developments in electricity-driven metallurgical and cement-making processes open new opportunities for industrial synergism and symbiosis. The increase in climate change and CO\textsubscript{2} emissions awareness is shifting the global community’s attention toward clean energy conversion and
renewable energy resources, and as such these industries are also starting to understand the importance of switching towards green equipment and energy resources. For example, an Austrian steelmaker is converting three of its blast furnace plants to electric arc furnaces, and a Canadian steelmaker in Ontario is on the same path. The adoption of such environmentally friendly production systems can make the adoption of synthetic silicate minerals for ERW viable. Another attractive opportunity is the integration of silicate production processes with technologies such as cement production and geological sequestration, which would allow for minimizing the environmental footprint from cradle (silicate synthesis) to grave (soil amendment).

The research hypothesis for synthesizing reactive silicate minerals for ERW application is that these materials can be produced with higher weathering rates than their natural counterparts. Fast-weathering silicates such as merwinite and bredigite are found in steelmaking slags (Figure 3), and these materials have been shown to be more reactive than natural minerals such as olivine both under chemoorganotrophic bioleaching conditions and under accelerated carbonation conditions. It has also been found that the composition of synthetic silicates can be customized, with the potential to harness enhanced benefits in agricultural yields by doping silicate minerals with plant nutrients, much like P and V are sequestered in some metallurgical slags (Figure 3) during steel refining.

The following research objectives and hypotheses should be investigated to evaluate the technical and practical feasibility of utilizing synthetic silicates for ERW in agricultural settings:

- **Synthesizing various fast-weathering silicate minerals via solid-state sintering.** The hypothesis is that those silicate minerals with a high Ca:Si ratio, and not containing Al, will weather significantly faster and more predictably in soil ERW settings. Such minerals include (Figure 3): akermanite (Ca₂MgSi₂O₇), bredigite (Ca₇Mg(SiO₄)₄), cuspidine (Ca₄Si₂O₇F₂), larnite (β-Ca₂SiO₄), calcio-olivine (γ-Ca₂SiO₄), merwinite (Ca₃Mg(SiO₄)₂), and pseudowollastonite (β-CaSiO₃).

- **Investigating the doping of plant nutrients (e.g., P, K, Mo, and Se) into the silicates, to increase their fertilizing ability.** The hypothesis is that as the silicates weather, they will release plant nutrients, with amorphous silica, and this can be an effective way of fertilizing and remineralizing soil while sequestering carbon.

- **Investigating mechanical activation and degree of crystallinity as means to increase the weathering rate of synthetic silicates.** The hypothesis is that silicates with crystal defects and disorders in their crystal structure will be more reactive under ERW soil settings.

- **Testing the synthesized materials in soils to determine their fertilizing ability and CO₂ sequestration ability.** The hypothesis is that the synthetic silicates will behave similarly to how steelmaking slags are known to rapidly weather and carbonate but will be safer because of the tuned chemical composition, and their behavior will be more predictable because of controlled mineralogy.
Conceptualizing an integrated industrial process to manufacture these synthetic silicates in a net-negative carbon way. The hypothesis is that synthetic silicate production can be combined with carbon capture and sequestration (CCS) via geological carbon storage, to enable supplying free alkaline earth metal oxides from natural carbonates, in a similar approach to that used in the production of carbon-neutral cement via integrated calcination-CCS.29

POTENTIAL FIELD TRIALS

A utilitarian role in the global carbon cycle is played by natural soils, as it demonstrates an approximate reservoir of 2500 Gt of carbon that far exceeds the atmospheric C reservoir of 800 GtC.30,31 There are two major natural pathways through which the atmospheric CO₂ is regulated by pedogenic processes in soils: by photosynthesis, which influences the soil organic carbon (SOC) pool, and via weathering of alkaline minerals, which controls the soil inorganic carbon (SIC) pool. Although many investigations to date have been conducted for increasing the SOC pool capacity,32–35 the SIC pool has received relatively limited attention, especially the amendment of soils by alkaline silicate minerals for building up the capacity of the inorganic pathway.

Given that the CO₂ sequestration capacity of alkaline minerals accessible deposits outnumbers the estimates of carbon content present in fossil fuel reserves,1 some of these minerals can play a significant role in minimizing the hazardous effects of excessive CO₂ presence in the atmosphere. The ERW approach has candidate materials made up of calcium and magnesium silicates, including the serpentine group ((Mg,FeII)₃Si₂O₅(OH)₄) minerals, the olivine group ((Mg,Fe)₂SiO₄) minerals such as fayalite (Fe₂SiO₄) and forsterite (Mg₂SiO₄), and the pyroxene group ((Ca,Na,FeII,Mg)(Cr,Al,FeIII,Mg,Mn,Ti,V)Si₂O₆) minerals such as enstatite (MgSiO₃) and wollastonite (CaSiO₃).36 As an example, all carbon that can be expected to be emitted from the currently recognized reserves of natural gas, oil, and coal can in theory be completely sequestered by the global reserves of serpentine and peridotite (olivine and pyroxene).37

The process of ERW consists of the amendment of soils with alkaline earth minerals.38 Magnesium- or calcium-rich silicate minerals are finely milled/crushed, and the powder is added to soils. The mineral weathering process releases the alkaline earth metal cations. Concurrently, the carbonate anions originating from the soil microbial process or the atmosphere, are dissolved in the soil pore water. Alkaline earth metal cations react with carbonate anions to form carbonate or bicarbonate salts.39 These salinities either accumulate in the A, B, or C soil horizons upon precipitation as SIC, or the groundwater carries them through underlying aquifers, and finally, these salts are accumulated in large water bodies and oceans. The solubility of carbonates at a particular soil pH would identify the long-term fate of CO₂ sequestered through either pathway, but the atmospheric CO₂ concentration can be effectively reduced through either mechanism of the ERW technique.38 From a practical aspect, ERW is deployable in a similar way to how the pH of soils can be controlled or corrected by either the addition of powdered carbonate-rich rocks to agricultural soils, or by blending such rocks with fertilizers, peat, and compost.18 This conventional process is known as liming owing to the conventional use of limestone and other calcium carbonate-based materials.30 Liming in the agricultural context of soil pH neutralization has been shown to be a net-positive CO₂ emission practice,41,42 hence the use of silicates rather than carbonates is needed to achieve the negative emissions goal of ERW. Forested and urban soils can similarly be used to sequester atmospheric CO₂ concentrations for the long term.43,44

Charcoal, humus, microorganisms, and decomposed plants and animal residues make up the SOC pool, whereas primary carbonates such as calcite (CaCO₃) and secondary carbonates such as dolomite ((CaMg(CO₃)₂) are included in the SIC pool.45 These primary and secondary carbonates can be categorized into lithogenic and pedogenic carbonates, respectively. The detrital particles, which are derived from carbonate bedrock (particularly limestone) and formed under marine conditions, are referred to as primary or lithogenic carbonates. Pedogenic carbonates are the secondary carbonates in soils and subsoils. These are
further classified into calcitic pedogenic carbonates (which are derived from pre-existing carbonates and are formed by calcite remobilization) and silicatic pedogenic carbonates (which come into existence because of silicate weathering). Calcitic carbonates do not play any role in net carbon sequestration, as they are formed from pre-existing carbonates. In contrast, the silicatic pedogenic carbonates are composed of the carbonation products of alkaline earth silicate minerals, which deliver net positive carbon sequestration.46

In ambient weathering, naturally occurring rocks weather slowly, from an anthropogenic point of view rather than a geological timescale. In the ERW process, alkaline silicate minerals are milled into fine powder form and exposed to the atmosphere under reaction-accelerating conditions. The milling increases the specific surface area of minerals, which accelerates the weathering process.38 The minerals can also be potentially pretreated for improving the weathering rate via mechanical, chemical, biological, or thermal means.47,48 However, such pre-treatment processes result in a drawback of high operational energy consumption.49,50 Certain soil and crop conditions accelerate the rate of silicate weathering and SiC accumulation, and these facts have been verified at relatively short timescales (months to years) under controlled and uncontrolled ambient settings using the fast-weathering natural mineral wollastonite.7,17,18

Wollastonite is a polymorphic substance, naturally found in three forms: triclinic wollastonite, monoclinic (or para-) wollastonite, and pseudo- or (cyclo-) wollastonite.54 The first two are chain-structured and low-temperature polymorphs, whereas the third one belongs to the cyclo-silicate family and is a high-temperature polymorph, as silicate tetrahedrons (SiO4)4- form a ring of three units (Si3O9)6- at high temperature. The most common synthesis process includes the mixing of limestone (or other calcium sources) and quartz (or other silicon dioxide source). The mixture is then calcined at a temperature range of 1200–1400°C. The most common synthesis process includes the mixing of limestone (or other calcium sources) and quartz (or other silicon dioxide source). The mixture is then calcined at a temperature of 1200°C. 

\[ \text{CaSiO}_3 \] is a polymorphic substance, naturally found in three forms: triclinic wollastonite, monoclinic (or para-) wollastonite, and pseudo- or (cyclo-) wollastonite.54 The first two are chain-structured and low-temperature polymorphs, whereas the third one belongs to the cyclo-silicate family and is a high-temperature polymorph, as silicate tetrahedrons (SiO4)4- form a ring of three units (Si3O9)6-. The most common synthesis process includes the mixing of limestone (or other calcium sources) and quartz (or other silicon dioxide source). The mixture is then calcined at a temperature range of 1200–1400°C via a solid-state sintering process, which results in producing wollastonite.55,56

Åkermanite mineral is a product of contact metamorphism of dolostones and siliceous limestones, having the chemical formula Ca₂Mg(Si₂O₇). It can be synthesized through various means; however, the conventional sintering method is common. In this method, ceramics are heated at very high temperatures, which reduces mechanical strength and fosters grain growth. Åkermanite powder was produced by Wu et al.57 through the sintering process at 1370°C for 6 h, Hou et al. synthesized åkermanite powder at 1350°C for 4 h, and Bodor et al.16 prepared akermanite powder by sintering the precursors for 24 h at 1300°C.

Bredigite mineral, having chemical composition Ca₂Mg(SiO₄)₆, is a part of metasomatic rocks belonging to sanidinite facies. It is naturally formed under low pressure (less than 1–2 kbar) and high temperature (more than 800°C) conditions and is rarely found on Earth.59 Tavangarian and Emadi synthesized bredigite powders using a mechanical activation technique followed by annealing. Talc, amorphous silica, and calcium carbonate were used as initial reactants. The mechanical activation ranged between 10 to 60 h, whereas the subsequent annealing time was 1 h at a temperature of 1200°C.
Cuspidine is a fluorine-bearing sorosilicate mineral, having the chemical composition Ca₄(Si₂O₇)(F,OH)₂. The crystallization phase of cuspidine is monoclinic. Bodor et al. synthesized cuspidine by heating calcium oxide, fumed silica, and calcium fluoride at 1100°C for 2 h, under an inert atmosphere of Ar.

Merwinite is an orthosilicate mineral, having the chemical formula Ca₃MgSi₂O₈. Hafezi-Ardakani et al. synthesized merwinite at 1300°C, and Bodor et al. synthesized merwinite by milling the precursors for 2 h, followed by 20 h of sintering at 1500°C.

Calcio-olivine (γ-C₂S) and larnite (β-C₂S) are the low- and high-temperature polymorphs of dicalcium silicate (C₂S; Ca₂SiO₄). Calcio-olivine is orthorhombic whereas larnite is monoclinic. Fang et al. studied the mineral’s evolution and strength development by accelerated carbonation curing of β-C₂S and γ-C₂S phases. Both phases were sintered at 1450°C for 3 h. For avoiding the transformation of β-C₂S to γ-C₂S, to obtain larnite, the sintered samples were rapidly cooled.

SYNTHESIS AND MORPHOLOGY

Negative emissions technologies target the removal of CO₂ from the atmosphere as a way of combating global warming. ERW is a vital negative emissions technology that, applied globally, could remove gigatonnes of CO₂ per year from the atmosphere. In ERW, silicate minerals exposed to the atmosphere trap CO₂ via mineral carbonation as thermodynamically stable carbonates. From a fundamental and technological standpoint, the present challenge is that the most reactive naturally-occurring silicates are not abundant, and even those may weather too slowly in colder and dryer regions of the world, such as the Canadian Prairies. In order to design novel fast-weathering and nutrient-doped synthetic silicates for ERW in colder and dryer regions, a basic understanding of their structure and reactivity is necessitated at the nanoscale. Because of the complexity involved in experimentally characterizing mineral surfaces, recent theoretical and computational studies that complement experimental efforts have focused on exploring and understanding the structure-property relationships at silicate surfaces. Nonetheless, these computational and experimental studies are still in their infancy, resulting in a lack of clarity regarding the atomic-scale structure of low-index silicate surfaces and basic atomistic mechanisms and dynamics of CO₂ interaction with various facets of silicates.

The majority of the computational studies in the literature exploit the well-known atomistic simulation methods such as density functional theory (DFT) and empirical potentials-based molecular dynamics (MD) to model reactive silicate surfaces and their interaction with additive molecules. These two methods have their advantages as well as disadvantages. For instance, DFT offers basic insights into the thermodynamics of surface stability with the atomic and electronic structure of silicate surfaces and interface charge transfer with additive molecules. However, DFT is limited by the system size and simulation time since these calculations are extremely expensive because of large surface slab models that are necessitated to mimic silicates. An inherent limitation of DFT calculations is that they are performed at 0 K, which does not offer information about surface kinetics and dynamics. On the other hand, empirical potentials-based MD offers a window into kinetics but is unable to provide information at the electronic level. In addition, MD is limited in applicability because it heavily depends on the choice and availability of force fields. In general, because of the complexity involved in mimicking silicate surfaces, it appears that a concerted effort is required to successfully study the dynamics of CO₂ interaction with silicate surfaces, which will be crucial to developing new negative emission technologies based on ERW.

Because DFT has proved to be a useful tool in predicting the structure and properties of complex materials, we recently employed DFT within the framework of the Vienna ab initio Simulation Package (VASP) to predict the atomic-scale structure low index surfaces of wollastonite (CaSiO₃) in its most common triclinic phase using surface slab models consisting of 240 atoms. Owing to the triclinic phase, wollastonite exhibits different surface layer atomic arrangements and symmetry along different families of (100) planes. We find that the respective surface energies of (100), (010), and (001) surfaces of wollastonite are 1.349 J/m², 1.103 J/m², and 1.104 J/m², indicating that (010) and (001) exhibit similar stabilities, whereas (100) is the least stable. Geometrically and energetically minimized atomic-scale models of (001), (010), and (100) surfaces of wollastonite are given in Figure 4. The normal and side views of the surface atomic arrangement in wollastonite evidently display the complexity associated with studying such systems. Remarkably, in each of the three surfaces, atomic layers could either constitute calcium, oxygen, or silicon, or a combination of these atoms, which further dictate the surface stability. Such intricacy is also present along the
and families of planes. Perhaps, this is one of the potential reasons for the lack of fundamental research on low-index wollastonite surfaces. For instance, although much is known about the surface structure and properties of well-studied complex materials such as titanium dioxide, cerium oxide, strontium titanate, etc., the same cannot be argued about wollastonite or silicates in general. Moreover, several wollastonite low-index surfaces are Type II symmetric according to Tasker classification, which requires careful treatment for ensuring appropriate surface cleavage so as to avoid surface energy divergence. If we move on from pure surfaces and consider surface defects, there are hardly any studies focused on their formation and stability. Because oxygen defects are ubiquitous in most materials having oxygen sublattices, they are likely to influence the surface structure and reactivity of wollastonite. In addition, dopants are often added to improve or tune the material properties, but not much is known about the role of defects and dopants in stabilizing and influencing the reactivity of wollastonite surfaces.

Based on our preliminary efforts targeting silicate surfaces and the current status of work in the field, several potential approaches could be undertaken in order to expedite and maximize the use of these technologically relevant materials. In order to design novel ERW materials at the macroscale, a fundamental understanding of their structure and reactivity is necessitated at the nanoscale. Although a macroscopic description of ERW is known, studies that uncover basic mechanisms and kinetics at the nanoscale are necessary to identify materials for ERW. Future studies illuminating the thermodynamic preference of various silicate facets that exhibit enhanced reactivity would be welcome. Atomistic-level DFT calculations that include quantum effects will be suitable to study thermodynamics and interface charge transfer in silicate-adsorbate systems. Although empirical potential-based MD is expected to offer reasonable trends, ab initio Molecular Dynamics (AIMD) will be more appropriate because of the complexity involved in
investigating the reaction kinetics at the interface between silicate minerals and soil pore water solution. Studies focused on unraveling the influence of defects and dopants in altering the reaction dynamics at interfaces of minerals and solid solutions would be valuable. Ultimately, studies addressing the fundamental aspects of CO₂ adsorption on silicate surfaces would be timely. For instance, insights pertaining to whether CO₂ prefers chemisorption or physisorption and if certain facets prefer molecular versus dissociative adsorption are expected to shed light on the atomic scale mechanisms of CO₂ capture in these minerals. Additional efforts that investigate surface coverage-dependent mechanisms for CO₂ adsorption on silicate surfaces would aid in estimating the total amount of CO₂ adsorbed. Overall, the aforementioned fundamental studies in tandem with experimental efforts will be imperative to guide the large-scale synthesis of novel silicates for ERW. As mentioned earlier, a co-author of the present study recently conducted first-principles modeling of CO₂ adsorption on wollastonite surfaces for ERW application. The study used DFT to investigate the thermodynamic behavior of CO₂ adsorption on wollastonite surfaces. The study found that the bent CO₂ geometry bridging between the calcium atoms of wollastonite is the most favorable location for CO₂ sequestration and indicated the importance of this binding site and the likelihood of this geometry while designing the reactive silicates for ERW application to capture and sequester CO₂.

ENVIRONMENTAL AND ECONOMIC CONSIDERATIONS

Synthetic fertilizer is a critical component of modern and climate-smart agriculture. However, the production of synthetic fertilizer is not without environmental and economic costs. Currently, approximately 14.6 million metric tons of phosphorus fertilizers as P are estimated to be consumed annually, in order to produce adequate food, fuel, and fiber supplies for an increasing global population.

Recently there has been a push to consider the circularity of nutrients in the food-energy-water nexus. One result of this has been the deployment of struvite (NH₄MgPO₄·6H₂O) as a slow-release fertilizer, recovered from human and animal wastes. Using recovered struvite has the potential to reduce the quantity of nitrogen and phosphorus discharged to the environment in areas in which it will cause damage, such as eutrophication of receiving waters, and the corresponding impacts of eutrophication such as fish kills, etc. Tonini et al. found that societal costs for recovering phosphorus from sewage sludge were 81% lower than for rock-derived phosphorus. Previous work has focused on the environmental impact of the recovery of these materials for wastewater. Suggesting that alternatives to conventional phosphorus fertilizers are a critical component for future sustainable agriculture.

Reactive silicates have the potential to be utilized as agricultural amendments while also enriching the soil with added nitrogen and phosphorus. These slow-weathering materials can add the necessary nutrients to the soil, and because of their inherently longer weathering spans, release them continuously over a long period of time. This is particularly relevant as it reduces the potential for nutrient runoff. quantified the potential environmental costs and benefits of using enhanced weathering for potential soil carbonation in Brazil and found a net benefit to using basalt rock for enhanced weathering. Their benefits were lower than some other studies, as they considered environmental costs, such as transportation which offset some of the anticipated benefits, which is critical to include from a holistic environmental impact perspective.

Multiple current challenges exist with respect to understanding the environmental and economic impacts of enhanced rock weather on soil health and CO₂ sequestration. The first is accounting for all of the environmental impacts and economic implications. Tools such as life cycle assessment (LCA) and techno-economic assessment (TEA) have the potential to frame these issues systematically. The second is scale. Assuming that economies of scale will apply, the synthesis process will be less environmentally and economically intensive as production operations increase in size. A third is the regionality of application for ERW, in that it may achieve greater benefits in some geographic areas when compared to others.

Life cycle assessment (LCA) is a systematic tool for determining the environmental impacts of a product or process across its lifetime and for the evaluation of tradeoffs. It allows for the comparison of environmental impacts across all stages of a product or process’s lifetime, to prevent burden-shifting among stages (Figure 5). To assess the true potential benefits of slow-weathering silicates for agricultural purposes, a consistent set of scopes, boundaries and functional units need to be applied across studies. In addition, if the purpose of the silicates is to replace conventional fertilizer products, their function must be compared.
to the function of conventional fertilizer products. Transportation is also relevant to consider, particularly when products are moved over long distances, or compared to traditional agricultural fertilizer products such as manure. Utilizing a standardized framework for comparing silicates that not only enrich the carbon content of soil through slow weathering but also have the potential to replace conventional fertilizers is critical to understanding the environmental and economic impacts and implications.

CONCLUSIONS

The proposed approach to ERW aims at synthesizing silicate minerals with a high weathering rate to be suited for use in alkaline soils of the colder and drier agricultural lands of Western Canada and the Western United States. The following is a summary of the main investigations/future directions discussed in the present work:

- Investigating the doping of these minerals with plant nutrients for improved fertilizing ability.
- Determining the weathering mechanisms at the atomic scale and rates under normal and accelerated weathering conditions.
- Studying the role of mechanical activation and degree of crystallinity in improving their weathering performance.
- Testing the synthesized minerals for altering the agricultural soils and gauging their benefits in terms of CO$_2$ capture and agriculture fertilizing capability.
- After a successful performance, conceptualizing an integrated industrial process for manufacturing these silicates at a large scale in a net-negative carbon emissions pathway.

Limitations of the study

The cost of the synthesized minerals via doping of nutrient fertilizers could become one of the major challenges with this approach. It is, therefore, important to conduct a techno-economic analysis of the manufacturing process, which can be optimized by utilizing the waste process heat from industrial units. This information will also help in conducting a comparative analysis with other carbon capture, utilization and storage (CCUS) solutions currently present in the market, to better tackle the global warming problem.

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REFERENCES

1. Lackner, K.S. (2003). A guide to CO₂ sequestration. Science 300, 1677–1678. https://doi.org/10.1126/science.1079033.

2. Beerling, D.J., Kantzas, E.P., Lomas, M.R., Wade, P., Eufrasio, R.M., Renforth, P., Sarkar, B., Andrews, M.G., James, R.H., Pearce, C.R., et al. (2020). Potential for large-scale CO₂ removal via enhanced rock weathering with croplands. Nature 583, 242–248. https://doi.org/10.1038/s41586-020-2448-9.

3. Schuiling, R.D., and Knijgsman, P. (2006). Enhanced weathering: an effective and cheap tool to sequester CO₂. Clim. Change 74, 349–354. https://doi.org/10.1007/s10584-005-3485-y.

4. Renforth, P. (2019). The negative emission potential of alkaline materials. Nat. Commun. 10, 1401. https://doi.org/10.1038/s41467-019-09477-9.

5. Haque, F., Chiang, Y.W., and Santos, R.M. (2019). Alkaline mineral soil amendment: a climate change ‘stabilisation wedge’? Energies 12, 2299. https://doi.org/10.3390/en12122299.

6. Beerling, D.J. (2019). Can plants help us avoid seeding a human-made climate catastrophe? Plants People Planet 1, 310–314. https://doi.org/10.1002/ppp3.10066.

7. Haque, F., Santos, R.M., and Chiang, Y.W. (2020). CO₂ sequestration by wollastonite-amended agricultural soils – an Ontario field study. Int. J. Greenh. Gas Control 97, 103017. https://doi.org/10.1016/j.ijggc.2020.103017.

8. Zamanian, K., Zhou, J., and Kuzyakov, Y. (2021). Soil carbonates: the unaccounted, irrecoverable carbon source. Geoderma 384, 114817. https://doi.org/10.1016/j.geoderma.2020.114817.

9. Poggie von Strandmann, P.A.E., Tooley, C., Mulders, J.I.P.A., and Renforth, P. (2022). The dissolution of olivine added to soil at 4°C: implications for enhanced weathering in cold regions. Front. Clim. 4, 827696. https://doi.org/10.3390/fclim2022.827696.

10. Bertagni, M.B., and Porporato, A. (2022). The carbon-capture efficiency of natural water alkalization: implications for enhanced weathering. Sci. Total Environ. 838, 156524. https://doi.org/10.1016/j.scitotenv.2022.156524.

11. Statistics Canada. (2022). Land Use, Census of Agriculture Historical Data. https://www150.statcan.gc.ca/r1/db1/en/tv.action?pid=3210015301.

12. Slessarev, E.W., Lin, Y., Bingham, N.L., Johnson, J.E., Dai, Y., Schimmel, J.P., and Chadwick, O.A. (2016). Water balance creates a threshold in soil pH at the global scale. Nature 540, 567–569. https://doi.org/10.1038/nature20319.

13. Economic Research Service (2017). Major Land Uses. https://www.ers.usda.gov/data-products/major-land-uses/major-land-uses/.

14. Broche, A. (2020). Mineral Commodity Summaries - Wollastonite. https://www.usgs.govcenters/nmic/wollast.

15. Lefebvre, D., Goglio, P., Williams, A., Manning, D.A., de Azevedo, A.C., Bergmann, M., Meersmans, J., and Smith, P. (2019). Assessing the potential of soil carbonation and enhanced weathering through Life Cycle Assessment: a case study for Sao Paulo State, Brazil. J. Clean. Prod. 233, 468–481. https://doi.org/10.1016/j.jclepro.2019.06.099.

16. Bodor, M., Santos, R.M., Krikova, L., Elsen, J., Vlad, M., and Van Gerven, T. (2013). Susceptibility of mineral phases of steel slags towards carbonation: mineralogical, morphological and chemical assessment. Eur. J. Mineral. 25, 533–549. https://doi.org/10.1127/0935-1221/2013/0025-2300.

17. Haque, F., Santos, R.M., and Chiang, Y.W. (2020). Optimizing inorganic carbon sequestration and crop yield with wollastonite soil amendment in a microplot study. Front. Plant Sci. 11, 1012. https://doi.org/10.3389/fpls.2020.01012.

18. Janiwal, H., Haque, F., Vanderburgt, S., Santos, R.M., and Chiang, Y.W. (2022). Mineral-soil-plant-nutrient synergies of enhanced weathering for agriculture: short-term investigations using fast-weathering wollastonite skarn. Front. Plant Sci. 13, 929457. https://doi.org/10.3389/fpls.2022.929457.

19. DeCristofaro, N. (2015). Utilization of CO₂ in High Performance Building and Infrastructure Products (US DOE OSTI Technical Report). https://doi.org/10.2172/1301860.

20. Caserini, S., Barreto, B., Lanfredi, C., Cappello, G., Ross Morrey, D., and Grosso, M. (2019). Affordable CO₂ negative emission through hydrogen from biomass, ocean liming, and CO₂ storage. Mitig. Adapt. Strateg. Glob. Change 24, 1231–1248. https://doi.org/10.1007/s11027-018-9835-7.

21. Renforth, P. (2022). Novel materials for ocean alkalinity enhancement. Geochemical Carbon Dioxide Removal Research in Progress Meeting.

22. Climate Reality Project (2016). Follow the Leaders: How 11 Countries Are Shifting to Renewable Energy. https://www.climeretrialtoproject.org/blog/follow-leader-how-11-countries-are-shifting-renewable-energy.

23. Post, E. (2022). Record Renewable Addition for 2021 and 2022 Despite Supply Bottlenecks. Prove Solar and Wind’s Resilience. https://energypost.eu/record-high-renewables-additions-for-2021-and-2022-despite-supply-chain-bottlenecks-prove-solar-winds-resilience/.

24. van Aalst, L. (2021). Steelmaker Voestalpine to Convert Three Blast Furnaces to EAFs by 2030. S and P Global Commodity Insights. https://www.spglobal.com/commodityinsights/en/ market-insights/latest-news/metas/060921-steelmaker-voestalpine-to-convert-three-blast-furnaces-to-eafs-by-2030.

25. Van Dongen, M. (2022). Take a Deep Breath — the End of a Century of Coal-Fired Steel Pollution in Hamilton Is on the Horizon. https://www.thespec.com/news/hamilton-region/2022/06/15/fallout-hamilton-steel-pollution-arcelormital-dofasco.html.

26. Chiang, Y.W., Santos, R.M., Monbaliu, A., Gyselbrecht, K., Martens, J.A., Mattos, M.L.T., Gerven, T.V., and Meeschaert, B. (2013). Effects of bioleaching on the chemical, mineralogical and morphological properties of natural and waste-derived alkaline materials. Miner. Eng. 48, 116–125. https://doi.org/10.1016/j.mineng.2012.09.004.

27. Chai, Y.E., Miller, Q.R., Schaefer, H.T., Barpaga, D., Bakshoodeh, R., Bodor, M., Van Gerven, T., and Santos, R.M. (2021). Pressurized in situ X-ray diffraction insights into super/subcritical carbonation reaction pathways of steelmaking slags and constituent silicate minerals. J. Supercri. Fluids 171, 105191. https://doi.org/10.1016/j.supflu.2021.105191.
carbonation curing. J. Wuhan Univ. Technol. -Mat. Sci. Edit. 25, 1053–1060. https://doi.org/10.1007/s11595-020-2355-9.

63. Longo, R.C., Cho, K., Brüner, P., Welle, A., Gerdes, A., and Thissen, P. (2015). Carbondation of wollastonite (001) competing hydration: microscopic insights from ion spectroscopy and density functional theory. ACS Appl. Mater. Interfaces 7, 4706–4712. https://doi.org/10.1021/ami508313g.

64. Kundu, T.K., Rao, K.H., and Parker, S.C. (2003). Competitive adsorption on wollastonite: an atomistic simulation approach. J. Phys. Chem. B 109, 11286–11295. https://doi.org/10.1021/jp0580367.

65. Manzano, H., Durgun, E., Abdolhosseinei Qomi, M.J., Ulm, F.-J., Pelleng, R.J.M., and Grossman, J.C. (2011). Impact of chemical impurities on the crystalline cement clinker phases determined by atomistic simulations. Cryst. Growth Des. 11, 2964–2972. https://doi.org/10.1021/cg200212c.

66. Durgun, E., Manzano, H., Pelleng, R.J.M., and Grossman, J.C. (2012). Understanding and controlling the reactivity of the calcium silicate phases from first principles. Chem. Mater. 24, 1262–1267. https://doi.org/10.1021/cm203127m.

67. Sanna, S., Schmidt, W.G., and Thissen, P. (2014). Formation of hydroxyl groups at calcium-silicate-hydrate (C-S-H): coexistence of Ca−OH and Si−OH on wollastonite (001). J. Phys. Chem. C 118, 8007–8013. https://doi.org/10.1021/jp500170h.

68. Hohenberg, P., and Kohl, W. (1964). Inhomogeneous electron gas. Phys. Rev. 136, B864–B871. https://doi.org/10.1103/PhysRev.136.B864.

69. Kohl, W., and Sham, L.J. (1966). Self-consistent equations including exchange and correlation effects. Phys. Rev. 140, A1133–A1138. https://doi.org/10.1103/PhysRev.140.A1133.

70. Allen, M.P. (2004). Introduction to molecular dynamics simulation. Computational Soft Matter: From Synthetic Polymers to Proteins. Lecture Notes, NIC Series 23, 1–28.

71. Kresse, G., and Hafner, J. (1993). Ab initio molecular dynamics for liquid metals. Phys. Rev. B Condens. Matter 47, 558-561. https://doi.org/10.1103/physrevb.47.558.

72. Kresse, G., and Joubert, D. (1999). From ultrasoft pseudopotentials to the projector augmented wave method. Phys. Rev. B 59, 1758–1775. https://doi.org/10.1103/PhysRevB.59.1758.

73. Luan, B., and Dholabhai, P.P. (2002). First principles modeling of CO₂ adsorption on (100), (010), and (001) surfaces of wollastonite for applications in enhanced rock weathering. Surf. Sci. 724, 122143. https://doi.org/10.1016/j.susc.2022.122143.

74. Diebold, U. (2003). The surface science of titanium dioxide. Surf. Sci. Rep. 48, 53–229. https://doi.org/10.1016/S0167-5729(02)00100-0.

75. Mullins, D.R. (2015). The surface chemistry of cerium oxide. Surf. Sci. Rep. 70, 42–85. https://doi.org/10.1016/j.surfrep.2014.12.001.

76. Pai, Y.-Y., Tylan-Tyler, A., Irvin, P., and Levy, J. (2018). Physics of SrTiO₃-based heterostructures and nanostructures: a review. Rep. Prog. Phys. 81, 036503. https://doi.org/10.1088/1361-6633/aa892d.

77. Phoon, B.L., Lai, C.W., Juan, J.C., Show, P., and Chen, W. (2019). A review of synthesis and morphology of SrTiO₃ for energy and other applications. Int. J. Energy Res. 43, 5151–5174. https://doi.org/10.1002/er.4505.

78. Tasker, P.W. (1979). The stability of ionic crystal surfaces. J. Phys. C Solid State Phys. 12, 4977–4984. https://doi.org/10.1088/0022-3719/12/22/036.

79. Car, R., and Parrinello, M. (1985). Unified approach for molecular dynamics and density-functional theory. Phys. Rev. Lett. 55, 2471–2474. https://doi.org/10.1103/PhysRevLett.55.2471.

80. Janiwala, H., Santos, R.M., Lauzon, J.D., Dutta, A., and Chiang, Y.W. (2020b). Controlled release fertilizers (CRFs) for climate-smart agriculture practices: a comprehensive review on release mechanisms, materials, methods of preparation, and effect on environmental parameters. Environ. Sci. Pollut. Res. Int. 29, 53967–53995. https://doi.org/10.1007/s11356-022-20890-y.

81. Sena, M., Rodríguez-Morris, M., Seib, M., and Hicks, A. (2020). An exploration of economic valuation of phosphorus in the environment and its implications in decision making for resource recovery. Water Res. 172, 115449. https://doi.org/10.1016/j.watres.2019.115449.

82. Liu, Y., Villaalga, G., Ayres, R.U., and Schroder, H. (2008). Global phosphorus flows and environmental impacts from a consumption perspective. J. Ind. Ecol. 12, 229–247. https://doi.org/10.1111/j.1530-9290.2008.00025.x.

83. Tonini, D., Saveyn, H.G.M., and Huygens, D. (2019). Environmental and health co-benefits for advanced phosphorus recovery. Nat. Sustain. 2, 1051–1061. https://doi.org/10.1038/s41893-019-0416-x.

84. Sena, M., and Hicks, A. (2018). Life cycle assessment review of struvite precipitation in wastewater treatment. Resour. Conserv. Recycl. 139, 194–204. https://doi.org/10.1016/j.resconrec.2018.08.009.

85. Sena, M., Seib, M., Noguera, D.R., and Hicks, A. (2021). Environmental impacts of phosphorus recovery through struvite precipitation in wastewater treatment. J. Clean. Prod. 280, 124222. https://doi.org/10.1016/j.jclepro.2020.124222.

86. Hu, Y., Scarborough, M., Aguirre-Villegas, H., Larson, R.A., Noguera, D.R., and Zavala, V.M. (2018). A supply chain framework for the analysis of the recovery of biogas and fatty acids from organic waste. ACS Sustainable Chem. Eng. 6, 6211–6222. https://doi.org/10.1021/acssuschemeng.7b04932.