

Monitoring Pedogenic Inorganic Carbon Accumulation Due to Weathering of Amended Silicate Minerals in Agricultural Soils.

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Abstract

The present study aims to demonstrate a systematic procedure for monitoring inorganic carbon induced by enhanced weathering of comminuted rocks in agricultural soils. To this end, the core soil samples taken at different depth (including 0-15 cm, 15-30 cm, and 30-60 cm profiles) are collected from an agriculture field, the topsoil of which has already been enriched with an alkaline earth metal silicate containing mineral (such as wollastonite). After transporting to the laboratory, the soil samples are air-dried and sieved. Then, the inorganic carbon content of the samples is determined by a volumetric method called calcimetry. The representative results presented herein showed five folded increments of inorganic carbon content in the soils amended with the Ca-silicate compared to control soils. This compositional change was accompanied by more than 1 unit of pH increase in the amended soils, implying high dissolution of the silicate. Mineralogical and morphological analyses, as well as elemental composition, further corroborate the increase in the inorganic carbon content of silicate-amended soils. The sampling and analysis methods presented in this study can be adopted by researchers and professionals looking to trace pedogenic inorganic carbon changes in soils and subsoils, including those amended with other suitable silicate rocks such as basalt and olivine. These methods can also be exploited as tools for verifying soil inorganic carbon sequestration by private and governmental entities to certify and award carbon credits.

Introduction

CO₂ is a major greenhouse gas (GHG), and its concentration in the atmosphere is increasing continuously. Preindustrial global average CO₂ was about 315 parts per million (ppm),

and as of April 2020, the atmospheric CO₂ concentration increased to over 416 ppm, hence causing global warming¹. Therefore, it is critical to reduce the concentration of this heat-

trapping GHG in the atmosphere. Socolow² has suggested that to stabilize the concentration of atmospheric CO₂ to 500 ppm by 2070, nine 'stabilization wedges' will be required, where each stabilization wedge is an individual mitigation approach, sized to achieve 3.67 Gt CO₂ eq per year in emissions reduction.

Carbon capture and storage (CCS) is the main technology to reduce the CO₂ from the atmosphere, as recommended by the Mission Innovation initiative, launched at the United Nations Climate Change Conference 2015³. To capture atmospheric CO₂, the three main storage options available are ocean storage, geological storage, and mineral carbonation⁴. Focusing on mineral carbonation, CO₂ is stored by converting alkaline earth metals, mainly calcium- and magnesium-rich silicates, into thermodynamically stable carbonates for geological timeframes (over millions of years)⁵. For example, olivine, pyroxene, and serpentine group minerals have the potential to undergo mineral carbonation⁶; however, under normal conditions, these reactions are limited by slow reaction kinetics. Therefore, to speed up the process under ambient conditions, finely comminuted (crushed/milled) forms of these silicates can be applied to agricultural soils, a process referred to as terrestrial enhanced weathering⁷. Soil is a natural sink to store CO₂, presently being a reservoir for 2500 Gt of carbon, which is thrice the atmospheric reservoir (800 Gt carbon)⁸. Pedogenic processes in soils and subsoils regulate atmospheric CO₂ by two major natural pathways, namely the organic matter cycle and the weathering of alkaline earth metal minerals, affecting organic and inorganic carbon pools, respectively⁹.

It is estimated that almost 1.1 Gt of atmospheric CO₂ is mineralized through chemical rock weathering annually¹⁰. Silicate rocks rich in calcium and magnesium

(e.g., basalt) are regarded as the primary feedstocks for enhanced weathering^{9,11,12}. Once crushed silicate-containing minerals are applied to agricultural fields, they begin to react with CO₂ dissolved in soil porewater, concluding with the mineral precipitation of stable carbonates^{11,13}. Olivine^{14,15}, wollastonite (CaSiO₃)¹³, dolerite, and basalt¹⁶ are among minerals which have demonstrated carbon sequestration potential through enhanced weathering in previous studies. Despite the greater availability, and hence possibly greater CO₂ sequestration capacity, of magnesium silicates, there are concerns about their application for enhanced weathering in croplands due to their potential environmental impact as a result of Cr and Ni leaching and the possible presence of asbestiform particulates^{11,15,17,18}. As a calcium-bearing silicate, wollastonite is herein highlighted as a prime candidate for this process due to its high reactivity, simple chemical structure, being environmentally benign as well as facilitating the production of carbonates due to the weaker bonding of Ca ions to its silica matrix^{12,19,20,21}. Wollastonite that is mined in Kingston, Ontario, Canada, and is presently commercialized by Canadian Wollastonite for agricultural applications, does not contain elevated levels of hazardous metals. The worldwide wollastonite reserves are estimated to be over 100 Mt, with China, India, USA, Mexico, Canada, and Finland as the top productive countries²².

Enhanced weathering of silicate mineral is reckoned to promote soil health, notably crop yield increase and plant growth improvement, leading to the potential reduction in the application of synthetic fertilizers, which can further contribute to GHG emissions reduction^{11,18,19}. Previous studies have reported that the application of Ca-rich silicate minerals to soils supplies basicity for neutralizing acidity in the soil medium, favoring crop production^{23,24,25}. This also impedes

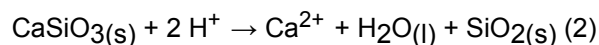
toxic metals mobilization, susceptible to acidic conditions, and enhanced weathering could be useful for retarding erosion through soil organic matter increment¹¹.

Equations 1-3 show how pedogenic carbon sequestration as inorganic carbonates is possible by amending soils with wollastonite. Ambient CO₂ enters the soil through rainwater or is produced in soil by microbial activity degrading organic compounds. Once in contact with soil porewater, carbonic acid is formed, which dissociates to form bicarbonate and proton (Equation 1). In the presence of plants, root exudates, such as citric acid and maleic acid, are released, which also provide protons in the system. These protons facilitate the dissolution of wollastonite in the soil through releasing Ca ions and leaving behind amorphous silica (Equation 2). The released Ca ions ultimately react with the bicarbonate to precipitate as carbonates (crystalline calcite or other varieties, depending on geochemical conditions) (Equation 3). This formed calcium carbonate becomes part of the soil inorganic carbon (SIC) fraction²⁶.

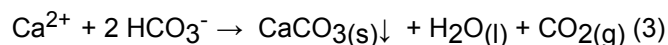
Ambient CO₂ solvation:



Wollastonite dissolution (H⁺ from the dissociation of carbonic acid and root exudates):



Pedogenic inorganic carbonate precipitation:



In our recent work, enhanced weathering through the application of wollastonite to agricultural soils, as a limestone-alternative amendment, has been found effective for CaCO₃ precipitation in topsoil, both at laboratory and field scales,

and over short (few months) and long (3 years) terms. In the field studies, chemical and mineralogical assessments have revealed that the SIC content increases proportionally to wollastonite application dosage (tonne·hectare⁻¹)¹³. In laboratory studies, the mineralogical analysis showed the presence of pedogenic carbonate due to carbon sequestration¹⁹. Pedogenic carbonate formation in soil depends on several factors, most notably: topography, climate, surface vegetation, soil biotic processes, and soil physicochemical properties²⁷. Our previous study²³ determined the role of plants (a leguminous plant (green bean) and a non-leguminous plant (corn)) on wollastonite weathering and inorganic carbonate formation in soil. Our ongoing research on the pedogenic carbon formation and migration in soils and subsoils includes investigating the fate of soil carbonates in agricultural soil, first formed in topsoils due to mineral weathering at various depths and over time. According to Zamanian et al.²⁷, the naturally occurring pedogenic carbonate horizon is found farther from the surface as the rate of local precipitation increases, with the top of this horizon commonly appearing between a few centimeters to 300 cm below the surface. Other ambient and soil parameters, such as soil water balance, seasonal dynamics, the initial carbonate content in parent material, soil physical properties, also impact the depth of this occurrence²⁷. Thus it is of significance to sample soils to a sufficient depth at all opportunities to obtain an accurate understanding of the original and the incremental levels of SIC resulting from enhanced weathering of silicates.

At the field scale, an important limitation is the use of low application rates of silicate soil amendments. As there is limited knowledge on the effect of many silicates (such as wollastonite and olivine) on soil and plant health, commercial producers avoid testing higher application rates that could

result in significant carbon sequestration. As a result of such low application rates, as well as the large area of crop fields, a research challenge commonly faced is to determine changes in SIC when values are relatively low, and to recover and isolate the silicate grains and weathering products from the soil to study morphological and mineralogical changes. In our past work, we reported on how physical fractionation of the wollastonite-amended soil (using sieving) enabled a better understanding of the weathering process, especially the formation and accumulation of pedogenic carbonates²⁸. Accordingly, the higher contents of wollastonite and weathering products were detected in the finer fraction of soil, which provided reasonably high values during analyses, ensuring more precise and reliable results. The findings highlight the importance of using physical fractionation, through sieving or other segregation means, for reliable estimation of the sequestered carbon accumulation in silicate-amended soils. However, the degree of fractionation could vary from soil to soil and from silicate to silicate, so it should be further researched.

Accurate measurement of SIC is critical for establishing a standard and scientific procedure that can be adopted by various researchers interested in analyzing the evolution of SIC and (and organic carbon) over time and depth of the soil. Such methodology enables farmers to claim carbon credit as a result of SIC formation in their field soils. The following protocol describes, in detail: (1) a soil sampling method to be used following soil silicate amendment, which accounts for the statistical significance of the analyzed soil data; (2) a soil fractionation method that improves the accuracy of quantifying changes in pedogenic inorganic carbonate pool as a result of enhanced silicate weathering, and (3) the calculation steps used to determine the SIC sequestration rate as a result of soil silicate amendment. For the purpose

of this demonstration, wollastonite, sourced from Canadian Wollastonite, is assumed to be the silicate mineral applied to agricultural soils, and the agricultural soils are considered to be similar to those found in Southern Ontario's farmlands.

The procedure involving amending agricultural soil with wollastonite (e.g., determining the amount of wollastonite to apply per hectare, and the method to spread it over the soil) was described in our previous study¹³. The study area in our prior and present work is rectangular plots; therefore, the direct random sampling method is appropriate for such studies. This is a commonly used method owing to its low cost, reduced time requirement, and ability to provide adequate statistical uncertainty. Similarly, depending on the various field conditions and the level of statistical significance desired, zonal or grid sampling methods can also be used. Accuracy in soil sampling is essential to reduce statistical uncertainty as a result of sampling bias. When statistics are used, achieving less than 95% confidence (i.e., $p < 0.05$) is not considered "statistically significant." However, for certain soil studies, the confidence level may be relaxed to 90% (i.e., $p < 0.10$) owing to the number of uncontrolled (i.e., naturally varying) parameters in the field conditions that affect the general precision of measurements. In this protocol, two sets of samples are collected in order to investigate SIC content and other chemical, mineral, and morphological properties of the soil throughout its vertical profile.

Protocol

1. Soil sampling method and core collection

1. Divide the mapped and a demarcated agricultural land area of interest into different plots based on the land elevation, historical crop yield, and/or land management strategy. Determine the leveling of each plot using a

GPS receiver, classify crop yield based on historical farm records (below-average, average, above-average), and the land management strategy used for each plot (types of soil amendments used, if any). Place the flags at the boundaries of each plot to ease subsequent sampling.

NOTE: **Figure 1** shows the sectioning of the rectangular area under study into four plots (A, B, C, D). Such an experimental design and information will be helpful to check the statistical significance of the analyzed data. Furthermore, it can be appropriate for irregular farmlands

and be convenient for aligning sampling according to a parameter deemed necessary, from the orientation of crop rows to the direction of terrain, runoff, dominant wind, sun path, etc. These four plots were considered in order to facilitate a field filming campaign.

2. Use the directed random sampling method to collect cores across each plot. Subdivide each plot following a grid pattern into 25 sub-plots (**Figure 2**). Collecting 25 cores is above the traditionally minimum recommend number of cores (15-20).

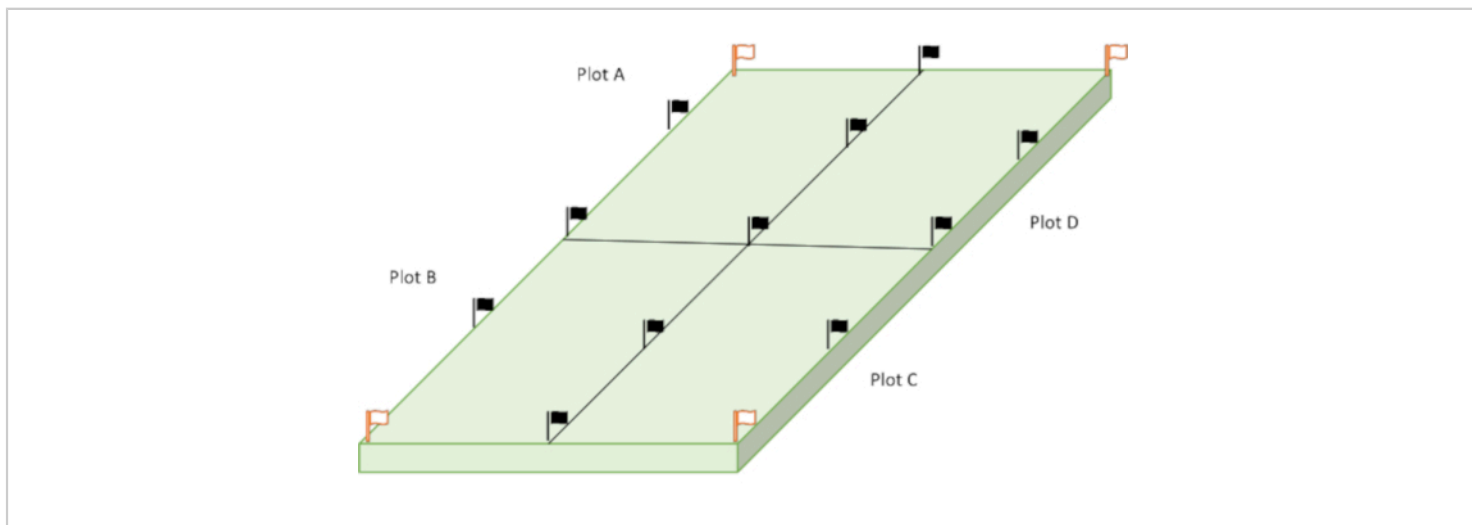


Figure 1: Representation of the plots used for sample collection (each plot represents an area of 5 m × 10 m (totally four x 50 m²)). Black flags delimit each plot boundary to ease sampling, and white flags mark locations for deep sampling. [Please click here to view a larger version of this figure.](#)

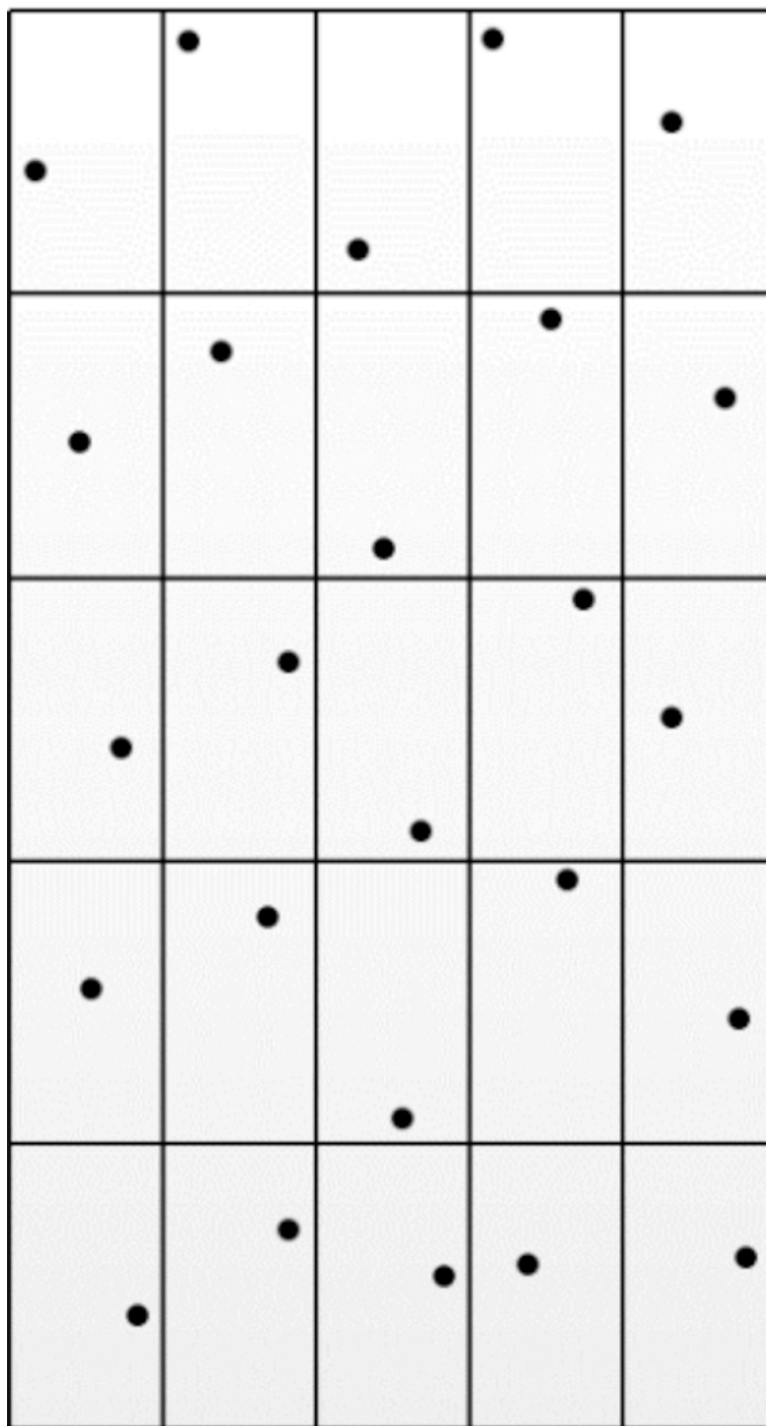


Figure 2: Sub-sectioning of each plot for collecting core samples (each sub-section represents an area of 1 m x 2 m), based on directed random sampling method. [Please click here to view a larger version of this figure.](#)

3. Collect core samples from random points within each sub-plot, one per sub-plot. Use a soil probe or a soil core sampler to collect the soil core down to three depth zones of 0-15 cm, 15-30 cm, and 30-60 cm to account for the SIC variation with depth due to silicate soil amendment.

NOTE: Depending on the type of soil and the probe/sampler used, a different sampler may be required to collect the 30-60 cm sample.

4. Use an extendable auger (or similarly capable sampler) to collect deep soil samples from the white flag locations in **Figure 1**, down to additional three depth zones of 60-100 cm, 100-175 cm, and 175-250 cm. These samples account for the soil characterization variation within these depths as well as evaluate background SIC level in the investigated land area, down to the upper depth of the naturally occurring pedogenic carbonate horizon.

NOTE: Based on the local properties in site (e.g., depth of groundwater table), the deepest zone may be modified in different locations.

5. Transport the soil samples into buckets, one for each sampled depth at each plot. Hand-blend the soils in each bucket thoroughly. Place the portable moisture tester into the mixed soil sample. Wait until the moisture content fixes at a stable point on the gauge of the device. Press the holder button and record the value as the real-time moisture content of blended soils.
6. Store the composite samples in sealed bags. Label bags properly with information about the plots (A, B, C, or D), the soil depth (0-15 cm, 15-30 cm, 30-60 cm, 60-100 cm, 100-175cm, 175-250 cm), and date of sampling.

2. Soil fractionation prior to chemical analysis

1. Air-dry the soil samples as soon as possible after sampling to minimize the oxidation of soil carbon. For this, place the soil samples in cardboard boxes (2.5" x 3" x 3") and place the boxes in a drying cabinet at 50 °C for 24-48 h, until the soil is dry. Store the air-dried samples in sample bags until further analysis.
2. Prior to soil fractionation, run the soil samples through a 2-mm sieve to remove large fragments of rocks and plant remains.
3. Oven-dry the sieved soils by placing the samples in a muffle furnace maintained at 105 ± 2 °C for at least 15 h.
4. For soil fractionation, place 1 kg of the oven-dried sample onto the top mesh of the sieve shaker consisting of different mesh sizes (710 to 50 μ m). Shake the sieves at 60 rpm for 15 min. Pan fractions <50 μ m are preferably used for analyses, as this is the pedogenic carbonate-enriched soil fraction.

NOTE: Other soil fractions can also be tested to yield additional data for verification of SIC accumulation due to enhanced weathering of amended silicates.

3. Pedogenic inorganic carbon sequestration determination

1. To determine the inorganic carbon content of soil samples using calcimetry analysis, place 5 g of a sieved soil sample in an appropriate Erlenmeyer flask. Suspend the sample in 20 mL of ultrapure water. Add 7 mL of 4 M HCl to a small flat-bottomed glass test tube, then place this tube upright inside the flask using a pair of tweezers.
2. Carefully attach the flask to the calcimeter by affixing the rubber stopper. The burette water levels on the

calcimeter should have been previously adjusted as required, and blanks and CaCO_3 standards should have been once run on the calcimeter as needed.

3. Shake the flask, thereby knocking over the acid tube, until the water level in the burette reaches a constant value, and no bubbling is observed in the solution (this takes approximately 5 min).
4. Calculate the CaCO_3 -equivalent ($\text{CaCO}_3(\text{eqv})$) content of the sample ($\text{g}, \text{CaCO}_3(\text{eqv}) \cdot (\text{kg}, \text{soil})^{-1}$) based on the volume change observed in the burette, and the blank and CaCO_3 calibration values, using the appropriate calcimetry formula. SIC content is obtained by converting the $\text{g}, \text{CaCO}_3(\text{eqv}) \cdot (\text{kg}, \text{soil})^{-1}$ value into $\text{kg}, \text{CO}_2 \cdot (\text{tonne}, \text{soil})^{-1}$ or $\text{kg}, \text{C} \cdot (\text{tonne}, \text{soil})^{-1}$.

1. Calculate the $\text{CaCO}_3(\text{eqv})$ content of the sample using the below formula:

$$w(\text{CaCO}_3(\text{eqv})) = 1000 \times \frac{m_2(V_1 - V_3)}{m_1(V_2 - V_3)} \times \frac{100 + w(\text{H}_2\text{O})}{100} \quad (5)$$

(4)

Where:

$w(\text{CaCO}_3(\text{eqv}))$ = the carbonate content of the oven-dried soil

m_1 = the mass of the test portion

m_2 = the mean mass of the calcium carbonate standards

V_1 = the volume of carbon dioxide produced by the reaction of the test portion

V_2 = the mean volume of carbon dioxide produced by the calcium carbonate standards

V_3 = the volume change in the blank determinations

$w(\text{H}_2\text{O})$ = the water content of the dried sample

NOTE: steps 3.1 to 3.4 are conducted based on a standard protocol²⁹.

5. For measuring bulk density (BD) of soil ($(\text{tonne}, \text{soil}) \cdot \text{m}^{-3}$), place a sufficiently large aliquot of the oven-dried soil sample in a container with a known volume. Weigh the sample using a scale. The ratio of the dried weight to the volume of the sample is considered as BD.

NOTE: The alternative devices for calculating "undisturbed bulk density" are introduced in the discussion.

6. Calculate the Areal SIC ($\text{kg}, \text{CO}_2 \cdot (\text{hectare})^{-1}$) using the following formula:

$$\begin{aligned} SIC_{areal} \left(\frac{\text{tonne CO}_2}{\text{hectare}} \right) &= SIC_{measured} \left(\frac{\text{kgCO}_2}{\text{tonne soil}} \right) \times BD \left(\frac{\text{tonne soil}}{\text{m}^3} \right) \times \\ &DT (m) \times \frac{1}{1000} \left(\frac{\text{tonne}}{\text{Kg}} \right) \times 10000 \left(\frac{\text{m}^2}{\text{hectare}} \right) \end{aligned}$$

Where:

A = the surface area

DT = depth thickness

7. Calculate the Total SIC (SIC 0-60 cm, $\text{kg}, \text{CO}_2 \cdot (\text{hectare})^{-1}$) for each plot, using the areal SIC values obtained for each depth, as follows:

$$SIC_{Plot A} = SIC_{0-60 \text{ cm}} = SIC_{0-15 \text{ cm}} + SIC_{15-30 \text{ cm}} + SIC_{30-60 \text{ cm}} \quad (6)$$

8. Add the Total areal SIC (SIC 0-60 cm, $\text{kg}, \text{CO}_2 \cdot (\text{hectare})^{-1}$) content for each plot (A, B, C, D) investigated, and obtain the average mean as follows:

$$\begin{aligned} Mean SIC_{areal} \left(\frac{\text{kgCO}_2}{\text{hectare}} \right) &= \frac{(SIC_{Plot A} + SIC_{Plot B} + SIC_{Plot C} + SIC_{Plot D})}{4} \quad (7) \end{aligned}$$

9. Divide the Mean areal SIC ($\text{kg,CO}_2 \cdot (\text{hectare})^{-1}$) obtained from Eq. 7 by the application rate of silicate mineral/rock used for the soil amendment ($(\text{tonne, silicate}) \cdot (\text{hectare})^{-1}$).

NOTE: This will provide the amount of pedogenic inorganic carbon sequestered in terms of kg of CO_2 per tonne of silicate applied ($\text{kg, CO}_2 \cdot (\text{tonne, silicate})^{-1}$). If a multi-year investigation is done, or a control plot without silicate amendment is present, this step needs to be modified to account for total sequestration and total amendment over a longer-term, or year-over-year values, or net pedogenic carbon sequestration.

Representative Results

The SIC content of soils can be determined using various methods, including an automated carbon analyzer or a calcimeter. The automated carbon analyzer for total soil carbon determination measures the CO_2 pressure built-up in a closed vessel³⁰. In calcimetry, the evolved volume of CO_2 released after acidification, typically by the addition of concentrated HCl acid, of the carbonate-containing sample is measured. The calcimetry method is relatively simple, involving simple chemical procedures, thus suitable for analyzing many field samples quickly with high precision (i.e., reproducible values) and adequate accuracy (i.e., values close to the accurate carbonate content). In the directed random sampling method used in this study, the samples from each plot are thoroughly hand-blended, then dried to obtain a homogenous representative soil sample prior to analyzing its SIC content. The calcimeter analysis is conducted in triplicates for each sample.

The elemental composition of soil samples can be determined either by Wavelength Dispersive X-ray Fluorescence spectroscopy (WDXRF) or by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In the case of the latter, soil samples must be acid digested prior to analysis. The mineral composition is best determined by powder X-ray Diffraction (XRD). The resulting diffractogram provides qualitative information about the presence of crystalline mineral phases, which can be quantified via the Rietveld refinement technique, best aided with the use of an internal standard. The elemental and mineralogical composition can be used to infer the depth that silicates and weathering products have reached at sampling time. Therefore, they can confirm the transport from topsoil towards subsoil, where carbonates can be stored for the long-term. The morphology of soil particulates can be studied by a scanning electron microscopy (SEM) and can be combined with energy dispersive spectroscopy (EDS) for semi-quantitative elemental microanalysis. Morphological analysis can be used to identify residual silicates, weathering products and gain a mechanistic understanding of the weathering phenomena (such as dissolving surfaces, newly precipitated crystals, and formation of amorphous materials). Mineralogical and elemental microanalysis results can also be used to further verify the calcimetry results. The presence of accumulated carbonate phases, such as calcite (CaCO_3), may be evident in diffractograms and can be found by compositional signature among soil particulates.

Table 1 shows a typical set of data for a wollastonite-amended soil (collected from 0-15 cm and unsieved) compared to a control untreated soil, in terms of the soil pH, the calcimetry results, and the calcium ion concentration obtained using microwave digestion followed by ICP-MS. The pH of the wollastonite-amended soil is higher by 1.15 units compared to the control, and the $\text{CaCO}_3(\text{eqv})$ content is nearly five times greater than the control. The calcium concentration in the wollastonite-amended soil is also higher, by almost seven times. Alone, ICP-MS cannot differentiate which calcium mineral, such as wollastonite or calcite, is mainly contributing to these calcium concentrations. Still, it is expected that the calcium concentration difference will be more significant than the carbonate difference since the amended soil will have both more wollastonite and more carbonates than the control soil. WDXRF and XRD analysis of these samples can help to further clarify the main oxides and mineral phases present in the samples, respectively.

The $\text{CaCO}_3(\text{eqv})$ content (calcimeter results) over a vertical profile (0-15, 15-30, and 30-60 cm) are demonstrated in **Table 2**. Accordingly, the highest content (of unsieved samples) was $10.13 \text{ g, CaCO}_3(\text{eqv}) \cdot (\text{kg, soil})^{-1}$, detected in 0-15 cm depth zone. The 15-30 cm samples showed the lowest amount of $\text{CaCO}_3(\text{eqv})$. The $\text{CaCO}_3(\text{eqv})$ content increased again in 30-60 cm zone. The results from two deep profile samples also suggest the much higher content of carbonates in deeper layers (60-100 cm profile). Based on the results of shallow and deep samples, it is implied that there are two zones enriched in carbonates. The first is the depth zone of 0-15 cm, representative of weathering products due to wollastonite application, given the significant increase versus the control. The other zone includes deeper samples, starting at around 30 cm and increasing to great extent down to 1 m. Since deeper samples are generally indicative of soil's parent materials, it can be inferred that carbonates at this zone are of geological origin. **Table 2** also depicts a comparison of the unsieved and sieved sample (pan fraction) to investigate the impact of fractionation on the carbonate content. Based on this, the carbonate content is slightly higher in the pan fraction, implying possibility of accumulation of carbonates in smaller particles, in agreement with our previous study²⁸.

The various oxides present in the soil can be determined by WDXRF, as exemplified in **Table 3** for the control soil. Silica (SiO_2) is the main oxide present, which is the primary component of sandy loam soil, and the texture of this sample includes 11 g/kg gravel, 551 g/kg sand, 295 g/kg silt, and 155 g/kg clay. The Ca content of the soil (2.59 wt %) obtained by WDXRF is greater than that determined by ICP-MS (0.96 wt%). This is because the WDXRF result is normalized to 100 wt%, which slightly inflates values as non-detectable components such as organics are not accounted for. Moreover, the digestion method used to prepare samples for ICP-MS likely did not fully dissolve all soil minerals, so ICP-MS values are slightly underestimated. Hence, the use of WDXRF combined with ICP-MS allows for estimating an upper and a lower bound on the true Ca (and Mg) concentration. Thus, they can be used to monitor the transport of silicates and weathering products, including carbonates, as a function of depth.

The XRD pattern of a wollastonite-amended soil is presented in **Figure 3**. The main peaks present are quartz (SiO_2) at 26.65° , and albite ($\text{NaAlSi}_3\text{O}_8$) at 28.07° , which are predominant minerals in sandy loamy soils³¹. The additional peaks of wollastonite and calcite are also present as a result of wollastonite addition and calcite formation. The calcite is identified by a main peak at 29.40° 2θ , and a minor peak at 39.40° . The high calcimeter reading for amended soil is due to the formation of calcite, at least in part as amorphous carbonates that can also form under ambient conditions³². WDXRF and XRD can also help in the characterization of the wollastonite used. The nominal elemental composition of the wollastonite used in this study, sourced from Canadian Wollastonite's Ontario mine, includes 26% silicon (55% SiO_2), 18% calcium (26% CaO), 4.0% magnesium (9% MgO), 1.8% sulfur, 0.11% nitrogen, 0.10% P_2O_5 , 0.10% K_2O , 11 ppm copper, and 1.1 ppm zinc. The main mineral phases present in this wollastonite, as determined by XRD analysis, include wollastonite, diopside ($\text{CaMgSi}_2\text{O}_6$), and quartz (SiO_2).

Figure 4a shows SEM images of the wollastonite-amended soil after a period of several weeks of weathering. The fine needle-shaped wollastonite is noticeable in the amended soil sample, present along with other larger soil particles. A closer look at these wollastonite particles (**Figure 4b**) helps to gain a deeper insight into the morphological changes occurring at the surface. The microanalysis of the wollastonite surface is possible by obtaining an elemental mapping of the sample (**Figures 4c-f**). The EDS spectrum of the mapped area reveals its semi-quantitative chemical profile in **Figure 4g**. The elemental maps clearly show Si and Ca as the main components of wollastonite. Mg is not a major component of wollastonite, as evidenced by absence of Mg signal from the needle-shaped particles, but it is present in minor quantities in other soil particles, which can include diopside particles. The C map does not distinguish between the carbonate formed on the wollastonite surface and the organic matter already present in the soil, and it is also dominated by carbon signal coming from the carbon tape below the sample. **Figure 5** shows spot EDS analysis on the smaller fragments, at 40000x, scattered in the soil sample and shown in **Figure 4b** (at 2,000x) marked within the yellow circle. Spot EDS analysis at two different points indicates that this fragment is rich in C and O, suggesting that it is made up primarily of organic matter, which matches the amorphous particle morphology. Additionally, by looking at the Ca:Si ratio, SEM-EDS analysis can be potentially used to identify signs of wollastonite weathering in soil, such as leaching of Ca from the wollastonite or the fate of the formed carbonates in the soil.

Using the calcimeter reading of the soil amended with wollastonite, the pedogenic inorganic carbon sequestration rate can be calculated using the steps outlined in section 3 of the Protocol. To this end, the difference of calcimeter reading for analyzed sample and its corresponding control should be calculated for the depth of interest. Then a factor of 0.44 is applied to the difference to convert $\text{CaCO}_3(\text{eqv})$ to CO_2 . In case of the 0-15 cm depth samples presented in table 2, deducting the calcimeter reading of the control ($2.51 \text{ g, CaCO}_3(\text{eqv}) \cdot (\text{kg, soil})^{-1}$) from of 0-15 cm depth reading ($10.13 \text{ g, CaCO}_3(\text{eqv}) \cdot (\text{kg, soil})^{-1}$), results in a net amount of $3.35 \text{ kg, CO}_2 \cdot (\text{tonne, soil})^{-1}$ sequestered at this depth. Considering only the soil thickness of 0.15 m, and a disturbed BD of $1.01 \text{ tonne} \cdot (\text{m}^{-3})$ measured in the laboratory, the Areal SIC is then can be calculated using Equation 5. Based on the ratio between undisturbed and disturbed BD and the uncertainty existing in reporting BD due to climatic and land use factors, we have estimated the undisturbed BD of our 0-15 cm layer to be $1.386 \pm 0.23 \text{ tonne} \cdot (\text{m}^{-3})$. Considering the uncertainty present in calcimeter reading, we determined the cumulative uncertainty of calculated $\text{SIC}_{\text{Areal}}$, using a Gaussian equation for normally-distributed errors method, to be $\pm 39\%$. Accordingly, we estimate the sequestered CO_2 in the 0-15 cm layer of our field to be $6.96 \pm 2.71 \text{ tonne, CO}_2 \cdot (\text{hectare})^{-1}$. Using similar procedure, the Areal SIC of 15-30 cm and 30-60 cm layers can also be calculated (for this field, control values were not available to demonstrate this calculation). Summing up the values for the full 0-60 cm profile, the estimated sequestered carbon could be determined in the study area.

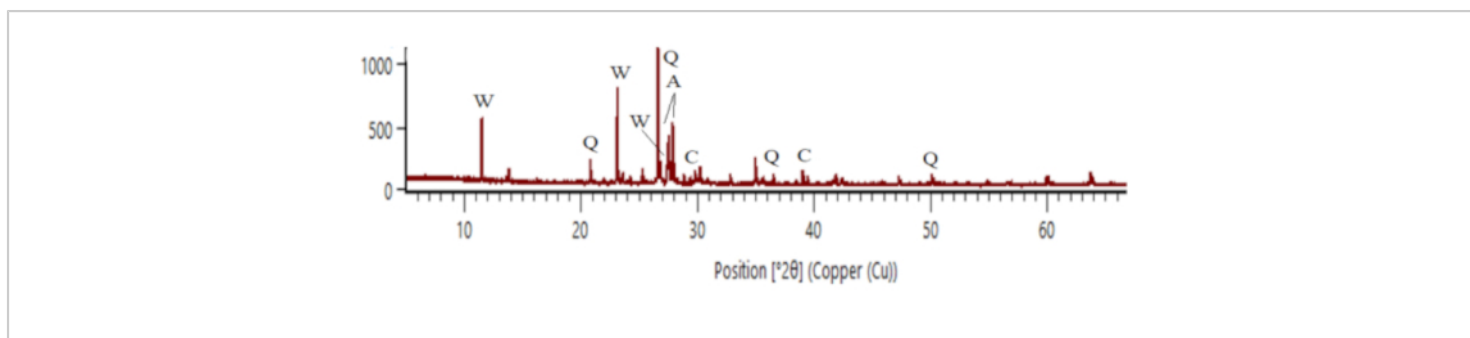


Figure 3: XRD diffractogram showing the mineralogical phases present in a wollastonite-amended soil (W: wollastonite, Q: quartz, A: albite, C: calcite). Diffractogram determined by commercial X-ray diffraction and analysis software. The diffractometer operated with Cu K α radiation at 45 kV and 40 mA, and the diffraction patterns were collected over a 2θ range of 5–70°. [Please click here to view a larger version of this figure.](#)

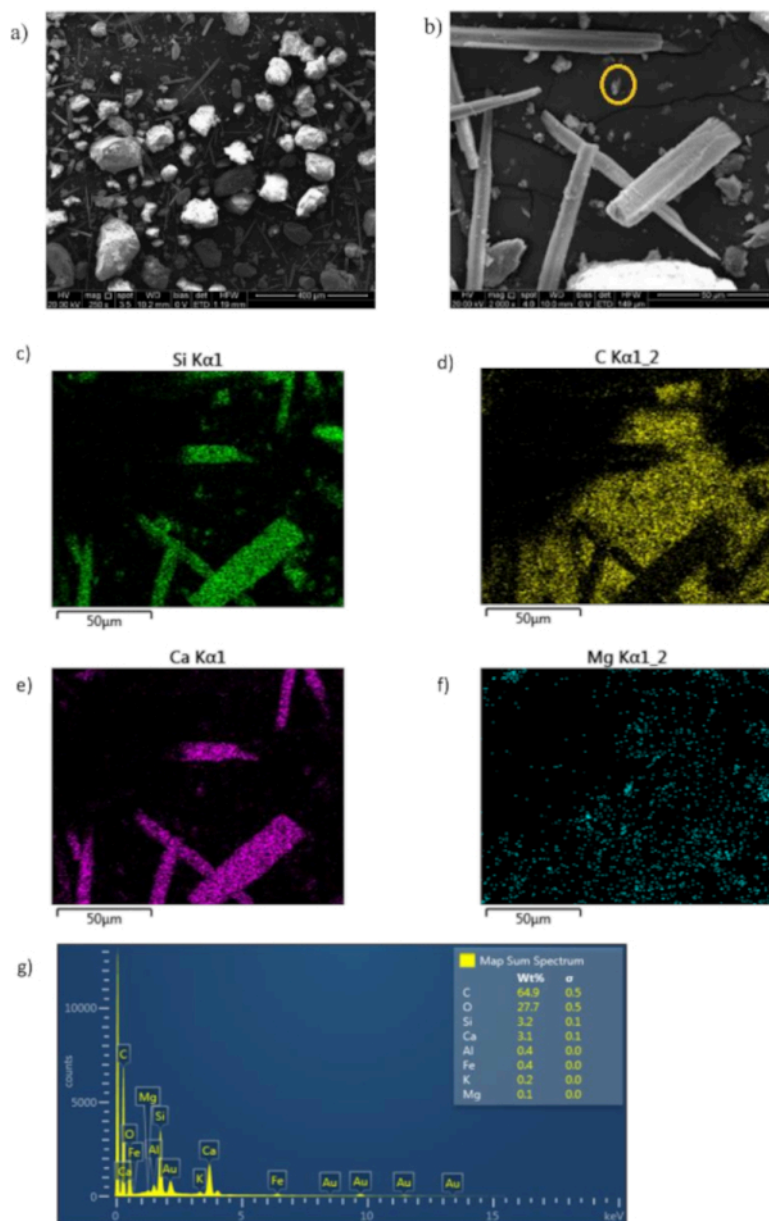


Figure 4: SEM-EDS analysis. (a) SEM image of a wollastonite-amended soil at 250x and 400 µm scale; (b) closer view of the weathered wollastonite grains present in the soil at 2000x and 50 µm scale; (c-f) EDS elemental mapping of Si, C, Ca, and Mg present in the area visualized in **Figure 4b** at 2,000x and 50 µm scale; (g) EDS spectrum and semi-quantitative elemental composition of the area visualized in panel b. SEM-EDS data was collected using scanning electron microscope, which was equipped with energy dispersive spectroscopy used for elemental composition analysis of selected areas and spots with an excitation volume at 20 kV. Prior to SEM-EDS analysis, the samples were mounted on carbon tape and sputter-coated with gold. [Please click here to view a larger version of this figure.](#)

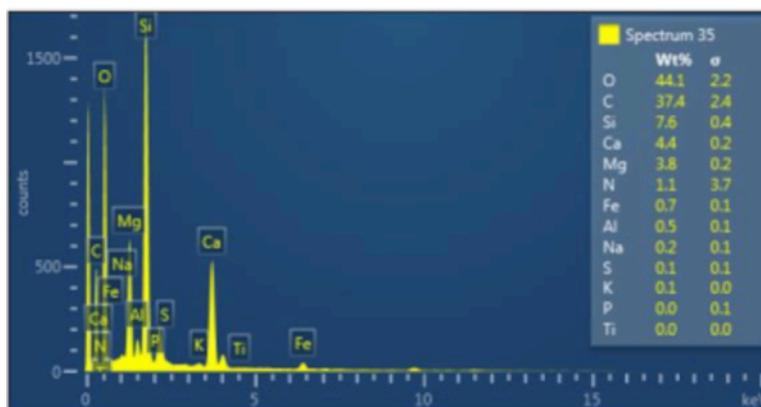
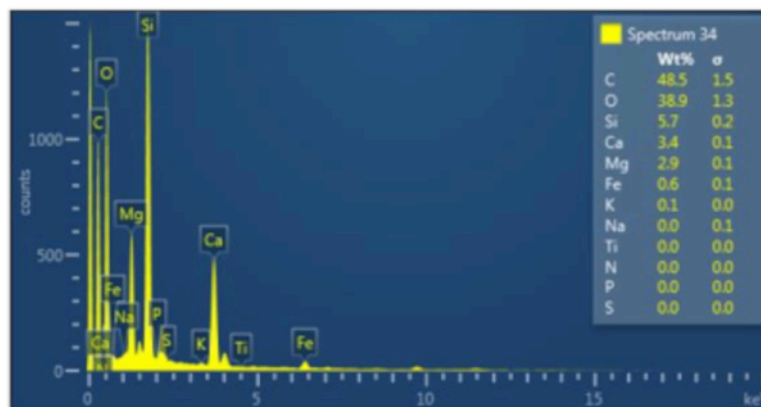


Figure 5: SEM image of encircled particulate shown in Figure 4b at 40,000x and 2.5 µm scale, and EDS spectrum and semi-quantitative elemental composition of two spots marked on the SEM image. [Please click here to view a larger version of this figure.](#)

Sample	pH ^a	Calcimeter measurement (g,CaCO ₃ (eqv)/kg,soil)	Ca concentration from ICP-MS (mg,Ca/kg,soil) ^b
Control (no amendment)	6.42 ± 0.05	4.5 ± 0.5	9566.6 ± 86.8
Wollastonite amended soil	7.57 ± 0.04	21.9 ± 0.1	66044.1 ± 534.6
^a The pH of the samples was determined using a 1:5 ratio of soil and 0.01M CaCl ₂ solution, followed by 30 min shaking and 1 h settling time before taking the pH measurement of the clear supernatant (Pansu and Gautheyrou, 2006).			
^b The samples were microwave digested in concentrated HNO ₃ prior to ICP-MS analysis; the use of HF is often recommended for digesting soils and silicates, but is avoided here to reduce the safety risk of the analysis (HF is a very toxic chemical that requires extreme care and appropriate handling).			

Table 1: Comparison between the untreated control soil and wollastonite-amended soil based on chemical analyses (pH, calcimetry, and ICP-MS).

Sample	SIC content (g,CaCO ₃ (eqv)/(kg,soil))
Depth zone of 0-15 cm (pan fraction)	12.33 ± 3.53
Depth zone of 0-15 cm	10.13 ± 2.68
Control value of depth zone of 0-15 cm	2.51 ± 0.50
Depth zone of 15-30 cm	4.23 ± 1.00
Depth zone of 30-60 cm	9.20 ± 0.09
Deep profile 1 (0-30 cm)	4.41 ± 0.06
Deep profile 1 (30-60 cm)	1.56 ± 0.03
Deep profile 1 (60-100 cm)	32.32 ± 1.36
Deep profile 2 (0-30 cm)	4.56 ± 0.62
Deep profile 2 (30-60 cm)	18.43 ± 0.41
Deep profile 2 (60-100 cm)	131.54 ± 1.89
Samples of depth zone of 0-15 cm were collected using a probe sampler. Samples of depth zones of 15-30 cm and 30-60 cm were collected using a Dakota probe sampler. Deep profile samples were collected using an extended auger sampler.	

Table 2: The CaCO₃(eqv) content in different depths of the soil based on the calcimetry results.

Oxides in soil	Wt%
SiO ₂	65.19
Al ₂ O ₃	14.76
Fe ₂ O ₃	6.20
CaO	3.62
K ₂ O	2.98
P ₂ O ₅	2.11
MgO	1.69
Na ₂ O	1.45
TiO ₂	1.25
SO ₃	0.37
MnO	0.16
BaO	0.11
ZrO ₂	0.10

Table 3: WDXRF data of the composition of the various oxides present in the control soil. Duplicate samples, in loose powder form, were analyzed for 20 min using standardless Omnia method, under helium and at 1 kW power, and concentrations were calculated as oxides. The average sum before normalization was 69.8 wt%, with the balance being porosity and undetectable light elements (H, C, O, N). The average concentrations of the detected oxides present in amounts greater than 0.10 wt% were selected and normalized to 100%.

Discussion

Given that collecting samples from fertilized agricultural fields is usually difficult, it is suggested that samples should be collected before nutrient application. It is also advisable to avoid collecting samples from frozen fields. The sampling depth may vary in different areas depending on the ease of sampling over the vertical profile, and the depth of the water table. The selected soil sampling device is dependent

on the soil structure and depth of interest³³. While it is more convenient to use hand probes/augers in the case of shallow samples, usually a more advanced version (e.g., extendable auger) is recommended for recovering subsoil samples³³. In the predominance of tight clays or cemented sands, some difficulties may appear during the extracting cores due to friction and torquing of the sampler³³. One issue for inorganic carbon verification campaigns is the choice of appropriate interval for tracking the uptake of carbon in soils,

as it may be variable over long intervals (e.g., 5 to 10 years)³⁴. Although there is no prescribed frequency for re-sampling, the moderately long intervals (e.g., yearly or bi-yearly) is believed to enhance the chance of reliably tracking SIC changes³⁵.

There are also a few challenges complicating measuring the inorganic carbon using different analyses. First is regarding the possible slow dissolution of carbonate species during calcimetry analysis, especially when there is entrapment of carbonates inside particle aggregates, or even within the original silicate particles; this reduces the contact of the acidic solution, slowing or even impeding the dissolution of carbonates and the resulting degassing of CO₂ during calcimetry analysis. The other difficulty that may arise is during mineralogical analysis, in terms of the detection of weathering/sequestration products, and due to the heterogeneity of the soil, which hampers XRD and SEM-EDS analyses, at least by making it more difficult to reach conclusive results³⁶. The fractionation procedure was found to be beneficial in our prior work²⁸ for concentrating the pedogenic carbonates and residual silicates in a single soil fraction (pan fraction), allowing more precise chemical, mineral, and morphological analyses to be done. Other studies have indicated that accumulated organic carbon is more likely to be stored in fine particle aggregation of agricultural soils^{37,38}, similar to the particle analyzed in **Figure 5**. Furthermore, the higher surface area of fine silicate rock particles leads to a higher weathering rate comparing to the coarser fraction¹⁵. However, fractionation could vary from soil to soil and even may not be required for soil containing large amounts of carbonates and silicates. Also, its need or benefit should be further verified for different soil types and various silicate amendments than the ones used in our prior work.

We have demonstrated methods for detecting and analyzing SIC due to application of wollastonite to agricultural soils in the current study. Although these techniques could be utilized for investigating SIC in the soils amended with other enhanced weathering candidates, such as basalt and olivine, the mineral of choice may have different effects on the soil, which should be considered during the analysis. For example, the weathering process may take longer for some minerals compared to others. This is can be due to dissimilar dissolution rate of several minerals, concluding in different mineralization rate in short and long terms. The other issue is concerned with occurrence of precipitated carbonates over vertical profile of the soil, which could vary based on the silicate mineral properties and resulting geochemical conditions of the soil, inductive or not to immediate carbonate precipitation in the shallow soil. Accordingly, amendment of soils with some types of silicates could yield significant pedogenic carbonate formation in deeper layers, in contrast to the shallow accumulation of carbonates due to weathering of wollastonite detected in our studied fields. Core samplers have been widely used for extracting undisturbed samples and measuring undisturbed BD in the field³⁹. Since BD is a function of several climatic parameters and practice settings, and it may vary both spatially and temporally, a reasonable number of replicates is required to yield an acceptable range of BD uncertainty in the study area³⁹. This is particularly necessary for addressing big uncertainties in SIC_{areal} calculated estimates, such as the value determined in the current study (i.e., $\pm 39\%$).

Thermogravimetric analysis (TGA) can also be used to determine the calcium carbonate content in the soil by measuring the mass loss in the temperature range of 500–800 °C, which is the decomposition temperature range for CaCO₃⁴⁰. Automated carbon analyzer or TGA methods

are suitable for analyzing soil samples from smaller confined areas, such as a pot experiment, since these methods require only 20 milligrams of soil sample for analyses. Therefore for agricultural studies, the calcimetry results are deemed more precise and accurate given the larger mass of sample analyzed (10 g versus 20 milligrams), the triplicate readings obtained, and the use of pure calcium carbonate as the method standard. More details and examples can be found in Haque et al.³⁶. Due to the co-occurrence of geological- and atmospheric-driven pedogenic carbonates in soil, distinguishing between different sources is of significance. Stable isotopic ($\delta^{13}\text{C}$) and radiogenic (^{14}C) carbon signatures, as well as isotopic oxygen signatures, are regarded as the robust tools for identifying the source of carbon in soil^{16,41,42,43}. Such analysis can further verify the sequestration of atmospheric CO_2 in studies aiming to monitor the fate of pedogenic carbonate in soils.

While conventional carbon detection methods (e.g., mass measurement) are suitable for local carbon markets, more systematic methods are required when it comes to verification objectives in regulated markets³⁵. The verification method described here is adaptable for monitoring pedogenic inorganic carbon sequestration in various agricultural soils amended with alkaline earth metal silicate-containing rocks, such as wollastonite, basalt, and olivine. This type of validation is essential for carbon credit programs, which can benefit farmers that sequester carbon in their fields.

Disclosures

The authors have no conflict of interest.

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