

Communication

Characterization of Physically Fractionated Wollastonite-Amended Agricultural Soils

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Abstract: Wollastonite is a natural silicate mineral that can be used as an agricultural soil amendment. Once in the soil, this mineral undergoes weathering and carbonation reactions, and, under certain soil and field crop conditions, our previous work has shown that this practice leads to accumulation of inorganic carbon (calcium carbonate). Mineral carbonation is the carbon sequestration approach with the greatest potential for sequestration capacity and permanency. Agricultural lands offer vast areas onto which such minerals can be applied, while benefiting crops. This work illustrates a technique to separate wollastonite-containing soils into different fractions. These fractions are characterized separately to determine organic and inorganic content, as well as to determine the chemical and mineral composition. The aim is to detect the fate of wollastonite in agricultural soils, and the fate of weathering/carbonation products in the soil. The soils used in the study were collected from soybean and potato farmlands in Southern Ontario, and from an experimental pilot plot. Soil fractionation was done using sieving, and soil fractions were analyzed by a calcimeter, X-ray diffraction, and loss-on-ignition. Acid digested samples were measured by Inductively Coupled Plasma Mass Spectrometry. Carbonates and wollastonite were enriched by fractionation.

Keywords: enhanced weathering; mineral carbonation; mineral soil amendment; soil inorganic carbon; climate change mitigation

1. Introduction

Mineral carbonation of alkaline earth minerals, mainly calcium and magnesium-rich silicates, is the carbon sequestration approach with the greatest potential for sequestration capacity and permanency. Agricultural lands offer vast areas worldwide onto which such minerals can be applied [1–3]. In addition to the agricultural soil's carbon sequestration, inorganic carbon sequestration in urban soil can also aid atmospheric carbon dioxide removal [4–6]. Renforth et al. [7], Renforth and Manning [8], and Washbourne et al. [9] studied carbon sequestration in urban soils used for construction projects, and reported soil inorganic carbon (SIC) accumulation due to enhanced weathering of alkaline minerals. Manning et al. [10] studied the effect of adding finely ground basaltic quarry fines (basalt and dolerite), in combination with compost, to soils meant for land restoration projects, on the SIC accumulation as well as on plant growth.

Wollastonite that is mined in Ontario, Canada, is a natural mineral, rich in calcium silicates (primarily CaSiO_3 , secondarily $\text{CaMgSi}_2\text{O}_6$) that, when added to the soil, can improve the soil fertility, by undergoing weathering reactions: releasing calcium, silica, and associated plant nutrients (Mg, Fe, S, K) into the soil, as well as forming carbonates (inorganic carbon) by reacting with the dissolved CO_2 present in the soil porewater [11–13]. Determining the amount and composition of carbonate products

is an essential requisite for understanding the fundamental phenomena regarding weathering and carbonation reactions and to verify that carbon sequestration is occurring.

When in soil, the amended alkaline minerals and the precipitated carbonates are associated with the soil particles/aggregates and are present in relatively low amounts, which makes identification and quantification challenging using conventional analytical techniques. Techniques such as calcimetry become less reliable at low concentration levels, while techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), and energy dispersive spectroscopy (EDS) are not ideal for highly heterogeneous materials due to a small sample size that is characterized. This necessitates the separation from soil, or the concentration in soil, of silicates and carbonates, before further analysis. Physical fractionation of soil could provide wollastonite and/or carbonate-rich fractions of soil, and the analysis of the different fractions of the soil would provide a new perspective on wollastonite's roles and fate in the agricultural soil.

Soil is naturally heterogeneous, both in terms of particle/aggregate size, and particle/aggregate composition. Thus, soil fractionation helps us to obtain more homogeneously-sized fractions. Analysis of the distribution of minerals in the soil fractions provides more detailed geochemistry data and is a robust soil data framework [14,15]. Soil fractionation is usually performed by dry sieving [16], which causes mechanical disintegration of the aggregates when dry soil is exposed to rotary sieving [17]. Most of the previous studies have used soil fractionation to study the soil organic matter [18–21] or silicon mobility in the soil profile [22,23]. Such studies have not reported the inorganic carbon content in the different soil fractions, which marks the novelty of the present study.

In our previous work, Haque et al. [24] studied the benefits of the wollastonite soil amendment, both in terms of plant growth and inorganic carbon sequestration. In that study, collected soils were analyzed for inorganic carbon content after sieving the soil through a 200- μm mesh, to remove coarse materials that were not important for analysis. Given that 90% of the wollastonite used in that study had a particle size less than 25.9 μm , much of the collected material, less than 200 μm in size, was made up of other soil particles/aggregates. Wollastonite and its weathering/carbonation products were a minor component of the sieved soil. Chemical analysis of these soil samples produced small-value results (<0.70 wt.%) for total inorganic carbon (TIC). In fact, at the application rate of wollastonite-to-soil used in that study, and, according to wollastonite carbonation stoichiometry, the maximal TIC value possible in these tests would have been 1.29 wt.%. Such low values are a challenge to accurately and precisely quantify using calcimetry. Mineralogical analysis was not reported in that study since the calcium carbonate and calcium silicate peaks of interest were not quantifiably visible from the diffraction patterns obtained. Thus, the conclusions reached in that study did not include fundamental understanding of the weathering or carbonation reactions. This necessitates soil fractionation to more accurately and precisely quantify the inorganic carbon content of the wollastonite-amended agricultural soils in order to study the mineralogy of the weathering/carbonation reactants and products. Analyzing the minerals of different soil fractions would help us to understand which soil fractions store carbonates in greater quantity, and also provide new insight into the weathering and carbonation reactions.

For the present work, agricultural soils were collected from soybean and potato farmlands in Southern Ontario, and from an experimental pilot plot at the University of Guelph. The main objective of this study is to use a sieving technique to separate alkaline mineral-amended soil into different fractions, and to then characterize these different soil fractions for elemental and mineral composition, and for inorganic and organic carbon content. The aim of this study is to detect the fate of alkaline minerals added to the agricultural soil and also the fate of weathering/carbonation products (carbonates and silica). By fractionating the agricultural soil and identifying one or more fractions that have greater amounts of inorganic carbon than the unfractionated soil, it is then possible to verify the results obtained by analyzing the whole soil. The rationale is that inorganic carbon can only be concentrated if it is actually present, and is not a measurement artifact. The chemical and mineralogical characterization of soil fractions provides a better understanding of the roles and fate of wollastonite.

2. Materials and Methods

2.1. Soil Sampling and Wollastonite Used

Soils from three different locations were used in this study. First, agricultural soil was collected from a commercial field located in Woodstock, Ontario (43°08'57.7" N 80°37'29.8" W). Wollastonite had been applied to this land at an application rate of 4.94 tonne·ha⁻¹, and tilled to a depth of 2.5 cm. Following wollastonite application, soybeans seeds were planted at a rate of 420,078 seeds·ha⁻¹ along with 0.173 tonne·ha⁻¹ of muriate of potash. After a period of five months (June to October, 2018), the soil was sampled. The collected soil was characterized as sandy loamy (gravel 1.1%, sand 55.1%, silt 29.5%, clay 15.5%) with a pH of 6.63 and 3.2 wt.% dry organic matter content. Climatic data from this site (Figure S2) is presented in the Supplementary Materials.

Second, soil was sampled from an experimental pilot plot maintained on the Thornbrough building rooftop at the University of Guelph (Guelph, ON, Canada). The soil used in this experimental plot had been collected from the Woodstock farm prior to wollastonite application at the farm. The soil used in this pilot plot was mixed (to a depth of 15 cm) with 5 wt.% and 10 wt.% wollastonite, which is equivalent to an application rate of 98.8 tonne·ha⁻¹ and 197.7 tonne·ha⁻¹, respectively, and soybeans were grown in these amended soils. Soils were collected at the conclusion of the 14-week experimental trial. Climatic data from this site (Figure S3) is presented in the Supplementary Materials. For both the experimental pilot plot and the commercial soybean field, the unamended soil initially collected acted as the control.

The third sampling site was a potato field located at Alliston, Ontario (44°14'57.3" N, 79°49'26.7" W), where wollastonite was used at a rate of 1.235 tonne·ha⁻¹ in part of the farm, and tilled to a depth of 2.5 cm. In all of the farm, dolomitic lime, as the liming agent, and a fertilizer (160 units of N and 80 units of K) had also been applied. The soil type was determined to be sandy loam (gravel 0.5%, sand 57.1%, silt 35.9%, clay 7.0%) with 1.7 wt.% dry organic matter content. These soils were sampled post-harvest in late September 2018, from both the land areas with and without (control) wollastonite application. Climatic data from this site (Figure S1) is presented in the Supplementary Materials.

The field soils were sampled using a soil core sampler (JMC) down to 15 cm of soil depth, and several kilograms of cores collected from points widely distributed in each plot/field were thoroughly blended in a bucket, which is followed by quartering into replicate samples prior to characterization analyses. The soil from the rooftop was sampled, using a soil core sampler (1.27-cm diameter) at five different points radially distributed within each microplot and down to full depth (15 cm). Additionally, >1 kg of cores were thoroughly hand-blended, followed by quartering into replicate samples prior to all soil analyses.

Wollastonite applied in this research was sourced from Canadian Wollastonite's Ontario mine. Coarser textured wollastonite, with a d (0.5) particle size of 13.8 µm (wet laser diffraction, by volume) and d (0.9) value of 83.7 µm, was applied on the soybean field and the potato field. Finer wollastonite, with a d (0.5) particle size of 8.2 µm (by volume) and d (0.9) value of 63.7 µm, was used in the rooftop experiment. The mined mineral used in this study was mainly comprised of wollastonite (CaSiO₃), diopside (CaMgSi₂O₆), and quartz (SiO₂) mineral phases, as identified by the XRD analysis. The CaCO₃ content (calimeter reading) in coarse and fine wollastonite was found to be 2.09 wt.% CaCO₃ (or 9.2 g CO₂/kg soil) and 3.82 wt.% CaCO₃ (or 16.8 g CO₂/kg soil), respectively. Elemental composition of the wollastonite includes 26% silicon (55% SiO₂), 18% calcium (26% CaO), 4.0% magnesium (9% MgO), 1.8% sulfur, 0.11% nitrogen, 0.10% P₂O₅, 0.10% K₂O, 11 ppm copper, and 1.1 ppm zinc.

2.2. Separation Technique

The soils were dried by placing samples in a muffle furnace (Thermo Scientific F48055-60, Waltham, MA) maintained at 103 ± 2 °C for at least 15 h. For sieving, the dried samples were sieved using a sieve shaker consisting of different mesh sizes (710 to 50 µm), at 60 rpm for 15 min. Sieved fractions used for analysis included 500–250 µm, 250–100 µm, 100–75 µm, 75–50 µm, and <50 µm, which are respectively

referred hereafter as fractions 250, 100, 75, 50, and pan. Above 500 μm , soil fractions mainly consisted of gravel, and were not analyzed.

2.3. Characterization Techniques

The agricultural soil fractions were analyzed by calcimetry, loss-on-ignition (LOI), and XRD. Acid-digested samples were measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Calcimetry is used for determining inorganic carbon content in agricultural soil samples. During wollastonite weathering, calcium ions from the dissolving wollastonite react with the bicarbonate ions dissociated from the dissolved atmospheric/soil CO_2 , which leads to the formation and precipitation of calcium carbonate. During wollastonite carbonation, carbonate ions react at the wollastonite particle surface with calcium ions coming from within the particle, and carbonate is deposited on the particle surface or in close proximity. Either of these processes adds to the inorganic carbon fraction of the soil, which can be determined by use of a calcimeter (Model 08.53, Eijkelkamp, Netherlands). Soil fraction samples were suspended in MiliQ water (5 g in 20 mL), to which 7 mL of 7 M HCl was added within a sealed Erlenmeyer flask connected to a graduated water-filled manometer-style column that recorded the released CO_2 volume [25]. The amount of released CO_2 is then converted into the amount of CaCO_3 , which is an equivalent value, as other alkaline earth metal carbonates could also be present. The calcimetry results were statistically analyzed using R software (The R Foundation) by applying Tukey's HSD (honestly significant difference) test to determine similarity groups for each set of triplicate data. Tukey's test was applied to three separate batches of data: rooftop samples, soybean farm samples, and potato farm samples. The numerical data for these analyses are given in Table S1 in the Supplementary Materials.

The LOI method was used to determine the organic matter (OM) content of the different soil fractions. OM is an important parameter of the soil profile, both as a carbon sink and as a measure of soil health. This value was determined to analyze the effect of wollastonite application on the OM content of soils. Air-dried soil samples (5 g) from the different fractions were weighed into tared porcelain crucibles and dried at 105 $^\circ\text{C}$. The crucibles were reweighed to determine the oven-dry weight ($W_{105\text{ }^\circ\text{C}}$ in g), before placing it in a muffle furnace at 360 $^\circ\text{C}$ for 4 h [26]. A temperature of 360 $^\circ\text{C}$ was chosen to minimize the decomposition of carbonates, which occurs at higher temperatures. The crucibles were allowed to cool in a desiccator before reweighing ($W_{360\text{ }^\circ\text{C}}$ in g). The loss in weight between 105 $^\circ\text{C}$ and 360 $^\circ\text{C}$ gives the OM content of the soil (Equation (1)) [26].

$$OM \% = \frac{(W_{105\text{ }^\circ\text{C}} - W_{360\text{ }^\circ\text{C}})}{W_{105\text{ }^\circ\text{C}}} \times 100 \quad (1)$$

Mineralogical analysis of the agricultural soil fractions was conducted by using XRD (Empyrean, Panalytical, Netherlands) and HighScore Plus software (Malvern Panalytical, UK). The diffractometer operated with Cu $K\alpha$ radiation at 45 kV and 40 mA, and the diffraction patterns were collected over a 2θ range of 5–70 $^\circ$.

The different agricultural soil fractions were analyzed for their elemental calcium concentration to identify which fraction comprised a greater amount of calcium minerals, which relates to the fractions enriched with wollastonite and/or calcium carbonate. Samples of 0.1 g of the oven-dried soil fractions were digested in 10 mL of 2 vol.% nitric acid (trace metal grade, Fisher Scientific, Hampton, NH, USA) in a block heater for 1 h at 90 $^\circ\text{C}$. The digested sample was syringe filtered (0.45 μm) and diluted to 100 mL of MiliQ water containing 1000 ppb of lead as the internal standard. The Ca^{2+} concentration (mg Ca/kg soil) in acid digested samples was determined using ICP-MS (NexION, Perkin Elmer, Waltham, MA, USA). Samples are introduced to an argon plasma, where individual atoms become positively-charged ions that then enter a quadrupole mass analyzer, are separated through mass ratio, and are detected at high and low concentration ranges [27].

3. Results and Discussion

The calcimeter analysis of the different agricultural soil fractions obtained via sieving is shown in Figure 1. The soils sampled from the experimental pilot rooftop (RFT), where the soils had been amended with 5 wt.% and 10 wt.% wollastonite by weight, are denoted as 5% RFT and 10% RFT, respectively. The soils contained a higher amount of calcium carbonate (CaCO_3 wt.%) when compared to the control plot (not amended with wollastonite), which is expected due to the weathering/carbonation reactions when CO_2 is sequestered. Figure 1a for the rooftop samples shows that the amount of CaCO_3 is higher in all the fractions, especially in the pan fraction, for both the 5 wt.% and 10 wt.% RFT samples, as compared to the control. The even more important observation in this case is that the different soil fractions contained different amounts of CaCO_3 , and the highest amounts were observed in the soils that passed through the 50- μm sieve, i.e., the ones from the pan: 1.57 wt.% CaCO_3 (which is equivalent to 6.91 g CO_2/kg soil) and 2.19 wt.% CaCO_3 (equivalent to 9.64 g CO_2/kg soil) for the lower and higher amended soils (Figure 1a), respectively. Tukey's HSD groups for these samples also confirm that they are statistically different from the other fractions of the same soils. In our previous study, Haque et al. [24] reported a soil inorganic carbon content of 0.606 wt.% (~ 2.67 g CO_2/kg soil) for the agricultural soil sieved through 200 μm , which is much less than the value reported in this study for the 5 wt.% and 10 wt.% wollastonite amended rooftop soil fractions from the pan ($< 50 \mu\text{m}$). This implies that soil fractionation results in isolating soil that contains most of the pedogenic calcium carbonate.

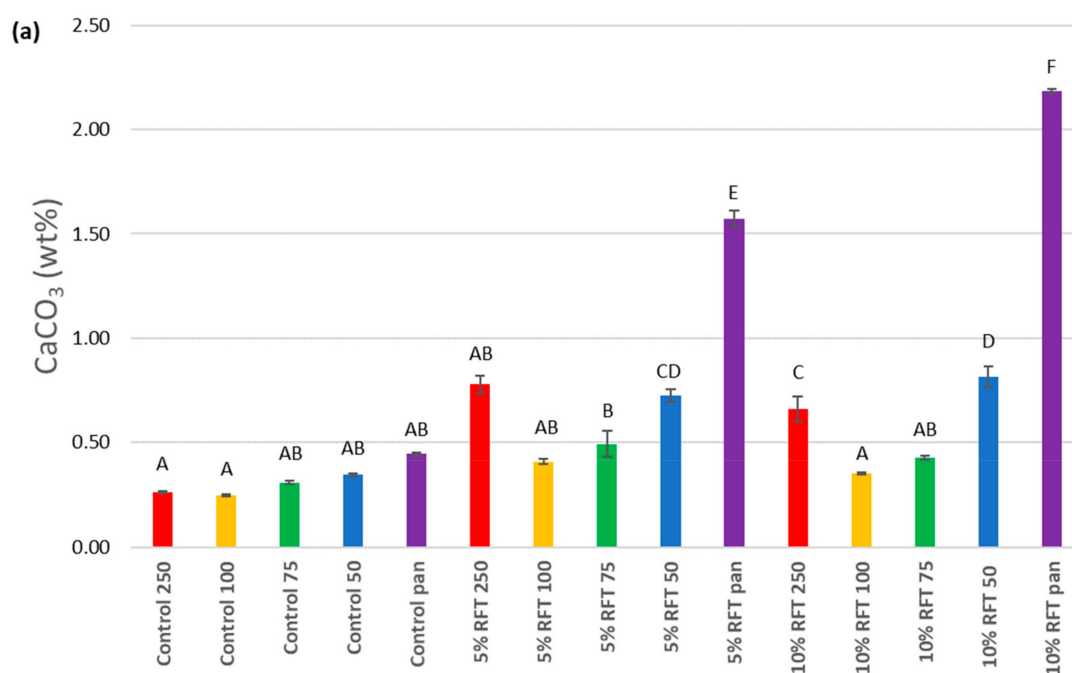


Figure 1. Cont.

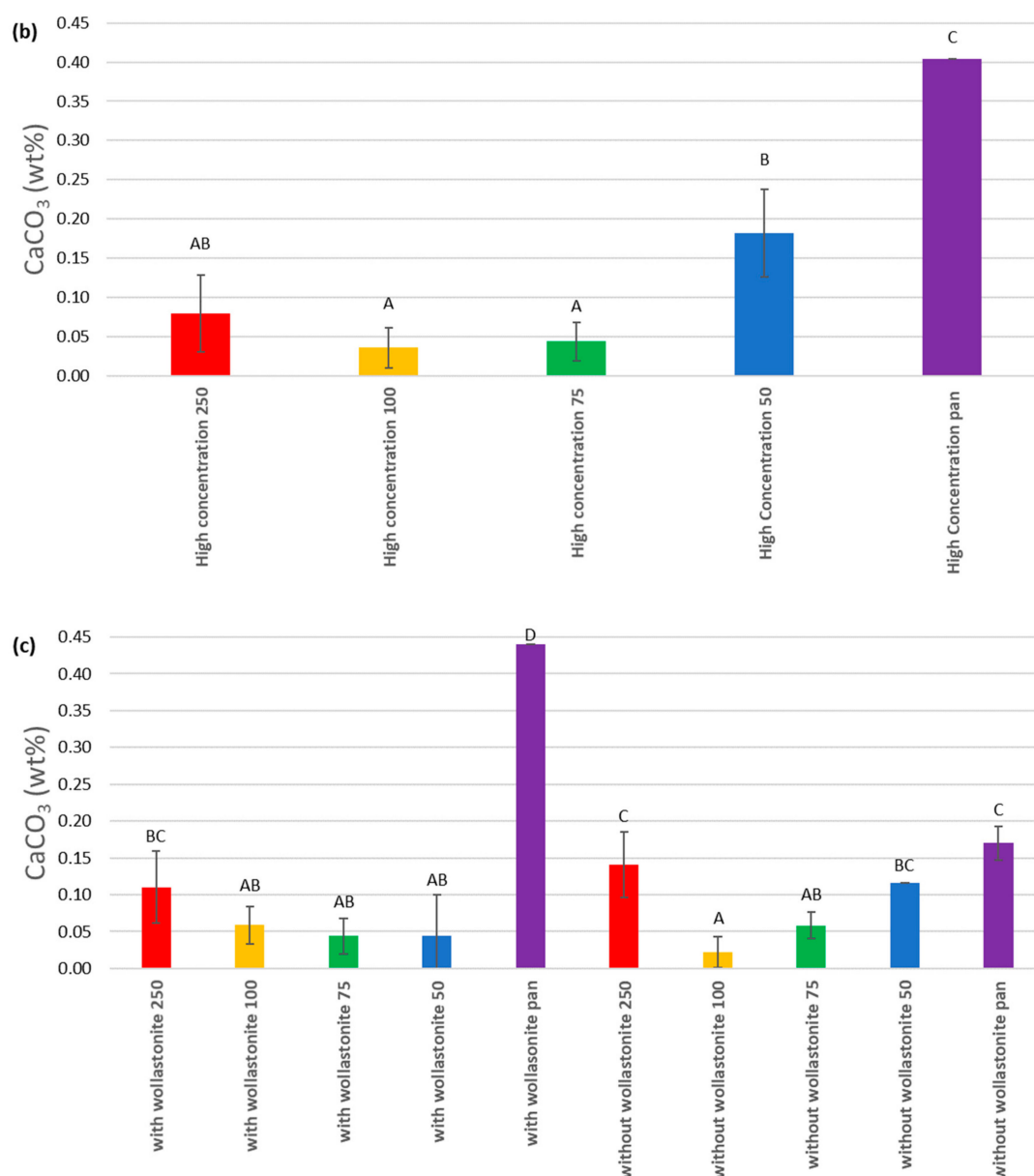


Figure 1. Calcimeter analysis of the soil fractions fractionated from the soils sampled at three different sites: (a) rooftop "control" and amended plots ("RFT"), (b) soybean farm ("high concentration"), and (c) potato farm ("with" and "without" wollastonite). Color coding relates to sieve sizes, error bars represent the standard deviation of triplicate samples, and lettering relates to Tukey's HSD test groups.

From Figure 1b, for the soil sampled from the soybean field, denoted as "high concentration" because of the wollastonite field application rate of $4.942 \text{ tonne}\cdot\text{ha}^{-1}$ used (the highest used in that farm), it can be seen that the amount of CaCO₃ in the 250- μm to 50- μm sieve agricultural soil fractions is much lower (0.04–0.18 wt.% CaCO₃, or 0.18–0.79 g CO₂/kg soil) compared to the fraction from the pan (0.40 wt.% CaCO₃, or 1.76 g CO₂/kg soil). Like with the rooftop soils, the pan fraction from the soybean farm soil is found to be statistically different than the other fractions of the same soil, according to Tukey's HSD test groups. For the soils sampled from the potato field (Figure 1c), the pan fraction of the wollastonite-amended soil (denoted as "with wollastonite pan") contained higher CaCO₃ as compared to the pan fraction of the control soil ("without wollastonite pan"), which suggests that carbonate formed as a result of wollastonite weathering and/or carbonation. Tukey's HSD test confirms that the amended pan fraction belongs to a different group than all other fractions.

Figure 2 shows the organic matter (OM) content of the three fractionated soils. Analyzing the enriched pan fraction, the OM content of the control is 1.9 wt.%. In addition, 5 wt.% RFT sample has 0.9 wt.% (~50% less than that of the control), and the 10 wt.% RFT samples contain 0.6 wt.% (~70% less than that of the control). It is possible that the high amendment ratio used in the rooftop experiments led to a slight decrease in organic carbon content of the soils, which was also reported in Haque et al. [24]. It is important to note that such a high amendment ratio is not expected to be utilized in field crops, but rather, in field crops, a similar amount of wollastonite would be amended over several years. Thus, a negative impact of a high application rate is not expected in field crops, which is corroborated by the field sampling data shown here and discussed next. More importantly, for the control and RFT sample fractions, no clear trend with a sieved fraction size is seen for these three samples. In the control, OM content is higher for the smaller fraction, but, for the RFT samples, the intermediate fractions have slightly higher OM content. Sieving is a physical separation that does not fully disturb aggregates, so it is possible that the concentration of OM in finer fractions in the control is a sign that this soil was less consolidated, while the soils used in the plot trials, and amended with wollastonite, became more consolidated. This concentrated more OM in larger size fractions. Soil consolidation is a potential effect of the wollastonite amendment reported by some users in Ontario that we have contacted. However, our research group is yet to scientifically verify this claim.

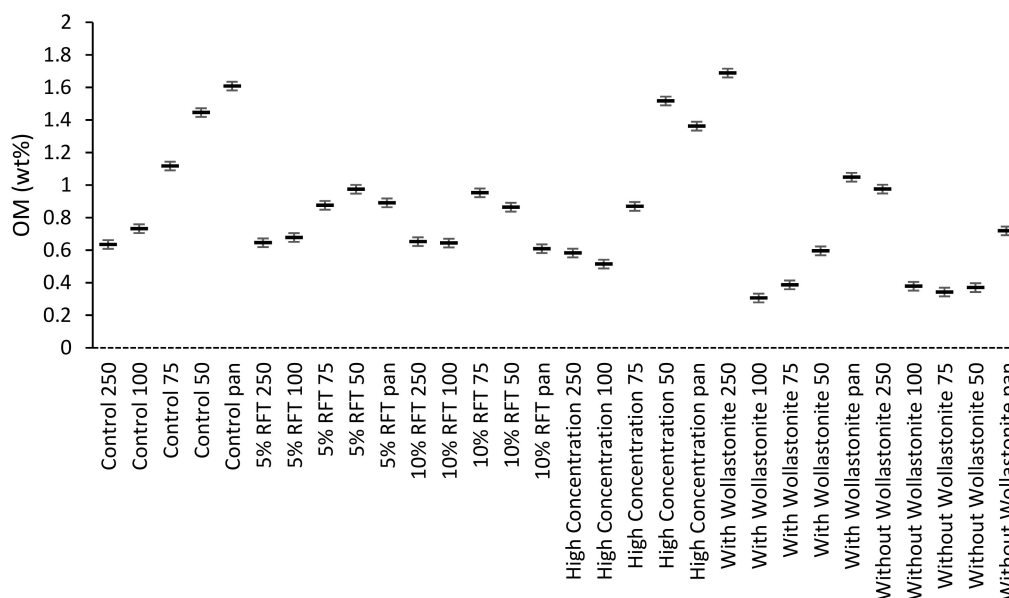
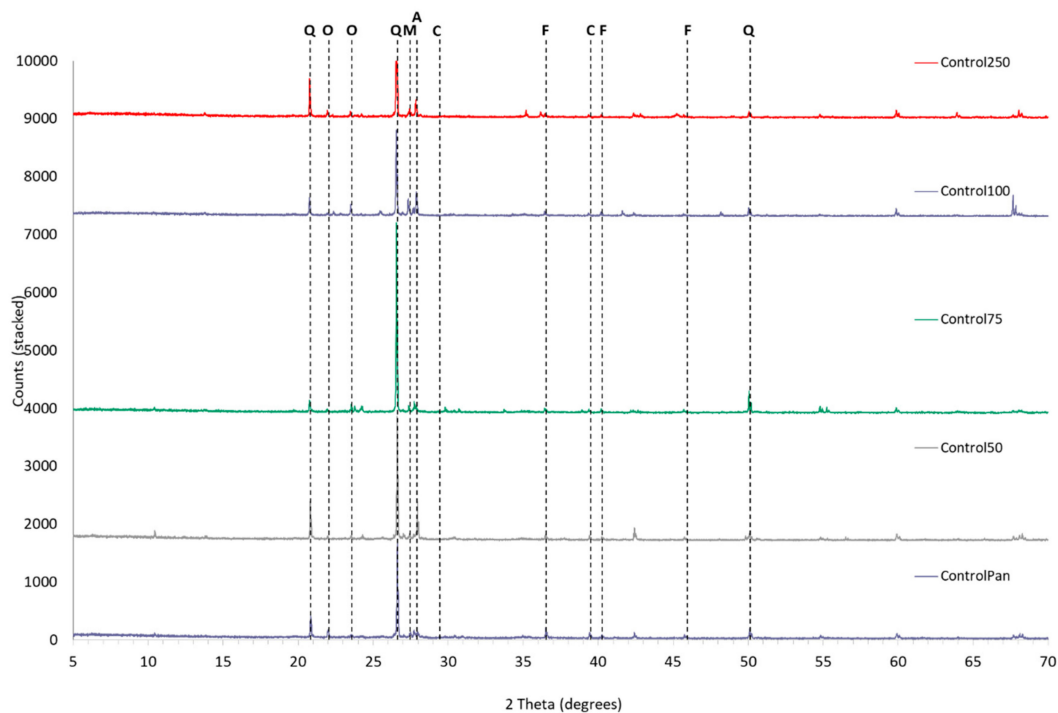


Figure 2. Organic matter (OM) content, determined by LOI, of the three different soils fractionated by dry sieving. Error bars represent the standard deviation of triplicate samples.

In the field-collected samples, both the soybean soil and the potato soil showed OM content spread widely among the different size fractions, but with differing trends. The soybean soil OM content had a similar trend to that of the control (which is soil obtained and characterized as-received from the soybean farm pre-amendment), with greater OM content in finer fractions, and similar total OM content. As we previously hypothesized, this could indicate less consolidated soil. The potato soils, both amended and unamended, presented the highest OM content in the largest fraction (250 μm) followed by the smallest fraction (pan). The difference between these two was that the wollastonite-amended agricultural soil had slightly greater OM content. Thus, looking at both the soybean and potato soils, the wollastonite amendment at field-scale with field crop-appropriate amendment levels did not negatively affect the OM content of soils, which is a desirable outcome for farming. According to OM testing, fractionation does not aid, on its own, in reliably gaining more insight on soil organic carbon content, accumulation, or depletion, versus analysis of the soil as a whole (with conventional preparations). This may explain why soil fractionation is not commonly reported in

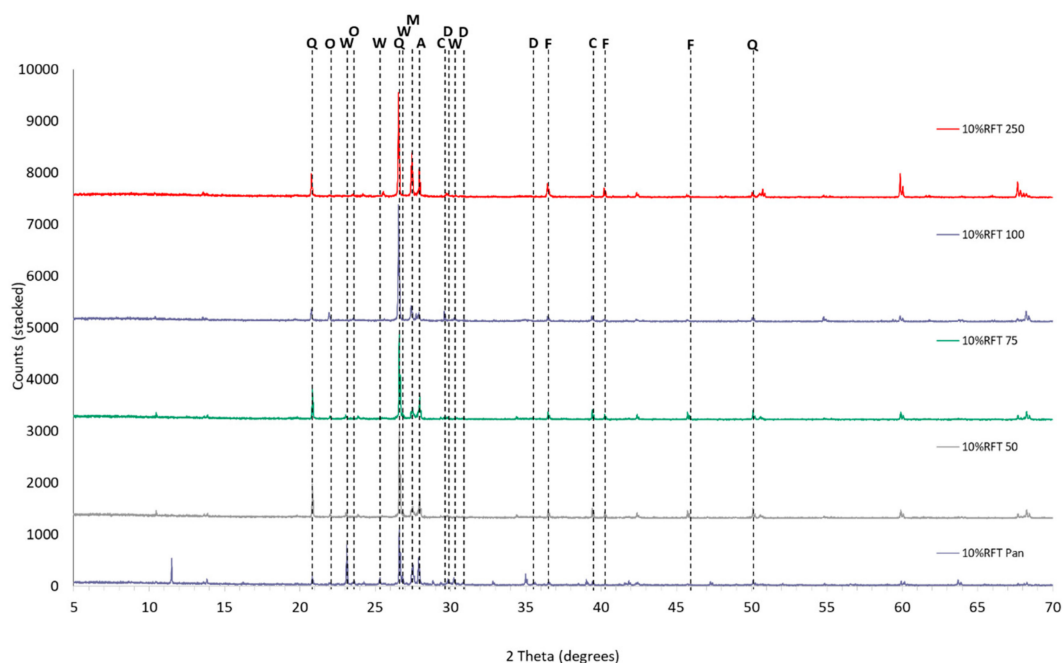
soil carbon sequestration literature that typically focuses on soil organic carbon. Our work, on the other hand, shows the value of fractionation for inorganic carbon analysis, as seen in calcimetry analysis, and the following results.

Overall, 10 wt.% RFT soil fractions showed a higher amount of calcium carbonate compared to other samples (Figure 1). Therefore, the mineralogy of the 10% RFT soil sample is discussed herein, in comparison with the control soil. On Figure 3a, the control soil fractions showed the major discernable (i.e., not overlapping) peaks for quartz (SiO_2) at 26.65° , albite ($\text{NaAlSi}_3\text{O}_8$) at 28.07° , orthoclase (KAlSi_3O_8) at 22.09° , microcline (KAlSi_3O_8) at 27.50° , and ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5(\text{H}_2\text{O})$) at 36.65° , as well as other discernable peaks from these phases, and two main peak locations of calcite. These, like many Canadian soils, contain quartz and albite, together with a range of other minerals [28]. None of the control soil fractions showed clear signs of the presence of calcite, which is identified by a main peak at 29.40° 2θ , and minor peaks at 39.40° and 43.14° . Such calcite peaks are visible in RFT soil (Figure 3b), primarily in the pan fraction, but also, to a lesser extent, in the $100 \mu\text{m}$ fraction. Given that the control soil shows less evidence of the presence of calcite, especially in the pan, these results can be interpreted as indicating that the carbonate product of wollastonite is enriched in the smaller-sized soil fractions. This correlates well with the greater inorganic carbon content of the finest fraction determined by calcimetry.



(a)

Figure 3. Cont.



(b)

Figure 3. XRD diffractograms of: (a) control soil fractions, and (b) 10 wt.% rooftop soil fractions. Size fraction order of diffractograms, from top to bottom: 250 μm , 100 μm , 75 μm , 50 μm , and pan. Lettering relates to the main peaks of major mineral phases: albite (A), calcite (C), diopside (D), ferrihydrite (F), microcline (M), orthoclase (O), quartz (Q), and wollastonite (W).

Additionally, wollastonite and diopside peaks are visibly present in the pan RFT soil fraction, as well as in the 50- μm and 75- μm fractions, though to a lesser extent than the pan. Diopside ($\text{CaMgSi}_2\text{O}_6$) is the second most abundant mineral present in the wollastonite ore mined in Ontario, and, thus, is present in the amended soils. The principal wollastonite peaks occur (in 2θ order) at 23.20° , 25.28° , 26.88° , and 30.06° . The peak at 26.88° is not clearly visible in soil samples as the main quartz peak at 26.65° nearly overlaps, but the other peaks are not present in the control soil. Diopside peaks occur at 29.85° , 35.48° , and 30.88° , in decreasing order of magnitude. All of these are visible in the pan fraction of RFT soil. Wollastonite and diopside peaks are not visible in the RFT soil fractions greater than 75 μm . This correlates well with the particle size of the wollastonite amendment used in the rooftop trials: d_{32} of 4.37 μm and $d(0.9)$ of 63.7 μm , determined by laser diffraction. It is, thus, shown that soil fractionation by size can be used to concentrate fine silicate minerals amended to soil. In the case of coarse minerals, density-based fractionation can potentially be used and will be investigated in future research. The combination of calcimetry and XRD analyses on fractionated agricultural soil, as a result of concentration of mineral phases of interest, also serves to confirm with greater certainty that the results obtained by analyzing the whole soil, as in Haque et al. [24], are genuine and not analytical artifacts. If wollastonite and calcite phases are present in detectable quantities in smaller soil fractions, then it will be present in the whole unfractionated soil even when present in quantities near or below detection limits.

Calcium concentration in the control soil and in the 5 wt.% and 10 wt.% wollastonite-amended rooftop soil samples, after fractionation by sieving, is shown in Figure 4. These samples were chosen for analysis by ICP-MS since a higher application rate of wollastonite was used in the rooftop experimental plot, which makes it easier to discern if the calcium concentration detected is attributable to the original soil composition, to newly formed pedogenic carbonates (i.e., CaCO_3), or to the amended wollastonite (which contained calcium both in the form of CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$). The two finest 5 wt.% RFT soil fractions (50 μm and pan) showed significantly greater calcium concentration when

compared to the other fractions. These fractions in the amended soil contained 1.9 and 1.5 times, respectively, as much calcium as the similarly-sized fractions of the control. The finest 10 wt.% RFT soil fraction (pan) contained seven-fold greater amount of calcium compared to the control pan sample. This analysis further elucidates that fractionation resulted in enriching the finer soil fraction in wollastonite and calcium carbonate. Alone, ICP-MS cannot differentiate what mineral contributes most to these calcium concentrations, but, together with calcimetry and XRD results, it is possible to estimate how much calcium is present as calcite and how much calcium is present as silicates. For example, the ratio of the CaCO_3 amount between pan and 100- μm fractions, determined by calcimetry $((0.45 \text{ wt.})/(0.25 \text{ wt.}) = 1.8)$ is very similar to the ratio from the ICP-MS results $((9567 \text{ mg/kg})/(4951 \text{ mg/kg}) = 1.9)$. This suggests that nearly all calcium present in the control soil is in the form of CaCO_3 . In the case of the 10 wt.% RFT soil, the same ratios from calcimetry and ICP-MS are, respectively, 6.3 and 9.1. This discrepancy can be linked to the presence of significant quantities of unreacted silicates present in this soil, which was confirmed by XRD.

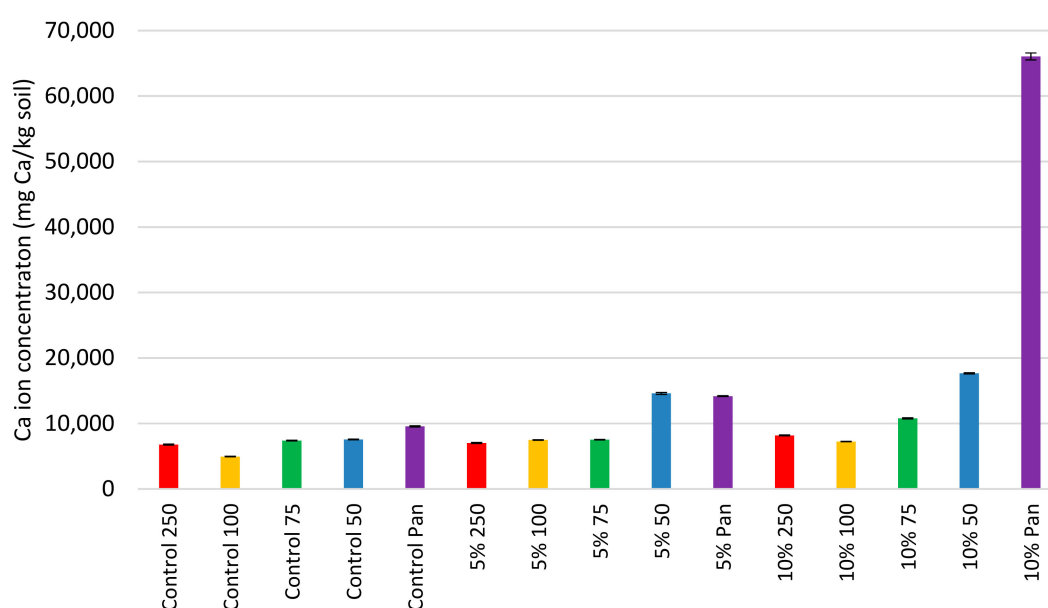


Figure 4. Calcium concentration in the samples obtained from fractionated control, 5 wt.% RFT, and 10 wt.% RFT soils, determined by ICP-MS after acid digestion. Error bars represent the replicate measurement (five) relative standard deviation.

Besides dry sieving, the next step in this research should be to fractionate the agricultural soil by density, using heavy liquids, such as sodium polytungstate and sodium metatungstate [29,30]. These are non-toxic chemicals that can be used to prepare mixtures in water with varying high densities, in the range of $1.0\text{--}3.1 \text{ g}\cdot\text{cm}^{-3}$, which enables the separation of wollastonite as well as calcite, which have average densities of $2.84 \text{ g}\cdot\text{cm}^{-3}$ and $2.71 \text{ g}\cdot\text{cm}^{-3}$, respectively [31], from other soil components. In particular, it would be useful to first perform dry sieving to concentrate amended fine silicates and calcium carbonate in a fine fraction. This is followed by heavy liquid separation, which could potentially generate a wollastonite-rich and a carbonate-rich fraction. Another phase that could be separated using this method is the amorphous silica product of silicate weathering/carbonation. Amorphous silica is not directly quantifiable by XRD, but it can be identified, when in high enough concentration, by a characteristic bump near the location of the main quartz peak [32]. Its concentration can be semi-quantitatively determined using internal standards [33]. Amorphous silica could not be identified in the present study, even after fractionation, due to its expected small concentration in soils (a fraction of the wollastonite content). Therefore, heavy liquid separation as a subsequent fractionation

step could make this amorphous phase visible in XRD diffractograms, or could be detected by ^{29}Si nuclear magnetic resonance [34].

4. Conclusions

Results from physical fractionations of the agricultural soil by means of sieving provided a deeper insight on the weathering/carbonation reactions of wollastonite, as shown by the calcimetry, XRD, LOI, and ICP-MS analyses. For calcimeter, in sieved samples, pan samples (<50 μm) showed the highest amount of calcium carbonate, which was followed by the soil fraction <75 μm . This confirms the wollastonite amendment sequester CO_2 in agricultural soil as inorganic carbon. Fractionation did not provide as much insight on organic carbon content of soils, since OM content does not reliably become concentrated in a particular size fraction. This is likely affected by the degree of soil consolidation. The LOI analysis did suggest that wollastonite amendment does not pose a negative effect on soil organic carbon content when applied at field conditions and amendment loadings, unlike the apparent reduction seen with high loadings in rooftop plot trials. By XRD, the extra peaks for amended and unreacted wollastonite and diopside, and those for the calcium carbonate formed were clearly observed in the 10 wt.% RFT soil fractions retained by 75- μm and 50- μm sieves, but were most concentrated in the pan fraction. These qualitative results agreed well with quantitative calcium concentrations determined by ICP-MS analysis of acid digested soils. In turn, calcimetry and XRD results aided in the interpretation of the ICP-MS, in terms of clarifying the speciation of calcium as carbonate or silicate in the different fractions.

Physical fractionation of the wollastonite amended agricultural soil by using the sieving method, which provided a better understanding of the wollastonite weathering/carbonation products, especially inorganic carbonate, in the different soil fractions. It is recommended that soil amended with wollastonite or any other alkaline silicate minerals can be analyzed following fractionation using sieving. The soil fractions with smaller particle/aggregate size are rich in wollastonite and weathering/carbonation products, which provides reasonably high values during analyses. This ensures more precise and reliable results. This is particularly crucial for verification of carbon sequestration in carbon credit programs. For soils amended with low wollastonite application rates, as seen in the case of the soybean and potato field scenarios evaluated in this study, the use of heavy liquids for fractionation will be even more beneficial, since they might segregate pre-sieved fractions further. This makes it possible to detect wollastonite and weathering/carbonation products, including amorphous silica, in even smaller quantities. Such a separation could also aid in answering a question that remains open for discussion: namely, if wollastonite undergoes weathering or carbonation. This is because, using the present techniques, it was not possible to confirm if carbonate and silica products of both processes were present as distinct particles, or still attached or coating remnants of wollastonite, which is often observed in accelerated carbonation. Concentrating carbonates and amorphous silica would allow easier inspection by visual techniques, such as scanning or transmission electron microscopy. The results and recommendations from this study will be applied in our future work on soil carbon sequestration by alkaline mineral amendment, at pilot and field scales.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-163X/9/10/635/s1>. Figure S1: Temperature and Precipitation graph for 1981 to 2010 Climate Normals from Alliston, ON, Canada, Figure S2: Temperature and Precipitation graph for 1981 to 2010 Climate Normals from Woodstock, ON, Canada, Figure S3: Kitchener/Waterloo, ON (Canada) weather historical data from June to October of 2018 during the experiment, Table S1: Tukey's Honest Significant Difference (Tukey's HSD) method data for calcimeter results; ordered by groups; position is the placement on Figure 1 in the main text. Supplementary Material—Climatic Data. Supplementary Material—Statistics Data.

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References

1. Kwon, S.; Fan, M.; Dacosta, H.F.; Russell, A.G. Factors affecting the direct mineralization of CO₂ with olivine. *J. Environ. Sci.* **2011**, *23*, 1233–1239. [[CrossRef](#)]
2. Hartmann, J.; West, A.J.; Renforth, P.; Köhler, P.; De La Rocha, C.L.; Dürr, H.H.; Scheffran, J.; Wolf-Gladrow, D.A.; Wolf-Gladrow, D.A. Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. *Rev. Geophys.* **2013**, *51*, 113–149. [[CrossRef](#)]
3. Manning, D.A.C.; Renforth, P. Passive Sequestration of Atmospheric CO₂ through Coupled Plant-Mineral Reactions in Urban soils. *Environ. Sci. Technol.* **2012**, *47*, 135–141. [[CrossRef](#)] [[PubMed](#)]
4. Jo, H.-K.; McPherson, G.E. Carbon Storage and Flux in Urban Residential Greenspace. *J. Environ. Manag.* **1995**, *45*, 109–133. [[CrossRef](#)]
5. Jorat, M.E.; Kolosz, B.W.; Goddard, M.A.; Sohi, S.P.; Akgun, N.; Dissanayake, D.; Manning, D.A. Geotechnical requirements for capturing CO₂ through highways land. *Int. J. GEOMATE* **2017**, *13*, 22–27. [[CrossRef](#)]
6. Leake, J.R.; Renforth, P.; Edmondson, J.; Manning, D.A.C.; Gaston, K.J. Designing a carbon capture function into urban soils. *Proc. ICE Urban Des. Plan.* **2011**, *164*, 121–128.
7. Renforth, P.; Manning, D.; Lopez-Capel, E. Carbonate precipitation in artificial soils as a sink for atmospheric carbon dioxide. *Appl. Geochem.* **2009**, *24*, 1757–1764. [[CrossRef](#)]
8. Renforth, P.; Manning, D.A. Laboratory carbonation of artificial silicate gels enhanced by citrate: Implications for engineered pedogenic carbonate formation. *Int. J. Greenh. Gas Control* **2011**, *5*, 1578–1586. [[CrossRef](#)]
9. Washbourne, C.-L.; Lopez-Capel, E.; Renforth, P.; Ascough, P.L.; Manning, D.A.C. Rapid Removal of Atmospheric CO₂ by Urban Soils. *Environ. Sci. Technol.* **2015**, *49*, 5434–5440. [[CrossRef](#)]
10. Manning, D.; Renforth, P.; Lopez-Capel, E.; Robertson, S.; Ghazireh, N. Carbonate precipitation in artificial soils produced from basaltic quarry fines and composts: An opportunity for passive carbon sequestration. *Int. J. Greenh. Gas Control* **2013**, *17*, 309–317. [[CrossRef](#)]
11. Hangx, S.J.; Spiers, C.J. Coastal spreading of olivine to control atmospheric CO₂ concentrations: A critical analysis of viability. *Int. J. Greenh. Gas Control* **2009**, *3*, 757–767. [[CrossRef](#)]
12. Moosdorf, N.; Renforth, P.; Hartmann, J. Carbon Dioxide Efficiency of Terrestrial Enhanced Weathering. *Environ. Sci. Technol.* **2014**, *48*, 4809–4816. [[CrossRef](#)] [[PubMed](#)]
13. Haque, F.; Chiang, Y.W.; Santos, R.M. Alkaline Mineral Soil Amendment: A Climate Change ‘Stabilization Wedge’? *Energies* **2019**, *12*, 2299. [[CrossRef](#)]
14. Woodruff, L.; Cannon, W.F.; Smith, D.B.; Solano, F. The distribution of selected elements and minerals in soil of the conterminous United States. *J. Geochem. Explor.* **2015**, *154*, 49–60. [[CrossRef](#)]
15. Birke, M.; Rauch, U.; Stummeyer, J. How robust are geochemical patterns? A comparison of low and high sample density geochemical mapping in Germany. *J. Geochem. Explor.* **2015**, *154*, 105–128. [[CrossRef](#)]
16. Dudhaiya, A.; Santos, R.M. How Characterization of Particle Size Distribution Pre- and Post-Reaction Provides Mechanistic Insights into Mineral Carbonation. *Geosciences* **2018**, *8*, 260. [[CrossRef](#)]
17. Kemper, W.D.; Rosenau, R.C. Aggregate stability and size distribution. In *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods—Agronomy Monograph No. 9*; American Society of Agronomy: Madison, WI, USA, 1986; pp. 425–442.
18. Kaiser, M.; Ellerbrock, R. Functional characterization of soil organic matter fractions different in solubility originating from a long-term field experiment. *Geoderma* **2005**, *127*, 196–206. [[CrossRef](#)]
19. Sun, K.; Jin, J.; Kang, M.; Zhang, Z.; Pan, Z.; Wang, Z.; Wu, F.; Xing, B. Isolation and Characterization of Different Organic Matter Fractions from a Same Soil Source and Their Phenanthrene Sorption. *Environ. Sci. Technol.* **2013**, *47*, 5138–5145. [[CrossRef](#)]
20. Christensen, B.T. Physical fractionation of soil and structural and functional complexity in organic matter turnover. *Eur. J. Soil Sci.* **2001**, *52*, 345–353. [[CrossRef](#)]
21. Diochon, A.C.; Kellman, L. Physical fractionation of soil organic matter: Destabilization of deep soil carbon following harvesting of a temperate coniferous forest. *J. Geophys. Res. Biogeosci.* **2009**, *114*, G01016. [[CrossRef](#)]

22. Cornelis, J.-T.; Weis, D.; Opfergelt, S.; Van Ranst, E.; Dumon, M. Past and current geochemical conditions influence silicon isotope signatures of pedogenic clay minerals at the soil profile scale, Ethiopia. *Chem. Geol.* **2019**, *524*, 174–183. [[CrossRef](#)]
23. Bayon, G.; Delvigne, C.; Ponzevera, E.; Borges, A.; Darchambeau, F.; De Deckker, P.; Lambert, T.; Monin, L.; Toucanne, S.; Andre, L. The silicon isotopic composition of fine-grained river sediments and its relation to climate and lithology. *Geochim. Cosmochim. Acta* **2018**, *229*, 147–161. [[CrossRef](#)]
24. Haque, F.; Santos, R.M.; Dutta, A.; Thimmanagari, M.; Chiang, Y.W. Co-benefits of wollastonite weathering in agriculture: CO₂ Sequestration and promoted plant growth. *ACS Omega* **2019**, *4*, 1425–1433. [[CrossRef](#)] [[PubMed](#)]
25. Chen, L.; Flynn, D.F.B.; Jing, X.; Kühn, P.; Scholten, T.; He, J.-S. A Comparison of Two Methods for Quantifying Soil Organic Carbon of Alpine Grasslands on the Tibetan Plateau. *PLoS ONE* **2015**, *10*, e0126372. [[CrossRef](#)]
26. Schulte, E.E.; Kaufmann, C.; Peter, J.B. The influence of sample size and heating time on soil weight loss-on-ignition. *Commun. Soil Sci. Plant Anal.* **1991**, *22*, 159–168. [[CrossRef](#)]
27. Tanner, S.D.; Baranov, V.I. Theory, design, and operation of a dynamic reaction cell for ICP-MS. *At. Spectrosc.* **1999**, *20*, 45–52.
28. Schönenberger, J.; Momose, T.; Wagner, B.; Leong, W.H.; Tarnawski, V.R. Canadian Field Soils I. Mineral Composition by XRD/XRF Measurements. *Int. J. Thermophys.* **2012**, *33*, 342–362. [[CrossRef](#)]
29. Madella, M.; Powers-Jones, A.; Jones, M. A Simple Method of Extraction of Opal Phytoliths from Sediments Using a Non-Toxic Heavy Liquid. *J. Archaeol. Sci.* **1998**, *25*, 801–803. [[CrossRef](#)]
30. Callahan, J. A nontoxic heavy liquid and inexpensive filters for separation of mineral grains. *J. Sediment. Res.* **1987**, *57*, 765–766. [[CrossRef](#)]
31. Wollastonite-1A Mineral Data. Available online: <http://www.webmineral.com/data/Wollastonite-1A.shtml#.XTe9uPJkjiU> (accessed on 23 July 2019).
32. Santos, R.M.; Van Audenaerde, A.; Chiang, Y.W.; Iacobescu, R.I.; Knops, P.; Van Gerven, T. Nickel Extraction from Olivine: Effect of Carbonation Pre-Treatment. *Metals* **2015**, *5*, 1620–1644. [[CrossRef](#)]
33. Bodor, M.; Santos, R.M.; Kriskova, L.; Elsen, J.; Vlad, M.; Van Gerven, T. Susceptibility of mineral phases of steel slags towards carbonation: Mineralogical, morphological and chemical assessment. *Eur. J. Mineral.* **2013**, *25*, 533–549. [[CrossRef](#)]
34. Chemtob, S.M.; Rossman, G.R.; Stebbins, J.F. Natural hydrous amorphous silica: Quantitation of network speciation and hydroxyl content by ²⁹Si MAS NMR and vibrational spectroscopy. *Am. Mineral.* **2015**, *97*, 203–211. [[CrossRef](#)]



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