

# Silicon exportation by crops alters soil mineralogy and clay fraction

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## Research Article

**Keywords:** Mineral evolution, silicon dynamic, crop cultivation, silicon exportation

**Posted Date:** March 1st, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-187973/v1>

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# Abstract

## Aims

Silicon (Si) dynamic in system controls mineral evolution. We expected that the Si exported from soil due to soybean cultivation would affect Si forms and clay minerals. The objective of this study was to evaluate Si forms in the soil-plant system in areas with different soybean cultivation times in order to respond how Si exportation affects soil mineralogy.

## Methods

Oxisols under soybean cultivation for 2, 8 and 40 years were evaluated and an adjacent area with native vegetation was used as the control treatment. The total and available Si in the soil and in the roots, aerial part of the plants and in the soybeans were evaluated, as well as the physical, chemical and mineralogical attributes of the soil.

## Results

We estimated that 12 to 15 kg/ha of Si were exported by soybean grains per cultivation. The Si exportation for 40 years decreased the available Si contents in the soil by 9%, compared to the native field. The total Si contents in the clay fraction after 40 years of cultivation were 29% lower when compared to the native field. As a consequence of the soil cultivation for 40 years, we observed a decrease in the clay content and a clay dissolution, changing the clay mineral fraction.

## Conclusions

The Si exportation by soybean grain promotes changes in particle size contents and mineral fraction of cultivated soils. Our results highlighted that Si, should be taken into account in a suitable fertilization process in agricultural lands submitted to intensive use.

## Introduction

Silicon oxide ( $\text{SiO}_2$ ) is the most abundant cation in the earth's crust. The presence of Si in terrestrial ecosystem compartments depends on environmental factors such as: climate, topography, soil source material, weathering and biotic factors (i.e. vegetation, microorganisms) as well as soil use and management (Alexandre et al. 1997; Sommer et al. 2006; Street-Perrott and Barker, 2008; Alexandre et al. 2011; White et al. 2012).

In the soil/vegetation system, minerals are the reserves of silicon (Si), represented by tectosilicates, which are resistant to weathering, called lithogenic silicates (Henriet et al. 2008) while the phyllosilicates start to control the primary source of Si for the plants because they are susceptible to rapid dissolution (Henriet et al. 2008). The total Si content in the soil depends on the mineralogy of the soil and it ranges from 5 to 470 g  $\text{kg}^{-1}$  (Mckeague and Cline, 1963). Part of the Si in the ecosystem is in the vegetable form of biopals (phytoliths). These structures are originated from plants that present the ability to store Si in their tissues. Phytoliths are formed from

monosilicic acid ( $\text{H}_4\text{SiO}_4$ ) present in the soil solution that is absorbed by the root system of vegetables and, subsequently, deposited in the inter and intracellular spaces along the leaves and stems, forming silicified structures representing phytolites (Parr and Sullivan 2005). Plants store Si in the form of phytolites in many plant tissues, especially at the end points of transpiration (Hodson et al. 2005; Schaller et al. 2013).

The Si biogeochemical cycle in the rock/soil/vegetation system determines the mineralogical evolution of these compartments (Cornelis and Delvaux 2016). The amount of Si in the compartments is also determined by human activity, for example, irrigation, and the change of native vegetation by agricultural crops (Cornelis and Delvaux 2016). In arable land, it is known that the Si cycle, as well as its magnitude in two different ways, is influenced by the export of Si from the soil by harvesting grains, which reduces the storage of relatively soluble phytolites in the topsoil (Vandevenne et al. 2012).

Phytoliths represent an important reservoir of biogenic silica in acidic soils from tropical and subtropical regions. Phytoliths are released during the degradation of organic matter in the litter horizon and later transferred to deeper horizons or evacuated by air or hydrographic route (Bartoli 1981). Studies show that the solubility of phytolites is close to that of amorphous silica, while their dissolution rates are between those of quartz and vitreous silica, with similar pH dependence. The production of phytoliths more susceptible to dissolution, in the words of Alexandre et al. (1997), may be an evolutionary response to environmental pressure, perhaps a shortage of Si, as for example in Oxisols.

In the literature, several authors have studied mineral changes due to plant growth and development. Korchagin et al. (2019) evidenced the dissolution of the clay fraction, releasing Al and forming HIMs in response to the action of eucalyptus root. Bortoluzzi et al. (2012) evidenced the loss of the clay fraction and mineral alteration in response to the extraction of K in grapevine. Low composition of 2:1 clay mineral was found in experiments involving no fertilization of potassium (K), as well as with the addition of K, when testing the absorption by vegetables (Moterle et al. 2016; 2019). Oort et al. (2016) in a 42-plot experiment in Versailles observed the partial dissolution of smectite by microdivision through the alteration of fine phyllosilicate minerals or a process of neoformation of secondary phases of Si, Al and/or Fe released by dissolution of clays in acidic medium. Studies on Si cycling had already been performed, and some of them have elucidated the plant absorption and the bioavailability of Si in soils (Blecker et al. 2006; Henriot et al. 2008), as well as the Si balance in terrestrial environments (Chadwick and Chorover 2001), however, none of them were associated to the Si exportation from commercial crops and related to soil mineralogical alteration. In this sense we expected that the Si exportation by plants play an important role in the mineral evolution of the soil, which the mechanism is still poorly understood. This information may aid the fertilization managements considering Si in new formulations, although this element is not an essential nutrient for plants.

We know that plants absorb Si from the soil solution in the form of monosilicic acid  $\text{Si}(\text{OH})_4$  (Tisdale et al. 1993). The return of Si to the soil can occur through the plant debris after death and the release of Si in the form of monosilicic acid and in the form of phytolites, structures that are rich in Si and more stable (Piperno 2006). In the Si biogeochemical cycle, if there is a change in the amounts of Si in these compartments, there may be degradation of biogenic (biopals) and inorganic (clay) silicate minerals releasing Si from the reserve compartments for more available forms of Si. There may also be a recombination of Si in coprecipitation with other elements and neoforming other clay minerals (Bortoluzzi et al. 2018). The small clay minerals, in turn, can

dissolve, as evidenced by Korchagin et al. (2019) and Bortoluzzi et al. (2012), which contributes to replenish the available Si in the soil.

The objective of this study was to evaluate if the mineral elements of the soil are affected by agricultural cultivation, discussing the Si exportation as a mechanism of mineralogical alteration. For this, we evaluated Si forms in the soil and plant system in areas with different times of soybean cultivation.

## Materials And Methods

### *Experimental place and soil classification*

The soils were collected in January 2018 in the town of Água Santa - RS (Figure 1 a), at 650 m of altitude, 28°10'37" S, 52°02'02" O. The climatic classification of the place is according to Köppen-Geiger, with an average temperature of 20.6 °C and an average annual rainfall of 1409 mm, belonging to the Atlantic Forest biome.

The soil was classified as typical Latossolo Bruno Distrófico (Oxysoil) after morphological description and classification of a soil profile located in the native field, at an altitude of 740 m, 28°16'0.408" S, 52°1'57.396" W (Figure 1), according to SBCS (2018).

The history of the studied places, reported by the owner, shows that the areas cultivated for 2 and 40 years were occupied by native forest and the area cultivated for 8 years was covered by native grassland prior to cultivation. However, before native forest, it is believed that the predominant vegetation would be the grassland. Soybean crop is grown annually in the summer season and grasses such as ryegrass or oats for grazing in the winter. There are no records of the exact rates of limestone and fertilizers used in each area annually.

Fig 1 Location of the town of Água Santa/RS, Brazil, where data were collected to perform the study (a), opening the trench for soil classification (b) and description of the soil profile located in the native field (c)

### *Collection of soil, plants and preparation of samples*

The experiment consisted of four treatments, being four areas with different times of land use (native field, 2-year soybean crop, 8-year soybean crop and 40-year soybean crop).

### *Soil collection*

Soil sampling was carried out on January 17, 2018, in all areas with different times of land use. Ten replicates were performed, each one comprising 10 subsamples collected with an auger at a depth of 0-20 cm. The experimental design was completely randomized.

### *Collection of plants*

Plant sampling was performed on the same day of soil collection and in all areas with different times of land use. Whole plants were collected, that is, aerial part together with the root. In the three cultivation areas, soybean plants were collected in the R1 stage. In the native field, the natural cover plants present in that period were collected, where grass species prevailed.

The plants were collected in order to have three replicates, being each one composed of five soybean plants and plants from the native field present in the area of 1 m<sup>2</sup>. After collection, the samples were sent to the laboratory, where the plant material was washed in a detergent solution and rinsed in distilled water to remove the detergent. The plant material was dried in a forced circulation chamber at 65 °C until constant weight, after which the root and aerial part were separated and grounded in a Willey mill. After grinding, the plant material was packed in paper bags and sent to predetermined analyzes.

### *Grain collection and sample preparation*

At the end of the soybean crop cycle, grain samples were collected from three replicates of 5 plants from each treatment. The grains were manually traced and the samples were sent to the XRF analysis.

## ***Evaluations***

### ***Soil size***

The granulometric analysis was performed on the soil samples, using the pipette method (Gee and Bauder 1986). The samples were subjected to the burning of organic matter and subsequently to chemical (NaOH 0.1 mol L<sup>-1</sup> + NaPO<sub>3</sub> 0.07 mol L<sup>-1</sup>) and mechanical (stirring for 16 h on a horizontal shaker) dispersion. Afterwards, the sand (> 0.053 mm) fractions were obtained by sieving and silt (0.002 - 0.053 mm) and clay (<0.002 mm) by pipetting.

### ***Soil density analysis***

Soil density was determined by the volumetric cylinder method, with undisturbed samples, using the mass of the dry soil divided by the volume of soil collected in the the cylinder. The density was obtained by averaging soil samples collected every 5 cm in the 0 - 20 cm layer.

### ***Chemical characterization of the soil***

The organic matter content of the soil was determined according to Embrapa (2011), where the pH and SST indices and the levels of P, K, Ca, Mg, Mn and Al were determined according to Tedesco et al. (1995).

### ***Elementary analysis by X-ray fluorescence***

The analysis of the total contents of the chemical elements was performed in the source rock, in the total fraction of the soil and in the clay fraction. The elements expressed in the form of oxides were determined using the X-ray Fluorescence (XRF) technique in the soil samples, being all of them analyzed in the form of powder pressed to 25 tons, forming tablets.

In addition, samples of undisturbed soybean plants were analyzed in the XRF with the main purpose of quantifying the Si content exported by the grains. Besides that, the contents of other chemical elements present in the grains of the crop were also verified.

The determination was made using a Bruker S2 Ranger XRF equipment, which is basically a compact Energy Dispersible X-ray spectrometer (EDX), with a 50W high-voltage maximum power generator, 50 KV voltage and power intensity, current of 2 mA, with X-ray tube of anode material (Pd - Lead). It has a XFLASH detector with 129 eV resolution and Berilio window, operation in air, He and vacuum, analyzes from Na (Sodium) to U (Uranium).

### ***Analysis of available Si in the soil***

The determination of Si in the soil was performed by colorimetry. After extraction with 0.01 mol L<sup>-1</sup> of calcium chloride, 10 g of soil were used, and 100 ml of the extracting solution were added. The reading was performed on a UV-Visible Spectrophotometer at a wavelength of 660 nm (Korndörfer et al. 2004).

### ***Available Si in the plant samples***

The Si extraction process in the plant was performed through the oxidation of the organic matter, that is, the elimination of carbon from plant tissue with hydrogen peroxide (digestion). 0.1000 g of the ground vegetable material was weighed and 3 ml of NaOH (500 g L<sup>-1</sup>) were added. The reading was performed on a Visible UV Spectrophotometer at a wavelength of 410 nm (Korndörfer et al. 2004).

### ***Analysis of phytoliths in the soil***

The separation of phytoliths in soil samples from the native field and from the area cultivated for 40 years was carried out using the method proposed by Madella (1998) for simplified extraction of phytoliths, using sodium polytungstate with a density of 2.35 g/cm<sup>3</sup>, and it was performed directly on air-dried fine textured soil. Three slides per horizon of each soil profile were examined in order to identify phytoliths in a petrographic microscope with 400 x magnification. Phytoliths were identified based on the International Code for Phytolith Nomenclature - ICPN 1.0 (Madella et al. 2005) and International Code for Phytolith Nomenclature - ICPN 2.0 (Neumann et al. 2019). The extracted phytoliths were weighed and the percentage of phytoliths present in the analyzed portion of the soil was estimated.

#### *Mineralogical characterization of soil samples*

The clay and silt fractions of the soil samples were characterized mineralogically using the X-ray diffraction equipment (XRD), available at the Centro Tecnológico de Pedras, Gemas e Jóias of Rio Grande do Sul (CT Pedras), in the city of Soledade/RS.

The detailed methodology for mineralogical analysis can be found in Bortoluzzi; Poleto (2013) and the identification keys are found in Brindley and Brown (1980). The samples must be ground beforehand.

Afterwards, they were subjected to pre-treatments that consisted of: dispersion by mechanical agitation or ultrasound; granulometric separation by sedimentation or centrifugation; the aliquots containing the representative fractions of the particle sizes of the ground material were subjected to powder XRD analysis (disoriented sample, scanned in 3-55° 2θ XRD) and in samples oriented on air-dried glass slides (XRD scan 3-55° 2θ) and after solvation in ethylene glycol (DRX scan of 3-55° 2θ) and after heating under temperatures of 150 °C , 350 °C and 550 °C in a muffle furnace (DRX scan of 3-55° 2θ).

## Statistical analysis

The results of the analysis of granulometry, soil density, organic matter, XRF, Si available in the soil and Si in the plant were subjected to analysis of variance using the F test. For the treatments that showed a significant difference, the comparison of means was performed by the Tukey test ( $p < 0.05$ ).

## Results

### *Effect of cultivation time on soil physical and chemical properties*

The area cultivated for 40 years showed 14% less clay and 25% more silt compared to the control (native field), demonstrating that the longer the soil cultivation time, the lower the clay content and the greater the silt content. There was no significant difference between the sand content from the 40-year crop area and the native field (Figure 2).

**Fig 2** Granulometry of soil from the native field, and from areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

Same letters at the top of the bars indicate that there was no significant difference for the fractions of the granulometric distribution (clay, silt and sand content) among treatments according to the Tukey test ( $P < 0.05$ )

The lowest organic matter content and the highest density of the soil were observed in the soil cultivated for 40 years (Table 1).

Table 1 - Organic matter content (OM) and soil bulk density (BD) from native field and from areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

Treatments	OM	BD
	g/kg	g/cm <sup>3</sup>
Native Field	46.12 a	1.18 b
2-year crop	46.65 a	1.20 b
8-year crop	46.28 a	1.28 b
40-year crop	42.60 b	1.36 a

\* Means followed by the same letter in the column do not differ statistically from each other, using the Tukey test at 5% of error probability.

The highest pH value and potential acidity were found in the place cultivated for 40 years. The pH of the 2 and 8-year cultivated areas and the native field showed no statistical difference. The lowest values of potential acidity were found in the native field and in the 8-year crop, consequently the highest levels of exchangeable aluminum were found in these same treatments. The levels of manganese were higher in the native field and in areas cultivated for 2 and 8 years (Figure 3).

**Fig 3** Content of pH, pH TSM, aluminum and manganese in the soil of the native field and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

\*Means followed by the same letter in the same element do not differ statistically from each other, by the Tukey test at 5% of error probability

The highest levels of P and K were found in the 8-year crop and the lowest values in the native field. The highest values of Ca and Mg were found in the 40 and 2-year crops and the lowest levels were found in the native field (Figure 4).

**Fig 4** Phosphorus, potassium, calcium and magnesium contents in the soil of the native field and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

\*Averages followed by the same letter in the same element do not differ statistically from each other, using the Tukey test at 5% of error probability.

#### *Si available in the soil and Si in the plant*

The highest levels of Si available in the soil were found in the 2-year crop, which did not differ statistically from the native field. The highest Si content in the aerial part of the plant was shown by the vegetation of the native field, as well as in the roots (Figure 5).

**Fig 5** Values of available Si in the soil and total Si in the roots and aerial part of plants from native field and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

\*Averages followed by the same letter in the same element do not differ statistically from each other, using the Tukey test at 5% of error probability

#### *Elementary analysis of soil by XRF*

The XRF analysis of the total soil fraction showed that the highest SiO<sub>2</sub> content was found in the 40-year crop, followed by the 2 and 8-year crops. The native field and the rock were the treatments with the lowest SiO<sub>2</sub> content. The highest content of Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O were also found in the rock and in the native field (Table 2).

Table 2 – XRF analysis of rock and total soil fraction from the native field and from areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

Elem.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	MnO	CaO	BaO	SO <sub>3</sub>
Treat.	%											
Rock	66.56 d	20.61 a	9.33 b	1.09 d	1.00 ns	0.68 a	0.12 d	0.11 ns	0.10 d	0.10 d	0.03 ns	0.00 d
N.F.	68.21 c	17.4 b	9.38 a	2.06 c	1.00	0.55 b	0.23 c	0.13	0.22 b	0.22 c	0.00	0.33 a
2- year	72.13 b	15.34 c	7.41 c	2.32 a	0.93	0.50 c	0.27 b	0.13	0.24 a	0.25 b	0.00	0.25 b
8- year	72.13 b	15.34 c	7.41 c	2.32 a	0.93	0.50 c	0.27 b	0.13	0.24 a	0.25 b	0.00	0.25 b
40- year	72.39 a	15.39 c	7.08 d	2.27 b	1.00	0.50 c	0.34 a	0.13	0.17 c	0.31 a	0.00	0.22 c

\* Averages followed by the same letter in the column do not differ statistically from each other, using the Tukey test at 5% of error probability.

The XRF analysis of the total soil fraction showed the highest content of CaO and P<sub>2</sub>O<sub>5</sub> in the area cultivated for 40 years, followed by the 2 and 8-year crop, while the lowest levels were found in the native field and in the rock. The contents of MgO, ZrO<sub>2</sub> and BaO showed no difference between the treatments studied (Table 2).

The XRF analysis of the clay fraction of the soil showed the highest SiO<sub>2</sub> content in the 2-year crop, followed by the native field. The areas of 8 and 40-year crop presented the lowest SiO<sub>2</sub> content. The highest levels of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> were found in the native field (Table 3).

Table 3 – XRF analysis of the clay fraction of the soil from the native field and in the areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

Elements	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	MnO
Treatment	%								
N.F.	34.76 b	25.94 a	11.46 a	1.37 c	1.50 c	0.43 c	0.00 ns	0.10 d	0.06 c
2-year	51.73 a	10.25 d	7.05 d	2.08 a	1.40 c	0.50 c	0.00	0.13 c	0.17 b
8-year	31.45 c	16.44 b	9.04 c	2.01 a	1.83 b	0.60 b	0.00	0.15 b	0.21 a
40-year	24.54 d	14.20 c	10.34 b	1.84 b	2.57 a	1.04 a	0.04	0.19 a	0.22 a
Elements	CaO	BaO	SO <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	V <sub>2</sub> O <sub>5</sub>	SrO	Nd <sub>2</sub> O <sub>3</sub>	Cl	CeO <sub>2</sub>
Treatment	%								
N.F.	23.07 c	0.00 b	0.07 d	0.00 b	0.00 b	0.06 d	0.00 b	1.02 d	0.00 ns
2-year	22.88 d	0.00 b	0.33 b	0.00 b	0.00 b	0.07 c	0.00 b	3.31 b	0.00
8-year	35.68 b	0.00 b	0.29 c	0.00 b	0.00 b	0.10 b	0.00 b	2.02 c	0.00
40-year	39.08 a	0.10 a	0.63 a	0.30 a	0.10 a	0.15 a	0.09 a	4.14 a	0.02

\* Averages followed by the same letter in the column do not differ statistically from each other in the same element, using the Tukey test at 5% of error probability; ns = Non-significant by the F test.

The XRF analysis of the clay fraction of the soil indicated that the highest contents of CaO, MgO, Cl, K<sub>2</sub>O, ZrO<sub>2</sub>, SO<sub>3</sub>, SrO, MnO, La<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, BaO and Nd<sub>2</sub>O<sub>3</sub> were found in the 40-year crop. The levels of P<sub>2</sub>O<sub>5</sub> and CeO<sub>2</sub> showed no difference among the treatments studied (Table 3).

#### *Elementary analysis of grains by XRF*

The XRF analysis of soybean plants showed the highest levels of K<sub>2</sub>O, CaO, SiO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, MnO and ZnO in the 2-year crop. The highest levels of Al<sub>2</sub>O<sub>3</sub> and BaO were present in the area of 40 years of cultivation. The contents of Na<sub>2</sub>O, MgO, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, Cl, I, CuO, Sb<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Rb<sub>2</sub>O, La<sub>2</sub>O<sub>3</sub> did not present statistical difference among the studied treatments (Table 4).

Table 4 - XRF analysis of soybean collected in the 2, 8 and 40-year cultivated areas

Elements	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	CaO	CeO <sub>2</sub>	BaO
Treatment	%										
2-year	9.13 a	3.54 b	0.49 ns	1.10 a	15.53 ns	17.18 a	3.13 ns	0.39 a	11.33 a	0.61 ab	0.30 b
8-year	9.80 a	4.56 b	0.49	1.10 a	17.70	11.69 b	3.97	0.00 b	9.80 a	0.95 a	0.00 c
40-year	5.79 b	6.44 a	0.59	0.52 b	15.67	10.56 b	2.59	0.00 b	6.85 b	0.00 b	1.15 a
Elements	SO <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	Cl	Na <sub>2</sub> O	ZnO	Cs <sub>2</sub> O	I	CuO	Sb <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub>	Rb <sub>2</sub> O
Treatment	%										
2-year	3.19 ns	0.00 ns	0.38 ns	32.87 ns	0.18 a	0.20 a	0.02 ns	0.02 ns	0.02 ns	0.00 ns	0.00 ns
8-year	2.77	0.00	0.35	36.60	0.12 b	0.03 b	0.00	0.00	0.00	0.00	0.00
40-year	2.72	2.05	0.34	39.00	0.08 c	0.09 ab	0.05	0.00	0.05	0.15	0.04

\* Means followed by the same letter in the column do not differ statistically from each other in the same element, using the Tukey test at 5% of error probability. ns = Non-significant by the F test.

### *Si balance*

In order to assess the Si contents of the plant, rock, clay fraction and soybean grains, the Si balance was performed. After 8 years of cultivation, the Si contents of the clay fraction decreased by 2 g/kg and after 40 years, these contents were reduced by 6 g/kg (Figure 6). The Si content in the dry matter seems to increase in the area cultivated for 8 years, however, after 40 years the Si content was lower, as a consequence, the Si exported by grains was around 12 to 20 kg/ha per year of cultivation, totaling a negative balance of 500 kg/ha of Si extracted from the grains in 40 years of cultivation (Figure 7).

**Fig 6** Total Si content in the plant (roots and aerial part), in the rock and in the clay fraction of the soil, in the native field, and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm

**Fig 7** Si content in the dry matter of the native field, and in areas cultivated for 2, 8 and 40 years; Si content in soybean and the estimate of Si export according to the soil cultivation time of 2, 8 and 40 years, evaluated at a depth of 0-20 cm

Note: The estimate of the dry mass production of 1200 kg/ha was used for native fields and 7945 kg/ha for soybean according to literature data. The annual soybean grain production was estimated in 3600 kg per hectare.

### *Phytolytes analysis*

Phytolytic analysis identified the presence of the morphotypes: elongate cavate, elongate sinuate, cylindrical sinuate, rectangular aerolate, rectangular nodulate and globular nodulate in the native field soil (Figure 8A) and the morphotypes: acicular, saddle, elongate smooth, bilobate, rondel, rectangular and saddle in the soil cultivated for 40 years (Figure 8B). The quantification of phytoliths determined by weighing showed that 0.63% of the native field soil and 0.36% of the cultivated soil were composed of phytoliths.

**Fig 8** Phytolith forms found in the native field soil (A) and in the area cultivated for 40 years (B). A1: Elongate cavate; A2: Elongate sinuate; A3 Elongate cavate; A4: Cylindric sinuate; A5: Rectangular aerolate; A6: Rectangular nodulate; A7: Globular nodulate. B1: Acicular; B2: Saddle; B3: Elongate smooth; B4: Bilobate; B5: Rondel; B6: Rectangular; B7: Saddle. Scale: 25  $\mu\text{m}$

### *Mineralogical soil analysis*

Mineralogical analysis of the soil demonstrates that the minerals that composed the clay fraction of the native field were muscovite ( $d=1.001\text{ nm}$ ), kaolinite ( $d=0.716\text{ nm}$ ;  $d=0.357\text{ nm}$ ;  $d=0.228\text{ nm}$ ), quartz ( $d=0.425\text{ nm}$ ;  $d=0.334\text{ nm}$ ), cristobalite ( $d=0.405\text{ nm}$ ;  $d=0.248\text{ nm}$ ;  $d=0.187\text{ nm}$ ) and calcite ( $d=0.386\text{ nm}$ ;  $d=0.302\text{ nm}$ ;  $d=0.209\text{ nm}$ ;  $d=0.191\text{ nm}$ ) (Figure 9 a).

The mineralogical analysis of the soil of the area cultivated for 2 years showed that there was no alteration of the mineralogical composition of the clay fraction when compared to the native field soil. Thus, the minerals found there were: muscovite ( $d=1.001\text{ nm}$ ), kaolinite ( $d=0.716\text{ nm}$ ;  $d=0.357\text{ nm}$ ;  $d=0.228\text{ nm}$ ), quartz ( $d=0.425\text{ nm}$ ;  $d=0.334\text{ nm}$ ), cristobalite ( $d=0.405\text{ nm}$ ;  $d=0.248\text{ nm}$ ;  $d=0.187\text{ nm}$ ) and calcite ( $d=0.386\text{ nm}$ ;  $d=0.302\text{ nm}$ ;  $d=0.209\text{ nm}$ ;  $d=0.191\text{ nm}$ ) (Figure 9 b).

Mineralogical analysis of the soil cultivated for 8 years showed that the minerals that were part of the clay fraction are muscovite ( $d=1.001\text{ nm}$ ), zeolite ( $d=0.935\text{ nm}$ ), kaolinite ( $d=0.716\text{ nm}$ ;  $d=0.357\text{ nm}$ ;  $d=0.228\text{ nm}$ ), quartz ( $d=0.425\text{ nm}$ ;  $d=0.334\text{ nm}$ ), cristobalite ( $d=0.405\text{ nm}$ ;  $d=0.248\text{ nm}$ ) and calcite ( $d=0.386\text{ nm}$ ;  $d=0.302\text{ nm}$ ;  $d=0.209\text{ nm}$ ) (Figure 9 c). The soil cultivated for 8 years showed absence of cristobalite peaks at a distance of  $d=0.187\text{ nm}$  and calcite at a distance of  $d=0.191\text{ nm}$  in relation to the native field (Figure 9 a) and 2-year crop treatments (Figure 9 b).

The mineralogical evaluation of the soil cultivated for 40 years showed that the minerals that were part of the clay fraction are kaolinite ( $d=0.716\text{ nm}$ ;  $d=0.357\text{ nm}$ ;  $d=0.228\text{ nm}$ ), quartz ( $d=0.425\text{ nm}$ ;  $d=0.334\text{ nm}$ ;  $d=0.223\text{ nm}$ ;  $d=0.213\text{ nm}$ ), cristobalite ( $d=0.405\text{ nm}$ ;  $d=0.248\text{ nm}$ ) and calcite ( $d=0.386\text{ nm}$ ;  $d=0.302\text{ nm}$ ;  $d=0.209\text{ nm}$ ) (Figure 9 d). The soil cultivated for 40 years showed an absence of muscovite peaks at a distance of  $d=1.001\text{ nm}$ , cristobalite at a distance of  $d=0.187\text{ nm}$  and calcite at a distance of  $d=0.191\text{ nm}$  in relation to the native field (Figure 9 a) and 2-year crop treatments (Figure 9 b) and absence of zeolite in relation to the treatment of 8 years of cultivation (Figure 9 c). The quartz peaks were present in greater quantity, and the peaks of distance  $d=0.223\text{ nm}$  and  $d=0.213\text{ nm}$  were only present in the soil cultivated for 40 years (Figure 9 d).

**Fig 9** X-ray diffraction of the clay fraction of the soil: a) native field; b) soil cultivated over a period of 2 years; c) soil cultivated over a period of 8 years; d) soil cultivated over a 40-year period, at a depth of 0-20 cm

The mineralogical evaluation of the samples saturated with calcium in the air-dried treatment showed that kaolinite ( $d=0.716\text{ nm}$  and  $d=0.357\text{ nm}$ ) has decreased its intensity in areas with 8 and 40 years of cultivation. The peaks of quartz ( $d=0.425\text{ nm}$  and  $d=0.334\text{ nm}$ ), cristobalite ( $d=0.405\text{ nm}$  and  $d=0.248\text{ nm}$ ) and calcite

( $d=0.209$  nm) increased their intensity in the soil cultivated for 8 and 40 years (Figure 9 a). It was not possible to observe differences in the mineralogical evaluation of the powdered soil (Figure 10 b).

**Fig 10** X-ray diffraction of the clay fraction of the soil: a) saturated with calcium and air-dried in oriented coverslips; b) powdered soil, in the native field and soil submitted to cultivation for 2, 8 and 40 years, at a depth of 0-20 cm

Figure 11 shows the X-ray diffraction patterns of the decomposed clay fraction saturated with Ca and solvated with ethylene glycol (Ca - EG). In the native field and areas of 2 and 8 years of cultivation, the peak of muscovite was present ( $d = 1.001$ ), and in the soil cultivated for 40 years, the peak of muscovite was not found. The relative proportion of diffracted intensity attributable to muscovite varied between 5.01-8.70%, while the surface area of kaolinite varied between 91.3-100% (Figure 11). In addition, the decomposition of the soil cultivated for 8 years showed the peak centered at  $d = 0.935$  nm, demonstrating that the zeolite group is present, which contributed to 0.84% of the diffracted intensity (Figure 11).

**Fig 11** Modeled X-ray diffraction patterns from the Ca-saturated clay fraction and solvated with ethylene glycol (Ca - EG): a) native field b) soil cultivated over a period of 2 years c) soil cultivated over a period of 8 years d) soil cultivated over a 40-year period, at a depth of 0-20 cm. The patterns were decomposed between  $3^\circ$  and  $14^\circ$  ( $2\theta$ ), corresponding to the (001) clay mineral peaks

The mineralogical assessment of the native field and from the soil cultivated for 2, 8 and 40 years showed that the minerals that were part of the silt fraction are basically quartz ( $d=0.425$  nm;  $d=0.334$  nm;  $d=0.245$  nm;  $d=0.228$  nm;  $d=0.223$  nm;  $d=0.213$  nm,  $d=0.197$  nm and  $d=0.182$  nm) and cristobalite ( $d=0.405$  nm), with no difference among the treatments applied and the studied soils (Figure 12 a, 12 b, 12 c and 12 d).

**Fig 12** X-ray diffraction of the silt fraction of the soil: a) native field b) soil cultivated over a period of 2 years c) soil cultivated over a period of 8 years d) soil cultivated over a 40-year period, at a depth of 0-20 cm

## Discussion

### *Effect of cultivation time on soil physical and chemical properties*

The lower clay levels found in the 8 and 40-year cultivated areas indicated that the absorption of Si by the vegetation and subsequent exportation contribute to the dissolution of minerals from the soil. The increase in silt content, resulting from the transformation of sand to silt and later to clay, demonstrates the degradation of primary minerals from lithogenic silicates, which when released can be recombinant to synthesize new-formed clay. These clay-size minerals can, in turn, dissolve and contribute to replenish the availability of Si in the soil (Mckeague and Cline 1963).

The respiration of the roots releases  $\text{CO}_2$  and forms carbonic acid, a weak acid that significantly changes the pH of the soil (Cotter-Howels and Paterson 2000). When in extreme, acidic or mainly basic pH media, their dissolution potential is significantly increased (Feth et al. 1961), these pH conditions can also favor ion co-precipitation and mineral crystallization (Bortoluzzi et al. 2019).

The pH and TSM values, as well as the levels of Al, Mn, P, K, Ca and Mg are the result of the use of limestone and fertilizers in the crops, considering that there was no application of these products in the native field. The 8-year

crop has the highest P and K content, these elements are made available quickly by soluble fertilizers. The higher levels of Ca and Mg present in areas of 2 and 40 years of cultivation, are due to the use of higher doses of agricultural fertilizers that contain these elements, as informed by the farmer.

The organic matter content of the soil decreases over the years of cultivation and, consequently, the density of the soil increases, which was expected due to the maintenance of the carbon content of native areas compared to cultivated areas, as well as the traffic of agricultural machines in tillage areas, which can increase the density of the soil.

#### *Total and available Si in the soil and Si in the plant at different times of soil cultivation*

The highest values of Si available in the soil were found in the native field and in the 2-year crop, which is why Si cycling occurs through the current natural vegetation (native field) or recent land use (2-year cultivation). The native field, being basically composed of grasses, becomes more aggressive in the absorption of Si, explaining the higher levels of Si found in the aerial part and roots of the plants from the native field, however, as there is no export outside the system, this Si returns to the soil in the form of phytoliths, which are dissolved over time and the Si can be reused (Chadwick and Chorover 2001; Blecker et al. 2006; Henriot et al. 2008). When the native field area is cultivated, the Si contents present in the vegetation return to the soil with the total senescence of the native vegetation, thus explaining the higher Si content available in the 2-year crop.

Areas cultivated for 2 and 8 years had a higher Si content in soybean plants than that cultivated for 40 years, as the levels of Si available in the soil are higher, enabling luxury consumption by the plant, through transfer from soil to the grain, demonstrating that the greater Si export by the grain, the greater the Si available in the soil.

The highest total Si content of the entire fraction of the soil was found in the 40-year crop, present in poorly soluble primary minerals such as quartz and mostly in the sand and silt fractions. The clay fraction had the lowest total Si content, demonstrating that there was dissolution of the most soluble silicate minerals and the release of Si, which was absorbed by the plants and exported by the grains. In addition, over the years, there was a reduction in the storage of phytoliths in the topsoil of 0.63 to 0.36%, which was also observed by Vandevenne et al., 2012, evidenced by the wear of phytoliths in the soil cultivated for 40 years (Fig 8B), reducing the Si content from the clay fraction.

#### *Soil mineralogy at different times of soil cultivation*

In the mineralogical evaluation of the clay fraction, the soil cultivated for 40 years showed an absence of muscovite, cristobalite, calcite and zeolite peaks in relation to the other treatments (Figure 11). In addition, quartz peaks were found in greater quantities in this area (Figure 9d). The kaolinite peaks decreased their intensity while the quartz peaks increased their magnitude over the years of cultivation (Figure 10). The silt fraction showed no difference in mineral composition between the native field and cultivated soil (Figure 12).

The increase in the presence of quartz peaks occurs in areas cultivated for 40 years, due to its compact arrangement, it has high resistance to weathering, and is therefore the most abundant mineral in soils and in the sand and silt fractions, and often in the clay fraction (Allen and Hajek 1989; Drees et al. 1989; Inda Jr. et al. 2006). Si in soils is present in several minerals, mainly crystalline silicates, such as quartz, plagioclase, feldspar, minerals rich in clay and amorphous silica (Sauer et al. 2006). The partial dissolution of minerals, such as muscovite and zeolite solubilizes structural elements like K and Al, transforming the minerals into quartz.

The kaolinite present in the studied soils reduced the intensity of its peaks over the years of cultivation, indicating small changes that can lead to its transformation to soil oxides. Kaolinite is one of the clay minerals often found in tropical and subtropical soils and is normally considered the most stable among the phyllosilicates (Allen and Hajek 1989; Dixon 1989; Luchese et al. 2001; Meurer 2000), originated from primary minerals, such as feldspars and micas, or from secondary ones, through the degradation of 2:1 clays, its occurrence being quite expressive in the clay fraction of tropical soils, such as Oxisols (Kämpf and Curi 2003; Ker 1997).

Calcite is one of the most important representatives of the carbonate group, occurring in a wide variety of soils (Allen and Hajek 1989; Schulze 1989) commonly associated with clay minerals (Moore and Reynolds Jr. 1997), calcite is present in the studied soils and the absence of the peak  $d = 0.191$  nm in soils cultivated for 8 and 40 years is due to the absorption of calcium by the cultivated plants and extraction in the grains, leading to its solubilization.

Other studies demonstrated that soil cultivation can promote changes in soil mineralogy. Grape production in an area cultivated over 40 years promotes the transformation of illite into vermiculite, induced by the lost of K in the interlayer despite fertilization practices (Bortoluzzi et al. 2012). The modification of the mineralogy, according to Bortoluzzi et al. (2019) also occurred in vineyard areas that received notable amounts of copper-based fungicides, causing metals accumulation in the soil profile together with high pH, presenting favorable conditions for the formation of copper-containing minerals in the rhizosphere.

The mineralogical evolution over time reported by Bakker et al. (2019) for different potassium treatments indicates a minimal but present influence of agronomic practices on soil mineralogy. As in the present study, it was observed that after 40 years of continuous cultivation, there was a change in the soil mineralogy, which must be monitored. Further studies with the use of fertilizer with Si should be performed in order to elucidate the Si balance in cultivated crops and its influence on soil mineralogy.

## Conclusion

We conclude that Si transfer from soil toward crop production was highlight as the major mechanism of soil mineral alteration.

Agricultural cultivation promotes an exporting process of Si via grain, which reduces the clay fraction contents, by clay mineral dissolution, altering soil mineralogy through the absence of muscovite, cristobalite, zeolite and calcite, and decreasing kaolinite proportion.

This study contributes to better understanding on Si dynamics in soils and may aid the fertilization management, emphasizing the Si restitution importance for soil and plants over time in agricultural lands.

## References

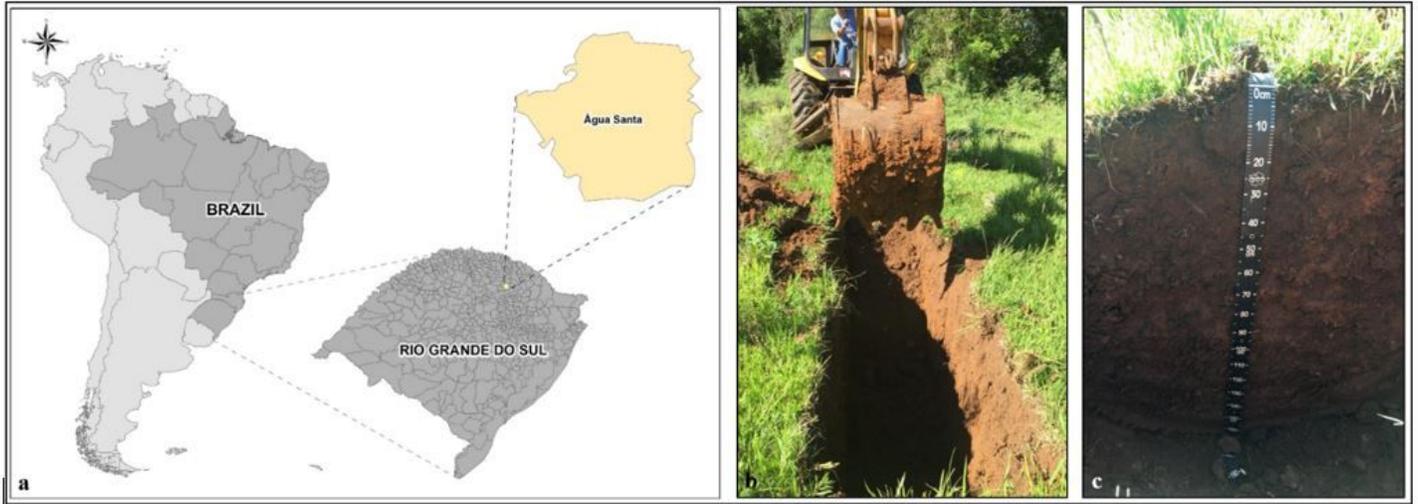
Alexandre A, Meunier JD, Colin F, Koud JM (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes. *Geochim Cosmochim Acta* 61:677-682. [https://doi.org/10.1016/S0016-7037\(97\)00001-X](https://doi.org/10.1016/S0016-7037(97)00001-X)

- Allen BI, Hajek BF (1989) Mineral Occurrence in Soil Environments. In: Dixon JB, Weed SB (ed) Minerals in Soil Environments, 2 rd edn. Soil Sci Soc Am J Madison, pp 199-278
- Alexandre A, Bouvet M, Abbadie L (2011) The role of savannas in the terrestrial Si cycle: A case-study from Lamto, Ivory Coast. *Glob Planet Change* 78:162-169. <https://doi.org/10.1016/j.gloplacha.2011.06.007>
- Bakker E, Lanson B, Findling N, Wander MM, Hubert F (2019) Mineralogical differences in a temperate cultivated soil arising from different agronomic processes and plant K-uptake. *Geoderma* 347:210-219. <https://doi.org/10.1016/j.geoderma.2019.04.010>
- Bartoli F (1981) Le cycle biogéochimique du silicium sur roche acide: Application à deux écosystèmes forestiers tempérés (Vosges). Dissertation, University of Nancy
- Blecker SW, Mcculley RL, Chadwick OA, Kelly EF (2006) Biologic cycling of silica across a grassland bioclimosequence. *Global Biogeochem Cycles* 20:GB3023 <https://doi.org/10.1029/2006gb002690>
- Bortoluzzi EC, Moterle DF, Rheinheimer DS, Casali CA, Melo GW, Brunetto G (2012) Mineralogical changes caused by grape production in a regosol from subtropical Brazilian climate. *J Soil Sediment* 12:854-862. <https://doi.org/10.1007/s11368-012-0509-x>
- Bortoluzzi EC, Poletto C (2013) Qualidade de sedimentos. In: Poletto C, Merten GH (ed) Metodologias para estudo de sedimentos: ênfase na proporção e na natureza mineralógica das partículas. 2 rd edn. ABRH, Porto Alegre, pp 35-90
- Bortoluzzi EC, Korchagin J, Moterle DF, dos Santos DR, Caner L (2019) Accumulation and Precipitation of Cu and Zn in a Centenarian Vineyard. *Soil Sci Soc Am J* <https://doi.org/10.2136/sssaj2018.09.0328>
- Brown G, Brindley GW (1980) X-ray diffraction procedures for clay mineral identification. In: Brindley GW, Brown G (ed) Crystal Structures of Clay Minerals and their X-ray Identification. Mineralogical Society, London, pp 305-361.
- Chadwick OA, Chorover J (2001) The chemistry of pedogenic thresholds. *Geoderma*, 100:321-353 [https://doi.org/10.1016/S0016-7061\(01\)00027-1](https://doi.org/10.1016/S0016-7061(01)00027-1)
- Cornelis JT, Delvaux B (2016) Soil processes drive the biological silicon feedback loop. *Funct Ecol* 30:1298-1310 <https://doi.org/10.1111/1365-2435.12704>
- Cotter-Howells JD, Paterson E. (2000) Minerals and soil development. In: Vaughan DJ, Wogelius RA (ed). *Environmental Mineralogy*. European Mineralogy Union-EMU, Eötvös University Press, pp 91-124.
- Dixon JB (1989) Kaolin and Serpentine Group Minerals. In: Dixon JB, Weed SB Minerals in Soil Environments. 2 rd edn. Soil Science Society of America, Madison , pp 467-526.
- Drees LR, Wilding LP, Smeck NE, Senkayi AL (1989) Silica in Soils: Quartz and Disordered Silica Polymorphs. In: Dixon JB, Weed SB Minerals in Soil Environments. 2 rd edn. Soil Science Society of America, Madison, pp 913-974.
- Donagema GK, Campos DVB de, Calderano SB, Teixeira WG, Viana JHM (2011) Manual de métodos de análise de solos. Embrapa Solos, Rio de Janeiro

- Feth JH, Rogers SM, Roberson CE (1961) Aqua de Ney – California: a spring of unique chemical character. *Geochim Cosmochim Acta* 22:75-77 [https://doi.org/10.1016/0016-7037\(61\)90107-7](https://doi.org/10.1016/0016-7037(61)90107-7)
- Gee GW, Bauder JW (1986) Methods of soil analysis. In: Klute, A. Particle-size analysis. 1 rd edn. American Society of Agronomy, Madison, pp 383-411.
- Henriet C, de Jaeger N, Dorel M, Opfergelt S, Delvaux B (2008) The reserve of weatherable primary silicates impacts the accumulation of biogenic silicon in volcanic ash soils. *Biogeochemistry* 90:209-223 <https://doi.org/10.1007/s10533-008-9245-0>
- Hodson MJ, White PJ, Mead A, Broadley MJ (2005) Phylogenetic variation in the silicon composition of plants. *Ann Bot* 96:1027-1046 <https://doi.org/10.1093/aob/mci255>
- Inda Jr. AV, Klamt E, Nascimento PC do (2006) Composição da Fase Sólida Mineral do Solo In: Meurer EJ (ed) *Fundamentos de Química do Solo*. 3 ed. Evangraf, Porto Alegre, pp 31-61.
- Kämpf N, Curi N (2003) Argilominerais em solos brasileiros. *Tópicos em Ciência do Solo*, Viçosa
- Ker JC (1997) Latossolos do Brasil: Uma Revisão. *Geonomos* 51:17-40. <https://doi.org/10.18285/geonomos.v5i1.187>
- Korchagin J, Bortoluzzi EC, Moterle DF, Petry C, Caner L (2019) Evidences of soil geochemistry and mineralogy changes caused by eucalyptus rhizosphere. *Catena* 175:132-143 <https://doi.org/10.1016/j.cat.2020.105744>
- Korndörfer GH, Pereira HS, Nolla A (2004) Análise de silício: solo, planta e fertilizante. GPSi/ICIAG/UFU, Uberlândia
- Luchese EB, Favero LOB, Lenzi E (2001) *Fundamentos da química do solo*. Freitas Bastos, Rio de Janeiro
- Madella M, Powers-Jones AH, Jones MK (1998) A Simple Method of Extraction of Opal Phytoliths from Sediments Using a Non-Toxic Heavy Liquid. *J Archeol Sci* 25:801-803 <https://doi.org/10.1006/jasc.1997.0226>
- Madella M, Alexandre A, Ball T (2005) International Code for Phytolith Nomenclature 1.0. *Ann Bot* 96:253-260 <https://doi.org/10.1093/aob/mci172>
- Mckeague JA, Cline MG (1963) Silica in soils. *Adv Agron* 15:339-396 [https://doi.org/10.1016/S0065-2113\(08\)60403-4](https://doi.org/10.1016/S0065-2113(08)60403-4)
- Meurer EJ (2000) *Fundamentos de Química do Solo*. Gênese, Porto Alegre
- Moore DM, Reynolds Jr. RC (1997) *X-Ray Diffraction and the Identification and Analysis of Clay Minerals*. Oxford University Press, New York
- Moterle DF, Kaminski J, Rheinheimer, D dos S, Caner L, Bortoluzzi EC (2016). Impact of potassium fertilization and potassium uptake by plants on soil clay mineral assemblage in South Brazil. *Plant Soil* 406:157-172. [doi:10.1007/s11104-016-2862-9](https://doi.org/10.1007/s11104-016-2862-9)

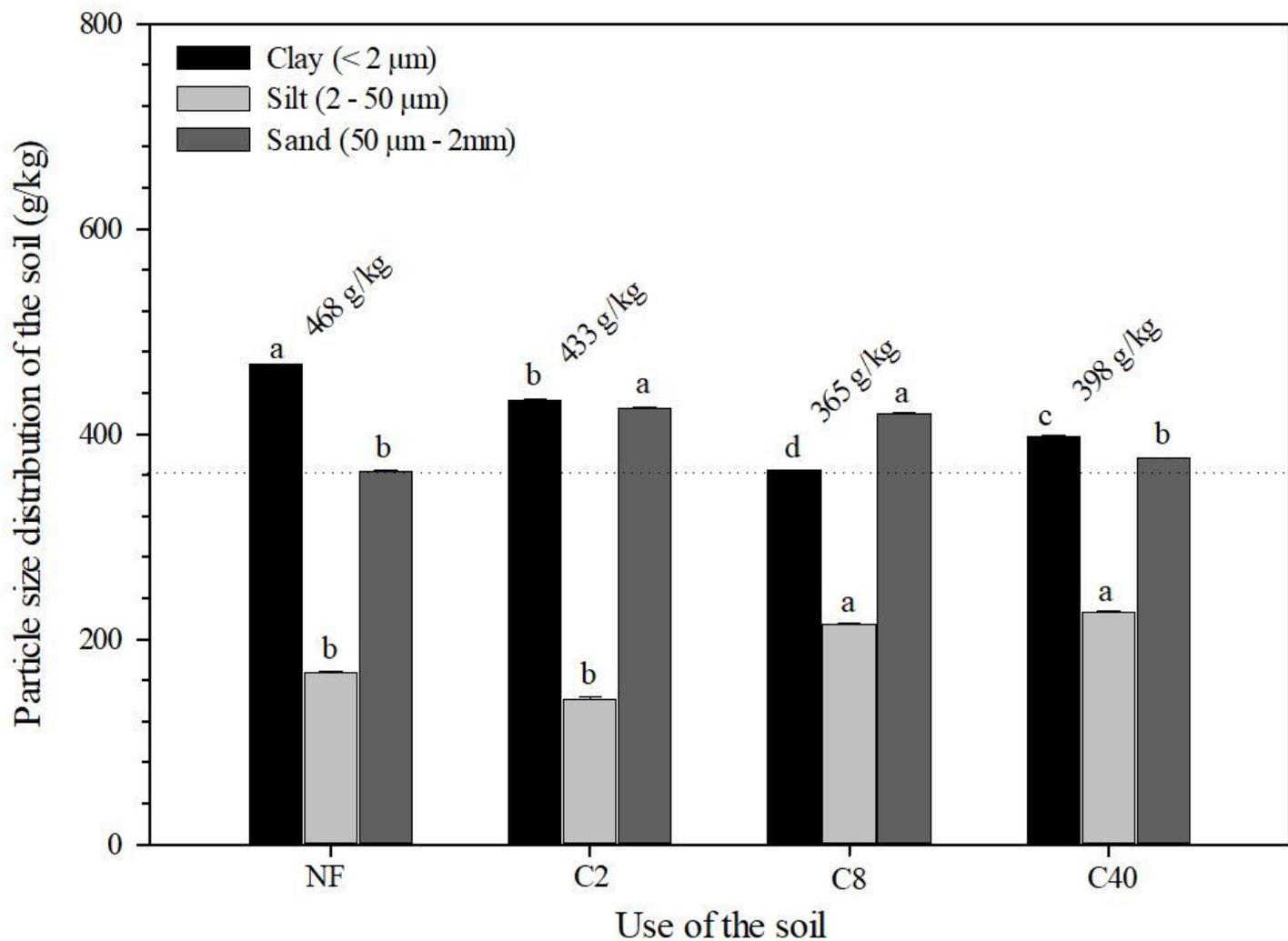
- Moterle DF, Bortoluzzi EC, Kaminski J, Rheinheimer DS, Caner L. (2019) Does Ferralsol clay mineralogy maintain potassium long-term supply to plants? *Rev Bras Cienc Solo* 43:e0180166
- Neumann K, Strömberg CAE, Ball T, Albert RM, Vrydaghs L, Cummings LS (2019) International Code for Phytolith Nomenclature (ICPN) 2.0. *Ann Bot* 124:189-199. <https://doi.org/10.1093/aob/mcz064>
- Oort V., Proix N. Paradelo, R., Delarue G., Breuil S., Baize, D. Richard, A. (2016) Indicateurs d'évolutions pédologiques infra-centenaires en Néoluvisol de loess nu, sous contrainte d'applications continues de matières fertilisantes. *Étude et Gestion des Sols* 23:143–162.
- Parr JF, Sullivan LA (2005) Soil carbon sequestration in Phytoliths. *Soil Biol Biochem* 37:117-124. <https://doi.org/10.1016/j.soilbio.2004.06.013>
- Piperno DR (2006) *Phytoliths: a comprehensive guide for archaeologists and paleoecologists*. AltaMira Press, Oxford
- Sauer D, Saccone L, Conley DJ, Herrmann L, Sommer M (2006) Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry* 80:89-108. <https://doi.org/10.1007/s10533-005-5879-3>
- Schaller J, Brackhage C, Paasch S, Brunner E, Běaucker E, Dudel EG (2013) Silica uptake from nanoparticles and silica condensation state in different tissues of *Phragmites australis*. *Sci Total Environ* 442:6-9. <https://doi.org/10.1016/j.scitotenv.2012.10.016>
- Schulze DG (1989) An Introduction to Soil Mineralogy. In: Dixon JB, Weed SB *Minerals in Soil Environments*. 2 ed., Soil Science Society of America, Madison pp. 1-34
- Santos HG dos, Jacomine PKT, Anjos LHC dos, Oliveira VA de, Lumbreras JF, Coelho MR, Almeida JA de, Araújo Filho JC de, Oliveira JB de, Cunha TJF (2018) *Sistema Brasileiro de Classificação de Solos*. Embrapa, Brasília
- Sommer M, Kaczorek D, Kuzyakov Y, Breuer J (2006) Silicon pools and fluxes in soils and landscapes-a review. *J Plant Nutr Soil Sci* 169:310-329. <https://doi.org/10.1002/jpln.200521981>
- Street-Perrott FA, Barker P (2008) Biogenic silica: a neglected component of the coupled global continental biogeochemical cycles of carbon and silicon. *Earth Surf Process Landf* 33:1436-1457. <https://doi.org/10.1002/esp.1712>
- Tedesco MJ, Gianello C, Bissani CA, Bohnen H, Volkweiss SJ (1995) *Análise de solo, plantas e outros materiais*. Departamento de Solos da Universidade Federal do Rio Grande do Sul, Porto Alegre
- Tisdale SL, Nelson WL, Beston JD, Haulin JL (1993) *Soil fertility and fertilizer*. Macmillan, New York
- Vandevenne F, Struyf E, Clymans W, Meire P (2012) Agricultural silica harvest: have humans created a new loop in the global silica cycle? *Front Ecol Environ* 10:243-248. <https://doi.org/10.1890/110046>
- White AF, Vivit DV, Schulz MS, Bullen TD, Evett RR, Agarwal J (2012) Biogenic and pedogenic controls on Si distributions and cycling in grasslands of the Santa Cruz soil chronosequence, California. *Geochim Cosmochim Acta* 94:72-94. <https://doi.org/10.1016/j.gca.2012.06.009>

# Figures



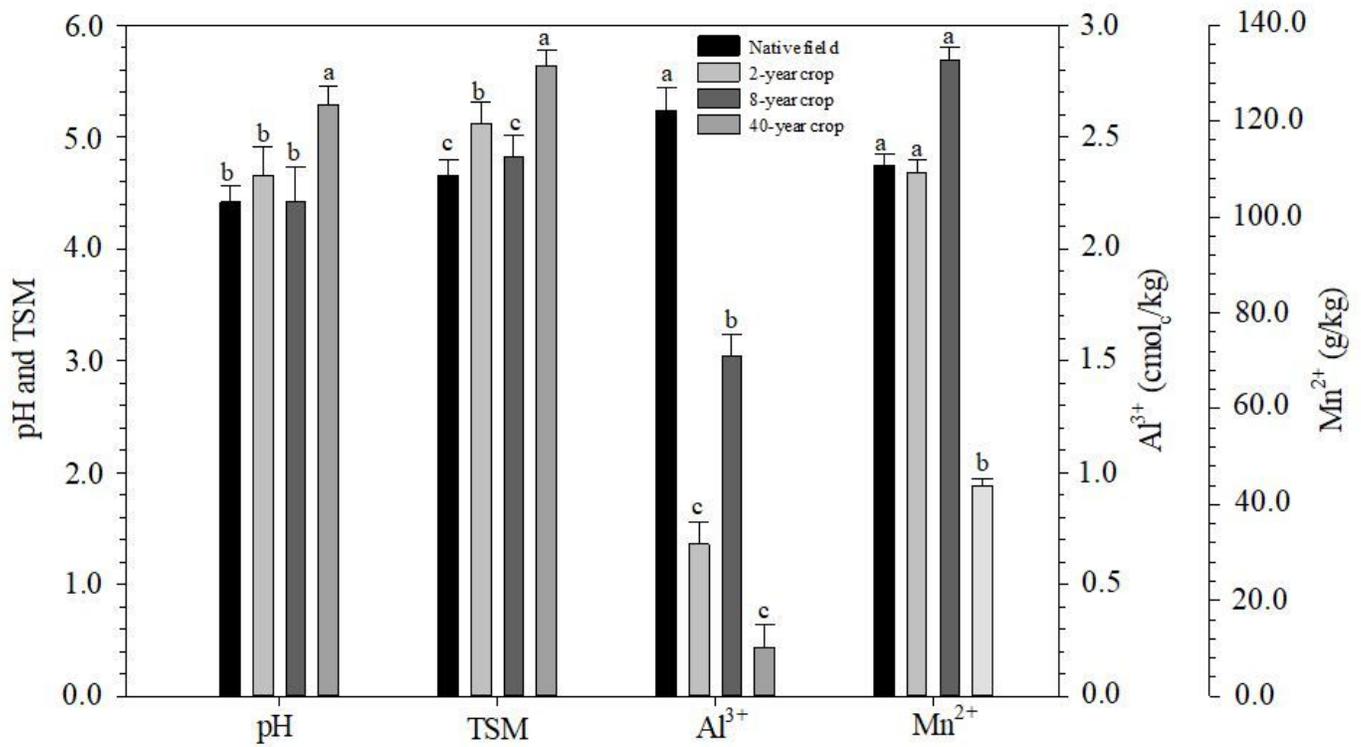
**Figure 1**

Location of the town of Água Santa/RS, Brazil, where data were collected to perform the study (a), opening the trench for soil classification (b) and description of the soil profile located in the native field (c)



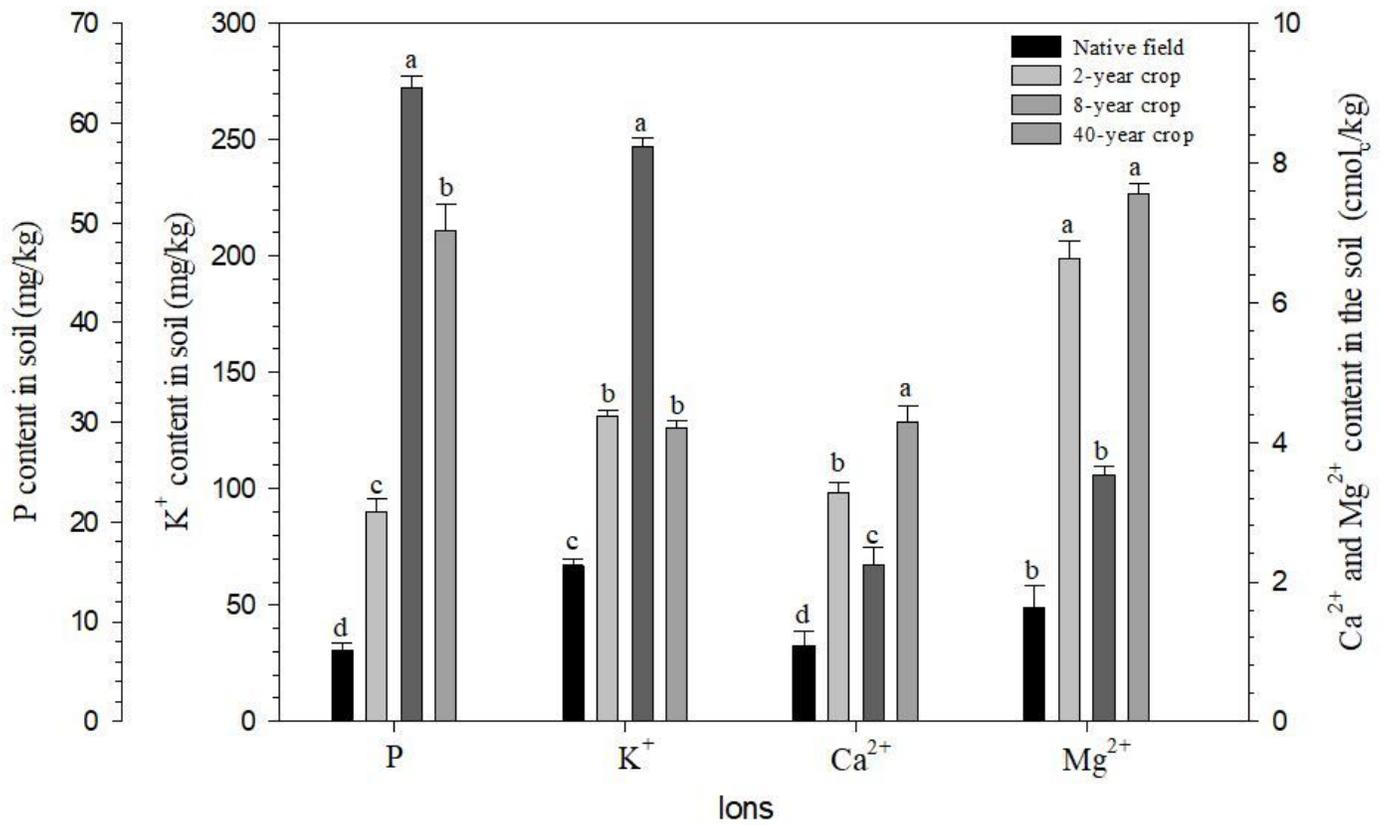
**Figure 2**

Granulometry of soil from the native field, and from areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm. Same letters at the top of the bars indicate that there was no significant difference for the fractions of the granulometric distribution (clay, silt and sand content) among treatments according to the Tukey test ( $P < 0.05$ ).



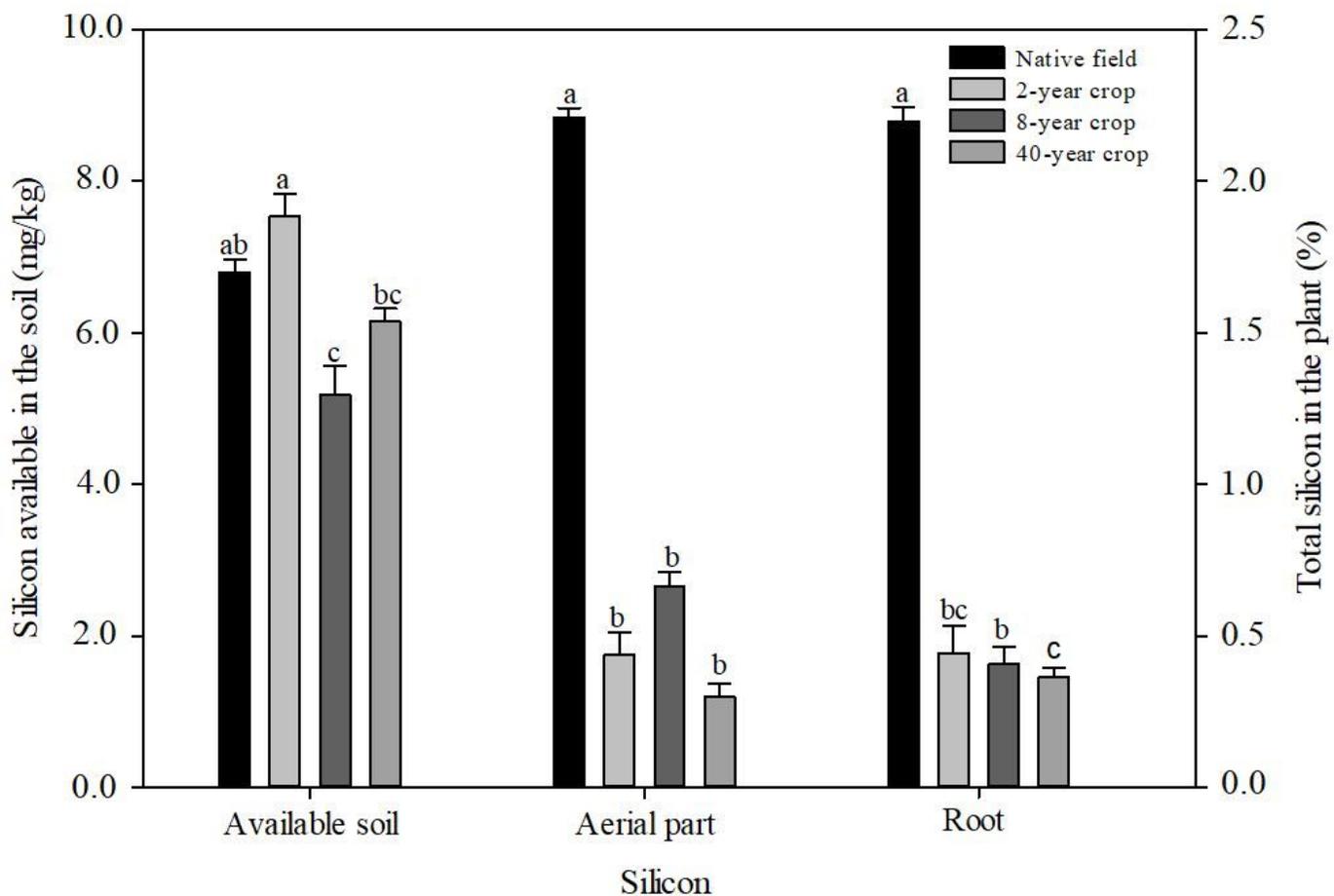
**Figure 3**

Content of pH, pH TSM, aluminum and manganese in the soil of the native field and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm \*Means followed by the same letter in the same element do not differ statistically from each other, by the Tukey test at 5% of error probability



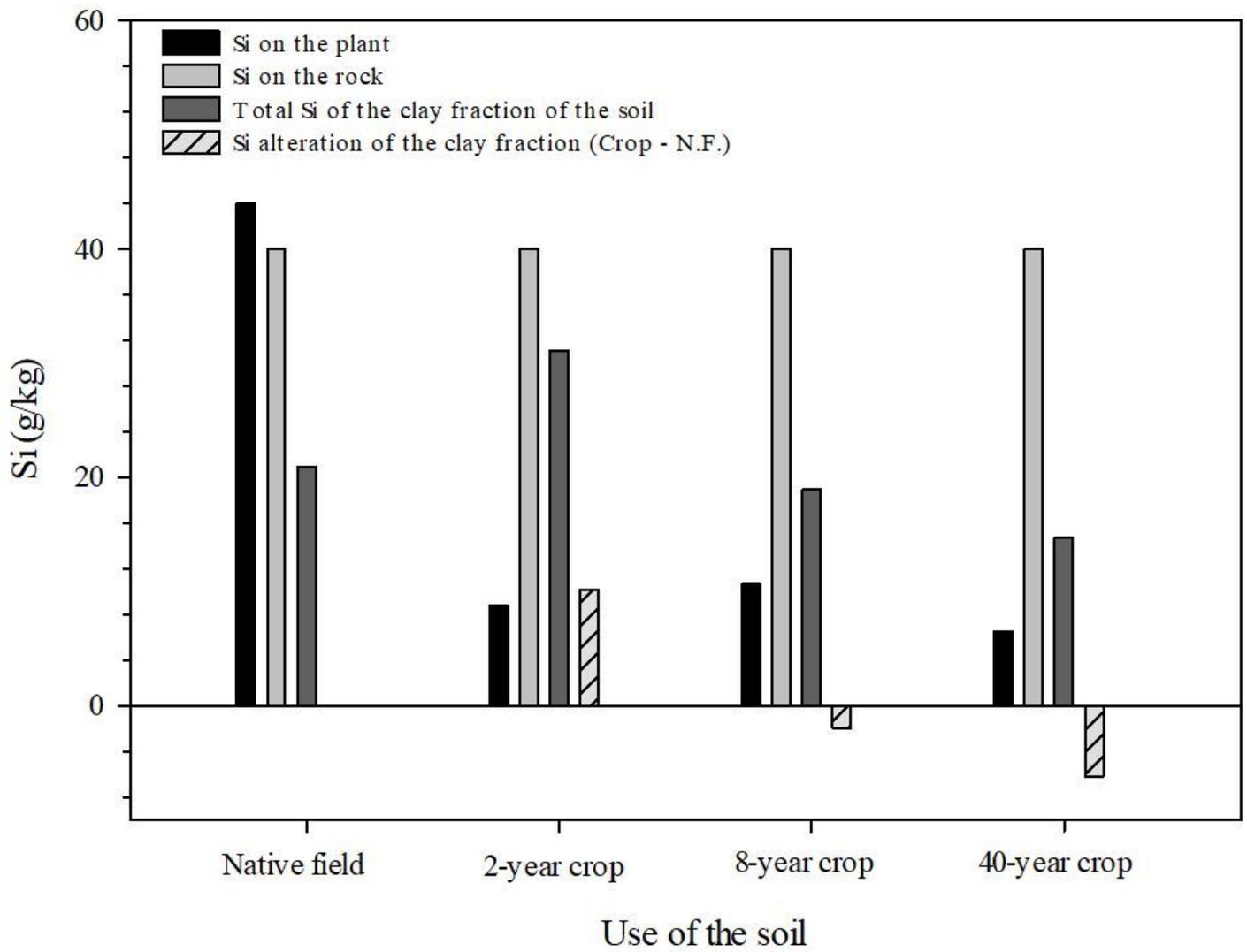
**Figure 4**

Phosphorus, potassium, calcium and magnesium contents in the soil of the native field and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm \*Averages followed by the same letter in the same element do not differ statistically from each other, using the Tukey test at 5% of error probability.



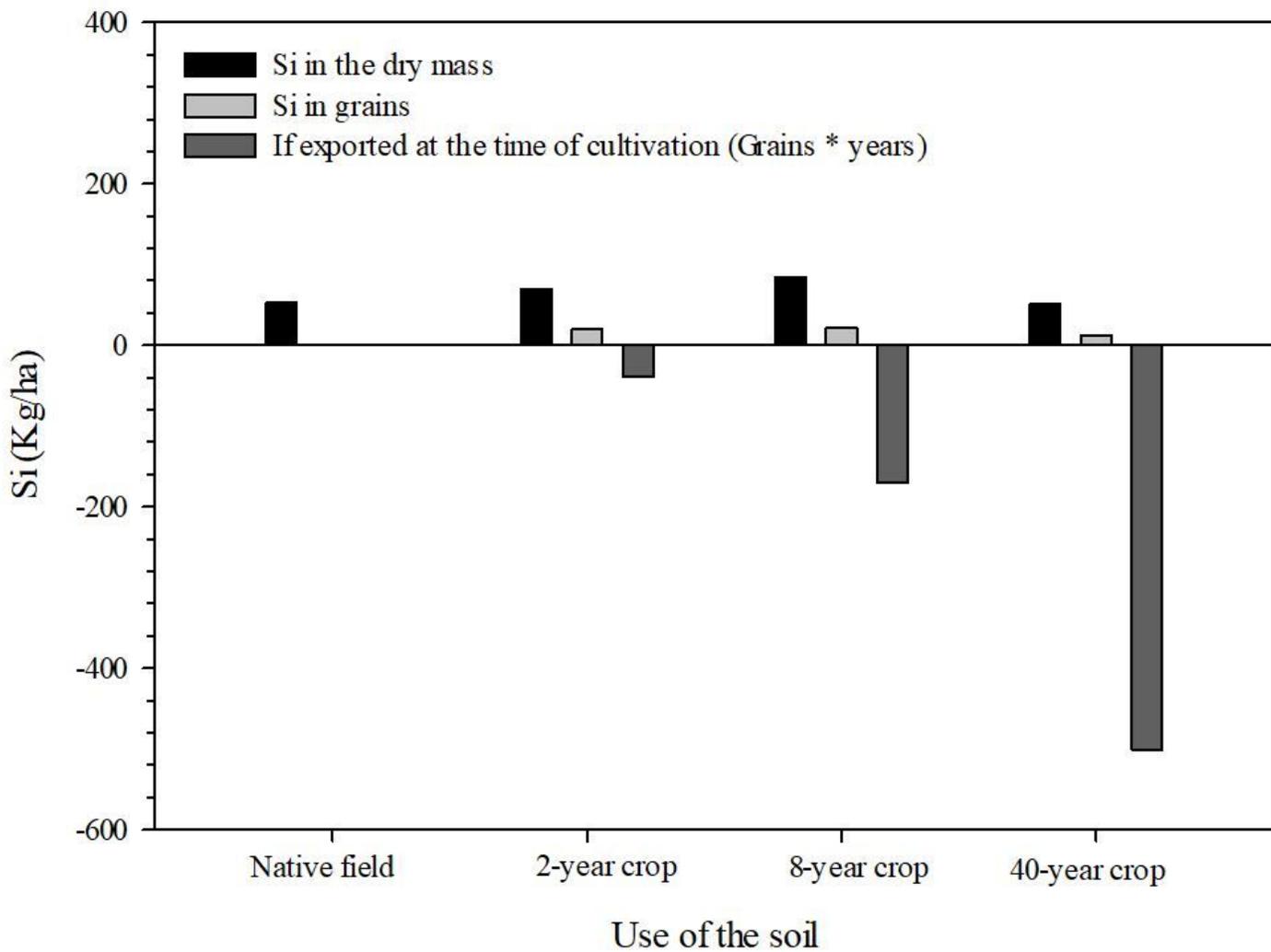
**Figure 5**

Values of available Si in the soil and total Si in the roots and aerial part of plants from native field and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm \*Averages followed by the same letter in the same element do not differ statistically from each other, using the Tukey test at 5% of error probability



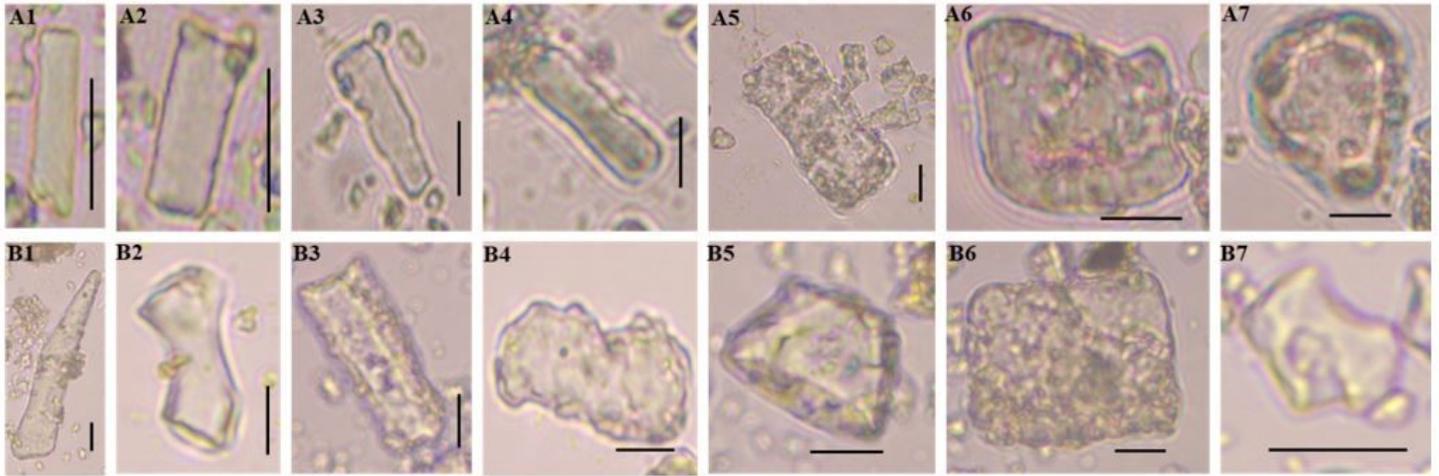
**Figure 6**

Total Si content in the plant (roots and aerial part), in the rock and in the clay fraction of the soil, in the native field, and in areas cultivated for 2, 8 and 40 years, evaluated at a depth of 0-20 cm



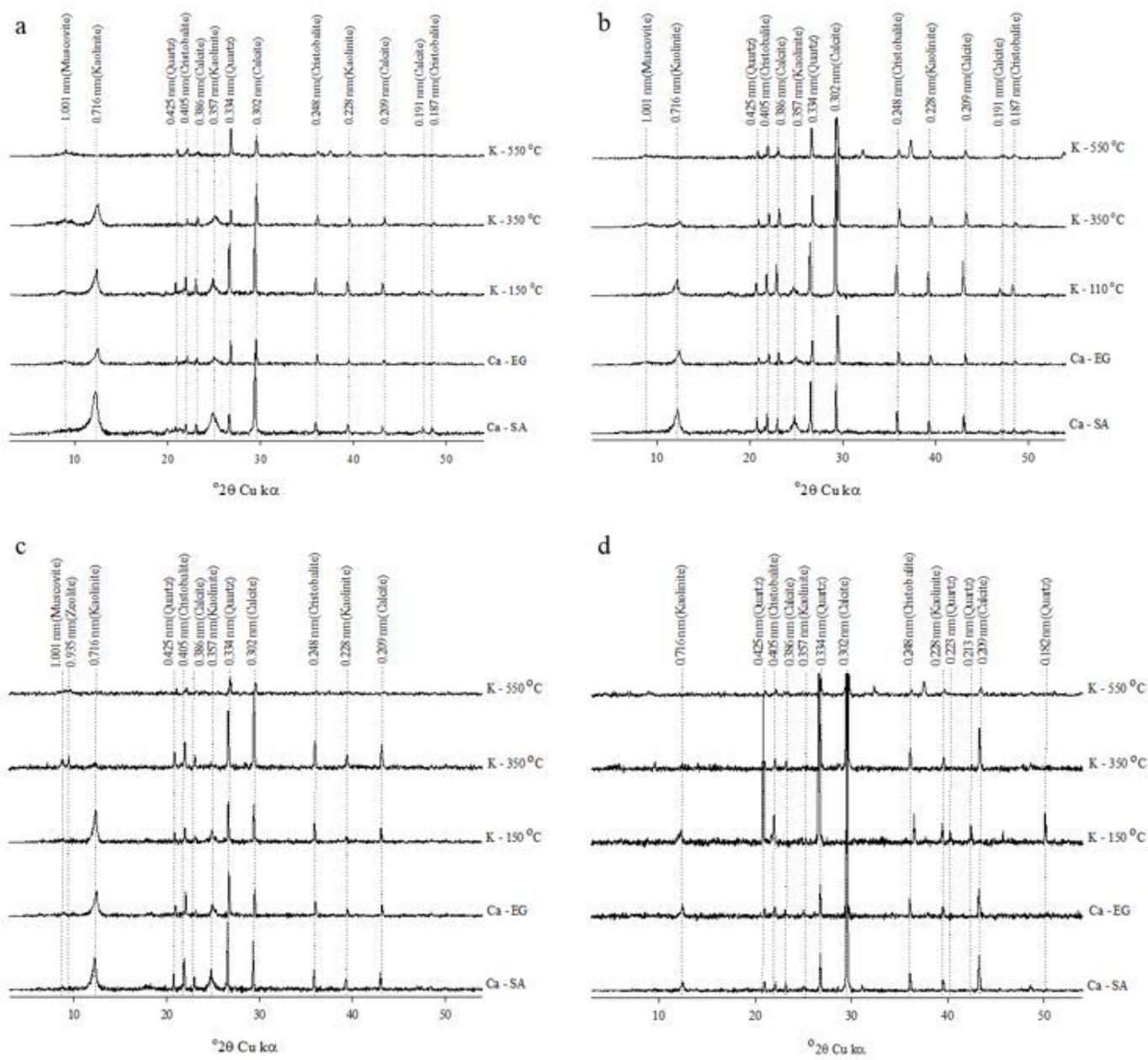
**Figure 7**

Si content in the dry matter of the native field, and in areas cultivated for 2, 8 and 40 years; Si content in soybean and the estimate of Si export according to the soil cultivation time of 2, 8 and 40 years, evaluated at a depth of 0-20 cm Note: The estimate of the dry mass production of 1200 kg/ha was used for native fields and 7945 kg/ha for soybean according to literature data. The annual soybean grain production was estimated in 3600 kg per hectare.



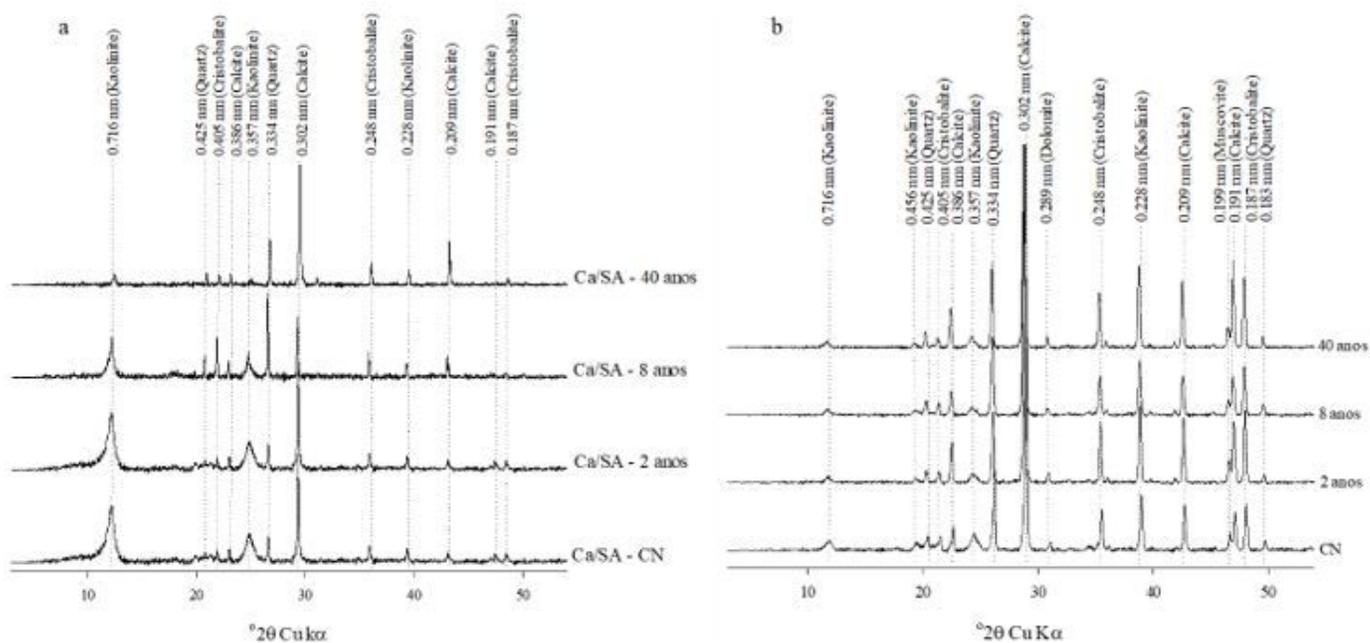
**Figure 8**

Phytolith forms found in the native field soil (A) and in the area cultivated for 40 years (B). A1: Elongate cavate; A2: Elongate sinuate; A3 Elongate cavate; A4: Cylindric sinuate; A5: Rectangular aerolate; A6: Rectangular nodulate; A7: Globular nodulate. B1: Acicular; B2: Saddle; B3: Elongate smooth; B4: Bilobate; B5: Rondel; B6: Rectangular; B7: Saddle. Scale: 25  $\mu$ m



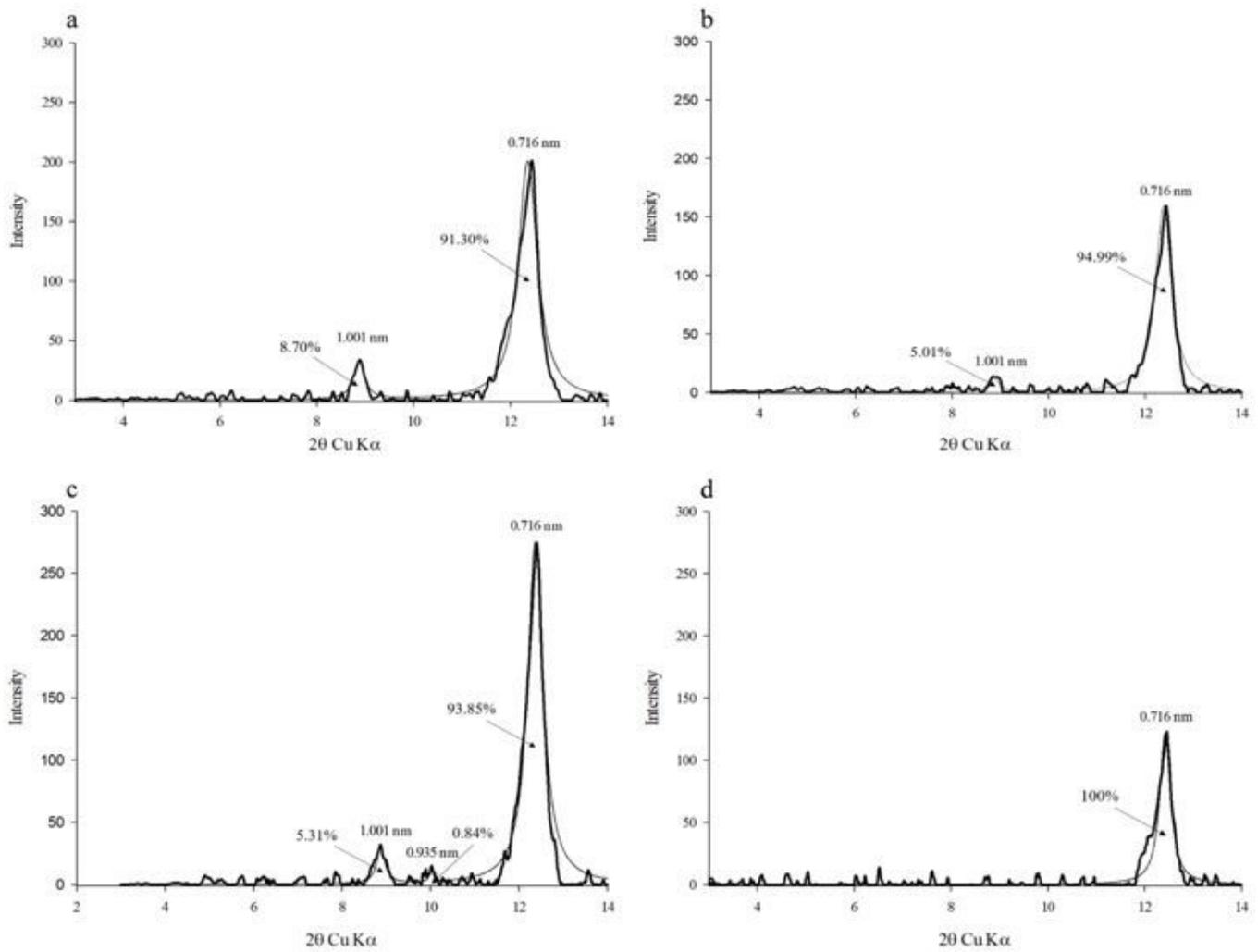
**Figure 9**

X-ray diffraction of the clay fraction of the soil: a) native field; b) soil cultivated over a period of 2 years; c) soil cultivated over a period of 8 years; d) soil cultivated over a 40-year period, at a depth of 0-20 cm



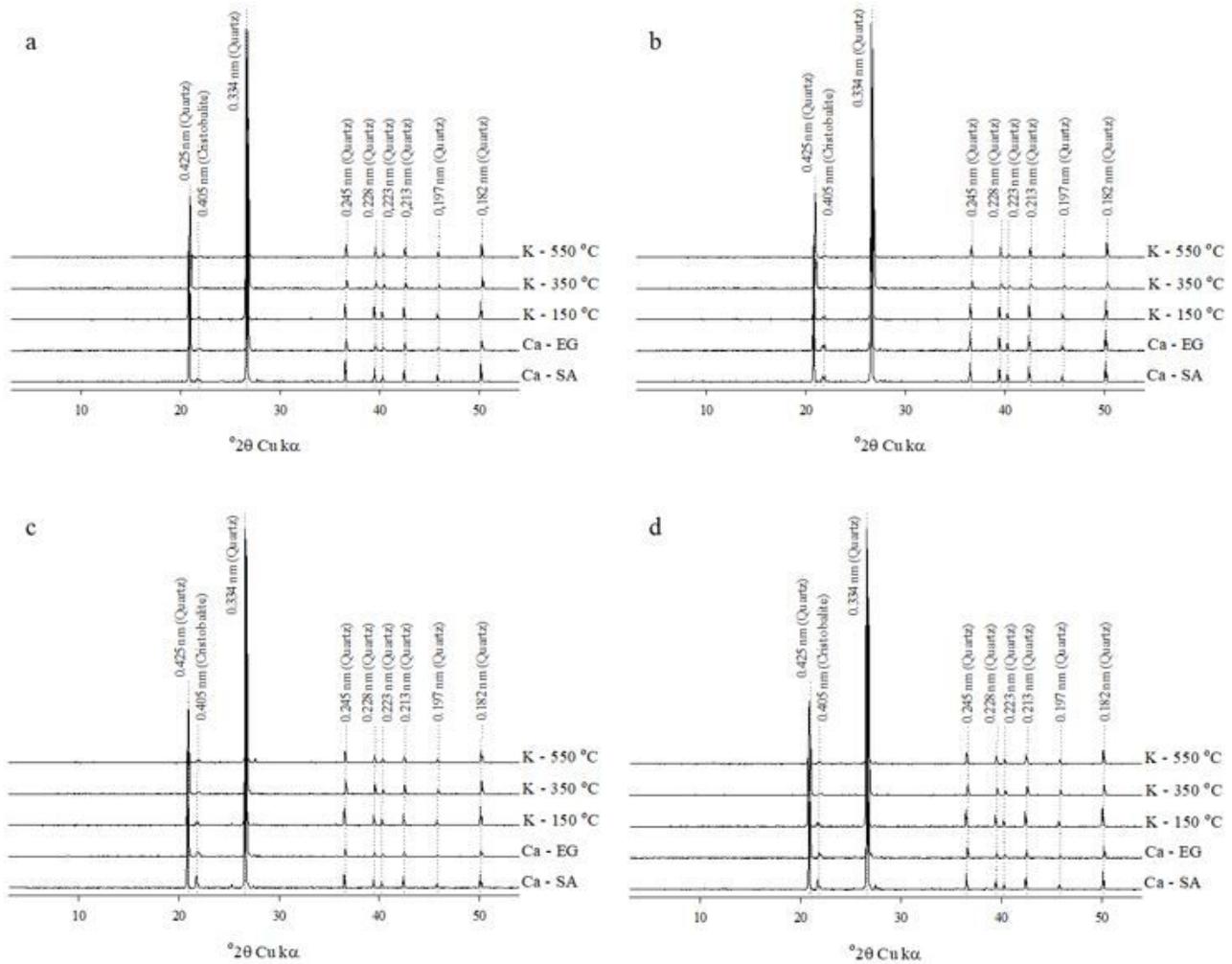
**Figure 10**

X-ray diffraction of the clay fraction of the soil: a) saturated with calcium and air-dried in oriented coverslips; b) powdered soil, in the native field and soil submitted to cultivation for 2, 8 and 40 years, at a depth of 0-20 cm



**Figure 11**

Modeled X-ray diffraction patterns from the Ca-saturated clay fraction and solvated with ethylene glycol (Ca - EG): a) native field b) soil cultivated over a period of 2 years c) soil cultivated over a period of 8 years d) soil cultivated over a 40-year period, at a depth of 0-20 cm. The patterns were decomposed between  $3^\circ$  and  $14^\circ$  ( $2\theta$ ), corresponding to the (001) clay mineral peaks



**Figure 12**

X-ray diffraction of the silt fraction of the soil: a) native field b) soil cultivated over a period of 2 years c) soil cultivated over a period of 8 years d) soil cultivated over a 40-year period, at a depth of 0-20 cm