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Multivariate Analysis with XRD Data as a Fingerprinting Technique to Study Burned Soils

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Abstract: Fire is a natural process with recognized recurrence. However, ongoing climate change and human activities are causing some disturbances in their natural regimes in most ecosystems. It is important to improve the methodologies used to evaluate the fire-induced changes in soils. This study aims at investigating the potential of the X-ray diffraction (XRD) technique to be used as a fingerprinting technique for burned soils. Multivariate analysis was employed to analyze the XRD data. Hierarchical Cluster Analysis (HCA) and local Partial Least Squares (PLS-2) models were performed. The soil samples are classified as Ferralsols and were collected from an Amazon region, Brazil, from forests, pastures and a slash-and-burn area. The studied temperatures ranged between 25 and 800 °C. Major differences were found for gibbsite, goethite and kaolinite contents due to dehydration. PLS-2 analysis presented better results than HCA as it provided information concerning the two features of the investigated soils, the collection site and the temperature. Therefore, it was possible to characterize soils from different sites and soils heated at different temperatures by using XRD data with multivariate analysis. Such methodology provided important information that may be used in areas with these environmental and soil conditions.

Keywords: X-ray diffraction; multivariate analysis; burning simulation; ferralsol

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1. Introduction

Fire is a natural process on Earth with recognized recurrency, resulting in fire regimes that have direct ecological effects and that act as selective forces for species. Fire regimes are important for multiple levels of biological organization, influencing populations, communities and ecosystems [1]. However, the ongoing climate change and human activities are causing some disturbances in the natural fire regimes in most ecosystems.

Many burnings are planned by people and employed as a management tool for agricultural purposes, e.g., clearings for shifting cultivation [2]. Prescribed fires are also performed to reduce fuel levels, aiming to minimizing the extent and severity of wildfires. Wildfires can start accidentally or by negligence (e.g., unattended campfires, discarded cigarettes) and the results are catastrophic when occurring in the presence of an abundant and dry fuel load [3].

Soil mineralogy may change when soil is burned both at low and high intensities, but mainly when fire is severe and reaches high temperatures and long durations. These changes are correlated with soil characteristics and can be short term, long term or permanent in nature [4]. The mineralogy of the clay fraction may be modified by heating, forming

more stable aggregates [5]. In addition, the cation exchange capacity may be affected by the transformation of clay minerals at high temperatures (>500 °C) [6].

It is important to improve the ability of estimating the fire-induced changes in soils and to develop inference methodologies to assess how soils are likely to respond to prescribed fires and wildfires. X-ray diffraction (XRD) in the Bragg–Brentano geometry may be employed as a fingerprinting technique to identify soil mineralogical changes induced by fire. Although the XRD technique allows the quantification of crystalline phases, for example, through the refinement of Rietveld structures, it was decided in this work to explore the basic but notable qualitative characteristics of XRD data. The correlation between the relative intensities makes the analysis of diffraction patterns simpler and friendlier to computational routines.

As the intensity of the XRD peaks were used to perform the analysis, and not the whole profile fitting with the Rietveld method, there may be some errors associated with the software in calculating the peak heights. In addition, the soil samples had complex matrices that should also be carefully considered in the results.

The relative intensities of the peaks of the different crystalline phases were correlated in order to develop a multivariate analysis as Hierarchical Cluster Analysis (HCA), Principal Component Analysis (PCA) and/or Partial Least Squares regression (PLS) that can be good tools for environmental and soil sciences [7]. Multivariate analysis consists of applying statistical procedures for the analysis of data that involve more than one variable. Large datasets may contain hidden structures, and multivariate analysis provides its decomposition in simpler components. Such processes allow the building of prediction models for different soil features [8].

Physical, chemical and mineralogical characterization from Amazon soils was performed by Souza et al., [9]. The authors carried out a laboratory analysis and XRD measurements with Latosols, Argisols, Nitosols, Plintosols, Neosols, Gleisols and Cambisols heated at different temperatures (25, 300 and 500 °C). The predominant minerals found in clay fractions were kaolinite, gibbsite, illite, chlorite and muscovite. Multivariate analysis with HCA and PCA were also performed to differentiate the soils according to their features. The authors claimed that there is still a need for research to be carried out in the Amazon region due to the high level of soil heterogeneity. Thermal alterations in soil mineralogy were also studied with XRD by Araya et al. [10]. The temperatures investigated (150, 250, 350, 450, 550, 650 °C) were previously reported in studies about prescribed fires and wildfires. The researchers identified important thresholds for major changes in soil mineralogy that are influenced by heating temperatures as the volatilization and transformation of some compounds.

Although there are studies about soil minerals and physical–chemical properties using XRD, there is still a lack of research concerning soil temperature and fire effects by using such a technique. An accurate quantification of minerals in soil samples is a long-standing problem in soil science. The good results obtained with XRD techniques on oxide mixtures and on soil samples of different compositions confirm the usefulness of the profile-matching mode for mineral quantification in soils. The Rietveld quantitative analysis applied to soil samples provides lower errors than those obtained by the classical method XRD (without requiring laborious sample pre-treatments) [11]. However, the presence of amorphous soil phases in burned soils must be taken into consideration to determine the percentage of soil minerals.

This study aimed at performing a simpler methodology, an exploratory investigation of burned soils using the XRD peaks and multivariate analysis. The potential of the XRD technique to be used as a fingerprinting technique for burned soils under controlled heating was studied. HCA and local PLS-2 models were developed with samples from the Amazon region, Brazil. Multivariate analysis was employed to investigate the burning effects in soil mineralogy.

2. Materials and Methods

Soil samples were collected from the Igarapé Bom Futuro basin in the Amazonian region at Porto Velho, Rondônia, Brazil (Figure 1). The soil is classified as Ferralsol [12], with a loam texture. Predominant vegetation is open ombrophilous forest and the mean annual precipitation is 2100 mm. Five different sites were studied: two forests (F), two pastures (P) and one slash-and-burn (SB) site. Due to some collecting difficulties (private area accessing, local conflicts, etc.), samples from 5 to 6 points in each site were collected and homogenized to obtain one composite sample per site. Samples were collected from 0 to 5 cm depth of mineral horizon.

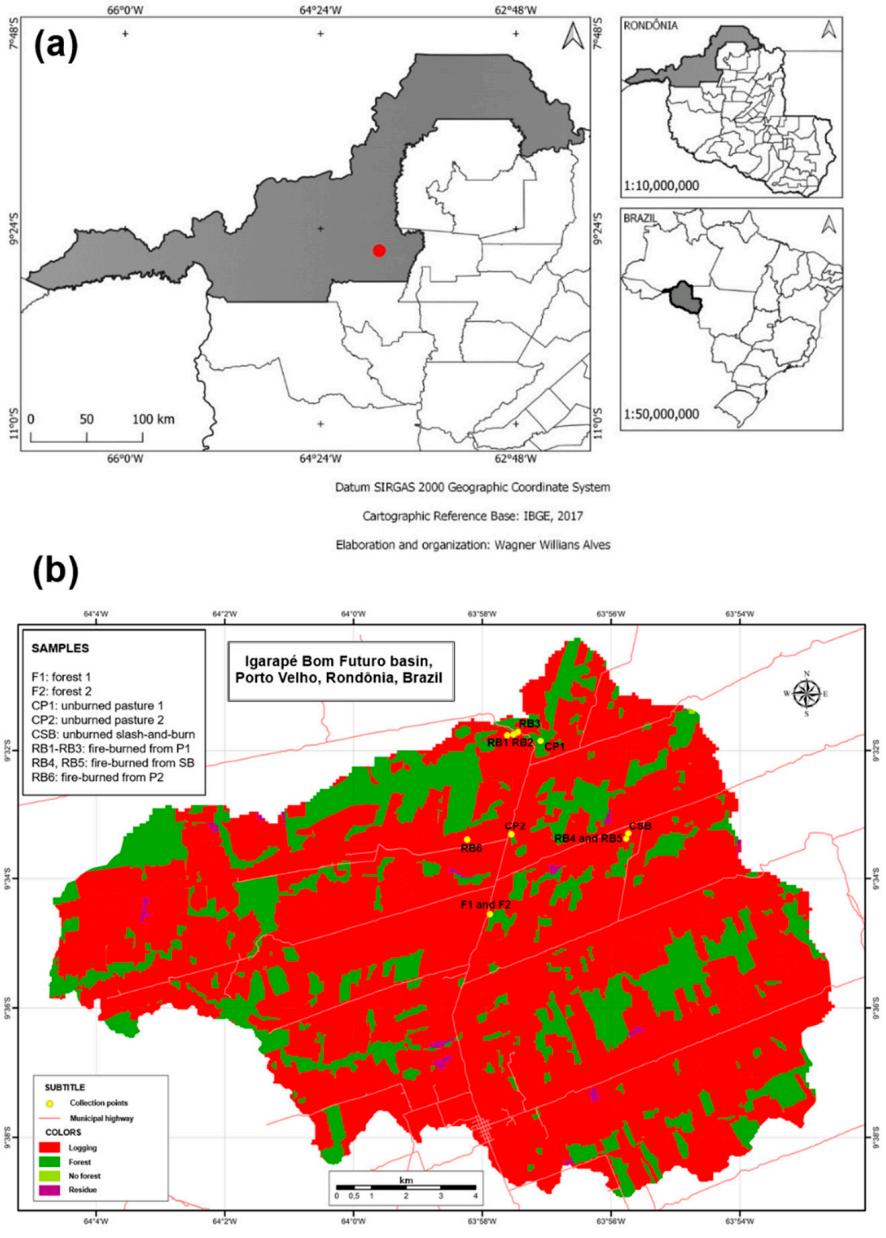

Figure 1. Study area at Rondônia, Brazil. F1—forest 1, F2—forest 2, P1—pasture 1, P2—pasture 2, SB—slash-and-burn. (**a**) Location of the studied area and (**b**) sampling points.

Prior to heating, samples were left to air dry at room temperature for 24 h, then grounded and sieved to grain size < 125 µm in order to obtain homogeneous samples. Simulated burning inside a muffle was performed to characterize mineralogical changes in the soil due to heating [13]. Temperature levels studied were 25 (no heating), 250, 400, 530, 600 and 800 °C. Approximately 5.0 g of sample was heated in a porcelain capsule, from

40 °C to the temperature peak, remaining for 20 min at this temperature. Then, the sample was left to cool outside the muffle.

After the heating treatments, the total number of analyzed samples was 30 (5 sites × 6 temperatures). For XRD measurements, the equipment employed was the PANalytical diffractometer model X'Pert PRO MPD (X'Pert PRO MPD, PANalytical, Almelo, The Netherlands) with CuKα radiation, Bragg–Brentano geometry. The voltage and current employed were 40 kV and 30 mA, respectively. The 2θ scanning interval ranged from 5° to 120°, angular step of 0.05° and 3.0 s counting time per point. Samples were rotated cyclically during the measurement for a period of 1.0 s.The qualitative mineralogical phase analysis was performed with HighScore Plus 3.0 software (Plus 3.0, PANalytical, Almelo, The Netherlands). Determining crystalline mineral phases is a matching peak process with diffraction patterns of minerals that are already in the software library. Such diffraction patterns have specific 2θ angles for each crystalline phase peak, with the respective intensity (%) that should appear in the diffraction pattern. Peaks with 100% intensity should be higher than 70% intensity peaks, since the preferred orientation can be discarded (small grain diameter). It is a good way to know whether the observed peak is derived from such a phase or whether it may be a superposition of other peaks. If the 70% peak appears, but not the 100% peak, it means that the sample does not contain such minerals.

To quantify the predominant crystalline phases and to certify their presence, a Rietveld refinement of crystalline structures was performed in the samples without heat treatment. The refinement was performed with the help of the High Score Plus software (Plus 3.0, PANalytical, Almelo, The Netherlands).

Table 1 presents some 2θ angles for crystalline phases studied with their respective peak intensities.

Table 1. Some crystalline mineral phase peaks and the intensity in which they appear in the XRD patterns. Data obtained from HighScore Plus 3.0 library. There are more peaks that are not presented here because they have lower intensities.

Crystalline Phase	Peak (2θ)	Intensity in the XRD Pattern (%)
Hematite	33.153	100
	35.612	70
	49.480	40
	54.091	45
Quartz	20.860	16
	26.640	100
	50.139	13
Kaolinite	12.457	100
	20.119	60
	24.993	100
Gibbsite	18.289	100
	20.300	70
Anatase	25.271	100
	47.980	23.7
Goethite	21.240	100
	36.658	61.9

The diffraction patterns were visually analyzed (as some small horizontal shifts can occur between different samples) and the maximum value of counts for each peak was registered in a data matrix. Therefore, the multivariate analysis was not performed with the full XRD patterns but with the main peaks' intensity values (maximum counts). The data matrix was constituted by 30 rows (samples) per 13 columns with the peaks' intensity values (variables). Full data may be accessed in the Supplemental Material. Multivariate

analysis was performed with R software [14] using ad hoc functions adapted from pls package [15].

2.1. Hierarchical Cluster Analysis

A Hierarchical Cluster Analysis (HCA) was performed with XRD data in order to examine the degree of association between the samples. Also known by cluster analysis, it is a statistical method for processing data. Such analysis is an unsupervised learning algorithm that works by organizing items into groups (clusters), considering how close they are to each other by calculating the Euclidean or Mahalanobis distance between them [16]. The analysis was performed using Matlab (R2009a, MathWorks, Inc., Portola Valley, CA, USA) (Ward's method, Euclidean distance). Data were autoscaled before running the HCA.

2.2. Partial Least Squares Analysis

To assess the interrelationships between the variables, we create two groups (henceforth, bold letters represent matrices): one with the intensities of the XRD peaks (**X**) and the other with the collection sites and the temperatures of heating (**Y**). Then, the relationship between variables was performed by multivariate Partial Least Square (PLS-2) analysis [17–19].

Variables within components were entered in a PLS model using a backward method. The final model had the lowest number of components with a similar explained variance of significant variables among models by monitoring the equivalent Root Mean Square error (RMS):

$$RMS = \sqrt{\sum_{i}^{n} \frac{(\hat{y}_i - y_i)^2}{n}} \quad (1)$$

where $(\hat{y}_i - y_i)$ was the difference between predicted and true value, and n the number of predictions [20]. The PLS-2 multivariate response model allowed high explained variances of both explanatory and result variables, as determined by R^2_X and R^2_Y fractions, respectively. A model with both R^2_X and R^2_Y values > 0.6 is considered acceptable to study associations between variables. A Variable Importance in the Projection (VIP) value ≥ 0.8 in at least one component and time point was considered a cutoff for entering significant variables (XRD peaks) in the PLS model [21]. The VIP values were computed as:

$$VIP_j = \sqrt{p\left(\frac{\sum_{k=1}^{h} SS(b_k \boldsymbol{t}_k)\left(\frac{\boldsymbol{w}_{jk}}{||\boldsymbol{w}_k||}\right)^2}{\sum_{k=1}^{h} SS(b_k \boldsymbol{t}_k)}\right)} \quad (2)$$

where $SS(b_k t_k) = b_k^2 t_k^t t_k$ is a fraction of variance in **Y** explained by the component k; p is the number of predictors (XRD peaks); h is the number of columns of **X** (XRD data matrix, i.e., mineral information); w_{kj} is the weight of the jth predictor variable in the component k; t_k, w_k and b_k are the kth column vectors of **T** (**X** scores in the **X** decomposition), **W** (the weight matrix in the NIPALS algorithm that relates the **X** matrix with the t_k components) and **B** (the vector that explains the relation between **Y** and the components $\mathbf{t}_k$), respectively. Explanatory (**X**) and result variables (**Y**) were visualized on correlation circles using their correlations with PLS components.

3. Results

The oxides hematite (Fe_2O_3) and anatase (TiO_2), the hydroxide goethite (FeO(OH)) and the silicates quartz (SiO_2) and kaolinite ($Al_2(OH)_4Si_2O_5$) were the crystalline mineral phases detected in unheated samples F1, F2, P2 and SB. In the unheated sample P1, the hydroxide gibbsite ($Al(OH)_3$) was detected as well as the silicates quartz and kaolinite. These minerals are commonly detected in Brazilian Ferralsols according to the literature [22].

Figure 2 presents the F2 unheated sample refined by the Rietveld procedure. The dominant crystallographic phases are quartz and kaolinite, shown in red and blue, respectively.

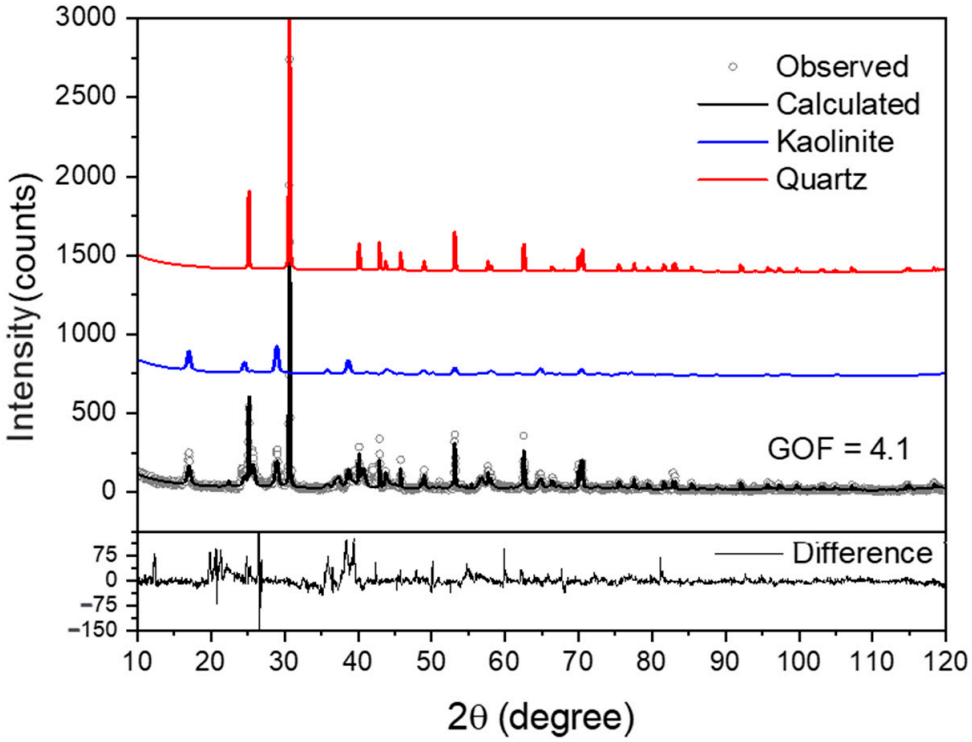

Figure 2. Rietveld refinement of unheated F2 sample. The simulated diffraction patterns of quartz and kaolinite are shown in red and blue, respectively. The crystallographic identification file from ICDD reference code used for both phases are 00-046.1045 for quartz (SiO_2—hexagonal P3221) and 00-029-1488 for kaolinite ($Al_2Si_2O_5(OH)_4$—monoclinic C12m1). The concentrations of phases were quartz 44%, kaolinite 33% and hematite, goethite and gibbsite the remainder.

In the fired samples, goethite and gibbsite were not detected in samples heated at temperatures greater than 250 °C. This occurs due to the loss of –OH in the dehydration process [23–25]. Another transformation observed after 530 °C was the dehydration of kaolinite [26,27]. The kaolinite mineral was not detected in samples heated at temperatures greater than 530 °C. The dehydration reaction can be described as [23]:

$$-OH \rightarrow H_2O \uparrow \quad (3)$$

The peaks used in the HCA and PLS-2 analyses were hematite (2θ = 33.475°), quartz (2θ = 20.775°, 25.575°, 36.475°, 39.475°, 40.275°, 42.375°, 44.725° and 50.075°), anatase (2θ = 22.225°), goethite (2θ = 21.325°), gibbsite (2θ = 18.289°) and kaolinite (2θ = 12.275° and 24.825°). Some peaks were not well defined or horizontally shifted, so the value used was the mean of two or three points adjacent to the maximum value. The data is given in the Supplementary Material (Table S1).

The HCA was performed with all samples collected from the five studied sites. The unheated (25 °C) and the heated samples (250, 400, 530, 600 and 800 °C) were included in the analysis. Figure 3 presents the HCA result from peak relative intensity. As may be observed in the figure, there is a tendency of differentiation by collection sites (F1 and P1 separated from F2, P2 and SB), rather than a differentiation of the samples by the heating temperatures.

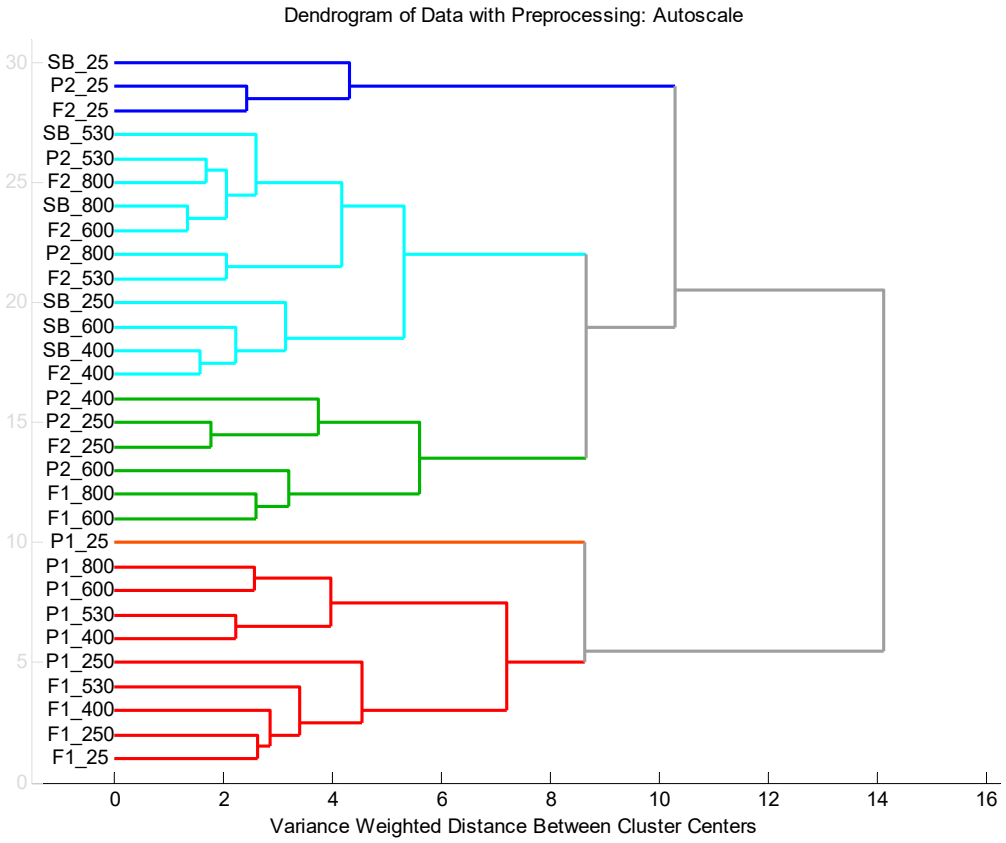

Figure 3. HCA (Hierarchical Agglomerative Analysis) performed in Matlab. Ward's method and Euclidean distance. The colors indicate the different clusters with variance weighted distance < 10. Labels: Site_HeatingTemperature. Unburned samples have "_25" in their label. F1—forest 1, F2—forest 2, P1—pasture 1, P2—pasture 2, SB—slash-and-burn. Two main groups are observed: F1 and P1, and F2, P2 and SB.

The same data were analyzed by the PLS-2 method. The peak intensities of the XRD patterns (counts) were considered the **X** matrix, and the collection sites and the heating temperatures the **Y** matrix. The gibbsite peak was not significant for the models and was then removed from the analysis. Figure 4 presents the correlation plot. Component t_1 and t_2 cumulative Q2 statistics are presented in Table 2.

From the plot in Figure 4, it can be stated that t_1 captures the collection site information while t_2 collects the heating temperature information. F1 and P1 (positive t_1 direction) have an inverse relationship to F2, P2 and SB (negative t_1 direction). In t_2, higher temperatures are in the positive direction, while the lower ones decrease gradually in the negative direction.

The plot in Figure 5 presents the variable importance in the projection for the minerals in the model. All variables lower than 0.8 in t_1 and t_2 have a low contribution in the modeling.

From Figure 4, it is possible to state that the most important minerals for differentiation among the collection sites are quartz and hematite (greater values in t_1), while the most important minerals for differentiation in reached temperature are kaolinite, goethite and anatase (greater values in t_2).

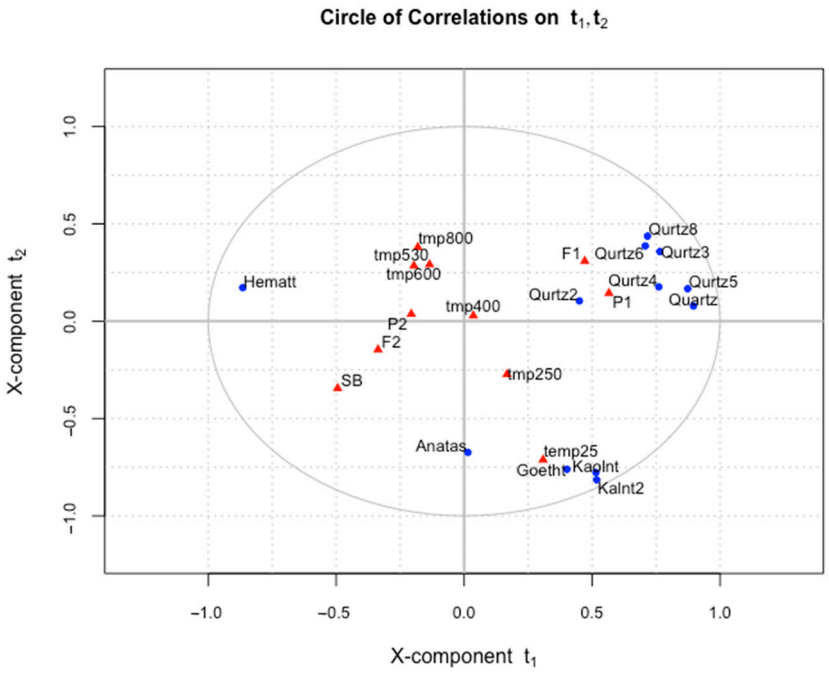

Figure 4. Correlation plot between components t_1 and t_2. Red points: heating temperature and collection sites. Blue points: minerals. Hematt—hematite. Qurtz—quartz (more than one peak was considered). Anatas—anatase. Goetht—gothite. Kaolnt—kaolinite (more than one peak was considered). Tmp—temperature.

Table 2. Cumulative Q2 statistic for components t_1 and t_2. F1—forest 1; F2—forest 2; P1—pasture 1; P2—pasture 2; SB—slash-and-burn; 25 to 800—heating temperatures in °C.

Component	F1	F2	P1	P2	SB	25	250	400	530	600	800
t_1	0.1647	0.0660	0.2124	0.0026	0.1788	−0.0095	−0.0301	−0.0525	−0.0480	−0.0323	−0.0417
t_2	0.1982	0.0235	0.1441	−0.0518	0.2375	0.4882	−0.0378	-0.785	0.0009	0.0097	0.0701

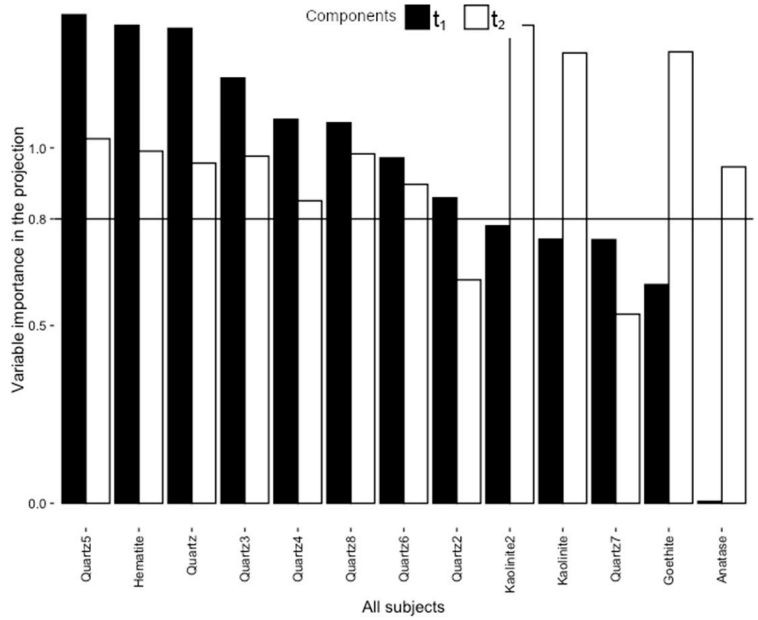

Figure 5. Graph of variable importance in the projection for components t_1 and t_2. All variables lower than 0.8 importance were removed from the model.

4. Discussion

The studied Brazilian Ferralsols presented hematite, gibbsite, goethite, kaolinite, anatase and quartz, which are minerals commonly found in the studied region [22]. These minerals can be transformed when the soil is heated, e.g., kaolinite transformation due to dehydration. The samples' XRD patterns presented some differences when the soil was heated at different temperatures. These differences may be slight and hard to study only by looking at the XRD peak values, which is a large dataset. An alternative is to perform the data analysis by means of statistical tools that provide the decomposition in simpler components. The HCA and the PLS-2 were efficient for understanding the heat effects in the mineralogy of the studied soil.

PLS-2 was able to differentiate soils in two characteristics—collection site and heating temperature—better than HCA. While HCA allowed a general overview of the samples' grouping, based on the most significative differences among the samples (which were due to the collection sites), PLS-2 exhibits extra information in the components t_1 and t_2. In such an analysis, the relationship between the transformation of the minerals and the heating temperature was visualized. Therefore, it was possible to use the XRD data as a fingerprint technique to evaluate the heated soils.

Regarding the relationship between the collection site and the heating temperature with the minerals in Figure 4, in t_1 all are similar, except for hematite that is totally different. Probably this mineral has different concentrations in the different locations. In t_2, the difference is clearly due to anatase, goethite and kaolinite, which have a completely different behavior to quartz and hematite.

Gibbsite, goethite and kaolinite were not detected after some temperature thresholds (gibbsite and goethite after 250 °C and kaolinite after 530 °C). The dehydration of kaolinite and goethite plays a main role in the analysis, as indicated by the plot in Figure 5 that represents the importance of each variable in the PLS-2 projections.

In general, multivariate methods are widely used in analytical chemistry but less diffused in materials' science and rarely used in X-ray diffraction. More systematic applications in crystallography started appearing in the literature from about 2000, and some groups started working to explore the potentialities and limitations of such methods, mainly in powder diffraction data analysis [8]. The employment of multivariate analysis using XRD data was performed by Souza et al. [9]. They developed a PCA with several soil attributes and found that it was possible to identify the relationship between such attributes and the variation of them among the soil classes. Another study was conducted by Bertacchini et al. [7], considering the collection sites of the samples and performing the multivariate models with the whole XRD patterns. They investigated the key role of the soil sampling procedure for geographical traceability and found the differences and homogeneity of collection sites and vertical profiles in the studied soils. Their results may be used in the planning process (number, type of samples) in extensive sampling. The present research, with Amazonian soils from Brazil, considered just the peaks' intensities from the XRD patterns, a simpler methodology to investigate the burned soils, and showed interesting results using multivariate analysis. These results were obtained from local models and may be applied in similar soils and climatic conditions. Further application to other soil types and climate conditions should be evaluated individually.

Some complexities that may arise when using XRD to analyze soils are the variable chemical and structural compositions of soil minerals, the thickness of diffracting domains, particle size, particle-size distribution and the sample weight or thickness in the holder [28]. Furthermore, the samples preparation, the XRD instrument alignment and the data collection procedures may influence the results. Some peaks can interfere with others, particularly the quartz ones, which overlap the kaolinite, maghemite and muscovite peaks.

To improve the developed analysis, one may increase the studied sample set and the temperature levels of heating and may employ data fusion of the XRD data with other fingerprinting techniques. The quartz phase may be removed for a better characterization

of burned soils with XRD and PLS-2, but the overall result shows that it is possible to analyze bulk samples and still obtain good fingerprints of fire-induced changes in soils.

5. Conclusions

The potential of the XRD technique as a fingerprinting method for burned soil was investigated using multivariate analysis. The minerals detected in the studied samples (Ferralsol) were hematite, anatase, goethite, quartz, gibbsite and kaolinite. It was possible to characterize the heated soil samples according to their sites of collection and heating temperatures with HCA and PLS-2 analysis. In the HCA analysis, the soil samples were grouped mainly according to their collection sites, while in the PLS-2 analysis it was possible to distinguish the collection site in component t_1 and the heating temperatures in component t_2. The samples were grouped mostly because of the differences in the goethite and kaolinite content. These differences were mainly due to the dehydration of such minerals, which occurred at 250 and 500 °C, respectively. Therefore, PLS-2 provided a better understanding of the dataset as it considered both X and Y matrices.

Our findings should be helpful for the development of new methodologies to measure the fire severity reached in soils, contributing to soil mineralogy and soil environment fields of knowledge.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12111402/s1. Table S1: X-ray diffraction data

Author Contributions: Conceptualization, D.R.R., F.L.M. and E.L.T.; methodology, D.R.R., X.B. and F.L.M.; software, X.B.; validation, D.R.R.; formal analysis, D.R.R. and X.B.; investigation, D.R.R., F.L.M. and E.L.T.; resources, E.L.T., F.L.M. and A.U.; data curation, D.R.R. and X.B.; writing—original draft preparation, D.R.R. and X.B.; writing—review and editing, J.M.-S., M.M.J.-V., A.U., F.L.M. and E.L.T.; visualization, D.R.R.; supervision, F.L.M. and E.L.T.; project administration, F.L.M. and M.M.J.-V.; funding acquisition, F.L.M., E.L.T. and M.M.J.-V. All authors have read and agreed to the published version of the manuscript.

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