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INFLUENCE OF PREFERRED ORIENTATION OF MINERALS IN THE MINERALOGICAL IDENTIFICATION PROCESS BY X-RAY DIFFRACTION

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ABSTRACT

The X-ray diffraction corresponds to one of the main techniques for characterization of microstructures in crystalline materials, widely used in the identification of minerals in samples of geological materials. Some minerals have a property called preferred orientation which corresponds to the orientation tendency of the crystals of ground minerals to orient themselves in certain directions according to a preferred crystallographic plane. This property affects the analysis by X-ray diffraction and this fact can generates erroneous results in the characterization. The purpose of this study is to identify the negative influence of the preferred orientation of a mineral in the generation of diffraction patterns obtained in the X-ray diffraction analysis. For this, a sample of muscovite, a mineral of mica group, was prepared by two different methods: the frontal method and the back loading method. In the analysis using the frontal method there was displacement of the XRD pattern in the abscissa axis, where it was observed changes in interplanar distance and angle 2θ values, which are essential information for characterization and identification of a mineral. In the analysis using the back loading method, the generated XRD pattern showed no displacement in the axis of abscissas and showed interplanar distance and angle 2θ values closer to the real values for the muscovite. The results showed that one can only make improvements to the process of sample preparation minimizing the effect of preferred orientation in the analysis. There is no need to change conditions of diffractometer measurements.

1. INTRODUCTION

The X-ray diffraction corresponds to one of the main techniques for characterization of microstructures in crystalline materials, widely used in the identification of minerals in samples of geological materials.

The phenomenon of X-ray diffraction results from a process in which X-rays are scattered by electrons of atoms without changing the wavelength [1], whenever certain geometric conditions are satisfied.

Upon reaching a material, X-rays can be scattered elastically without loss of energy by the electrons of the atoms (coherent scattering or Bragg scattering). After collision with the electrons of the sample, the X-ray beam changes its propagation direction keeping, however, the same wavelength of incident radiation.

When such dispersions are generated by electrons of a set of atoms arranged in a systematic way as in a crystalline structure, it can be seen that the phase relations between the scatterings become periodic and that the phenomenon of X-ray diffraction is observed at various angles of incidence of the beam, since its wavelength λ is of the order of magnitude of the interplanar distances [2].

If it is considered two or more planes of a crystalline structure, the conditions for the occurrence of X-ray diffraction will depend on the difference of the path of the X-ray beam and the wavelength λ of the incident radiation. This condition is expressed by Bragg's law, $\mathbf{n\,\lambda = 2\,d\,sen\theta}$, in which λ corresponds to the wavelength of the incident radiation, n to an integer, d to the interplanar distance for a set of planes {hkl} (Miller index) of the crystal structure and θ to the incident angle of X-rays (measured between the incident beam and the crystal planes) [3].

As most of the instrumental analytical techniques, the analysis by X-ray diffraction is susceptible to interferences which mask the results and generate errors in the analysis. Such interferences may be related to environmental conditions, instrumental conditions or related to the sample itself and its preparation. Among the factors of interference on the sample preparation it can be mentioned: inadequate particle size, variation of the grinding time and use of different methods of grinding (ball mill, rotating disc, an agate mortar) [4]. In the case of samples of certain minerals, there is still the preferred orientation which must be considered in the analysis of X-ray diffraction.

The preferred orientation is an intrinsic property of certain minerals which corresponds to the orientation tendency of the crystals of ground minerals to orient themselves in certain directions according to a preferred crystallographic plane. Some minerals of easy cleavage form needles or plates as they are placed on the specimen holder and when they are pressed. In this situation, the minerals show preferred orientation with increasing intensities of peaks which correspond to the cleavage planes [1]. This results in a higher frequency of occurrence of these plans and leads to the change in relative intensities of the reflections from other crystallographic planes [2]. Besides changing the intensity of the peaks, depending on the sample preparation, the preferred orientation also influences the angular position of the peaks generating displacement of the diffracted peaks, and thus determining incorrect values of interplanar distances. This fact represents a problem for the analysis by XRD, because the set of interplanar distances, such as the generated XRD pattern is unique and specific to each mineral [5-7], and since the d values are measurement incorrectly, the process of sample characterization is seriously affected and may lead to erroneous mineralogical identification results.

As the preferred orientation factor can be enhanced in the preparation of the sample during the fixing step (pressing) in the specimen holder, it is possible minimizing the effect of that property in the analysis of X-ray diffraction adapting the method of preparation samples [2, 8].

For this work, analyses were performed with a sample of muscovite, a mineral of mica group, which has perfect cleavage in one direction {001} and lamellar habit [9] which are properties directly related to preferred orientation.

Muscovite, whose composition is $KAl_2(Si_3AlO_{10})(OH,F)_2$, is one of the most common of the micas and occurs in a wide variety of geological environments. The mica structure is based on a composite sheet in which a layer of octahedrally coordinated cations is sandwiched between two identicals layers of linked $(Si,Al)O_4$ tetrahedra. For the muscovite, aluminium occupies this octahedric site. These sheets have a net negative charge, which is balanced by the introduction of K between them [10]. The sheets are joined to each other by van der Waals Bond, that explains the basal cleavage.

The purpose of this study was to identify the negative influence of the preferred orientation in the generation of diffraction patterns as well as in the identification process by mineralogical analysis of samples which were prepared by different preparation methods: the *frontal method* and the *back loading method*. The sample analyzed for this work is from pegmatitic rocks of the northeast portion of Minas Gerais State.

2. MATERIALS AND METHODS

2.1. Sample Preparation

The analyses of X-ray diffraction were performed at X-ray laboratory of Centro de Pesquisa Professor Manoel Teixeira da Costa, Instituto de Geociências, Universidade Federal de Minas Gerais - CPMTC-IGC-UFMG.

The sample of muscovite was ground in an agate mortar until a fine powder with a particle size of about 200 *mesh* was obtained. From the powdered sample were separated two aliquots of approximately 600mg each to be submitted to two different methods of preparing in the specimen holder: the *frontal method* and the *back loading method*.

The first aliquot was prepared by the frontal method which consists of pressing the powder against the base of the aluminum of the specimen holder, so that the surface of the powdered sample to be analyzed has been previously pressed.

The second aliquot was prepared by the back loading method which consists of pressing the opposite side of the sample which is indeed analyzed, with minimal interference in the distribution of crystals and thereby reducing the effect of preferred orientation.

2.2. Analysis by X-ray diffraction

The equipment used to perform the analyses was the PANalytical X'Pert PRO diffractometer with configuration θ-θ. The samples were irradiated by an X-ray tube with copper anode which emitted Kα radiation of wavelength 1.5418Å and operated at 45mA and 40kV. The radiation beam diffracted by the sample was collected by a proportional detector [11], where there was the formation of electrical pulses that were sent to a computer for processing and data storage. Scans of the samples were performed in a time step of the tube-detector system of 0.5 seconds and the angle step size equal to 0.02° 2θ, which generated analyses that lasted 27 minutes each test.

The samples characterization was done from the High Score Plus 2.0 (software from PANalytical) by comparing the generated diffraction patterns with reference standards organized into sheets available in the database PDF2 of the ICDD - *International Center for Diffraction Data*, which maintains crystallographic information such as the interplanar distances. In this procedure, the software performed a search for three to ten most intense peaks of each crystalline compound which was kept in the database and compared them with the peaks of the sample diffractogram. After the process of searching and comparison, the results values were expressed in increasing order of rank. The coincidence of values or a major proximity of values led to the identification of the mineral.

3. RESULTS AND DISCUSSION

3.1. Sample Prepared by Frontal Method

The obtained XRD pattern (Figure 1) showed significant displacement of peaks with changes in the interplanar distances and angle 2θ values. The changes in the values of *d* could be noted by comparing the interplanar distances of the XRD pattern with interplanar distances of the muscovite reference card which was kept in the database, as shown in Table 1.

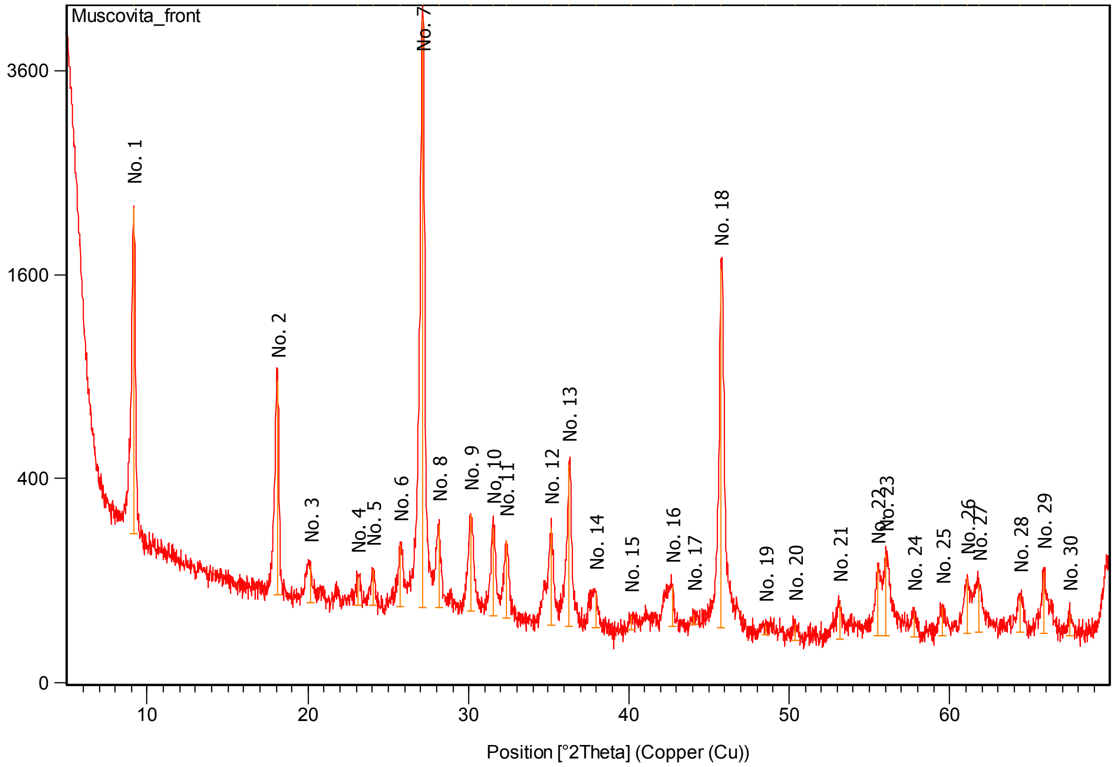

Figure 1. XRD pattern with peak displacement

Table 1. Interplanar distances of the top thirty peaks of the sample and of the reference card

Number Peak	Interplanar Distances (Å)		Accuracy Measures	
	Muscovita front Sample	Reference Card	Absolute Error	Relative Error (%)
01	9.64	9.95	0.31	3.1
02	4.90	4.97	0.07	1.4
03	4.40	4.47	0.07	1.6
04	3.84	4.30	0.46	10.7
05	3.70	4.11	0.41	9.9
06	3.46	3.95	0.49	12.4
07	3.28	3.88	0.60	15.5
08	3.17	3.73	0.56	15.0
09	2.96	3.48	0.52	14.9
10	2.83	3.34	0.51	15.3
11	2.77	3.32	0.55	16.6
12	2.55	3.19	0.64	20.1
13	2.47	3.12	0.65	20.8
14	2.37	2.99	0.62	20.7
15	2.24	2.86	0.62	21.7
16	2.12	2.79	0.67	24.0
17	2.05	2.60	0.55	21.2
18	1.98	2.57	0.59	23.0
19	1.88	2.50	0.62	24.8
20	1.81	2.49	0.68	27.3
21	1.72	2.46	0.74	30.1
22	1.65	2.45	0.80	32.7
23	1.64	2.40	0.76	31.7
24	1.60	2.38	0.78	32.8
25	1.55	2.25	0.70	31.1
26	1.52	2.24	0.72	32.1
27	1.50	2.21	0.71	32.1
28	1.45	2.20	0.75	34.1
29	1.42	2.15	0.73	34.0
30	1.39	2.13	0.74	34.7

During the search process of the most intense peaks of the minerals which were kept in the database and that had values of *d* which could be similar to the values of *d* of the diffractogram, it was expected to find the muscovite in the classification as the first candidate for mineral characterization of the diffractogram. However, muscovite was not listed among the first minerals suggested by the database, but it was listed with classification of 22nd mineral with the largest number of peaks with interplanar distances similar to those showed by the XRD pattern of the sample. As shown in Table 2, the database indicated other minerals which, in the process of search and comparison performed by the software, had a greater number of interplanar distances in common with the XRD pattern, which may induce the analyst to error if the sample is unknown and lead them to choose one of those minerals in an attempt to identify the material analyzed.

Table 2. Database indicating the muscovite as the 22nd mineral suggested to the characterization

Selected Candidate: 00-006-0263				
Nº	**Ref. Code**	**Score**	**Compound Name**	**Chemical Formula**
01	00-035-0550	37	Vuorelainenite	$(Mn, Fe)(V, Cr)_2O_4$
02	00-010-0467	35	Franklinite	$(Zn, Mn, Fe)(Fe, Mn)_2$...
03	00-031-1403	34	Osbornite, syn	TiNO.9O
04	00-044-1437	33	Teallite	$PbSnS_2$
05	00-041-1482	32	Zinnwaldite-/IT1M/RG	$KAl(FeLi)(Si_3Al)O_{10}F_2$
06	00-025-0417	30	Ulvospinel, ferrian, syn	Fe_5TiO_8
07	00-037-1469	30	Montroydite, syn	HgO
08	00-009-0381	29	Montroydite, syn	HgO
09	00-041-1471	29	Cattierite	CoS_2
10	00-031-0630	28	Manganochromite	$(Mn , Fe)(Cr, V)_2O_4$
11	00-031-1238	28	Chlorargyrite, syn	AgCl
12	00-006-0480	28	Chlorargyrite, syn	AgCl
13	00-002-0056	27	Illite	$KAl_2Si_3 AlO_{10}(OH)_2$
14	00-025-1408	27	Iron, rhodian	(Fe, Rh)
15	00-005-0519	27	Bismuth, syn	Bi
16	00-021-0159	27	Fluorite, yttrian	$(Ca, Ln)F_2$
17	00-031-0293	27	Fluorite, yttrian	$(Ca, Y)F_2$
18	00-003-0861	26	Gersdorffite	NiAsS
19	00-011-0014	26	Rammelsbergite, syn	$NiAs_2$
20	00-024-0518	25	Rammelsbergite	$NiAs_2$
21	00-042-1325	25	Unnamed mineral [NR]	$Bi_3(PO_4)_2O(OH)$
22	00-006-0263	25	Muscovite-2\ITM#1\RG	$KAl_2(Si_3Al)O_{10}(OH,$ ...
23	00-022-1012	25	Franklinite, syn	$ZnFe_2O_4$
24	00-005-0667	25	Cuprite, syn	Cu_2O
25	00-010-0319	25	Jacobsite, syn	$MnFe_2O_4$
26	00-011-0251	24	Froodite	Bi_2Pd

As the sample was known previously, a reference card of the muscovite was searched in the database and selected to characterize the diffractogram. However, the chosen card (22nd in the database) has not characterized all the peaks of the diffractogram, or just some interplanar distances of muscovite reference had values equal to or close enough to the interplanar distance values showed in the sample diffractogram, which generated an incomplete characterization, as shown in Figure 2.

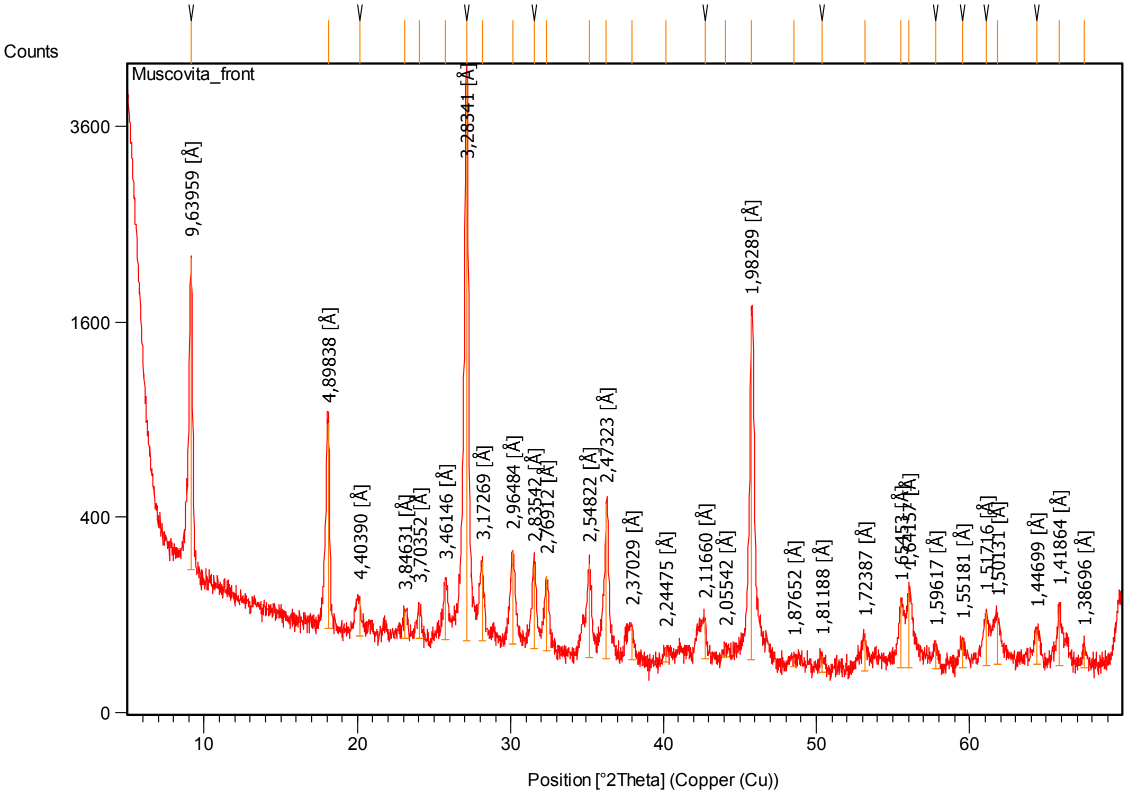

Figure 2. Diffractogram with incomplete characterization. Black markers on the extensions of the peaks indicate peaks not characterized by muscovite.

3.2. Sample Prepared by Back Loading Method

The analysis of the sample prepared by back loading method generated a diffractogram without displacements that changed significantly the interplanar distance and angle 2θ values, which favored the process of mineral identification. As can be seen in the Table 3, during the characterization, the first mineral suggested by the database was the muscovite.

Table 3. Database indicating the muscovite mineral as the first suggested to the characterization

Selected Candidate: 00-006-0263				
N°	**Ref. Code**	**Score**	**Compound Name**	**Chemical Formula**
01	00-006-0263	54	Muscovite-2\ITM#1\RG	$KAl_2(Si_3Al)O_{10}(OH,$ ...
02	00-019-0814	53	Muscovite-2\ITM#1\RG...	$K(Al, V)_2(SiAl)_4O_{10}$...
03	00-042-1399	49	Zinnwaldite-1\ITM\RG	$K(AlFeLi)(Si_3Al)O_{10}$...
04	00-003-0849	46	Muscovite	$H_4K_2(Al, Fe)_6Si_6O_{24}$
05	00-007-0042	44	Muscovite-3\ITT\RG	$(K, Na)(Al, Mg, Fe)_2$...
06	00-007-0032	41	Muscovite 2M1, syn	$KAl_2Si_3AlO_{10}(OH)_2$
07	00-041-1482	39	Zinnwaldite-\IT1M\RG	$KAl(FeLi)(Si_3Al)O_{10}$...
08	00-024-0594	39	Lepidolite-2\ITM#1\RG	$K(LiAl)_3(Si, Al)_4O_{10}$...
09	00-031-1045	39	Taeniolite-1\ITM\RG, ...	$KO.6(Mg, Li)_3\ Si_4$...
10	00-015-0237	39	Taeniolite, 1M, syn	$KO.6(Mg, Li)_3\ Si_4$...
11	00-038-0430	36	Iwakiite	$MnFe_2O_4$
12	00-026-0911	36	Illite-2\ITM#1\RG	$(K, H_3O)Al_2Si_3AlO_{10}$...
13	00-015-0256	34	Taeniolite 1M, syn	$KLiMg_2Si_4O_{10}F_2$
14	00-015-0506	33	Vanuralite	$(UO_2)_2AlOH(VO_4)_2$...
15	00-012-0300	31	Lopezite, syn	$K_2Cr_2O_7$
16	00-002-0056	31	Illite	$KAl_2Si_3AlO_{10}(OH)_2$
17	00-027-0159	30	Roquesite, syn	$CuInS_2$
18	00-042-0612	30	Lepidolite-3\ITT\RG	$K(Li, Al)_3(Si ,Al)_4O_{10}$
19	00-011-0060	29	Safflorite	$Co_{0.55}Fe_{0.41}Ni_{0.04}As_2$
20	00-023-0088	29	Safflorite	$(Co, Fe)As_2$
21	00-006-0615	28	W\PIustite, syn	FeO
22	00-002-0783	28	Breithauptite	NiSb
23	00-043-0692	28	Lepidolite-2\ITM\RG#2	$KLi(Al, Li)_2(Si_3Al)$...
24	00-035-0678	28	Bonshtedtite	$Na_3Fe(PO_4)(CO_3)$
25	00-010-0319	27	Jacobsite, syn	$MnFe_2O_4$
26	00-016-0344	27	Phlogopite-1\ITM\RG, ...	$KMg_3(Si_3Al)O_{10}\ F_2$
27	00-040-1250	27	Mgriite, syn	$CuAsSe_2$
28	00-029-1438	27	Yavapaiite, syn	$KFe(SO_4)_2$
29	00-024-0537	27	Ulvospinel, syn	Fe_2TiO_4
30	00-014-0565	26	Lepidolite-1\ITM\RG, ...	$K(Li, Al, Fe)_3Si_4O_{10}$...
31	00-034-0177	25	Ulvospinel, syn	Fe_2TiO_4
32	00-040-1500	25	Tausonite, syn	$SrTiO_3$
33	00-013-0227	25	Zinnwaldite-\IT1M\RG	$K(Li, Fe)_2AlSi_4O_{10}$…

At the moment it is indicated as the first candidate in the database, it is understood that the muscovite is the mineral which has the largest number of peaks in common with the sample diffractogram. Such comprehension could be confirmed by observing the characterized diffractogram (Figure 3), in which the muscovite removed all markers on the peaks and, consequently, the analysis was finished.

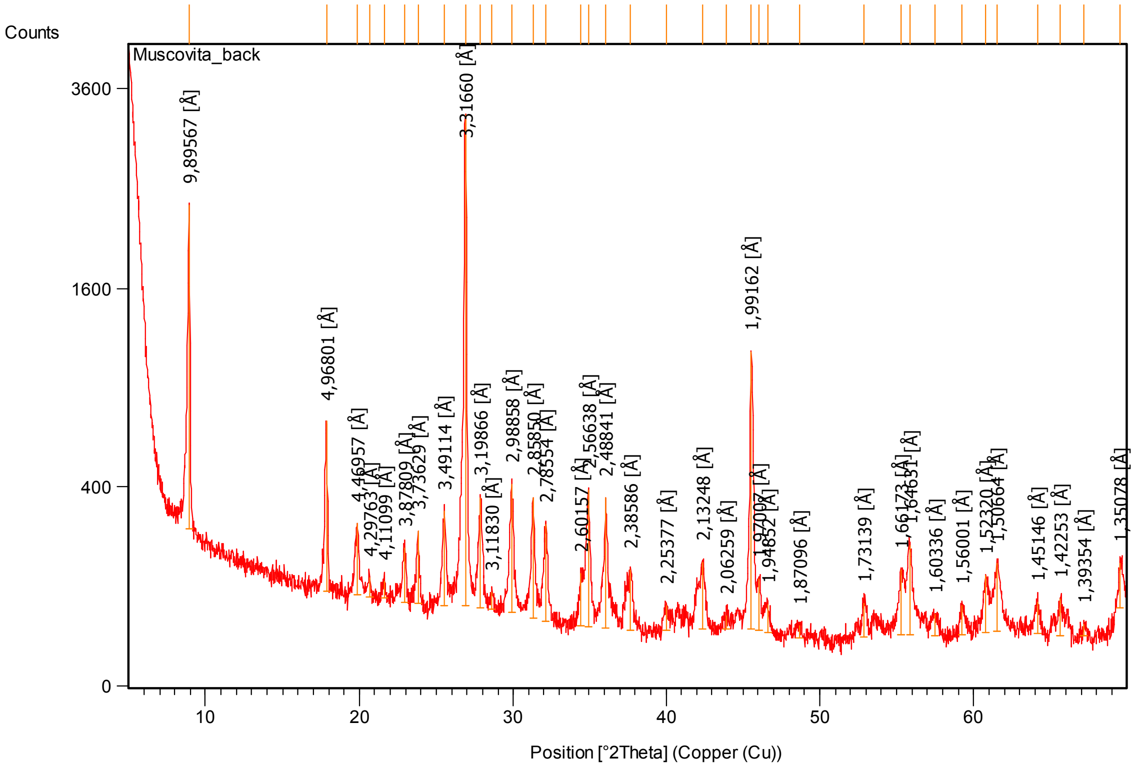

Figure 3. Diffractogram with full characterization. The total absence of black markers on the extensions of the peaks indicates that all peaks were characterized by muscovite.

The displacements in the XRD pattern of sample prepared by the *frontal method* can be viewed by the overlap of the diffractograms obtained for the samples prepared by both methods, as shown in Figures 4 and 5.

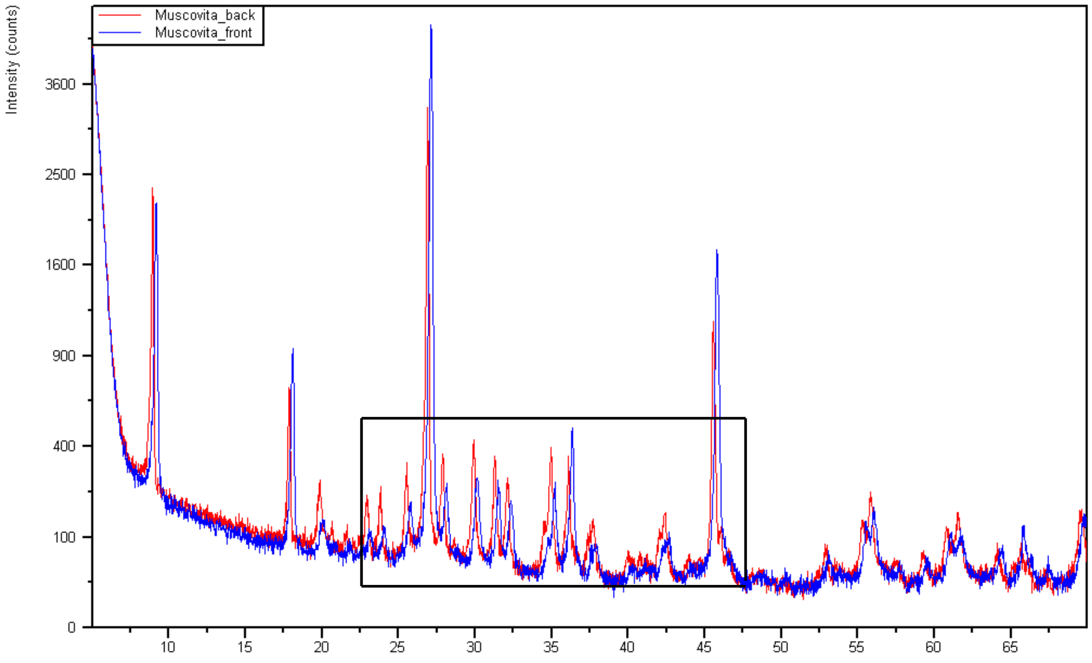

Figure 4. Overlap of diffraction patterns obtained from samples prepared by two different methods of preparation: front and back loading.

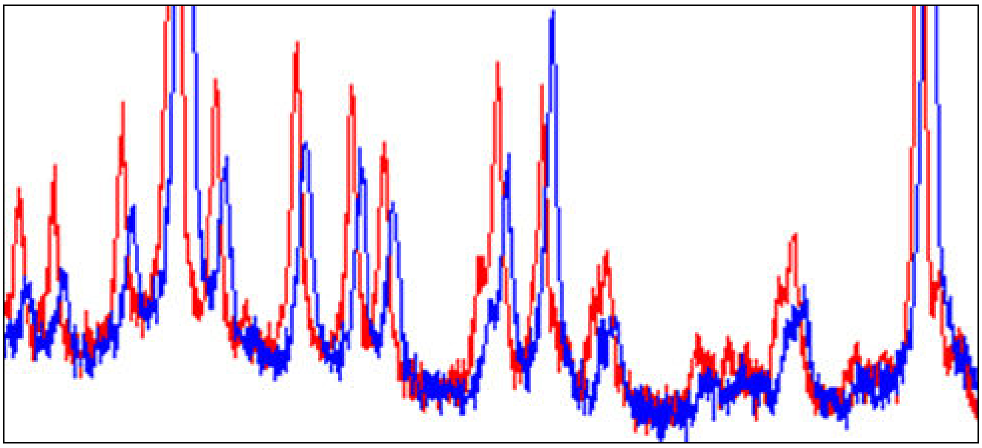

Figure 5. Expanded detail of the displacement of peaks

4. CONCLUSIONS

From the results it was possible to prove that the preferred orientation is a property that influences the analysis by X-ray diffraction negatively, favors the displacement of peaks, and leads to erroneous characterizations of the sample. However, it was noted that such influence can be minimized by proper preparation of the sample.

The two preparation methods used in this study, the *frontal method* of preparation proved to be inadequate for analysis of orientable minerals, because it showed large displacements of peaks in its XRD pattern and tended to an erroneous characterization of the sample. On the other hand, the *back loading* method was considered the most appropriate method, because, although it had small displacements in the XRD pattern, these displacements were considered insignificant, because they did not harm the sample characterization.

The problem created by the preferential orientation in analysis of X-ray diffraction can not be eliminated but it can be minimized by the back loading method of preparation. Other stages of preparation as particle size and grinding time should also be studied with the purpose to only implement improvements to the process of sample preparation to reduce the effect of preferred orientation in XRD patterns, thus, it is not necessary to change conditions of the diffractometer measures.

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