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Article

The Alteration Processes of the Weakly Magnetic Egyptian Black Sand Altered Ilmenite

Mohamed I Moustafa

Department of Civil Engineering, College of Engineering, Northern Border University
* Correspondence: ismail2251962@yahoo.com; Mohamed.Ibrahim@nbu.edu.sa

Abstract: One of the most extensively studied topics in dozens of studies is the alteration process of ilmenite, the formation of leucoxene and the presence of some impurity oxides; SiO_2 and Al_2O_3. The altered Egyptian black sand ilmenite grains of relatively lower magnetic characters are studied using the binocular microscope and the Cameca SX-100 microprobe instrument. Both of individual brown and black altered grains separated at 0.5 and 1 ampere values are investigated. The detection of the Various alteration phases, the mechanism of formation, their molecular formulas & limits, and the role of SiO_2&Al_2O_3 in alteration mechanisms are detected. The alteration phases includes: pseudorutile (psr) and leached pseudorutile (lpsr) of different phases in addition also to rutile. Few analyzed spots are detected to be leached ilmenite (lilm). Several Excel softwares are adopted to calculate the chemical formulas of each alteration phase. The contents of TiO_2 and Fe_2O_3 of all the investigated psr-lpsr in the study range between 59.16-86.56%, and 37.3-6.68%, respectively. The Ti/(Ti+Fe) ratio for these formulas ranges between 0.60 and 0.88. The psr-lpsr chemical formulas of all the investigated grains range as follows: $Fe_{2.01\text{-}0.50}Ti_3O_{8.97\text{-}4.50}(OH)_{0.03\text{-}4.50}$. The concluded lowest cationic iron content of the well defined accepted lpsr phase is 0.5 with a corresponding molecular formula of $Fe_{0.50}Ti_3O_{4.5}(OH)_{4.5}$. It was concluded that in the region of 68-70 TiO_2%, the mechanism of ilmenite alteration may be changed where neither all the analyzed TiO_2 of the spot nor all the calculated structural water are contained within the molecular formula of lpsr. There are other associated mineral phases containing for some TiO_2 and also some structural water which most probably are removed from the lpsr phase. As the analyzed spots are located at highly fissured locations, as the alteration process is relatively faster and the lpsr phase can be broken into rutile and hematite. Also, as the analyzed TiO_2 and structural and/or molecular water contents increase, as the darkness of the BSE image areas of the grain increases; this may reflect the existence of an individual TiO_2 phase; most probably rutile, mixed in homogeneity with the existed lpsr component. As the content of TiO_2 increases; within a definite TiO_2 range (80-85%), as the associated contents of Al_2O_3&SiO_2 increase. When the contents of the structural and/or molecular water contained within the lpsr phases decreases; the sum total oxides is more than 98%, the contents of Al_2O_3 are highly depleted. In the late alteration stages, the lpsr structure does not suddenly collapse but gradually producucing other associated mineral phases. The relatively enriched contents of SiO_2 and/or Al_2O_3 in some secondary rutile grains can be explained as most of the SiO_2% is associated with mol water or bearing for mol and/or str water necessary for the leachability of Fe^{3+} from the psr structure. The XRD patterns of the investigated grains before and after roasting at 1100 ^oC for one hour are detected and interpreted.

Keywords: altered ilmenite; leached ilmenite; leucoxene; pseudorutile; leached pseudorutile; exsolved intergrowth; X ray diffraction.

1. Introduction

The most abundant economic mineral of the Egyptian black sand is ilmenite followed by magnetite, garnet, zircon, rutile and monazite in a decreasing order of abundance. The Egyptian beach ilmenite partly altered to a greyish material which in a later stage is replaced by a very fine intergrowth of rutile-anatase product having a microporous structure [1]. Two post-depositional alteration varieties of the Egyptian beach ilmenite are distinguished. The first is the amorphous iron-titanium oxides due to alteration along borders, cracks or as thin rim separating fresh ilmenite relics from a broad outer zone of leucoxene. The second variety is the alteration to leucoxene; a very fine crystalline aggregates with a mottled appearance [2]. A highly leucoxenated secondary rutile grains; within the obtained rutile concentrate, as end product of ilmenite alteration were identified by [3,4]. Several types of magnetic and non-magnetic altered ilmenite varieties were detected by [5]. He put an explanation for the formation of each of these altered varieties.

So many papers were introduced about the alteration products of ilmenite. The discovery of a new mineral; arizonite, of a chemical composition closely corresponds to $Fe_2O_{3.3}TiO_2$, was reported by [6], and which was considered as merely weathered ilmenite by [7]. The nature and chemical composition of leucoxene are known to be variable [8-18].

The name pseudorutile was proposed for the product of oxidation and progressive partial removal of iron due alteration of ilmenite giving an intermediate iron titanate of a definite structure [19].

The ilmenite concentrates from several beach sand deposits were studied and concluded that most concentrates contain ore grains ranging from fresh ilmenite to a highly altered product approaching pure TiO_2 in composition [20].

The abundance co-occurrence of pseudobrookite and altered ilmenite was reported in Quilon sands, India [21]. [22] does not agree with the explanation of [21], unless the primary pseudobrookite was early present in the source area.

For ilmenite alteration of Ti/(Ti+Fe)> 0.7, the Al and Si levels increase rapidly with increasing Ti/(Ti+Fe) ratios, to maximum values near 1.5 wt% Al_2O_3 and 0.5 wt% SiO_2. This increase is due to co-precipitation or adsorption of these elements from the surrounding soil solutions onto the freshly-formed alteration products [23].

The alteration of ilmenite to psr decreases the cell volume up to 13% [24], while it is 6% by [25], and reaches to 40% by alteration to leucoxene leading to shrinkage cracks. The XRD pattern of psr in comparing with Rutile is similar with two additional lines of d-values 2.71 Åand 2.98 Å[24]. There are more extensive network of nanopores in the hydroxylian pseudorutile (HPR) than those of psr [26].

In recent two papers, most of the mineralogical features of the homogeneous Egyptian black sand ilmenite, the different exsolved intergrowths between ilmenite-other mineral components and the partially altered ilmenite grains were explained [27,28]. Although the alteration to pseudorutile is observed, further alteration to leucoxene is very rare in the studied sample from Rosetta ilmenite concentrate [29]. The chemical composition of the highly altered leucoxenated Egyptian beach ilmenite grains reflects that the TiO_2 ranges between 59.45 and 89.72%, the total iron content (Fe_2O_3) varies from 2.34 to 32.68%, whereas the SiO_2 content varies from 0.89 to 8.19% [30].

In the present article, some of the weakly magnetic altered ilmenite varieties are investigated to explain their mineralogical and chemical composition characters. Several Excel softwares are constructed for concluding the chemical formulas of the various ilmenite alteration products. The different alteration phases and their corresponding molecular formulas limits will be explained. The most accepted mechanism of their alteration processes are explained. The role of both of Al_2O_3 and SiO_2 in the process of ilmenite alteration will be also investigated.

2. Materials and Methods

A large bulk sample of the surfacial naturally highly concentrated beach black sand was collected from the beach area at the Mediterranean coast, 7 km to the east of Rosetta estuary, Egypt. Using both of wet gravity concentration; Full-size Wilfley shaking tables, magnetic separation; Reading cross belts separators, Carpco high intensity induced roll separator&Frantz iso-dynamic separator, and Carpco high tension electrostatic separator, each individual high grade economic mineral is obtained [5,27,28,31]. During the final magnetic refining of the obtained rutile concentrate, a bulk magnetic fraction is obtained. A relatively smaller representative sample is obtained from this bulk magnetic fraction and subjected to magnetic differentiation using the Frantz isodynamic magnetic separator to obtain six magnetic fractions and only one non magnetic fraction. In addition to the contained magnetic primary rutile grains, most of these fractions contain grains of altered ilmenite varieties [32].

The altered ilmenite grains obtained in the two individual magnetic fractions separated at 0.5 and 1 ampere values which are investigated in this article.

The altered ilmenite varieties obtained of these separated two individual magnetic fractions are investigated using the binocular and reflected microscopes. The grains are detected using a Cameca SX-100 electron microprobe analyzer (EMPA); institute of mineralogy and crystal chemistry, Stuttgart University, Germany. The analytical conditions are as described in [31]. Also, the same constructed Excel softwares of [31], to calculate the molecular formulas of leached ilmenite, pseudorutile, and leached pseudorutile are used.

3. Results and discussions

3.1. The separated magnetic fraction at 0.5 ampere

The obtained fraction is composed mainly of the black and brown coloured altered ilmenite varieties. The black grains are more abundant, angular, relatively finer, and with highly pitted surfaces than the brown coloured grains. The grains of light brown, reddish and yellowish brown colours are highly increased in the fraction [31]. A considerable number of the black coloured grains are stained to partially coated; from 5 to 90% of the grain's surface, with relatively lighter soft coloured material (dark brown, yellowish and reddish brown). Others are coated or stained with silica.

In this magnetic fraction several varieties of the brown coloured grains are detected. Three groups of grain varieties are investigated as follows:

3.1.1. The detected dark brown magnetic variety at 0.5 ampere

In this variety, seven dark brown grains are investigated. Some of the detected spots are either altered silicate minerals, or individual phases of TiO_2 and Fe_2O_3 obtained due to the breakdown of the formed lpsr.

The psr and lpsr spots for the three grains (Figure 1a-1c&Table 1), have TiO_2 contents range between 68.61 and 84.11% while Fe_2O_3 contents range between 6.68 and 20.7%. Their cationic iron ranges between 1.07 and 0.42 while the Ti/(Ti+Fe) ratio ranges between 0.74 and 0.88. The analyzed spot 1 of grain 1c is an impurity of a silicate mineral. All the analyzed spots of the grain (Figure 1a), are lpsr. In grain of (Figure 1b), the TiO_2 content attains 79.01% while the Fe_2O_3 content decreases to 12.72%. In grain of (Figure 1c), the TiO_2 content attains 84.11%, while the Fe_2O_3 content decreases to 6.68%. The cationic iron content ranges between 0.42 and 0.49. In the two grains (Figure 1b,1c), the new total oxides sum after applying the constructed psr Excel program (NT), is greater than 100% for each of the analyzed spots of the two grains; 104.5-106.11% for the grain 1b and 106.8-108.3% for the grain 1c. Then, either the calculated structural water and/or the content of the most abundant analyzed oxide (TiO_2) as included completely in the contained psr phase is incorrect. In both the two grains (Figure 1b,1c), comparing the original total oxides sum; before applying the constructed psr Excel program (OT), and NT for each of them, it is difficult to accept the calculated values of the corresponding contained str water (Table 1). The lowest OT value is 93.8% which reflects the maximum existence of 6.2% of str and/or mol water. On the other hand, the highest calculated H_2O% by using the adopted psr Excel program is 13.73%. It is remarked that in the lpsr structure, on reaching a TiO_2 content around 68-70%, the mechanism of ilmenite alteration seems to be changed. Also, as the analyzed TiO_2 content increases, as the the darkness of the BSE image areas of the grain increases from 1a to 1c. This may reflect the existence of an individual TiO_2 phase; most probably rutile, mixed homogeneously with the still existed survived lpsr component. Also, as the content of TiO_2 content increases (within a definite range, 80-85%), as the contents of Al_2O_3& SiO_2 increase.

The careful investigation of these three last grains reflects that several spots of these three grains are composed of individual phases for TiO_2 and Fe_2O_3. In such spots, it is incorrect to consider the analyzed contents of TiO_2 and/or Fe_2O_3 included completely in psr phases.

In the grain of (Figure 1d), the change of alteration mechanism is very obvious at TiO_2 contents in the range of 69-70%; spots 3&4 (Table 1). In each of the two spots 1&2, the individual content of TiO_2 and the individual value of the sum mixed contents Fe_2O_3+SiO_2+Al_2O_3 are very near. However, the investigation of the BSE images of the two spot areas reflects the breakdown of lpsr into individual phases where the formed Fe_2O_3 phase may be mixed with SiO_2 and Al_2O_3. The detected psr&lpsr spots of the grain have the chemical formulas of $Fe_{1.43-0.57}Ti_3O_{7.46-4.73}(OH)_{1.54-4.27}$ (Table1).

In the grain of (Figure 1e), the spots from 1 to 5 are corresponding to a definite silicate mineral, which contains definite amount of TiO_2. In these five spots as the contents of SiO_2+Al_2O_3+K_2O decrease, as the contents of TiO_2 increase (Table 1). The spots 6, 7, & 8 are lpsr, the mechanism of alteration for spot 8 is different than that for the other two spots. In fact, the calculated H_2O%; corresponding for the structural OH^- of spot 8 seems to be incorrect. The sum weight% of NT equals 107.7% after the addition of 11.03% of the calculated H_2O corresponding to the contained OH^-%. Each of the spots 9, 10, 11 & 12 is an individual TiO_2 phase mixed with minor Fe_2O_3. It seems that the grain (Figure 1e), was originally composed of major rutile component with minor exsolved intergrowths of ilmenite which altered to lpsr, and inclusions of a definite contained silicate mineral. In comparing the contents of SiO_2& Al_2O_3 and the values of OT & NT for the spots from 9 to 12, it can remarked that an appreciable contents of only Al_2O_3 are favorable with TiO_2 especially in the presence of str and/or mol water (Table 1). However, the detected psr&lpsr spots of the grain have the chemical formulas range of $Fe_{1.58-0.68}Ti_3O_{7.69-5}(OH)_{1.31-4}$ (Table 1).

In the grain of (Figure 1f), the analyzed spots from 1 to 6 are corresponding to a definite silicate mineral containing a definite content of TiO_2. Due to its alteration, considerable contents of SiO_2, Al_2O_3, CaO, MgO and K_2O are lost and an enrichment of TiO_2 from 6.68 to 72.26% is occurred. It should remarked that if these spots; especially spot 6, are investigated in the absence of their BSE image, it may identified as lpsr. On the other hand, the analyzed spots from 7 to 21 are lpsr while the spots from 22 to 24 are individual TiO_2 phases; most probably rutile, after the collapse of the altered lpsr. In these last three spots, the contents of Al_2O_3 and SiO_2 almost equal zero where the values of OT equal 99-100.5%. Then, in comparing them with the spots from 9 to 12 of the grain of (Figure 1e), it is remarked that with the removal of str and/or mol water, the presence of Al_2O_3 and SiO_2 with TiO_2 (more than 85% TiO_2), is not favorable. The detected psr&lpsr spots of the grain have the chemical formulas range of $Fe_{1.45-0.49}Ti_3O_{7.29-4.44}(OH)_{1.71-4.56}$ (Table 1).

In the grain of (Figure 1g), the analyzed spots from 1 to 13 are psr and lpsr. The TiO_2 contents range between 65.75 and 70.65%, the Fe_2O_3 contents range between 29.7 and 21.75%, and the Ti/(Ti+Fe) ratio ranges between 0.68 and 0.74. The contents of SiO_2, Al_2O_3 MgO and CaO are relatively lower while the contents of MnO are relatively higher than those of the other analyzed spots from 14 to 20. Also, in comparing the values of OT & NT; especially for the three spots 11, 12, and 13, it can remarked that the calculated structural water contents are not correct and the mechanism of psr alteration is changed. The analyzed spots from 14 to 20 are lpsr. Their TiO_2 contents range between 74.54 and 79.66%, Fe_2O_3 contents range between 13.55 and 7.09 wt%, and the Ti/(Ti+Fe) ratio ranges between 0.8 and 0.88. The mechanism of alteration for the first six spots is similar to that of the spots 11, 12, and 13. The spot 20 is composed of an individual TiO_2 phase; most probably rutile, it have relatively darker BSE image than others. Their contents of SiO_2, MgO, MnO, and CaO in addition to Fe_2O_3 are minimum while the content of Al_2O_3 still relatively higher and the spot still contains structural and/or molecular water; OT equals 96.19%. The spots of the grain have the chemical formulas of $Fe_{1.43-0.42}Ti_3O_{7.25-4.26}(OH)_{1.75-4.74}$ (Table1). However, many of these spots of grain 1g are not totally psr/lpsr phases. Other individual phases TiO_2 and Fe_2O_3 are also contained.

In these detected 7 grains (Figure 1a-1g), the analyzed spots have the chemical formulas range of Fe1.58-0.42Ti3O7.69-4.26(OH)1.31-4.74 (Table 1). The Ti/(Ti+Fe) ratio ranges between 0.66 and 0.88.

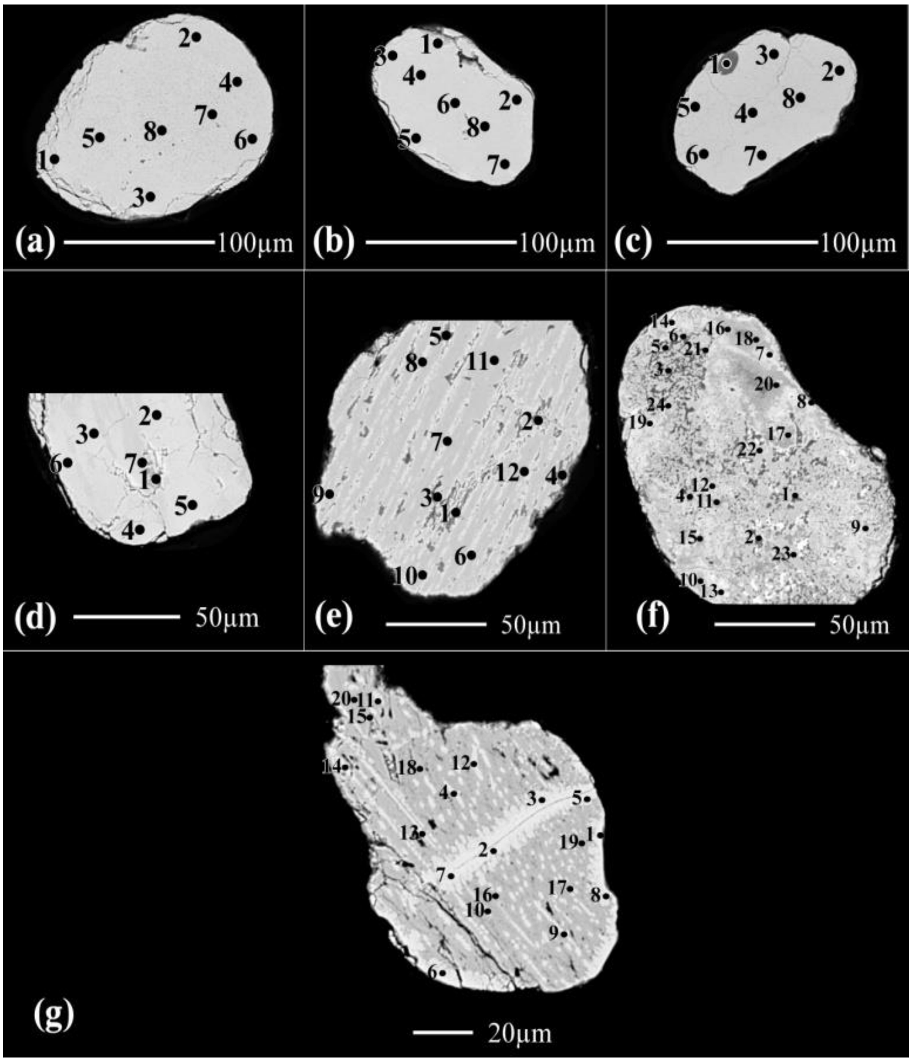

Figure 1. The back scattered electron (BSE) images of the altered brown ilmenite grains (**1a**) to (**1g**), separated as magnetic at 0.5 ampere value.

However, according to the BSE images of the grains of Figure (1), the spots having the lowest iron contents (0.49-0.42) are composed mainly of individual TiO_2 and Fe_2O_3 phases due to collapse of the majority of contained psr/lpsr phases. Then, The cationic Fe contents ranges between 0.42 and 0.49 are discarded as minimum values for the existence of psr-lpsr phases.

3.1.2. The detected brown, yellowish brown & brownish yellow varieties at 0.5

Forteen grains are investigated of this variety (Figure 2, Table 1). In the grain of (Figure 2a), all the analyzed spots are lpsr, the calculated structural water content in the calculated molecular formula are not accepted.

In the grain (Figure 2b), the spots from 1 to 7; except of spot 3, are lpsr. Spots 3 and 8 are located at highly fissured locations enriched with voids which accelerate the alteration of lpsr and its broken into individual TiO_2 and Fe_2O_3 phases. A considerable amount of hematite is lost and/or replaced with Al_2O_3. The contents of MnO in spots 3&8 are similar for MnO contents of the spots from 9 to 13 indicating that these two last spots may be also lpsr collapsed into individual TiO_2 and Fe_2O_3 phases.

In the grain (Figure 2c), , the spots from 1 to 4 are composed of lpsr and have relatively lighter BSE image tints, relatively lower contents of Al_2O_3, SiO_2, CaO & Cr_2O_3 and relatively higher contents of MnO while vice versa for the spots from 5 to 8.

The investigated psr-lpsr spots of the three last grains (Figure 2a-2c), have contents of TiO_2, Fe_2O_3, Fe, and Ti/(Ti+Fe) ratio range between 65.07-79.7%, 28.96-13.05%, 1.49-0.7, and 0.67-0.81, respectively. The detected lpsr phases inside them have the chemical formulas range of $Fe_{1.49-0.7}Ti_3O_{7.4-5.11}(OH)_{1.6-3.89}$ (Table 1).

In the grain (Figure 2d), spot 1 is a definite silicate mineral while the spots 2&3 are sphene. Both of the two spots 4&7 are mainly rutile with minor sphene. The spots 5&6 in addition to those from 8 to 12 are rutile with minor of Fe_2O_3 and sphene. Investigating the values of OT for these spots reflects the prescence of structural and/or molecular water. Also, it is detected that there are considerable contents of Al_2O_3, SiO_2 and CaO with the relatively higher contents of TiO_2. Then, both of the preexisting silicate mineral and sphene are altered and replaced with the enriched TiO_2 phase; most probably due to definite hydrothermal solutions affecting the area of source rocks bearing for them.

In the grain (Figure 2e), the analyzed spots 1 and 2 are lpsr but of different alteration phases. The analyzed spot 3 is inside a void while the analyzed spot 4 is beside the edge of the grain where the rate of alteration is highly accelerated and the lpsr is broken into two individual phases of Fe_2O_3 and TiO_2. Most of the contained ferric iron phase is leached out. The grain (Figure 2e), seems was originally ferriilmenite-titanhematite exsolved intergrowth where most of the hematite content is leached causing partially empty voids of various sizes and shapes. On the other hand, the ferriilmenite component is altered to lpsr. In comparing between the outside surrounding environment of spot 3 and the other three spots 1, 2 and 4 may reflects the association of Al_2O_3&SiO_2 at the spot location characterized by a relatively faster rate of alteration. In the grain (Figure 2f), the analyzed spots 1, 3 and 4 are lpsr. They have relatively lower contents of SiO_2, Al_2O_3 and CaO and relatively higher contents of MnO and MgO. Both of spots 2&5 have almost similar contents of TiO_2 like that of spots 1, 3 and 4. In contrast, the two spots have relatively lower contents of Fe_2O_3, MnO and MgO and relatively higher contents of SiO_2, Al_2O_3 and CaO. Also, the two spots have relatively higher contents of str and /or mol water. The value of OT of spot 2 equals 91.09% and that of spot 5 equals 90.89%. It is clear that the lpsr phases of spots 1, 3 and 4 are different than those of spots 2&5 which their contents of SiO_2&Al_2O_3 seem to be associated with the str and/or mol water characteristic for them.

The lpsr spots of these two last grains have contents of TiO_2, Fe_2O_3, Fe, and Ti/(Ti+Fe) ratio range between 73.63-83.14%, 18.73-11.62%, 0.97-0.5, and 0.75-0.86, respectively. The detected lpsr spots of the grains have the chemical formulas range of $Fe_{0.97-0.5}Ti_3O_{5.89-4.45}(OH)_{3.11-4.55}$ (Table 1).

The grain (Figure 2g), was originally a definite altered silicate mineral where most of the contents of SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O are leached out with the enrichment of the minor contained TiO_2. The detection of the various analyzed spots of the grain reflects that the decreasing of these oxide contents almost equals the increasing content of TiO_2. Note that the chemical composition of spot 1 seems as lpsr (Table 1, grain 2g).

Both of the two grains (Figure 2h,2i), have the similar lpsr phase which was broken into oxy- and/or oxyhydroxide iron and titanium individual phases. In the grain (Figure 2j), spots 1&2 are lpsr of a definite phase while spots 3&4 are lpsr of another different phase.

Both of the two grains (Figure 2k,2l), are collapsed lpsr into oxy- and/or oxyhydroxide iron and titanium individual phases. Comparing spots 1, 2 and 3 with spots 4&5 of grain 2k reflects the effect of the content of structural and/or molecular water on the darkness of BSE image of the analyzed spot areas. As their contents increase, as the darkness degree increases.

In the grain (Figure 2m), both of the analyzed spots 1,2 and 3 are a definite lpsr phase mixed with an individual Ti-phase. Not all the analyzed TiO_2 content is included within the lpsr structure. The spots from 4 to 9 are composed of mixed two individual phases of iron and titanium which occur as oxy- and/or oxyhydroxides. See both of the BSE image of grain (Figure 2m), and their corresponding OT% values (Table 1). The recorded lpsr spots of the two grains (Figure 2j,2m), have contents of TiO_2, Fe_2O_3, Fe, and Ti/(Ti+Fe) ratio range between 76.99-83.17%, 15.45-9.12%, 0.85-0.53, and 0.78-0.85, respectively. The detected lpsr spots of the grains have the chemical formulas range of $Fe_{0.85-0.53}Ti_3O_{5.54-4.58}(OH)_{3.46-4.42}$ (Table 1).

Also, the grain (Figure 2n, Table 1), is composed of mixed two individual phases of iron and titanium each as oxy-and/or oxyhydroxides. Spot 1 contains more structural and/or molecular water although have relatively lower TiO_2 content.

All the detected lpsr spots of the grains (Figure 2a-2n), have the chemical formulas range of $Fe_{1.49-0.50}Ti_3O_{7.4-4.45}(OH)_{1.6-3.46}$ (Table 1). The Ti/(Ti+Fe) ratio ranges between 0.67 and 0.86.

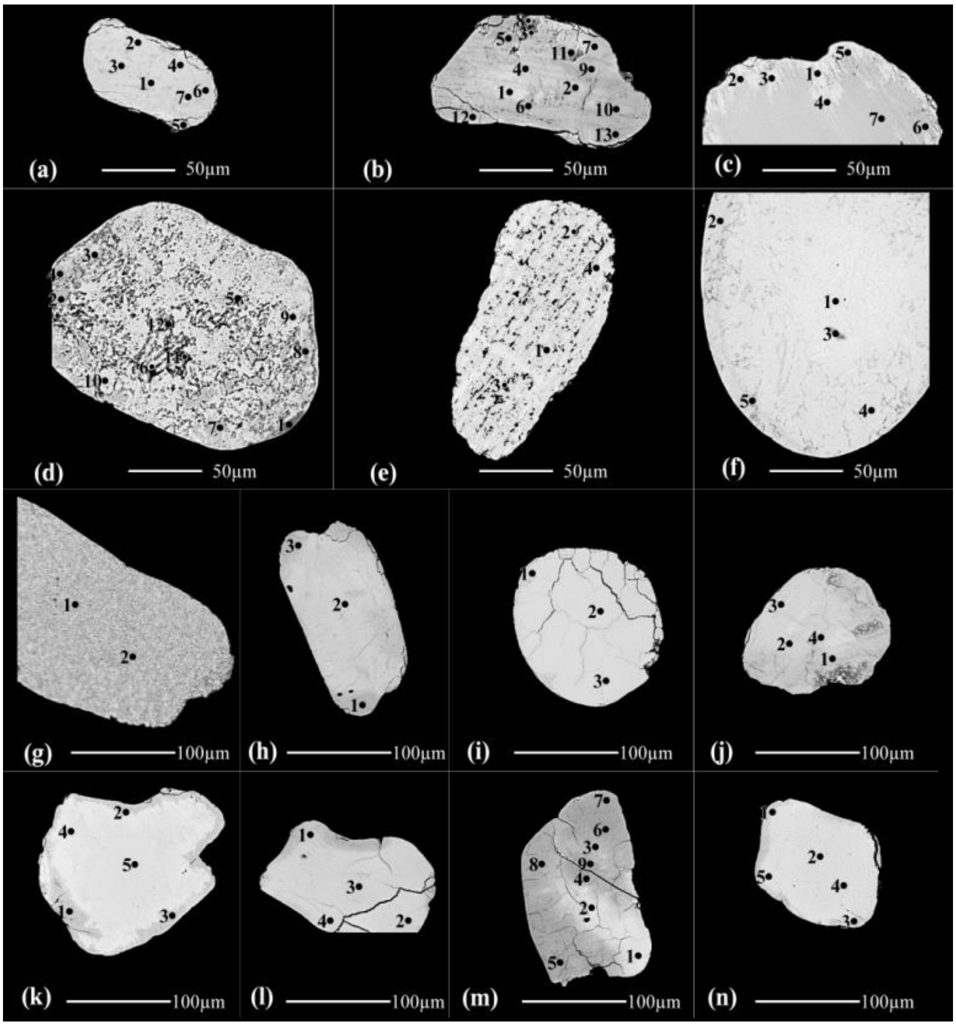

Figure 2. The back scattered electron (BSE) images of the altered brown, yellowish brown & brownish yellow ilmenite grains; (**2a**) to (**2n**), separated as magnetic at 0.5 ampere value.

Table 1. The microprobe chemical analyses and the corresponding molecular formula of the analyzed spots of the altered brown ilmenite grains; (Figure 1a-1g), the altered brown, yellowish brown&brownish yellow ilmenite grains; (Figure 2a-2n), the altered pale brown, yellow, creamy and white coloured ilmenite grains; (Figure 3a-3i), separated as magnetic at 0.5 ampere value.

Grains	Spots	SiO_2	MgO	MnO	CaO	ZnO	Fe_2O_3	Al_2O_3	Cr_2O_3	Na_2O	K_2O	TiO_2	O Total	OH%	H2O%	N Total	Fe_2	Ti_3	Ox	OHy	Losed Fe	Ti/(Ti+Fe)
1a	1	0.62	0.26	0.57	0.46	0.00	20.70	0.63	0.11	0.02	0.01	68.81	92.19	13.94	7.38	99.58	1.07	3	6.16	2.84	0.93	0.74
	4	0.68	0.25	0.51	0.51	0.08	19.42	0.61	0.12	0.00	0.01	70.50	92.69	15.22	8.06	100.75	0.99	3	5.93	3.07	1.01	0.75
	7	0.75	0.26	0.59	0.39	0.16	18.60	0.67	0.11	0.00	0.01	71.42	92.98	15.87	8.40	101.38	0.95	3	5.82	3.18	1.05	0.76
	8	0.74	0.25	0.51	0.37	0.03	18.51	0.64	0.14	0.01	0.03	72.15	93.37	16.26	8.61	101.99	0.93	3	5.75	3.25	1.07	0.76
1b	1	0.70	0.11	0.29	0.29	0.00	15.79	0.75	0.35	0.01	0.01	76.62	94.89	19.26	10.20	105.09	0.75	3	5.26	3.74	1.25	0.80
	2	0.74	0.12	0.20	0.32	0.00	14.22	1.01	0.30	0.00	0.01	76.88	93.80	20.17	10.68	104.49	0.70	3	5.11	3.89	1.30	0.81
	4	0.76	0.07	0.19	0.32	0.00	14.13	1.09	0.39	0.01	0.00	77.81	94.78	20.27	10.74	105.51	0.70	3	5.10	3.90	1.30	0.81
	8	0.90	0.11	0.11	0.32	0.06	12.72	1.13	0.45	0.04	0.04	79.01	94.89	21.20	11.23	106.11	0.65	3	4.96	4.04	1.35	0.82
1c	1	48.27	0.70	0.01	0.20	0.04	3.49	36.23	0.03	0.04	0.25	1.82	91.07	-223.24	-118.23	-27.16	208.70	3	730.28	-721.28	-206.70	
	2	0.92	0.17	0.09	0.39	0.03	7.78	1.62	0.63	0.05	0.03	82.15	93.83	24.53	12.99	106.82	0.49	3	4.46	4.54	1.51	0.86
	4	1.07	0.26	0.03	0.41	0.07	7.25	1.53	0.79	0.03	0.05	82.43	93.91	24.66	13.06	106.97	0.48	3	4.44	4.56	1.52	0.86
	8	0.87	0.24	0.06	0.37	0.14	6.68	1.40	0.70	0.03	0.04	84.11	94.65	25.67	13.60	108.24	0.43	3	4.29	4.71	1.57	0.87
1d	1	5.85	0.93	0.15	0.50	0.02	16.57	2.68	0.46	0.05	0.29	67.89	95.38	7.46	3.95	99.34	1.43	3	7.46	1.54	0.57	0.68
	2	1.71	0.51	0.41	0.37	0.01	23.28	1.12	0.25	0.01	0.03	68.66	96.34	10.09	5.34	101.68	1.30	3	6.89	2.11	0.70	0.70
	3	0.83	0.40	0.20	0.36	0.00	22.93	0.82	0.32	0.02	0.05	69.50	95.43	12.05	6.38	101.81	1.18	3	6.51	2.49	0.82	0.72
	4	1.08	0.50	0.29	0.40	0.03	21.81	0.97	0.35	0.05	0.04	70.60	96.10	12.48	6.61	102.71	1.16	3	6.43	2.57	0.84	0.72
	7	1.49	0.21	0.01	0.54	0.02	9.70	1.22	0.60	0.00	0.06	81.86	95.69	22.79	12.07	107.76	0.57	3	4.73	4.27	1.43	0.84
1e	1	46.02	6.23	0.09	0.62	0.10	16.12	10.21	0.03	0.10	3.82	7.53	90.85	-152.07	-80.53	10.32	45.23	3	152.35	-143.35	-43.23	
	5	35.55	6.48	0.17	0.44	0.01	18.82	8.20	0.03	0.06	2.18	22.43	94.38	-90.07	-47.70	46.67	12.90	3	45.17	-36.17	-10.90	
	6	1.60	0.87	0.43	0.14	0.07	27.95	0.55	0.10	0.03	0.11	64.32	96.15	6.04	3.20	99.35	1.58	3	7.69	1.31	0.42	0.66
	8	0.59	0.40	0.24	0.24	0.08	14.51	0.66	0.08	0.06	0.06	79.76	96.66	20.82	11.03	107.69	0.68	3	5.00	4.00	1.32	0.81
	9	0.16	0.13	0.10	0.23	0.03	3.18	0.93	0.04	0.06	0.01	91.11	95.97	30.76	16.29	112.26	0.19	3	3.54	5.46	1.81	
	12	0.03	0.03	0.07	0.18	0.01	1.25	1.12	0.12	0.06	0.02	94.13	97.01	32.31	17.11	114.12	0.12	3	3.34	5.66	1.88	
1f	1	36.56	1.09	0.12	1.10	0.00	3.76	25.65	0.06	0.04	0.14	6.68	75.20	-175.18	-92.78	-17.58	43.50	3	153.29	-144.29	-41.50	
	6	12.21	0.46	0.09	0.32	0.00	2.20	9.13	0.04	0.00	0.06	72.26	96.76	5.75	3.05	99.80	1.42	3	7.88	1.12	0.58	
	9	0.37	0.13	1.04	0.28	0.02	28.06	0.22	0.00	0.04	0.00	65.85	96.00	8.61	4.56	100.56	1.40	3	7.15	1.85	0.60	0.68
	13	0.42	0.08	0.94	0.32	0.08	26.55	0.16	0.05	0.02	0.00	67.53	96.14	10.20	5.40	101.54	1.30	3	6.84	2.16	0.70	0.70
	17	0.85	0.18	0.35	0.52	0.00	14.09	0.35	0.06	0.03	0.00	68.42	84.85	19.19	10.16	95.01	0.76	3	5.27	3.73	1.24	0.80
	21	0.01	0.01	0.25	0.04	0.01	13.60	0.00	0.03	0.00	0.01	86.56	100.49	24.26	12.85	113.34	0.49	3	4.44	4.56	1.51	0.86
	22	0.01	0.00	0.02	0.06	0.00	2.53	0.00	0.10	0.00	0.00	96.17	98.89	32.75	17.35	116.24	0.09	3	3.25	5.75	1.91	
	24	0.28	0.00	0.01	0.04	0.01	0.44	0.17	0.10	0.02	0.01	98.97	100.04	33.83	17.92	117.96	0.04	3	3.13	5.87	1.96	

Grains	Spots	SiO_2	MgO	MnO	CaO	ZnO	Fe_2O_3	Al_2O_3	Cr_2O_3	Na_2O	K_2O	TiO_2	O Total	OH%	H2O%	N Total	Fe_2	Ti_3	Ox	OHy	Losed Fe	Ti/(Ti+Fe)
1g	1	0.20	0.09	0.67	0.13	0.00	28.69	0.22	0.02	0.01	0.01	65.75	95.78	8.69	4.60	100.38	1.39	3	7.13	1.87	0.61	0.68
	10	0.40	0.13	0.53	0.31	0.00	24.98	0.40	0.08	0.03	0.03	68.71	95.59	11.60	6.14	101.73	1.21	3	6.58	2.42	0.79	0.71
	11	0.41	0.10	0.53	0.32	0.03	23.78	0.38	0.05	0.02	0.01	69.93	95.56	12.81	6.79	102.34	1.13	3	6.35	2.65	0.87	0.73
	12	0.54	0.16	0.39	0.38	0.07	22.09	0.46	0.04	0.01	0.01	70.46	94.60	13.90	7.36	101.96	1.06	3	6.16	2.84	0.94	0.74
	13	0.69	0.16	0.32	0.36	0.00	21.75	0.71	0.13	0.03	0.02	70.65	94.82	13.76	7.29	102.11	1.07	3	6.19	2.81	0.93	0.74
	15	1.04	0.21	0.13	0.45	0.14	13.40	1.12	0.12	0.05	0.03	75.04	91.71	19.90	10.54	102.25	0.73	3	5.17	3.83	1.27	0.81
	17	1.08	0.22	0.15	0.52	0.07	11.13	1.09	0.04	0.10	0.02	78.27	92.68	22.11	11.71	104.38	0.61	3	4.82	4.18	1.39	0.83
	19	1.20	0.21	0.13	0.57	0.10	9.14	1.17	0.02	0.07	0.00	79.66	92.24	23.59	12.50	104.74	0.54	3	4.60	4.40	1.46	0.85
	20	0.08	0.08	0.01	0.12	0.09	0.79	1.07	0.03	0.08	0.04	93.80	96.19	32.66	17.30	113.49	0.11	3	3.29	5.71	1.89	
2a	1	1.03	0.72	0.34	0.31	0.07	20.14	0.97	0.18	0.01	0.03	72.24	96.04	14.09	7.46	103.50	1.06	3	6.15	2.85	0.94	0.74
	4	1.02	0.75	0.40	0.34	0.03	19.66	1.01	0.27	0.05	0.04	73.30	96.86	14.51	7.68	104.54	1.04	3	6.07	2.93	0.96	0.74
	7	2.32	0.47	0.17	0.46	0.10	11.24	1.50	0.30	0.03	0.11	79.70	96.37	20.01	10.60	106.97	0.72	3	5.18	3.82	1.28	0.81
2b	1	0.90	0.42	0.52	0.21	0.00	24.15	1.18	0.38	0.00	0.03	68.83	96.61	10.44	5.53	102.14	1.28	3	6.81	2.19	0.72	0.70
	2	0.73	0.25	0.20	0.27	0.02	17.42	1.76	0.62	0.00	0.02	72.10	93.38	15.78	8.36	101.74	0.95	3	5.86	3.14	1.05	0.76
	3	0.75	0.22	0.03	0.29	0.00	6.15	3.17	0.77	0.02	0.02	72.84	84.25	23.07	12.22	96.47	0.57	3	4.71	4.29	1.43	
	7	0.65	0.20	0.17	0.23	0.00	13.49	1.51	0.60	0.01	0.01	75.40	92.28	19.81	10.49	102.77	0.73	3	5.18	3.82	1.27	0.80
	8	1.14	0.27	0.05	0.30	0.00	8.29	5.29	0.67	0.17	0.01	76.40	92.60	19.08	10.11	102.70	0.80	3	5.37	3.63	1.20	
	9	0.81	0.23	0.08	0.30	0.00	10.92	1.78	0.80	0.00	0.01	78.87	93.79	21.66	11.47	105.26	0.63	3	4.90	4.10	1.37	
	13	0.78	0.17	0.08	0.35	0.00	4.37	1.02	0.92	0.01	0.01	84.68	92.39	27.96	14.81	107.20	0.32	3	3.95	5.05	1.68	
2c	2	0.59	0.13	1.01	0.28	0.06	25.11	0.57	0.46	0.00	0.01	68.25	96.45	10.46	5.54	101.99	1.28	3	6.79	2.21	0.72	0.70
	4	0.39	0.17	1.13	0.22	0.08	25.00	0.38	0.32	0.00	0.01	69.34	97.04	11.29	5.98	103.02	1.23	3	6.63	2.37	0.77	0.71
	6	1.14	0.19	0.23	0.50	0.00	13.05	1.01	1.04	0.00	0.01	74.97	92.13	19.47	10.31	102.44	0.74	3	5.24	3.76	1.26	0.80
	8	1.15	0.16	0.20	0.51	0.05	13.89	0.96	0.93	0.05	0.02	77.16	95.08	19.34	10.24	105.32	0.75	3	5.26	3.74	1.25	0.80
2d	1	29.91	13.50	0.84	0.35	0.00	25.04	17.44	0.00	0.10	0.51	0.97	88.65	-169.17	-89.59	-0.94	376.74	3	1162.18	-1153.18	-374.74	
	3	22.18	0.02	0.03	20.69	0.00	0.49	0.49	0.01	0.00	0.01	56.16	100.08	-15.79	-8.36	91.72	3.22	3	12.66	-3.66	-1.22	
	6	1.72	0.23	0.92	1.70	0.00	2.52	3.73	0.09	0.19	0.11	74.06	85.27	23.03	12.20	97.47	0.62	3	4.74	4.26	1.38	
	7	6.94	0.10	0.16	6.76	0.00	1.43	1.10	0.04	0.08	0.04	82.06	98.69	18.91	10.01	108.70	0.83	3	5.44	3.56	1.17	
	8	1.28	0.32	0.67	1.26	0.00	3.40	3.16	0.09	0.18	0.04	85.32	95.70	25.34	13.42	109.13	0.49	3	4.37	4.63	1.51	
	12	1.19	0.12	0.27	1.02	0.00	1.21	1.71	0.06	0.14	0.06	91.73	97.52	29.59	15.67	113.19	0.26	3	3.74	5.26	1.74	
2e	1	0.34	0.57	0.43	0.15	0.00	17.35	0.71	0.14	0.07	0.03	74.75	94.53	17.93	9.50	104.02	0.85	3	5.47	3.53	1.15	0.78
	2	0.20	0.41	0.12	0.08	0.00	11.62	0.33	0.10	0.05	0.02	83.14	96.07	24.35	12.90	108.96	0.50	3	4.45	4.55	1.50	0.86
	3	1.04	0.09	0.03	0.10	0.00	2.87	2.04	0.10	0.06	0.04	84.43	90.78	28.62	15.16	105.94	0.29	3	3.89	5.11	1.71	
	4	0.04	0.22	0.04	0.01	0.00	7.77	0.11	0.05	0.01	0.00	89.72	97.96	28.46	15.07	113.03	0.29	3	3.84	5.16	1.71	
2f	1	0.72	0.32	0.21	0.24	0.00	18.73	1.43	0.43	0.08	0.07	73.63	95.85	15.56	8.24	104.10	0.97	3	5.89	3.11	1.03	0.75
	2	0.91	0.26	0.08	0.37	0.00	13.60	1.70	0.44	0.07	0.02	73.64	91.09	18.87	9.99	101.08	0.79	3	5.34	3.66	1.21	0.79
	3	0.72	0.31	0.16	0.23	0.00	17.99	1.30	0.41	0.02	0.03	74.07	95.25	16.43	8.70	103.95	0.92	3	5.74	3.26	1.08	0.77
	4	0.68	0.31	0.18	0.30	0.00	15.91	1.21	0.39	0.05	0.02	74.11	93.15	18.04	9.55	102.71	0.83	3	5.47	3.53	1.17	0.78
	5	1.01	0.25	0.08	0.44	0.00	12.30	1.73	0.52	0.08	0.03	74.47	90.89	19.76	10.46	101.35	0.74	3	5.20	3.80	1.26	0.80

Grains	Spots	SiO_2	MgO	MnO	CaO	ZnO	Fe_2O_3	Al_2O_3	Cr_2O_3	Na_2O	K_2O	TiO_2	O Total	OH%	H2O%	N Total	Fe_2	Ti_3	Ox	OHy	Losed Fe	Ti/(Ti+Fe)
2g	1	13.38	1.22	0.03	0.43	0.00	8.71	4.02	0.10	0.14	0.72	68.87	97.62	2.91	1.54	99.16	1.64	3	8.41	0.59	0.36	
	2	5.45	0.44	0.01	0.39	0.00	6.55	1.44	0.09	0.19	0.28	82.75	97.59	20.59	10.90	108.50	0.67	3	5.16	3.84	1.33	
2h	2	1.26	0.23	0.17	0.29	0.00	6.64	1.56	1.08	0.06	0.03	85.63	96.95	25.05	13.27	110.21	0.46	3	4.39	4.61	1.54	
2i	1	0.99	0.19	0.17	0.41	0.00	5.56	1.03	1.51	0.05	0.00	84.84	94.74	26.25	13.90	108.64	0.40	3	4.20	4.80	1.60	
	3	1.01	0.16	0.08	0.37	0.00	5.55	1.04	1.62	0.10	0.05	87.32	97.28	26.42	13.99	111.27	0.39	3	4.17	4.83	1.61	
2j	2	0.94	0.54	0.09	0.46	0.00	13.33	0.74	0.91	0.02	0.05	79.56	96.64	20.42	10.82	107.45	0.70	3	5.08	3.92	1.30	0.81
	4	0.94	0.16	0.03	0.37	0.00	5.30	0.62	1.37	0.08	0.04	88.36	97.27	27.41	14.51	111.78	0.34	3	4.02	4.98	1.66	
2k	1	0.61	0.17	0.03	0.42	0.00	3.75	0.72	0.90	0.05	0.03	87.49	94.16	29.09	15.40	109.57	0.27	3	3.78	5.22	1.73	
	2	0.62	0.15	0.03	0.32	0.00	4.12	0.67	0.73	0.05	0.05	87.88	94.63	29.07	15.40	110.02	0.27	3	3.78	5.22	1.73	
	3	0.65	0.12	0.02	0.33	0.00	4.02	0.67	0.80	0.02	0.06	88.98	95.68	29.17	15.45	111.13	0.26	3	3.77	5.23	1.74	
	4	0.86	0.15	0.00	0.42	0.00	2.98	0.73	1.38	0.07	0.05	91.48	98.12	29.25	15.49	113.61	0.26	3	3.77	5.23	1.74	
	5	0.77	0.17	0.02	0.41	0.00	2.74	0.67	1.41	0.00	0.03	91.72	97.93	29.60	15.68	113.61	0.24	3	3.71	5.29	1.76	
2l	1	1.05	0.20	0.03	0.42	0.00	3.39	2.06	1.06	0.04	0.05	88.22	96.52	27.40	14.51	111.03	0.35	3	4.06	4.94	1.65	
	4	1.03	0.21	0.08	0.37	0.00	2.79	1.82	1.10	0.07	0.05	89.26	96.77	28.13	14.90	111.67	0.32	3	3.95	5.05	1.68	
2m	2	0.78	0.19	0.09	0.20	0.00	11.07	2.64	0.18	0.08	0.03	81.63	96.89	21.62	11.45	108.33	0.64	3	4.92	4.08	1.36	0.82
	3	0.73	0.17	0.02	0.25	0.00	9.12	2.21	0.19	0.06	0.04	83.17	95.95	23.74	12.57	108.52	0.53	3	4.58	4.42	1.47	0.85
	5	0.75	0.15	0.07	0.27	0.00	5.23	1.61	0.24	0.06	0.01	85.39	93.77	27.37	14.50	108.27	0.35	3	4.04	4.96	1.65	
	9	0.67	0.14	0.06	0.26	0.00	5.01	1.55	0.24	0.05	0.02	87.35	95.36	27.86	14.76	110.11	0.33	3	3.97	5.03	1.67	
2n	1	0.90	0.17	0.05	0.41	0.00	4.62	1.05	0.59	0.03	0.02	85.82	93.66	27.90	14.78	108.44	0.32	3	3.96	5.04	1.68	
	5	0.88	0.15	0.03	0.29	0.00	3.83	0.99	0.69	0.08	0.04	90.05	97.02	28.87	15.29	112.31	0.28	3	3.82	5.18	1.72	
3a	2	1.03	0.24	0.08	0.53	0.00	9.89	3.14	0.60	0.09	0.02	78.37	93.98	20.59	10.90	104.89	0.70	3	5.09	3.91	1.30	0.81
	3	1.00	0.22	0.06	0.51	0.00	9.18	2.98	0.60	0.07	0.02	79.27	93.91	21.50	11.39	105.30	0.65	3	4.95	4.05	1.35	0.82
	5	0.98	0.24	0.04	0.40	0.00	10.39	2.90	0.81	0.12	0.05	80.73	96.66	20.83	11.03	107.69	0.69	3	5.05	3.95	1.31	0.81
	6	0.96	0.25	0.03	0.36	0.00	10.51	2.62	0.90	0.10	0.07	81.31	97.09	21.11	11.18	108.27	0.67	3	5.00	4.00	1.33	0.82
3b	1	1.87	0.48	0.09	0.50	0.00	4.19	2.30	0.82	0.06	0.05	82.13	92.49	24.89	13.18	105.67	0.48	3	4.45	4.55	1.52	0.86
	3	1.23	0.31	0.11	0.41	0.00	4.36	2.11	0.65	0.12	0.09	84.15	93.54	26.18	13.87	107.40	0.42	3	4.24	4.76	1.58	0.88
	5	1.70	0.39	0.03	0.39	0.00	3.83	2.17	0.97	0.12	0.08	86.61	96.28	25.98	13.76	110.04	0.43	3	4.28	4.72	1.57	0.88
3c	1	97.64	0.00	0.00	0.01	0.00	0.02	0.01	0.03	0.00	0.01	1.14	98.86	-271.13	-143.59	-44.73	340.60	3	1365.08	-1356.08	-338.60	
	2	0.73	0.13	0.05	0.31	0.00	3.22	1.16	1.75	0.07	0.01	88.11	95.54	28.38	15.03	110.57	0.30	3	3.89	5.11	1.70	0.91
	6	0.79	0.14	0.05	0.30	0.00	3.35	1.23	1.64	0.08	0.02	89.49	97.08	28.33	15.00	112.08	0.30	3	3.90	5.10	1.70	0.91

Grains	Spots	SiO_2	MgO	MnO	CaO	ZnO	Fe_2O_3	Al_2O_3	Cr_2O_3	Na_2O	K_2O	TiO_2	O Total	OH%	H2O%	N Total	Fe_2	Ti_3	Ox	OHy	Losed Fe	Ti/(Ti+Fe)
3d	1	10.89	4.09	0.13	0.17	0.00	8.40	4.86	0.10	0.03	0.82	67.82	97.32	2.35	1.25	98.57	1.79	3	8.52	0.48	0.21	
	2	9.28	3.73	0.07	0.28	0.00	7.78	4.79	0.11	0.08	0.61	70.15	96.87	5.92	3.14	100.00	1.57	3	7.81	1.19	0.43	
	4	7.54	3.32	0.07	0.14	0.00	6.33	3.81	0.11	0.04	0.19	75.80	97.35	12.28	6.50	103.86	1.18	3	6.62	2.38	0.82	
	7	10.33	0.51	0.05	0.16	0.00	3.47	0.77	0.10	0.06	0.27	83.36	99.09	18.28	9.68	108.77	0.74	3	5.61	3.39	1.26	
3e	1	3.48	0.30	0.01	0.30	0.00	4.49	5.10	0.43	0.09	0.08	83.47	97.76	20.76	11.00	108.76	0.68	3	5.15	3.85	1.32	0.81
	4	2.77	0.26	0.02	0.28	0.00	4.00	4.44	0.44	0.06	0.05	85.30	97.62	22.89	12.12	109.74	0.57	3	4.80	4.20	1.43	0.84
	6	1.78	0.20	0.00	0.30	0.00	4.40	3.82	0.42	0.02	0.03	86.42	97.41	24.54	12.99	110.40	0.49	3	4.52	4.48	1.51	0.86
3f	2	19.68	1.66	0.04	0.39	0.00	5.88	12.99	0.11	0.09	0.18	54.08	95.09	-20.82	-11.03	84.06	3.16	3	13.65	-4.65	-1.16	
	3	14.47	0.92	0.05	0.36	0.00	5.97	10.83	0.11	0.12	0.08	63.31	96.21	-5.62	-2.98	93.24	2.14	3	10.17	-1.17	-0.14	
	5	4.67	0.35	0.03	0.45	0.00	7.81	3.00	0.11	0.11	0.04	80.91	97.48	18.86	9.99	107.47	0.76	3	5.44	3.56	1.24	
	7	1.49	0.04	0.03	0.36	0.00	7.45	0.74	0.08	0.11	0.02	87.33	97.65	26.11	13.83	111.48	0.40	3	4.22	4.78	1.60	
3g	1	46.65	1.49	0.03	0.44	0.00	5.27	29.01	0.04	1.29	2.73	3.11	90.06	-198.23	-104.98	-14.92	119.83	3	403.44	-394.44	-117.83	
	3	30.48	0.00	0.00	28.84	0.00	0.14	0.56	0.01	0.02	0.00	41.06	101.11	-42.62	-22.57	78.54	6.04	3	21.07	-12.07	-4.04	
	5	30.06	0.00	0.03	28.43	0.00	0.21	0.78	0.03	0.01	0.01	41.21	100.76	-42.06	-22.28	78.49	5.97	3	20.86	-11.86	-3.97	
	6	5.10	0.00	0.00	0.46	0.00	0.18	0.09	0.06	0.00	0.03	84.87	90.80	27.97	14.81	105.61	0.28	3	4.05	4.95	1.72	
	9	0.05	0.02	0.00	0.32	0.00	0.27	0.00	0.05	0.01	0.03	100.31	101.05	34.20	18.11	119.16	0.03	3	3.07	5.93	1.97	
3h	3	28.34	0.01	0.00	26.51	0.00	1.11	2.44	0.01	0.00	0.01	41.92	100.33	-40.49	-21.45	78.88	5.75	3	20.25	-11.25	-3.75	
	4	27.51	0.02	0.00	25.23	0.00	2.31	1.18	0.00	0.00	0.00	43.76	100.00	-36.32	-19.24	80.76	5.26	3	18.82	-9.82	-3.26	
	5	2.04	0.38	0.11	0.99	0.00	3.33	8.81	0.02	0.18	0.06	72.12	88.04	16.90	8.95	96.99	0.94	3	5.81	3.19	1.06	
	6	0.20	0.02	0.00	0.71	0.00	2.33	0.44	0.00	0.00	0.02	96.97	100.68	31.91	16.90	117.58	0.13	3	3.38	5.62	1.87	
	10	0.01	0.01	0.00	0.56	0.00	0.35	0.00	0.01	0.02	0.01	100.07	101.02	34.07	18.04	119.06	0.04	3	3.08	5.92	1.96	
3i	1	0.51	0.10	0.03	0.24	0.00	5.97	0.87	0.78	0.05	0.00	84.72	93.27	27.49	14.56	107.83	0.34	3	4.01	4.99	1.66	
	4	0.48	0.09	0.00	0.22	0.00	5.97	0.88	0.79	0.04	0.01	86.01	94.49	27.64	14.64	109.13	0.33	3	3.98	5.02	1.67	
	8	0.51	0.08	0.00	0.21	0.00	5.59	0.81	0.79	0.11	0.03	89.22	97.36	28.16	14.91	112.27	0.31	3	3.91	5.09	1.69	
	10	0.60	0.10	0.01	0.10	0.00	4.91	0.82	0.83	0.11	0.03	90.30	97.80	28.64	15.17	112.97	0.28	3	3.84	5.16	1.72	

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3.1.3. The detected pale brown, yellow, and creamy coloured grain varieties at 0.5 ampere

Nine grains are investigated of this coloured grain varieties (Figure 3, Table 1). The grain (Figure 3a), is composed of a definite lpsr phase with variable amounts of structural and/or molecular water. Both of spots 1, 2 and 3 contain relatively higher amounts of str and/or mol water than those of spots 4, 5 and 6. The detected lpsr spots have contents of TiO_2, Fe_2O_3, Fe, and Ti/(Ti+Fe) ratio range between 77.38-81.31%, 10.89-9.18%, 0.72-0.67, and 0.81-0.82, respectively. The chemical formulas range are of $Fe_{0.72-0.67}Ti_3O_{5.14-4.95}(OH)_{3.86-4.05}$ (Table 1).

Except of spot 1 in the grain (Figure 3c), which is composed of silica, both of the three grains (Figure 3b,3c and 3e), are broken lpsr.

In the grain (Figure 3d), the contents of Al_2O_3 are varies directly with the contents of Fe_2O_3 in the analyzed spots. The contents of the analyzed Al_2O_3 are most probably related to the mechanism of psr alteration. It is clear that the contents of only SiO_2 are produced from an altered silicate mineral. In this grain as the TiO_2 contents enriched (more than 82%), as the contents of Al_2O_3 and structural and/or molecular water are highly decreases. The values of OT of the various analyzed spots are more than 98%.

In the grain (Figure 3f), spots 1, 2 and 3 are for a definite altered silicate mineral where most of SiO_2, Al_2O_3 and MgO contents are leached out while the TiO_2 contents are enriched. The spots 4, 5, 6 and 7 are mixed individual phases of Ti and Fe oxides.

Spot 1 of the grain (Figure 3g), is of a definite silicate mineral. The spots from 2 to 5 are sphene which seems have homogeneous chemical composition. The spots from 6 to 9 are for individual TiO_2 phase; most probably rutile. The contents of of Al_2O_3 in these last four spots indicate that the Al_2O_3 are not compatable with the well-defined rutile structure; TiO_2 ranges between 84.87 and 100.31%.

The spots from 1 to 4 of the grain (Figure 3h), are sphene. Comparing the chemical composition of spots 3, 4, with spot 5 may ensure that in spot 5 both of SiO_2 and CaO of sphene are leached by solutions containing both Al_2O_3 and Na_2O, leading to the enrichment of the immobile TiO_2. The spots from 6 to 10 are rutile after the leaching of sphene. These spots reflect the incompatibility of SiO_2& Al_2O_3 in the structure of rutile.

In the grain (Figure 3i), the spots of this grain are broken lpsr where they are composed mainly of individual TiO_2 phase and minor Fe_2O_3 phase.

3.1.4. The detected black coloured grains at 0.5 ampere

Seven black grains are investigated in the magnetic fraction of 0.5 ampere (Figure 4, Table 2). The grain (Figure 4a), is composed of Psr and lpsr phases. As the TiO_2 contents increase, as the contents of structural and/or molecular water increase. Also, according to the values of OT and NT of these spots, the calculated contents of structural water are not accepted. The presence of an individual TiO_2 phase associated with the lpsr phase is postulated (Table 2, grain 4a).

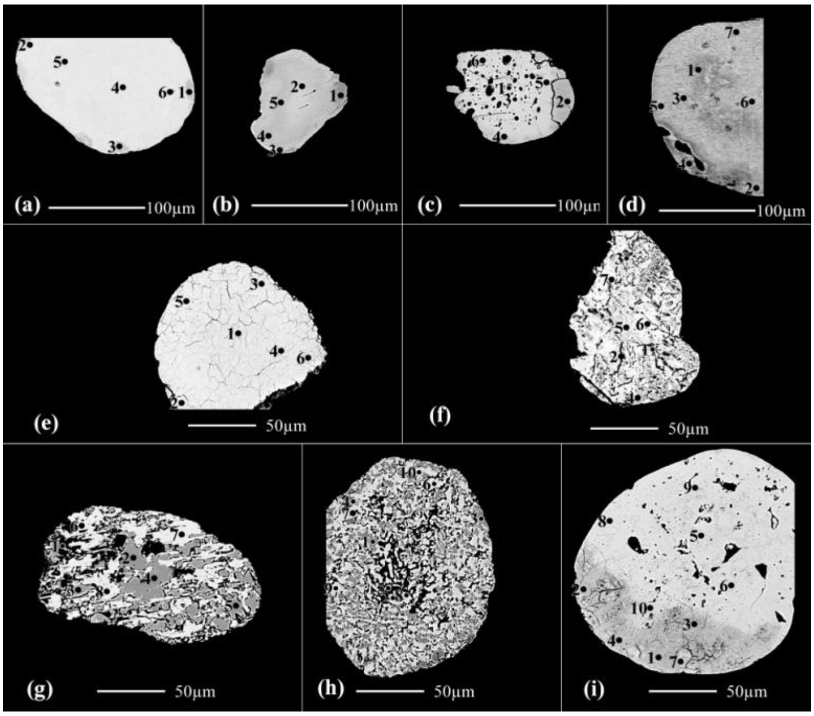

Figure 3. The back scattered electron (BSE) images of the altered pale brown, yellow, creamy and whitecoloured ilmenite grains; (**3a**) to (**3i**), separated as magnetic at 0.5 ampere value.

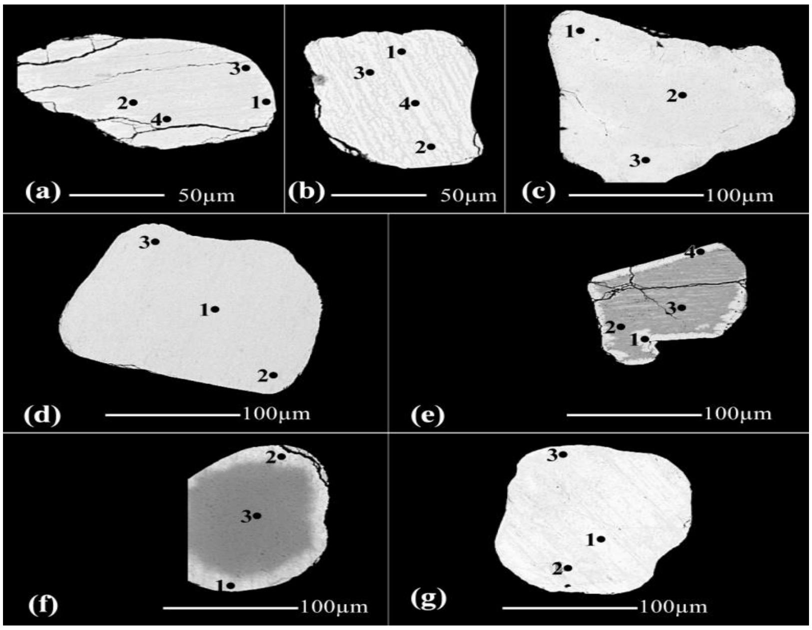

Figure 4. The back scattered electron (BSE) images of the altered black ilmenite grains; (**4a**) to (**4g**), separated as magnetic at 0.5 ampere value.

Table 2. The microprobe chemical analysis and the corresponding molecular formula of the analyzed spots of the altered black ilmenite grains; (Figure 4a-4g), separated as magnetic at 0.5 ampere value.

Grains	Spots	SiO_2	MgO	MnO	CaO	ZnO	Fe_2O_3	Al_2O_3	Cr_2O_3	Na_2O	K_2O	TiO_2	O Total	OH%	H_2O%	N Total	Fe_2	Ti_3	Ox	OHy	Losed Fe	Ti/(Ti+Fe)
Fig. 4a	1	0.44	0.18	0.93	0.20	0.00	29.35	0.26	0.19	0.04	0.03	64.15	95.76	6.97	3.69	99.45	1.51	3	7.48	1.52	0.49	0.66
	2	0.46	0.20	0.93	0.21	0.00	26.59	0.29	0.15	0.01	0.02	67.01	95.87	9.77	5.17	101.04	1.33	3	6.92	2.08	0.67	0.69
	3	0.58	0.22	0.80	0.24	0.00	24.25	0.35	0.23	0.09	0.04	68.44	95.23	11.54	6.11	101.35	1.22	3	6.59	2.41	0.78	0.71
	4	0.67	0.27	0.77	0.27	0.00	23.46	0.44	0.19	0.08	0.03	69.43	95.60	12.17	6.44	102.04	1.18	3	6.48	2.52	0.82	0.72
Fig. 4b	1	0.74	0.25	0.95	0.18	0.00	36.16	0.28	0.09	0.01	0.03	59.16	97.83	0.13	0.07	97.90	2.01	3	8.97	0.03	0.01-	0.60
	2	0.27	0.14	0.86	0.14	0.00	32.45	0.18	0.10	0.00	0.00	63.08	97.22	4.96	2.63	99.85	1.65	3	7.89	1.11	0.35	0.65
	3	0.27	0.08	0.71	0.16	0.00	30.98	0.16	0.08	0.01	0.02	63.76	96.22	6.34	3.36	99.58	1.55	3	7.60	1.40	0.45	0.66
	4	0.61	0.19	0.44	0.25	0.00	25.14	0.36	0.14	0.04	0.03	68.88	96.07	11.32	6.00	102.06	1.22	3	6.63	2.37	0.78	0.71
Fig. 4c	1	0.12	0.07	1.50	0.08	0.00	34.40	0.11	0.02	0.03	0.00	62.68	99.01	3.57	1.89	100.90	1.76	3	8.19	0.81	0.24	0.63
	2	0.12	0.12	1.48	0.08	0.00	33.86	0.11	0.02	0.01	0.02	63.10	98.92	4.06	2.15	101.07	1.73	3	8.08	0.92	0.27	0.63
	3	0.17	0.11	1.62	0.11	0.00	33.97	0.12	0.03	0.02	0.01	63.68	99.83	4.05	2.15	101.97	1.73	3	8.09	0.91	0.27	0.63
Fig. 4d	1	0.20	0.30	0.93	0.07	0.00	31.97	0.15	0.05	0.00	0.01	63.75	97.43	5.54	2.93	100.36	1.61	3	7.77	1.23	0.39	0.65
	2	0.28	0.39	1.51	0.10	0.00	30.44	0.15	0.04	0.02	0.02	64.02	96.96	6.17	3.27	100.23	1.58	3	7.64	1.36	0.42	0.65
	3	0.35	0.32	0.43	0.12	0.00	29.03	0.20	0.05	0.08	0.01	66.45	97.07	8.37	4.43	101.50	1.42	3	7.20	1.80	0.58	0.68
Fig. 4e	1	0.20	0.21	1.40	0.12	0.00	31.33	0.14	0.04	0.06	0.02	65.10	98.63	6.22	3.29	101.92	1.58	3	7.63	1.37	0.42	0.66
	2	0.57	0.32	0.99	0.31	0.00	20.69	0.41	0.15	0.05	0.02	71.12	94.64	14.56	7.71	102.35	1.04	3	6.04	2.96	0.96	0.74
	3	0.61	0.29	1.10	0.28	0.00	20.31	0.47	0.16	0.08	0.03	71.48	94.81	14.76	7.82	102.63	1.03	3	6.01	2.99	0.97	0.74
	4	0.51	0.26	1.21	0.29	0.00	20.74	0.36	0.14	0.07	0.03	72.51	96.12	14.91	7.90	104.02	1.02	3	5.97	3.03	0.98	0.75
Fig. 4f	1	0.34	0.29	0.32	0.13	0.00	24.03	1.32	0.31	0.04	0.02	71.62	98.41	12.10	6.41	104.82	1.18	3	6.50	2.50	0.82	0.72
	2	0.47	0.25	0.21	0.16	0.00	21.62	1.46	0.45	0.04	0.01	74.70	99.38	14.20	7.52	106.89	1.05	3	6.12	2.88	0.95	0.74
	3	0.97	0.16	0.03	0.35	0.00	7.45	1.72	0.95	0.08	0.06	85.65	97.42	24.80	13.14	110.55	0.48	3	4.42	4.58	1.52	0.86
Fig. 4g	1	0.42	0.25	0.42	0.14	0.00	31.32	0.25	0.16	0.04	0.01	64.26	97.25	5.98	3.17	100.42	1.57	3	7.68	1.32	0.43	0.66
	2	0.65	0.23	0.25	0.22	0.00	27.76	0.42	0.27	0.05	0.03	67.82	97.69	9.08	4.81	102.50	1.36	3	7.06	1.94	0.64	0.69
	3	0.66	0.16	0.34	0.27	0.00	25.37	0.50	0.29	0.05	0.05	69.50	97.18	11.07	5.86	103.05	1.24	3	6.68	2.32	0.76	0.71

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In the grain (Figure 4b), spot 1 is psr. Taking the calculated value of cationic iron of this spot into consideration (Table 2), it is detected that some amounts of analyzed iron still present as the divalent iron Fe^{++}. The psr of spot 1 is different than that of spots 2&3 which in turn are different than that of spot 4.

The values of OT for the analyzed spots of the other five grains (Figure 4c-4f), reflect that the grains are psr-lpsr of various chemical formulas. Some of their analyzed spots contain individual phases of TiO_2 in addition to the lpsr phases. As for example, the spots of 2, 3, and 4 of grain (Figure 4e), are lpsr of the same phase. The calculated NT values ensures that the calculated structural water is incorrect where the mechanism of alteration at these TiO_2 contents of the spots is changed.

The recorded psr-lpsr spots of the grains of (Figure 4), have contents of TiO_2, Fe_2O_3, Fe, and Ti/(Ti+Fe) ratio range between 59.16-74.7%, 36.16-20.31%, 2.01-0.48, and 0.6-0.75, respectively. The psr-lpsr spots of the grains have the chemical formulas range of $Fe_{2.01-0.48}Ti_3O_{8.97-4.42}(OH)_{0.03-4.48}$ (Table 2).

According to [33], within the pseudorutile composition range (60-71% TiO_2), the water content increased from ~ 2 to 4.5 wt.% with decreasing iron oxide content. The intermediate alteration phases comprised mixtures of TiO_2 with iron hydroxides.

In fact, within the given composition range of [33], the maximum limit of water content for the produced lpsr phases may be much more than the given maximum limit value. Even the lower limit value may be relatively lower than ~ 2%.

3.2. The separated magnetic fraction at 1 ampere

The magnetic fraction at one ampere is composed of light brown, brownish yellow and creamy coloured grains in addition to minor of the black grains. Most of the grains are spherical, sub-rounded to well rounded. The relatively coarser grains have highly pitted surfaces while the relatively finer ones have smooth surfaces.

Some grains of the magnetic fraction at 1 A are separated as light fraction of Clerici's solution (sp. Gr. = 4 g/cm^3). The grains have several coloured tints of pale brown, yellow, and cream with highly pitted surfaces. They contain a considerable number of the forementioned stained and coated grains.

Eight grains are investigated in the fraction (Figure 5, Table 3). Both of the two grains (Figure 5a,5b), are black , the five grains (Figure 5c-5g), have black cores and their surfaces are highly stained or partially coated with brownish, reddish, or yellowish white materials. The grain (Figure 5h), seems as locked grain between submetallic opaque mineral and altered light-coloured material.

Investigating the analyzed spots of grain 5a, reflects that as the TiO_2 contents increase, as the contents of str and/or mol water increase. Also, some of individual TiO_2 phase; most probably rutile, may be present with lpsr. The lpsr phase of spots 1&2 is different than that of spots 3&4.

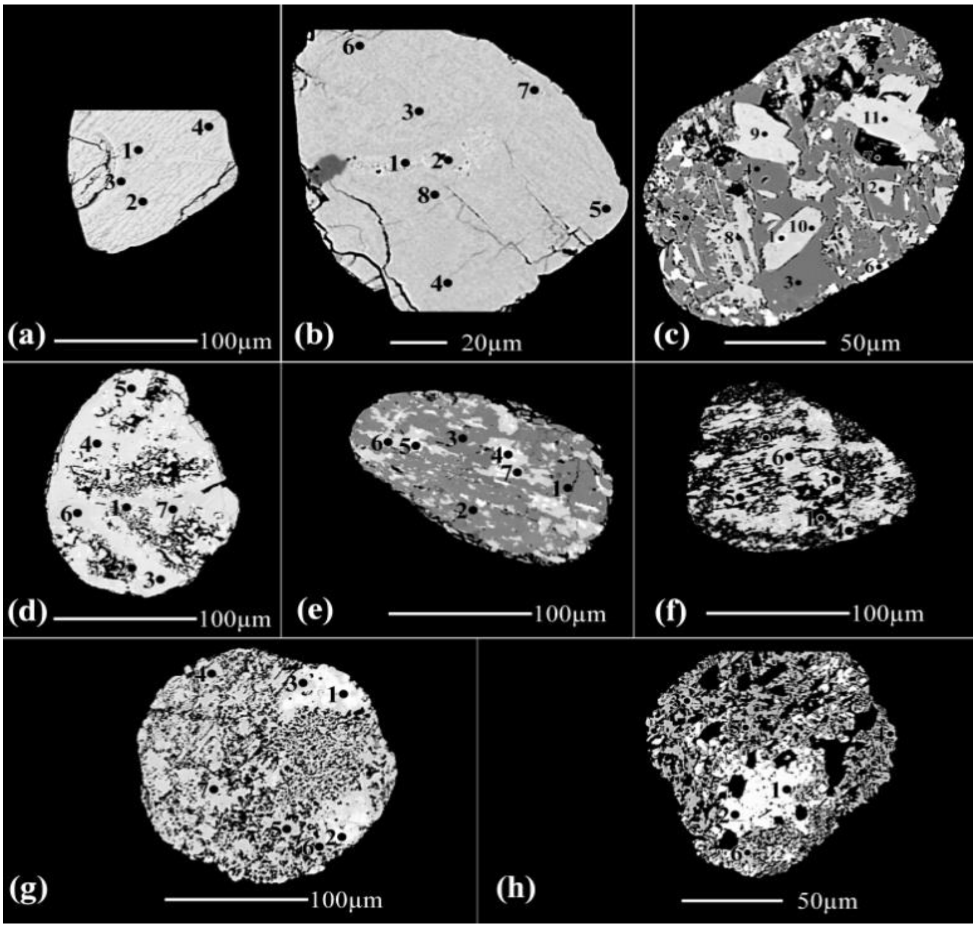

Figure 5. The back scattered electron (BSE) images of the altered black and brownish black coloured ilmenite grains; (**5a**) to (**5h**), separated as magnetic at 1 ampere value.

The grain (Figure 5b), is composed of lpsr except of spot 1 which is leached ilmenite containing 38.6% Fe_2O_3, 0.51% FeO, and a sum total oxides of 99.89%. The calculated chemical formula is $Fe^{2+}_{0.03}$ $Fe^{3+}_{1.94}$ Other cations $_{0.06}Ti_3O_9$ with a 0.97 as losed cationic iron.

In the brownish black grain (Figure 5c), spot 1 is an inclusion of titanomagnetite. The spots from 2 to 5 are sphene. The spots from 8 to 12 are ferriferous rutile where the contents of Fe_2O_3 decrease as the contents of TiO_2 increase and the OT values ranges between 100.3 and 100.8%. According to the BSE image of spot 6, it most probably a mixture of hydrated Ti and Fe oxide phases. On the other hand, spot 7 which is located inside a void, is ferriferous rutile where most of its iron content is leached.

The spots of grain (Figure 5d), contain an enriched TiO_2 phase; most probably rutile, after the alteration of a definite silicate mineral composed mainly of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and K_2O with minor TiO_2. The spots from 3 to 7 are highly enriched TiO_2 phase after the leaching for most of the other associated oxides. It was remarked that some spots of altered silicate minerals can be falsely considered as psr and lpsr according to their chemical compositions. Hence, both of the back scattered electron image (BSE) of the analyzed spot and the chemical composition analyses are at least required for the correct interpretation for such investigated situations. Also, it is obvious that the dependence on the powdered X-ray diffraction analysis (XRD) may be not enough to give correct decision during the investigation of some analyzed grains related to psr and lpsr alteration phases. The single crystal XRD may be more efficient technique in such situations.

The spots 1, 2 and 3 of the grain (Figure 5e), are sphene, both of spots 4&5 are leached ilmenite where the calculated contents of FeO, Fe_2O_3 and the losed iron value are 8.21%, 29.59% and 0.77 for spot 4; 19.99%, 21.04% and 0.55 for spot 5. Both of spots 6&7 are individual TiO_2 phases. Then, it is clear that sphene is substituted for preexisting ilmenite while the remaining ilmenite is altered to leached ilmenite.

The spot 1 of the grain (Figure 5f), is an altered silicate mineral. Spot 2 is mixture of silica and TiO_2. Spot 3 is ilmenite and rutile where most of the iron content is ferrous iron (Table 3); the other three spots are rutile.

The spots 1&2 of the grain (Figure 5g), are psr, spot 3 is broken lpsr to rutile and hematite. The spots from 4 to 7 are rutile after the leaching for most of the associated Fe_2O_3 contents causing many of scattered voids inside the grain.

The spots of 1,2 of the grain (Figure 5h), are leached ilmenite where the calculated contents of FeO, Fe_2O_3 and losed iron values are 28.8%, 12.05% and 0.33 for spot 1; 9.49, 29.63 and 0.76 for spot 2. The spots from 3 to 6 are rutile after the leaching of the associated Fe_2O_3; both rutile and hematite are obtained from a preexisting lpsr phase.

The detected psr-lpsr spots of the grains (Figure 5a,5b and 5g), have contents of TiO_2, Fe_2O_3, Fe, and Ti/(Ti+Fe) ratio range between 60.75-79.91%, 37.3-11.47%, 1.86-0.62, and 0.62-0.83, respectively. The detected lpsr spots of all the grains of (Figure 5), have the chemical formulas range of $Fe_{1.86-0.62}Ti_3O_{8.53-4.83}(OH)_{0.47-4.17}$ (Table 3).

3.3. The XRD results.

Table 3. The microprobe chemical analyses and the corresponding molecular formula of each analyzed spot of the altered black and browbnish black opaque ilmenite grains; (Figure 5a-5h), separated as magnetic at 1 ampere value.

Grains	Spots	SiO_2	MgO	MnO	CaO	ZnO	Fe_2O_3	Al_2O_3	Cr_2O_3	Na_2O	K_2O	TiO_2	O Total	OH%	H_2O%	N Total	Fe_2	Ti_3	Ox	OHy	Losed Fe	Ti/(Ti+Fe)
Fig. 5a	1	0.40	0.17	0.30	0.18	0.00	27.57	0.65	0.25	0.04	0.01	69.35	98.92	9.79	5.19	104.11	1.32	3	6.92	2.08	0.68	0.69
	3	0.71	0.25	0.21	0.42	0.00	13.63	1.14	0.47	0.05	0.05	78.89	95.81	20.48	10.84	106.65	0.70	3	5.07	3.93	1.30	0.81
Fig. 5b	1	0.13	0.06	0.47	0.05	0.00	39.18	0.06	0.03	0.07	0.02	59.87	99.96	-0.12	-0.07	99.89	2.03	3	9.03	-0.03	-0.03	
	2	0.06	0.05	0.44	0.08	0.00	37.30	0.01	0.01	0.03	0.02	61.74	99.74	2.03	1.08	100.81	1.86	3	8.53	0.47	0.14	0.62
	8	0.23	0.06	0.60	0.11	0.00	29.71	0.24	0.07	0.03	0.03	66.31	97.39	8.13	4.30	101.69	1.43	3	7.24	1.76	0.57	0.68
Fig. 5c	1	0.00	0.00	0.00	0.22	0.00	98.84	0.00	0.04	0.01	0.00	4.34	103.45	-86.63	-45.88	57.57	68.54	3	208.37	-199.37	-66.54	
	2	30.38	0.00	0.00	28.61	0.00	3.99	0.83	0.02	0.03	0.02	36.11	99.99	-50.38	-26.68	73.31	7.19	3	24.52	-15.52	-5.19	
	5	28.26	0.02	0.16	26.60	0.00	1.62	0.31	0.03	0.02	0.04	43.84	100.90	-36.59	-19.38	81.52	5.33	3	18.95	-9.95	-3.33	
	6	0.48	0.15	0.68	0.87	0.00	23.18	0.33	0.04	0.05	0.04	70.46	96.29	12.84	6.80	103.09	1.14	3	6.35	2.65	0.86	
	7	1.91	0.28	0.10	1.53	0.00	4.04	1.28	0.11	0.25	0.21	81.81	91.51	25.77	13.65	105.15	0.46	3	4.29	4.71	1.54	
	8	0.04	0.00	0.54	0.72	0.00	7.19	0.00	0.04	0.00	0.00	92.28	100.81	28.55	15.12	115.93	0.29	3	3.82	5.18	1.71	
	10	0.02	0.03	0.00	0.69	0.00	3.03	0.00	0.09	0.00	0.01	96.39	100.26	31.95	16.92	117.18	0.13	3	3.36	5.64	1.87	
	12	0.14	0.00	0.01	0.81	0.00	0.92	0.00	0.06	0.05	0.02	98.45	100.47	33.27	17.62	118.09	0.08	3	3.19	5.81	1.92	
Fig. 5d	3	0.03	0.03	0.00	0.01	0.00	1.35	0.00	0.02	0.01	0.02	98.09	99.55	33.68	17.84	117.38	0.05	3	3.14	5.86	1.95	
	5	0.00	0.00	0.03	0.04	0.00	0.68	0.00	0.00	0.02	0.01	98.44	99.22	34.18	18.10	117.32	0.03	3	3.07	5.93	1.97	
	7	0.11	0.00	0.00	0.05	0.00	0.40	0.00	0.00	0.04	0.02	99.68	100.30	34.26	18.14	118.44	0.02	3	3.06	5.94	1.98	
Fig. 5e	1	30.09	0.00	0.02	28.55	0.00	0.88	1.18	0.07	0.03	0.03	38.02	98.86	-46.67	-24.71	74.15	6.60	3	22.72	-13.72	-4.60	
	2	29.85	0.01	0.00	28.05	0.00	0.23	0.49	0.09	0.02	0.02	39.24	97.99	-43.74	-23.16	74.83	6.18	3	21.50	-12.50	-4.18	
	3	30.06	0.00	0.00	28.13	0.00	0.32	0.28	0.08	0.04	0.03	40.95	99.89	-41.84	-22.16	77.73	5.94	3	20.78	-11.78	-3.94	
	4	0.41	0.20	1.07	0.53	0.00	38.71	0.05	0.13	0.01	0.05	57.37	98.54	-1.98	-1.05	97.49	2.19	3	9.48	-0.48	-0.19	
	5	0.00	0.16	2.26	0.42	0.00	43.24	0.00	0.12	0.01	0.01	57.48	103.71	-4.66	-2.47	101.24	2.45	3	10.16	-1.16	-0.45	
	6	0.02	0.00	0.02	0.90	0.00	0.07	0.00	0.47	0.01	0.00	98.15	99.63	33.67	17.83	117.46	0.06	3	3.14	5.86	1.94	
	7	0.00	0.00	0.00	0.62	0.00	0.18	0.00	0.44	0.00	0.00	98.36	99.61	33.84	17.92	117.53	0.05	3	3.11	5.89	1.95	
Fig. 5f	1	43.69	4.87	0.05	0.42	0.00	15.28	11.64	0.05	0.15	3.26	9.04	88.45	-145.44	-77.03	11.42	35.81	3	122.37	-113.37	-33.81	
	2	78.87	0.95	0.00	0.16	0.00	2.19	2.07	0.03	0.10	0.59	10.83	95.79	-184.03	-97.46	-1.68	31.48	3	125.18	-116.18	-29.48	
	3	0.07	0.03	4.03	0.05	0.00	39.32	0.00	0.00	0.02	0.02	62.79	106.33	-0.45	-0.24	106.09	2.11	3	9.11	-0.11	-0.11	
Fig. 5g	1	0.95	0.37	0.72	0.33	0.00	31.19	0.82	0.30	0.10	0.02	60.75	95.54	3.01	1.60	97.14	1.80	3	8.32	0.68	0.20	0.63
	3	0.45	0.15	0.00	0.20	0.00	7.54	0.29	0.27	0.02	0.04	88.13	97.08	27.64	14.64	111.72	0.33	3	3.97	5.03	1.67	
	4	0.40	0.05	0.00	0.07	0.00	1.64	0.13	0.04	0.00	0.01	97.41	99.76	32.88	17.41	117.17	0.08	3	3.25	5.75	1.92	
	7	0.00	0.01	0.00	0.03	0.00	0.50	0.00	0.04	0.02	0.02	99.64	100.27	34.29	18.16	118.43	0.02	3	3.06	5.94	1.98	
Fig. 5h	3	1.58	0.26	0.00	0.20	0.00	1.47	0.82	0.00	0.05	0.05	95.32	99.76	30.74	16.28	116.04	0.19	3	3.58	5.42	1.81	
	6	0.52	0.01	0.02	0.13	0.00	0.85	0.40	0.02	0.01	0.01	97.26	99.24	33.04	17.50	116.73	0.08	3	3.24	5.76	1.92	

A small representative sample is taken from the magnetic fraction at 0.50 ampere. 200 grains are picked from each of the two detected coloured varieties; the various brown-coloured varieties and the black variety. The grains of each colour variety are splitted into two equal samples; each of 100 grains. One sample is subjected to the XRD and the other is roasted at 1100 ^{o}C for one hour and then treated using the XRD instrument. The sample of the non roasted brown coloured variety gave the composition of pseudorutile and rutile (Figure 6a) while after roasting gave the composition of rutile, pseudobrookite, and quartz (Figure 6b).

The results ensure the presence of individual TiO_2 phase (rutile), in association with the psr/lpsr alteration phases. Also, it is obvious that the hexagonal psr structure is unstable in comparison with the tetragonal rutile structure, a considerable TiO_2 content escaped from the broken psr structure and diffused inside the rutile structure. Both of the remaining TiO_2 and most of the Fe_2O_3 contents of the collapsed psr are modified into the orthorhombic pseudobrookite structure which seems to be more stable under the new prevailing conditions.

The sample of the non roasted black coloured variety gave the composition of rutile, hematite and quartz (Figure 6c) while after roasting gave the composition of pseudobrookite, rutile, hematite and quartz (Figure 6d). It is obvious that the presence of individual phases of TiO_2, Fe_2O_3, and SiO_2 affect the detection of individual psr/lpsr phases in X-ray diffractogram pattern.

It was noticed that after roasting most of the stained and/or coated materials are changed into translucent-transparent yellow and red primary rutile. Also, some of fibrous and very fine fragments of colourless silica are noticed in the container in which the magnetic grains are roasted.

A small representative sample (200 grains) is taken from the separated relatively lighter grains (sp. Gr. < 4 g/cm^3), of the magnetic fraction at 1 A. The grains are splitted into two equal samples, the first sample subjected to the XRD while the second subjected to roasting at 1100 ^{o}C for one hour and then treated using the XRD instrument. The first sample is composed of rutile with minor anatase and quartz (Figure 6e). The roasted sample gave the pattern of only rutile (Figure 6f). The detected mineral patterns are as accordance to the ASTM card numbers 4-0551, for rutile;19-182, for pseudorutile; 9-182, for pseudobrookite; 13-534, for hematite and 4-0477 for anatase.

The presence of anatase is not surprised. In some of the partially leucoxenated, or partially replaced ilmenite parts (e.g. by sphene), the final obtained TiO_2 polymorph of these parts may differ than that due to the leucoxenation of the non-altered; or the non-replaced, ilmenite component of the same grain. Also, the nature of the non-altered ilmenite component; whether normal ilmenite or ferriilmenite, the presence of exsolved titanhematite inside it, the orientation and relative percentage of such exsolved lamellae in the host ilmenite, may play another role in determining the formed type of the produced TiO_2 polymorph due to the difference of alteration rates. Because the rate of alteration could determine the type of the produced TiO_2 polymorph [13,34]. Then, the altered grains can contain more than one type of TiO_2 polymorph due to its complete leucoxenation.

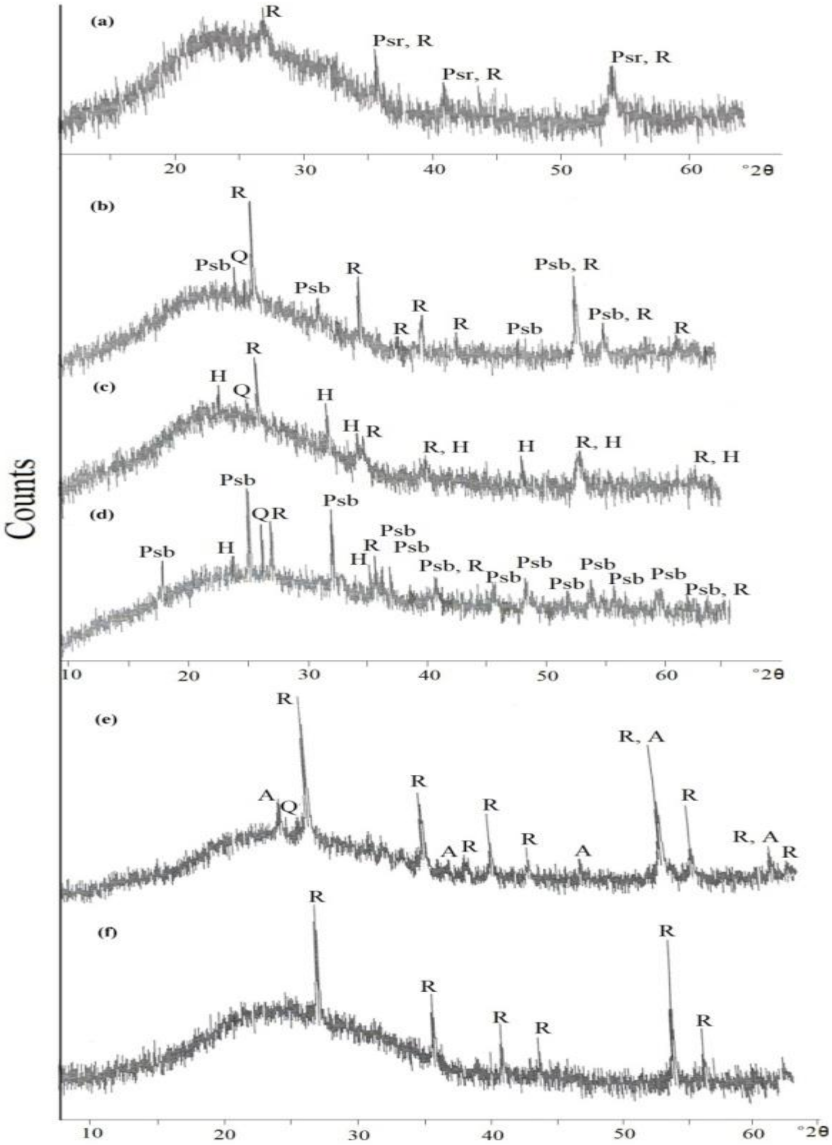

Figure 6. The X-ray diffractograms of the different altered ilmenite grains: the magnetic brown altered ilmenite of 0.5 ampere value before roasting (**a**) and after roasting (**b**); the magnetic black altered ilmenite of 0.5 ampere value before roasting (**c**) and after roasting (**d**); the non-magnetic altered ilmenite separated as light clerici's solution of 1ampere value before roasting (**e**) and after roasting (**f**).

3.4. The role of SiO_2 and Al_2O_3 in ilmenite alteration process

In many of the previous literatures, both of the recorded SiO_2& Al_2O_3 contents are considered as impurities and must be removed from the total oxides sum followed by the recalculation and correction of the other analyzed oxides. However, in case of lpsr phase spots, the most abundant analyzed oxide; TiO_2%, of the spot which will be highly affected by the recalculation and correction process. It increases with a relatively much more percent than the other analyzed oxides ; especially Fe_2O_3, the second major oxide of lpsr spot analysis. Then, if SiO_2 and/or Al_2O_3 are not impurities in a definite analyzed spot, but one or both them are originally associated with only TiO_2 or with only Fe_2O_3 then, some misleading results will be obtained due to the recalculation and corrections.

Aluminum and silicon are enriched due to iron depletion during the first stage of alteration, but their concentrations remain quite low, $Al_2O_3 \leq 0.4\%$ and $SiO_2 \leq 0.1\%$ [23,35]. For Ti/ (Ti+Fe) > 0.7, the aluminum and silicon levels increase rapidly with increasing Ti/(Ti+Fe) ratios, to maximum values near 1.5% Al_2O_3 and 0.5% SiO_2. This increase is due to co-precipitation or adsorption of these elements from the surrounding soil solutions onto the freshly-formed alteration products [23].

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The occurrence of gibbsite and clay minerals within the pores of the weathered grains was postulated. Then, the increase of Al and Si contents with the increase of Ti/(Ti+Fe) ratio as a consequence of the increase of abundance of pores available for crystallization of clay minerals, as ilmenite and pseudorutile alter isovolumetrically to porous rutile [18].

The presence of Al&Si is either inherited from original inclusions, kaolinite alteration of these inclusions or precipitated under pedogenic or early diagenetic conditions [34]. They are secondary mechanical enrichment [24].

In the process of ilmenite alteration and the formation of the various lpsr phases, it was detected that as both of the content of TiO_2 (within a definite TiO_2 range between 80-85%), and the associated str water increase, as the associated contents of Al_2O_3&SiO_2 increase. In fact, most of the detected lpsr spots having an appreciable contents of mol water, contain relatively higher contents of SiO_2 and Al_2O_3. This may indicates the ability of these two oxides for bearing mol water or OH^- anions. Then, both of SiO_2 and Al_2O_3 may be associated with the contained mol water in the altered grains [31].

Therefore, as the contents of str and/or mol water contained within the lpsr phases decrease; where the original total oxides sum (OT) is more than 98% and the contained TiO_2 is more than 85%, as the contents of SiO_2 and Al_2O_3 are highly depleted.

However, it was explained that the quantity of silica in most naturally occurring waters at near 25 °C probably is not controlled by the solubility of quartz. The decomposition of other silicates such as feldspars and the precipitation of various clays may be more important in regulating the quantities of silica found in natural waters [36].

3.4.1. The nature of SiO_2 and Al_2O_3 contents within psr and lpsr analyzed spots

The majority of the analyzed psr&lpsr spots of the altered ilmenite grains contain TiO_2 percent ranges between 58 and 80%, have appreciable contents of Al_2O_3 and/or SiO_2%. Most of their contents ranges between 2 and 3%. Only 28 spots out of 586 spot analyses have SiO_2 and Al_2O_3 contents relatively greater than 3%. In some few spots, the contents of CaO rarely reach considerable values (10.13%). However, in the majority of the analyzed spots both of CaO, Na_2O and K_2O are present but in negligible contents. In the forementioned 28 spots, the SiO_2 ranges between 0.75 and 13.38%, and the Al_2O_3 ranges between 0.31 and 9.13%. The calculated Si cations range between 0.04 and 0.77 while the calculated Al cations range between 0.02 and 0.59. In many of these spots, a clear negative correlation is present between Fe_2O_3 content and both of SiO_2 + Al_2O_3 contents. In fact, in many of these individual spots, if the contents of the included SiO_2% + Al_2O_3% are added to the present content of Fe_2O_3%, the sum of these three oxide contents gives the percentage which must be present totally of Fe_2O_3 taking into consideration the contained TiO_2% in the analyzed spot, and considering also that this detected individual analyzed spot is psr.

The investigation of psr and lpsr spot analyses reflects that the majority of spots contain a definite amount of str and may be also mol water contents. The deficiency than 100% for the sum of total analyzed oxides (OT) of each detected spot is considered corresponding to one or both of the two types of water. However, after applying the adopted psr Excel program, the deficiency than 100% for the sum of total analyzed oxides (NT) in this case will be corresponding only to the contained individual mol water.

It was detected that on applying the constructed Excel psr program for all the investigated psr/lpsr analyzed spots, the sum of the analyzed total oxides (NT); includes the calculated str water, ranges between 94.1 and 107.7%. Only 376 spot of psr/lpsr analyses have sum total oxides values less than 101%. The str and mol water ranges between 0.22 and 16.3%. The cationic iron ranges between 0.42 and 1.99. The recorded minimum total oxides sum after applying the constructed Excel psr program equals 94.1% which ensures the presence of appreciable molecular water content in some of these analyzed spots.

For all the investigated psr&lpsrs spots (586 analyses), if it was considered that the analyzed five oxides SiO_2, Al_2O_3, CaO, Na_2O and K_2O are impurities as reported by almost all the previous published studies, then the forementioned five oxides must be neglected and recalculating the percentages of the other remaining analyzed oxides, by multiplying each analyzed value in the following correction factor: $[100/100-(SiO_2+Al_2O_3+CaO+Na_2O+ K_2O)]$. On doing this, it was noticed that the mol and/or str water ranges between 0.35 and 17%. On applying the constructed Excel psr program, the sum of the analyzed total oxides (NT); which includes the calculated str water, ranges between 93.3 and 114.5%. Only 302 spot psr analyses have sum total oxides values less than 101%. The TiO_2 contents after such correction for the majority of the analyzed spots ranges between 58 and 83.7%. Only 7 spot analyses have corrected TiO_2 contents range between 84 and 93.6%. The cationic iron ranges between 0.12 and 1.97.

As a final result, the careful investigation of the analyzed psr-lpsr spots reflects the following assumptions about the presence of such detected impurity oxides as follows:

1- Both of SiO_2 and Al_2O_3; the most two major impurity oxides of the analyzed five impurity oxides, can be present as individual oxides inside the fissures and cracks of the altered ilmenite grains. Then, by neglecting them and recalculation the percentages of the remaining oxides of each spot, the spots should give an accepted results on applying the constructed Excel psr program. The case which is not achieved with the majority of the analyzed spots in this study.

2- One or more of these impurity oxides are associated with some or all of the analyzed Fe_2O_3 in addition to others which may be remnants of alteration of a preexisting definite silicate mineral containing minor of TiO_2 content. At definite geological conditions, considerable amounts of SiO_2, Al_2O_3, CaO and Fe_2O_3 present in the silicate mineral composition are removed and an enrichment of the contained TiO_2 content is occurred. There are several spots of several grains have such circumstances.

3- In other cases, SiO_2 and/or Al_2O_3 are replacing for an individual phase of Fe_2O_3. In such cases, both Fe_2O_3 and TiO_2 are two individual phases after ilmenite or following the breakdown of psr or lpsr in final alteration stages of ilmenite. Geothites and hematites can incorporate quite large amounts of Al in their structures [37].

4- The fourth assumption is that, in several other cases both of SiO_2 and Al_2O_3 are not present as impurities, they play an important role in the late stages of ilmenite alteration. They act as doners or acceptors of H_2O/OH^- in the alteration mechanisms of lpsr. In fact, the Al-OH bond is greater than the Fe-OH bond [38]. However, the enrichments of these oxides are noticed in the alteration mechanisms in which either the oxygen is replaced with OH^- or during the enrichment of the individual TiO_2 phase during the losing for most of str and/or mol water from the altered lpsr formula structure. Several authors studied the conversion of $Fe(OH)_3$ gel to β-FeOOH and α-Fe_2O_3 in the presence and absence of silicate ions [39,40]. At 60 ^{o}c the effect of silicate ions resemples that of phosphate; completely suppresses these two conversions, while is in contrast to the influence of sulphate ions which accelerate the conversion of the $Fe(OH)_3$ gel to β-FeOOH and delay the conversion from β-FeOOH to α-Fe_2O_3 [40]. Then, SiO_2 and/or Al_2O_3 may play a definite roles in some conversions of Fe- or Ti- oxyhydroxides of some suggested alteration Scenarios by the present author (under publication).

In some spot analyses of altered ilmenite grains have TiO_2 ranges between 80 and 90%, 19 spot analyses are detected to contain relatively higher contents of SiO_2, Al_2O_3 and CaO. The SiO_2 ranges between 1.78 and 11.84%, the Al_2O_3 ranges between 0.09 and 5.71% while CaO ranges between 0.1 and 6.76%. All of these spot analyses have accepted sum total oxides; very close to 100%, before and after neglecting these three oxides and recorrect the percentages of the remaining analyzed oxides. It is obvious that these three oxides are impurities and neither contain mol nor str water inside their structures. In these cases, there is not a psr formula structure and most of the contained TiO_2 and Fe_2O_3 are individual phases or both of them are present as one phase other than psr; most probably forriferous rutile. Really, on applying the constructed psr Excel program for these spot analyses; which have not psr structure, before and after neglecting the impurity oxides, the obtained results are not accepted. The sum of the total analyzed oxides in addition to the calculated structural water ranges between 105.06 and 112.35% before neglecting the oxides and ranges between 108.53 and 117.3% after neglecting them and recalculated the values of other remaining oxides. Then, such results are obtained when there is no a psr formula structure or at least not all the most major oxide in the analyzed spot (i.e. TiO_2), is present within only the psr formula structure, but there are also other individual phases containing for some of this major oxide (TiO_2).

According to the last explanation, the relatively enriched contents of SiO_2 and/or Al_2O_3 in some secondary rutile grains can be explained as most of the SiO_2% is associated with mol water or bearing for mol and/or str water necessary for the leachability of Fe^{3+} from the psr structure. It will be settled and remains inside the interspaces and pores of the remaining lpsr phase structure. During the growth of the final micro-, crypto-, or the triple twinned arrangement of secondary rutile polymorph starting from the core to the outside of the highly altered grain, the SiO_2 molecules may be either leached out from the interspaces or concentrated toward the outside on the periphery of the produced final alteration products.

4. Conclusions

The relatively weakly magnetic altered ilmenite grains separated individually at 0.5 and 1 ampere values, have an enrichment of the contained altered silicate minerals, silica, sphene, and individual phases of Ti and Fe. Also, a relatively higher contents of str water are present in the chemical formulas of the contained lpsr phases, in addition also to considerable volumes of voids and cracks. All of these components are the reason of the relatively lower magnetic characters of the investigated altered ilmenite grains.

Most of the recorded lpsr phases are considered extended composition range of the relatively higher stable psr phase $Fe_2Ti_3O_9$, where definite contents of Fe^{3+} are removed followed by replacing definite number of O^{2-} by similar number of OH^- to keep the psr anionic structure and achieve also its electrical neutralization.

It was detected that the investigated spots having the lowest iron contents (0.49-0.42) are composed mainly of individual TiO_2 and Fe_2O_3 phases due to collapse for most of contained psr/lpsr phases. Then, The cationic Fe contents ranges between 0.42 and 0.49 are discarded as minimum values for the existence of psr-lpsr phases. Then, the collapse of psr structure seems to be at cationic iron content just below 0.5. Some of the remaining survived lpsr phase may be exceptionally recorded at a cationic iron range of 0.50-0.40. However, the complete collapse for most of lpsr component phases into individual TiO_2 and Fe_2O_3 mineral phases, may be at the cationic iron ragion of 0.5-0.4.

The contents of TiO_2 and Fe_2O_3 of all the investigated altered spots in the present study range between 59.16-86.56%, and 37.3-6.68%, respectively. The Ti/(Ti+Fe) ratio for these spots chemical composition range between 0.60 and 0.88. The well defined accepted psr-lpsr chemical formulas of all the investigated grains in the study are as follows: $Fe_{2.01-0.50}Ti_3O_{8.97-4.5}(OH)_{0.03-4.5}$.

The comparison between the total oxides sum before (OT) and after (NT) applying the constructed psr Excel software for the various chemical analyses of the detected spots reflects that the calculated structural water contents for some of analyzed spots are not accepted, and there are individual phases of TiO_2; may be also of Fe_2O_3, other than psr/lpsr. Then, in the region of 68-70 TiO_2%, the mechanism of ilmenite alteration may is changed where neither all the analyzed TiO_2 of the spot nor all the calculated structural water are contained within the molecular formula of lpsr. There are other phases containing for some TiO_2 or Ti-oxyhydroxide which most probably are separated from the lpsr phase.

In case of grains composed originally of ferriilmenite-titanhematite exsolved intergrowth, most of the hematite content is leached causing partially empty voids of various sizes and shapes while the ferriilmenite component is altered to lpsr.

Also, as the analyzed TiO_2 and str and/or mol water contents increase, as the darkness of the BSE image for the region of the the analyzed spots increases. This may reflect the existence of an individual TiO_2 phase; most probably rutile, mixed in homogeneity with the existed lpsr component. Also, as the content of TiO_2 content increases (within a definite TiO_2 range of 80-85%); due to a relatively faster alteration rate, as the associated contents of Al_2O_3& SiO_2 increase. Also, as the contents of the str and/or mol water contained within the lpsr phases decreases (OT is more than 98%), as the contents of Al_2O_3 are highly depleted. Then, with the occurrence of the well-defined rutile structure; TiO_2 ranges between 85 and 100%, the contents of of Al_2O_3 are highly decreased indicating that the Al_2O_3 are not compatable with rutile structure.

After roasting at 1100 ^oC for one hour, it is obvious that the hexagonal psr structure is unstable in comparison with the tetragonal rutile, a considerable TiO_2 content escaped from the broken psr structure and diffused inside the rutile structure. Both of the remaining TiO_2 and most of the Fe_2O_3 contents of the collapsed psr are modified into the orthorhombic pseudobrookite structure which seems to be more stable under new conditions. It is detected also that minor contents of amorphous hydrated silica was contained with the psr of brown coloured grains. After roasting the water molecules were lost and the minor free SiO_2 molecules are recrystallized into quartz.

More than one polymorph of TiO_2; rutile and anatase, can be formed after alteration of psr and lpsr due to the difference of the alteration rates and may be also due to some of the associated impurity elements.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. Excel Software S1: The constructed Excel program for calculation of molecular formula of ilmenite (only for given one spot chemical analysis); Excel Software S2: The constructed Excel program for calculation of molecular formula of ilmenite (for given several spot chemical analyses); Excel Software S3: The constructed Excel program for calculation of molecular formula of leached ilmenite (only for given one spot chemical analysis); Excel Software S4: The constructed Excel program for calculation of molecular formula of leached ilmenite (for given several spot chemical analyses); Excel Software S5: The constructed Excel program for calculation of molecular formula of pseudorutile/leached pseudorutile (only for given one spot chemical analysis); Excel Software S6: The constructed Excel program for calculation of molecular formula of pseudorutile/leached pseudorutile (for given several spot chemical analyses).

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