Iraqi Journal of Agricultural Sciences –2025:56(3):1170-1183 Goran & Essa

EFFECT OF WATER REGIMES AND ORGANIC ACIDS ON Mg-INTERLAYERING FORMATION IN EXPANSIBLE 2:1 MINERALS IN SOME SOILS OF KURDISTAN REGION, IRAQ

A . H. Goran **S. K. Essa**
Researcher **Prof.**
Coll. Agri. Engin.Sci. **Coll. Agri. Engin. Sci.**
University of Salahaddin **University of Baghdad**
e-mail: salman.essa.52@gmail.com

ABSTRACT

This study was aimed to investigate the occurrence of chloritization phenomenon in these soils. Three of these pedons were chosen in soil sites differing in their agricultural exploitation, which included: one pedon in an uncultivated soil at Daratw . While the second pedon was dug in soil exploited by the cultivation of wheat at Bardarash . The third pedon was chosen as representative of a forest soil at Tawska Valley. Also, another two soil pedons were exposed to successive cycles of wet and dry, were chosen in Aski Kalak , and Altun Kupri districts. All studied soils were examined by X-ray diffractions. Results showed the presence of Mica, Smectite, Real chlorite and Kaolinite minerals in clay fraction of these soils. Results also, showed the precipitation of Brucite layer into Montmorillonite interlayers and caused to shifting Montmorillonite towards Chlorite mineral in Aski Kalak , Altun Kupri, and forest soil pedons, this was attributed to creation a suitable conditions to encouraged a chloritization phenomenon to occur in these soils.

Key words: wet-dry cycles , interstratified minerals, hydroxyl interlayer .

مجلة العلوم الزراعية العراقية- 2025 :56 (3):1170-1183 كوران وعيسى

أثر نظم الري والحوامض العضوية في تكون طبقة المغنيسيوم الداخلية في معادن 2:1 المتمددة في بعض ترب أقليم كوردستان / العراق

أحمد حازم كوران سلمان خلف عيسى
باحث أستاذ
كليةعلوم الهندسة الزراعية كلية علوم الهندسة الزراعية
جامعة صلاح الدين جامعة بغداد

المستخلص

أختيرت خمس بيدونات لترب ضمن أقليم كوردستان، لغرض الكشف عن حدوث ظاهرة الكلوره في تلك الترب. وقد أختيرت ثلاث منها ضمن مواقع لترب تختلف فيما بينها بالاستغلال الزراعي، إذ مثل البيدون الاول لتربة غير مستغلة زراعيا في منطقة داره تو، وكان البيدون الثاني ممثلا لتربة مستغلة بزراعة محصول الحنطة في منطقة برده رش، في حين أختير البيدون الثالث ضمن تربة غابات في منطقة توشكه. إما بيدوني الترب الاخرين، فقد تم أختيارهما ضمن مواقع تتعرض بأستمرار لدورات الترطيب والجفاف عند منطقتي التون كوبري وآسكي كلك. فحصت نماذج أطيان ترب الدراسة بوساطة الاشعة السينية الحائدة. إذ بينت النتائج وجود كل من معادن المايكا، السمكتايت، الكلورايت الحقيقي، والكاؤولينايت، ضمن دقائق مفصول الطين لتلك الترب. كذلك أظهرت النتائج حدوث ترسيب لطبقة البروسايت ضمن الطبقات الداخلية لمعدن المونتموريلونايت، والذي أدت الى تحول معدن المونتموريلونايت بأتجاه معدن الكلورايت، إذ تم ملاحظة تلك الظاهرة ضمن بيدونات تربة الغابات، أسكي كلك، والتون كوبري، نتيجة لتوافر الظروف المناسبة التي تشجع حدوث ظاهرة الكلورة في تلك الترب.

كلمات مفتاحية: دورة رطبة–جافة، معادن متداخلة، طبقات هيدروكسيل

Received: 27/1/2023, Accepted:3/5/2023, Published:30 June.

INTRODUCTION

Interlayered clays constitute undoubtedly one of the most intriguing types of clay minerals, by virtue of the large variety of possible Interlayer fillings. Interlayering manifests itself in a modification of the thermal stability of the clay mineral structure and it may occur within both smectite and vermiculite interlayer spaces. The presence of interlayer precipitates within smectite prevents their interlayer spaces from fully collapsing to 10 Å during heat treatment. Many different names have been assigned to ~ 14 Å interlayered minerals, such as swelling and collapsing chlorites, chlorite intergrades, soil chlorites, soil vermiculites, etc., because the reaction of these phases to diagnostic tests (i.e., glycerol or ethylene glycol solvation, and heat treatments) can vary (2, 5, 17). In more recent studies, the minerals have been termed hydroxy-interlayered smectites (HIS) and are considered to form a solid-solution series between smectite and chlorite (4, 8). Although interlayered clay minerals have been extensively studied, while the interlayering of smectite and vermiculite with a variety of different types of organic compounds which may lead to the formation of organo-clay nanocomposites or other types of clay–organic complexes (1). Many experimental studies on clay–organic complexes have focused on the preparation and properties of organo-clay nanocomposites (15, 16, 18, 19). These studies have clearly demonstrated an increase in the thermal stability of organics intercalated within clay mineral interlayers. Simultaneously, the intercalated organic matter stabilizes the clay mineral structure and protects the structure against full collapse to 10 Å during heat treatment (26). On the other hand, several soils with frequent wetting and drying cycles' as well as low SOM content suggested as optimal conditions for hydroxyl-interlayer prespetate within interlayers of 2:1 clay minerals (17, 25, 21). The aim of this study is to present evidence for the formation of Mg-interlayering within interlayers of 2:1 clay minerals, in some soils of Iraqi Kurdistan region of differing in their agricultural exploitation, and some of them were exposed to successive cycles of wet and dry.

MATERIALS AND METHODS

Five soil sites were chosen in different locations in Iraqi Kurdistan region. The selection of sites was according to the hypotheses that were previously developed to visualize the occurrence of chloritization phenomenon in these soils. The first hypothesis was that the content of organic matter is one of the main influencing factors in the occurrence of this phenomenon in these soils. Accordingly, three soil sites differing in their agricultural exploitation were chosen to prove the validity of this hypothesis, which included: one pedon in an uncultivated soil at Daratw (36 28 09. 167 N and 43 47 27. 637 E). While the second pedon was dug in soil exploited by the cultivation of wheat at Bardarash (36 31 58. 921 N and 43 36 17. 041 E). The third pedon was chosen as representative of a forest soil at Tawska Valley (36 31 58. 921 N and 43 36 17. 041 E). The second hypothesis, was supposed to expose the soil to successive cycles of wet and dry, may encourage the occurrence of the chloritization phenomenon in these soils. Accordingly, two soil sits were chosen, their pedons are continuously exposed to the fluctuation of the water table level, represented by Aski Kalak pedon located on the bank of the Upper Zab River (36 14 59. 296 N and 43 38 56. 120 E), and the second one was chosen on the bank of the Lower Zab River at Altun Kupri district (35 50 22. 794 N and 44 22 08. 938 E). Soil samples were collected from different horizons at each pedon. The collecting samples were air dried, crashed, and passed through the sieve of 2 mm openings, then some chemical and physical analyzes were done on it (Tables 1 and 2). The particle size distribution was determined according to international pipette method as described in (22). The Ec and pH of soil were measured using method of (22). Total $CaCO_3$ equivalent was determined by method of (22). While the cation exchange capacity (CEC) was determined according to the method described in (20). Total organic matter (OM) was determined by using Walkey and Black method as described in (6). Humic acid (HA) and fulvic acid (FA) were extracted from soil with a combined NaOH 0.1 N and $Na_4P_2O_7$ 0.1 *M* solution as described by (6). The mineralogical composition of the claysized fraction was determined by X-ray on parallel oriented clay of the Mg^{2+} and K^+ saturated clay samples. The Mg^{2+} saturated clay was treated with the X-ray in the air dry and ethylene glycol salvation. While the K^+ saturated clay was heated to 350^0C and 550^0C. X-ray analyses were made with a Philips – P.W 1840 diffractometer equipped with a graphite diffracted beam monochromatot using CuKα radiation.

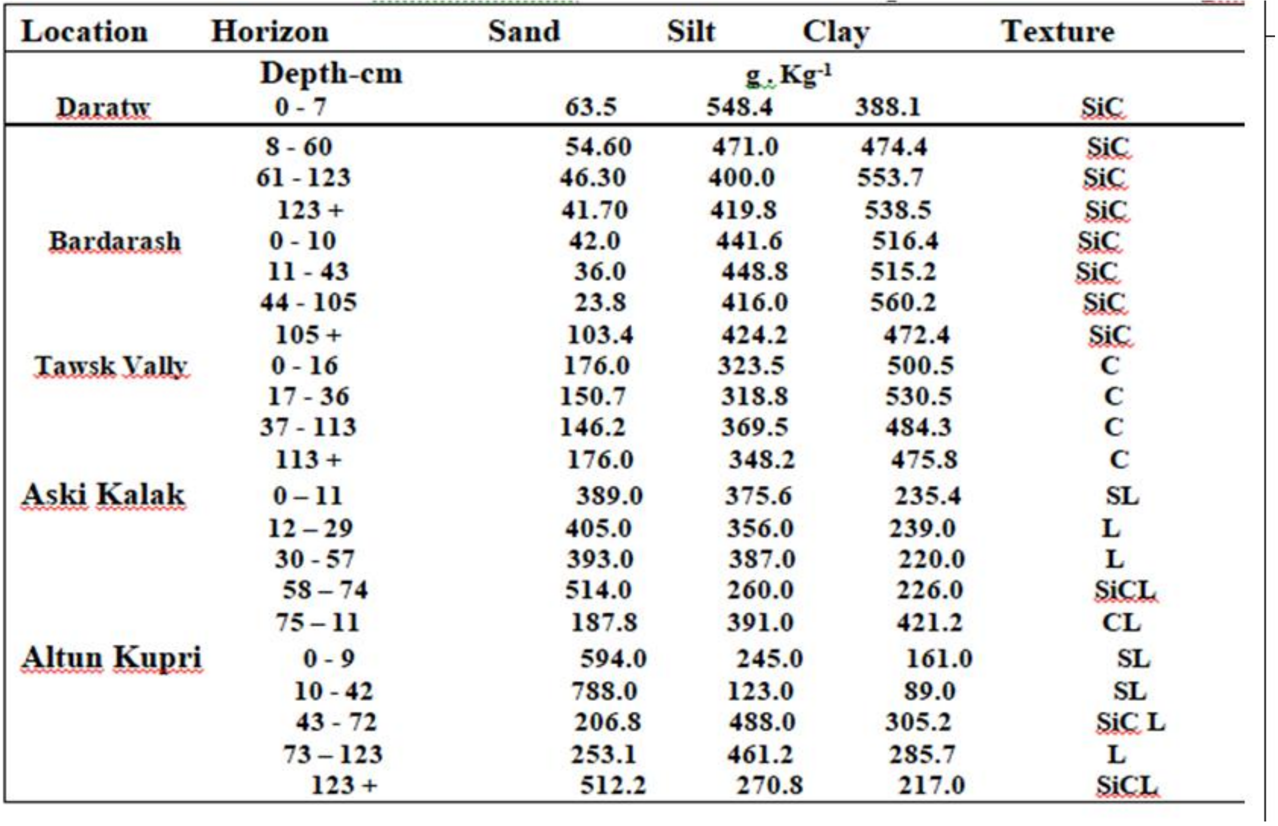
RESULTS AND DISCUSSIONS

Tables (1) and (2) shows some chemical and physical properties of studied soils. Results indicated that the range of pH values was between (7.35 – 8.43), reflecting that the reaction of all pedons was around moderate alkali to nutral, due to effect of calcareous parent material of these soils. Also, results showed there was no specific pattern for pH values with depth in all studied pedons. Results of Electrical conductivity (EC) indicate that all studied soils were non-saline, reflected by low values of EC (0.36 – 5.20 $dS.m^{-1}$). The low EC values and low soluble salt contents in all studied pedons attributed to desalinization process as affected by high amount of rainfall, and increasing of leaching rate through all studied pedons. Results in Table 1 show that the amount of total $CaCO_3$ were ranged between (185 – 455 $g.kg^{-1}$). The high content of $CaCO_3$ reflected a calcareous nature of studied soils. Results show that the amounts of total $CaCO_3$ were increased with depth in all studied pedons, reflect the effect of many factors, such as high leaching rate, calcification process, and calcareous parent material of these soils. Sheikh Abdullah, 2012 indicated, whether calcium carbonate present in parent material or transferred from other sources, the pedogenic processes of solution, translocation and deposition are responsible for sedimentation and accumulation of $CaCO_3$, and the depth of sedimentation upon the depth of depleted water which carried the Ca^{2+} and HCO_3^{-1} ions. The values of cation exchange capacity (CEC)

Table 1. Some chemical properties of studied soils

Location	Horizon	pH	EC	CEC	T.$CaCO_3$
	Depth - cm		ds . m^{-1}	Cmol C . kg^{-1}	g . kg^{-1}
Daratw	0 – 7	7.65	1.37	40.06	390
	7 – 60	8.22	0.43	40.60	455
	60 – 123	8.28	0.56	35.08	355
	123 +	8.20	0.68	43.40	320
Bardarash	0 – 10	8.01	1.09	41.14	300
	10 – 43	8.22	0.74	40.06	265
	43 – 105	8.10	1.46	35.71	260
	105 +	8.03	1.98	31.90	410
Tawsk Vally	0 – 16	7.39	0.91	44.95	288
	16 – 36	8.32	0.37	40.60	250
	36 – 113	8.26	0.36	36.79	335
	113 +	7.35	0.45	43.32	200
Aski Kalak	0 - 11	8.20	1.99	20.49	235
	11 - 29	8.17	0.85	16.22	185
	29 - 57	8.04	0.72	18.86	195
	57 - 74	7.84	0.77	20.49	230
	74 – 113	7.95	0.72	24.84	260
Altun Kupri	0 - 9	7.80	3.20	13.51	360
	9 - 42	7.88	1.81	10.37	330
	42 - 72	8.43	1.24	17.77	355
	72 - 123	8.18	1.02	16.24	315
	123 +	8.30	0.97	14.72	330

Table 2. Particle size distribution of soil particles in studied pedons



Location	Horizon	Sand	Silt	Clay	Texture
	Depth-cm		g . Kg^{-1}		
Daratw	0 - 7	63.5	548.4	388.1	SiC
	8 - 60	54.60	471.0	474.4	SiC
	61 - 123	46.30	400.0	553.7	SiC
	123 +	41.70	419.8	538.5	SiC
Bardarash	0 - 10	42.0	441.6	516.4	SiC
	11 - 43	36.0	448.8	515.2	SiC
	44 - 105	23.8	416.0	560.2	SiC
	105 +	103.4	424.2	472.4	SiC
Tawsk Vally	0 - 16	176.0	323.5	500.5	C
	17 - 36	150.7	318.8	530.5	C
	37 - 113	146.2	369.5	484.3	C
	113 +	176.0	348.2	475.8	C
Aski Kalak	0 – 11	389.0	375.6	235.4	SL
	12 – 29	405.0	356.0	239.0	L
	30 - 57	393.0	387.0	220.0	L
	58 – 74	514.0	260.0	226.0	SiCL
	75 – 11	187.8	391.0	421.2	CL
Altun Kupri	0 - 9	594.0	245.0	161.0	SL
	10 - 42	788.0	123.0	89.0	SL
	43 - 72	206.8	488.0	305.2	SiC L
	73 – 123	253.1	461.2	285.7	L
	123 +	512.2	270.8	217.0	SiCL

were ranged between (10.37 – 44.95 Cmol.Kg^{-1}). In general, the surface A and subsurface B horizons in all studied soils have a higher values of CEC. These results suggest the effect of organic matter and clay content and both of them were contributed to increases the CEC values of these soils. These results agree with (2,9,10,11), who studied some Iraqi soils, and found a high contribution of clay and organic matter in CEC of soil. Results of particle size distribution in Table 2 show that the range amount of clay fraction was between (89.0 – 560.2 g.kg^{-1}). In general the amount of clay in all pedons is at its maximum in the B horizon. The pattern of clay distribution decrease with depth then increases in B horizon then decrease in C horizon. Aziz, 2006 pointed that this type of clay distribution with depth may be due to the effect of different types of processes mainly pedogenic duo to effect of high leaching process in these soils, or to some extent to geomorphic processes. Silt and sand did not show specific pattern of distribution with depth in all studied pedons and they range from (123.0 – 548.4 g.kg^{-1}) and from (23.8 – 788.0 g.kg^{-1}) respectively. From the results of particle size distribution it is obvious that the texture of studied soils was ranged from silty clay to clay loam.

Organic matter and fractionations

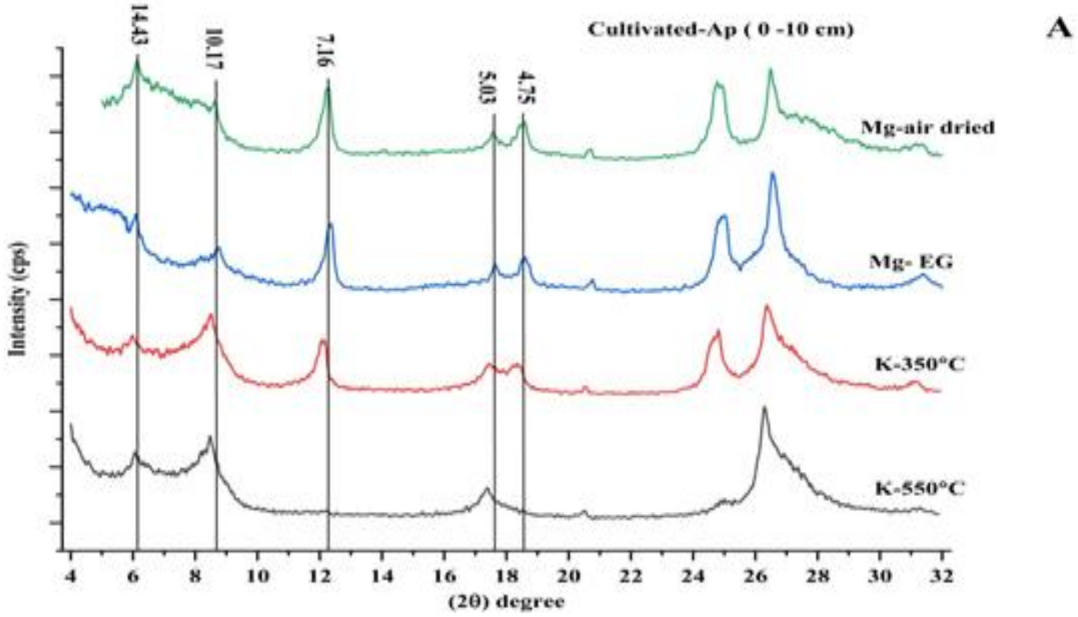
Results in Table 3 show the amount of organic matter and fractionations. The amount of total organic matter in studied soil samples ranged between (4.94 – 45.33 g.kg^{-1}) and the highest amount is obtained almost in surface horizons of all studied pedons. These results indicated that the amount of total organic matter was higher in the soil surface and decrease with depth, this is due to the accumulation of high amount of plant residuals at the upper part of soil. The highest amount of total organic matter was found in surface horizon of forest soil, while the difference between the amounts of organic matter in the studied soils may be due to many factors such as types of plant covering, difference between plant residual decomposition, and the ability of organic matter decomposition. Results in Table 3 show the value of humic acid in all studied soil samples, which ranged between (0.21 – 4.09 g.kg^{-1}) . The variation of humic acid values in these soils is due to differences in plant covering, and rate of their litters decomposition. These results agree with (12,21,24). Also the results show that the values of humic acid were high in surface soil and takes the same trend of organic matter distribution in soil pedon. Result in Table 3 show the values of fulvic acid , they ranged between (0.0 – 1.57 g.kg^{-1}). In general we found that the amount of fulvic acid in studied soils was quiet differ from humic acid trend, but at the same time it was following the organic matter distribution in all studied pedons. There is a good reason to expect a strong link between organic matter quality and the amount, mobility of organic acids in these soils. Zanelli et al., 2007 found a high acidity coupled with the presence of organic acids that act as ligands, accelerates the detachment of elements from primary minerals and from interlayer of clay minerals. Thus it seems plausible that differences in complexing ability of organic compound induced by the observed vegetation change should yield consequences for the composition of the mineral assemblage. In general the results in Table 3 show that the relative content of HA in all studied soils was much higher than that of FA in all studied soils, this indicated that the humification degree at these soils was high, and varied with vegetation types, the overall high degree of humification in the studied soils was directly related to the surface vegetation, and to increased surface soil moisture. Jin Li et al., 2022 have pointed out that the from most important indicators for increasing the humification degree in soil is the content of HA and FA, as well as the high ratio of HA/FA. The calculation of HA/FA ratio has been done for all studied soils (Table 3), where the HA/FA ratio is often used as an indicator of humus maturity. The higher the ratio, the higher the degree of humus decay and molecular complexity. The smaller the ratio the lower the degree of hums decay and molecular complexity (11, 12, 14). Results of Table (3) show, that the ratio of HA/FA has no specific trend in all studied pedons. As we find it increase in surface horizon and decreasing with depth as it is in Altun-Kupri and Daratw (Uncultivated soil) pedons, while at other times we fined this ratio increasing in B horizon and then decreased again with depth, as it is in Tawsk-Vally (Forest soil) , Bardarash (Cultivated soil), and Aski-Kalak pedons. As it seems and according to our belief that the distribution trend of HA/FA ratio throughout the all studied soils is controlled by many factors, such as plant coverage, the degree of organic residues decompositions, the content of HA and FA in organic residues, and the rate of leaching for decomposition products of organic residues downward in each pedon, which in turn depends on soil texture. This was consistent with the results of (9, 10, 13,14), who found that the values of HA/FA ratio was affected by accumulation of surface biomass, type of plant coverage, and the degree of organic residues decompositions.

Table 3. Total organic matter content and fractionation in the soil pedons

Location	Horizon	Total O.M	Humic A.	Fulvic A.	Humin	HA/FA
	Depth - cm		g.kg $^{-1}$			
Daratw	0 – 25	32.29	2.18	0.70	29.41	3.11
	25 – 53	11.20	1.18	0.55	9.47	2.14
	53 – 86	8.24	1.13	0.43	6.67	2.62
	86 – 112	4.94	0.21	0.07	4.66	3.00
Bardarash	0 – 15	29.65	2.11	1.26	26.28	1.67
	15 – 45	20.43	1.86	0.75	17.82	2.48
	45 – 74	11.86	4.09	0.32	7.45	12.78
	74 – 110	5.93	0.98	0.11	4.84	8.90
Tawsk Vally	0 - 25	45.33	3.86	1.57	39.90	2.45
	25 – 54	16.80	1.14	0.35	15.31	3.25
	54 – 75	8.90	1.22	0.08	7.59	15.25
	75 – 104	13.18	0.79	0.20	12.19	3.95
Aski Kalak	0 – 11	17.46	1.06	0.37	16.03	2.86
	11 – 29	12.52	0.86	0.18	11.47	4.77
	29 - 57	7.91	0.72	0.06	7.13	12.00
	57 – 74	5.93	0.34	0.05	5.50	6.80
	74 – 11	6.59	2.12	Nil	4.47	2.12
Altun Kupri	0 - 9	9.22	2.90	0.07	6.25	10.44
	9 - 42	6.19	1.31	0.04	4.84	32.75
	42 - 72	10.54	0.28	0.06	10.20	4.66
	72 – 123	8.57	0.42	Nil	8.15	0.42
	123 +	12.52	0.42	Nil	12.10	

Mineralogical properties of studied soils

The mineralogical composition of <2µ fractions for two horizons Ap and C_1 in all studied soils (Figs. 1-5) were examined by X-ray diffraction. In cultivated soil (Bardarash) , results in Fig (1A) representing the clay sample of Ap horizon, and show that the presence of 14.43 A^0 reflection in air-dried, Mg-saturated treatment, and continued presence without changed in all treatments, reflecting the presence of real chlorite in this horizon, confirming to that is the appearance of his third diffraction at d-spacing of 4.75 A^0 . The presence of 10.17 A^0 reflection in air-dried, Mg-saturated treatment and remaining without change in all treatments reflecting the presence of mica minerals in this soil, also the appearance of second order of mica with a high intensity at d-spacing of 5.03 A^0 confirmed the presence of Muscovite in this soil. This agrees with results obtained by many studies (1,2,3,4,8,9), who have shown that the distinguish between two types of mica minerals (Biotite and Muscovite) depending on the second order of mica at 5 A^0 , in Muscovite the peak of second order is always strong and high, while it is disappear or very weak in Biotite . Also, the six order of mica was used for distinguish between mica minerals, so the six order of Muscovite appear at 1.5 A^0 , while it is appear at 1.54 A^0 in case of Biotite. In Fig (1A) the Kaolinite is identified by 7.16 A^0 reflection and remains in air-dried, Mg-saturated, ethylene glycol salvation, and K-saturated with heat treatment to 350 ^{0}C , and disappear in K-saturated with heat treatment to 550 ^{0}C. Generally, the presence of real chlorite mineral, and the absence of smectite group minerals in Ap horizon of Bardarash soil, it can be interpreted in two ways, the first: is that the chlorite mineral is inherited from the parent material, and the second way: is the transformation of smectite mineral towards chlorite mineral by effect of chloritization phenomenon and this depending on the degree of interlayer filling. From our point of view, we agree with the first assumption, that is the chlorite mineral in this soil was inherited from the parent material, this is because the basal reflection of chlorite did not change in all treatments, and remained at d-spacing of 14 A^0 , therefor the mineral identified in sample is real chlorite. In C_K horizon of cultivated soil (Bardarash), Fig (1B) show the presence of smectite minerals in the clay fraction, which indicated by 14.47 A^0 reflection in air-dried, Mg-saturated treatment and shifts to an 17.20 A^0 reflection following ethylene-glycol salvation, and then shifts to an 10.35 A^0 reflection in K-saturated and heating to 350 and 550^{0}C. The increase in the intensity of diffraction line of 10 A^0 , with decrease in diffraction line of 14 A^0 in this sample on k-saturation with heating to 350 and 550 C^0 , reflectes the collapse in smectite layers, and indicates that the smectite in this soil was inherited from mica (1,2,3,16,18). Also, results of Fig (1B) show that the presence of 14.47 A^0 reflection in air-dried, Mg-saturated treatment, and continued presence without changed in all treatments, reflecting the presence of real chlorite in this soil. The presence of 10.35 A^0 reflection in air-dried, Mg-saturated treatment, and remaining without change in all treatments, reflecting the presence of Mica minerals in the clay fraction of this soil, while the appearance of second order of Mica with a high intensity at d-spacing of 5.03 A^0 confirmed the presence of Muscovite in this soil. Also, Kaolinite was diagnosed through presence of 7.17 A^0 reflection in treatments of air-dried, Mg-saturated , ethylene



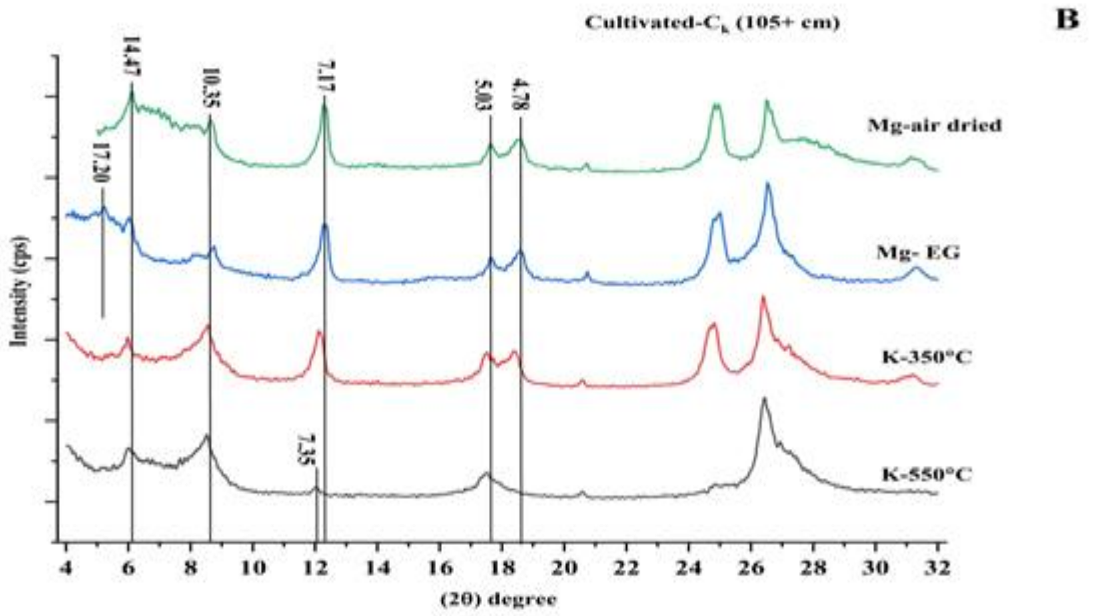


Fig. 1. X-ray diffraction curves of cultivated soil (Bardarash) A. A$_P$ horizon (0-10 cm), and B. C$_K$ horizon (105 + cm).

glycol salvation , and K-saturated with heat treatment to 350 ^{0}C , and disappeared in K-saturated with heat treatment to 550 ^{0}C . while the appearance of 7.35 A^0 reflection in K-saturated with heat treatment to 550 C^0 is represent the second order of real chlorite mineral. Examination results for clay fraction in A horizon of uncultivated soil at Daratw are shown in Fig (2A), which reveals almost the same mineralogical composition, as in the surface horizon of cultivated soil pedon, which was the presence of real Chlorite, Muscovite, and Kaolinite. In C$_C$ horizon of uncultivated soil, results in Fig (2B) show the presence of 14.36 A^0 reflection in air-dried, Mg-saturated treatment and remaining without change in all treatments, reflecting the presence of real chlorite mineral in clay fraction of this horizon. . The presence of 10.19 A^0 reflection in air-dried, Mg-saturated treatment, and remaining without change in all treatments, reflecting the presence of Mica minerals in the clay fraction of this soil, while the appearance of second order of Mica with low intensity at d-spacing of 5.03 A^0 confirmed the presence of Biotite in this horizon. Also, Kaolinite was diagnosed through presence of 7.15 A^0 reflection in treatments of air-dried, Mg-saturated , ethylene glycol salvation , and K-saturated with heat treatment to 350 ^{0}C , and disappeared in K-saturated with heat treatment to 550 ^{0}C . In A horizon of forest soil in Tawska Vally, Fig (3A) show the presence of smectite minerals in the clay fraction, which indicated by 14.63 A^0 reflection in air-dried, Mg-saturated treatment and shifts to an 16.63 A^0 reflection following ethylene-glycol salvation, and then shifts to an 10.21 A^0 reflection in K-saturated and heating to 350 and 550^{0}C. Results of Fig (3A), also show that the shifting of 14 A^0 reflection after heating to 350 ^{0}C to the basal spacing of 21.46 A^0 , and the diffraction peaks become shorter and broad, presumably due to presence of Mg-hydroxyl- interlayered between Smectite interlayer, which transferred to stable stage, while the heating to 550 ^{0}C cause to collapse the peak to 14.54 A^0 , which reflect loss of structural integrity. Chavez-Garcia et al., 2006 reported that heating the hydroxyl -interlayered of montmorillonite to 350 ^{0}C did not affect the basal spacing of reflection, and the diffraction peaks become shorter and broader, Also they showed that this d-spacing will decreases to 14 A^0 in K-saturated with heat treatment to 500 ^{0}C. According to our belief, the formation of Mg-hydroxy interlayer during chloritization process in Smectite at surface horizon of forest soil, may be due to the appropriate surrounding conditions in soil, which most prominent is the outputs of organic matter decomposition, such as organic acids (humic and fulvic acids), which were high in that horizon compared to the rest of the surface horizons of the studied soils. Also, Chavez-Garcia et al., 2006 mentioned that the formation of Mg-hydroxy interlayer in neutral to alkaline soil, and referred to formation of hydroxyl-interlayering Mg^{2+} may be favored in soil with enhanced concentrations of organic acids percolating the soil profile such as podzols. Also, Sokolova et al., (23) was identified the hydroxyl-interlayer in montmorillonite in top soils rich in soil organic matter. Examination results for clay fraction in C_C horizon of forest soil at Tawska Vally are shown in Fig (3B), which reveals the presence of smectite, Muscovite, and Kaolinite . In Ap horizon of (Altun-Kupri) pedon, Fig (4A) show the presence of smectite minerals in the clay fraction, which indicated by 14.60 A^0 reflection in air-dried, Mg-saturated treatment and expanded to 16.81 A^0 reflection following ethylene-glycol salvation, and then shifts to an 10.31 A^0 reflection in K-saturated and heating to 350 and 550^0C. While the appearance of 25.41 A^0 reflection in air-dried, Mg-saturated and then shifts to 14.84 A^0 and 14.76 A^0 reflections in K-saturated and heating to 350 ^{0}C and 550 ^{0}C respectively, indicating the presence of regular interstratified (Smectite-Chlorite) mineral (2). Also, results in Fig (4A) show the presence of 10.21 A^0 reflection in air-dried, Mg-saturated treatment, and remaining without change in all treatments, reflecting the presence of Mica minerals in the clay fraction of this soil. Kaolinite was diagnosed through presence of 7.18 A^0 reflection in treatments of air-dried, Mg-saturated , ethylene glycol salvation , and K-saturated with heat treatment to 350 ^{0}C , and disappeared in K-saturated with heat treatment to 550 ^{0}C .

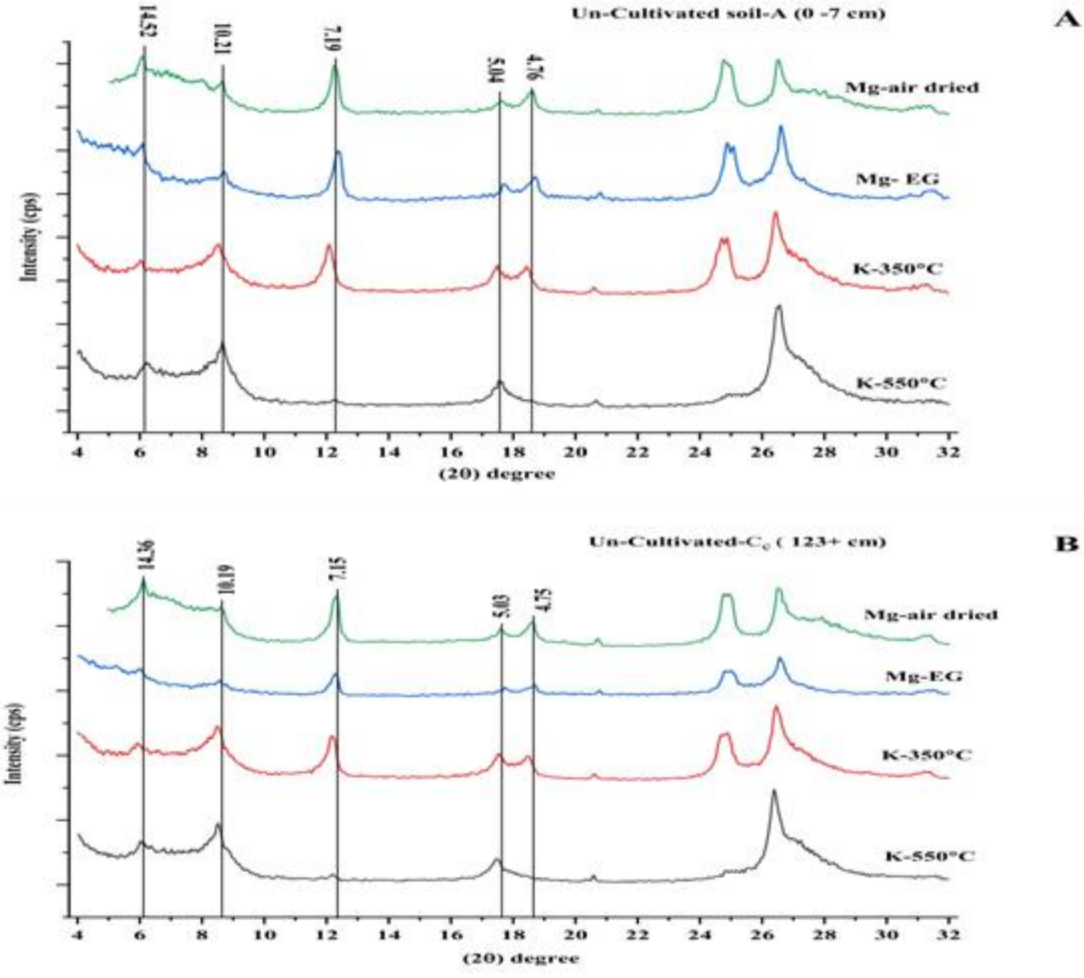


Fig. 2. X-ray diffraction curves of Uncultivated soil (Daratw) A. A horizon (0-7 cm), and B. C_C horizon (123 + cm).

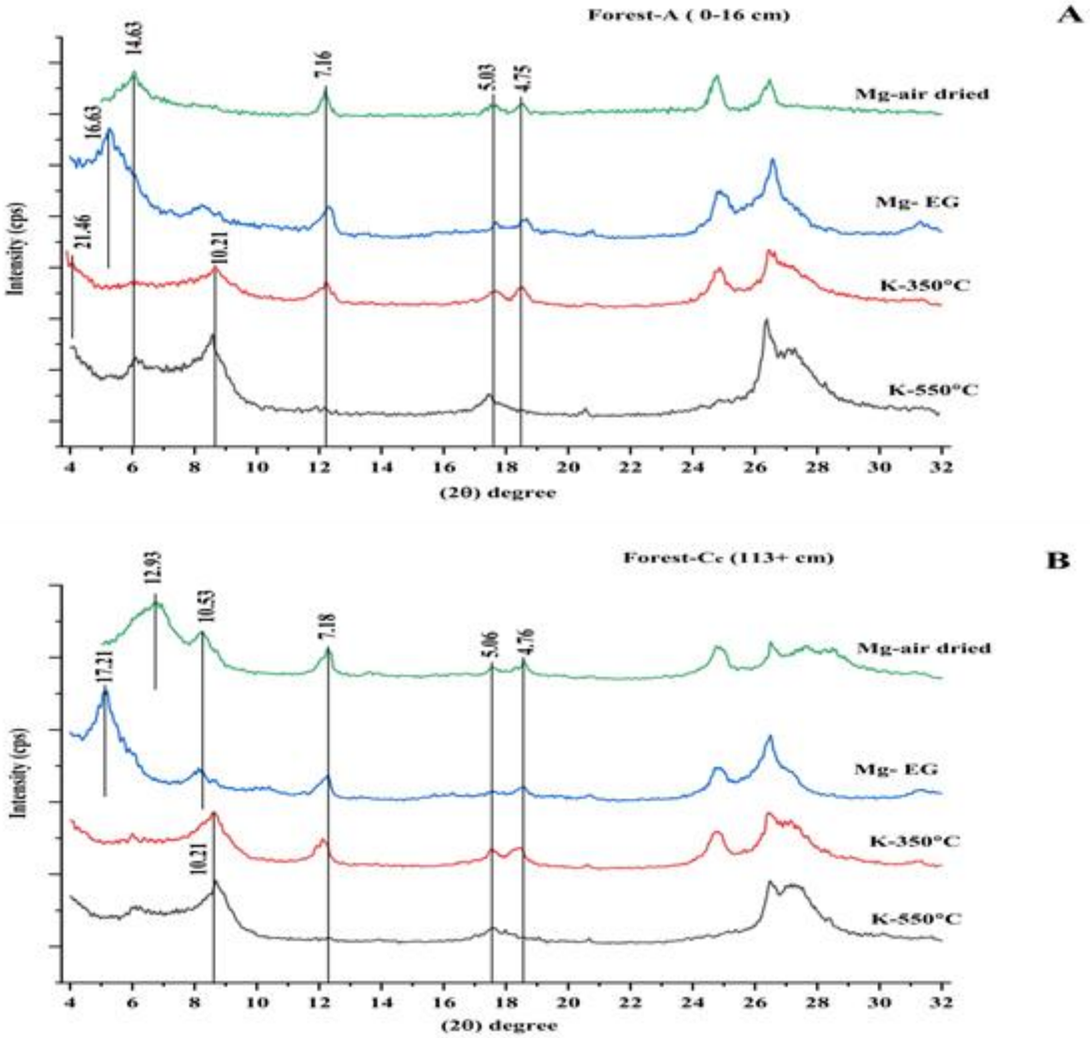


Fig. 3. X-ray diffraction curves of Forest soil (Tawska Vally) A. A horizon (0-16 cm), and B. C_C horizon (113 + cm).

Fig (4C) show the X-ray examination results of clay fraction in B_{K1} horizon of Altun-Kupri pedon, which indicated the presence of 15.06 A^0 reflection in air-dried, Mg-saturated treatment, that expanded to 24.54 A^0 reflection following ethylene-glycol salvation, and then shifts to an 14.99 A^0 reflections in K-saturated and heating to 350 ^{0}C and 550 ^{0}C . The response of 15.06 A^0 reflection to the ethylene-glycol salvation and expanded to 24.54 A^0 reflection, indicated the presence of Mg-hydroxide- Montmorillonite in that soil, this confirmed by shift this reflection to an 14.99 A^0 d-spacing in K- saturated with heating to the 350 ^{0}C and 550 ^{0}C, which indicate retention of Mg-hydroxy interlayer by Montmorillonite. It also, confirms that this horizon was subjected to continuous fluctuation of water table, which encouraged a chloritization phenomenon to occur. Al –Wotaify ,2012 found through his study of the Iraqi soils, that the process of water table fluctuation contributes greatly in chloritization phenomenon. Also, results of Fig (4C) show the presence of Muscovite and Kaolinite in clay fraction of B_{K1} horizon.

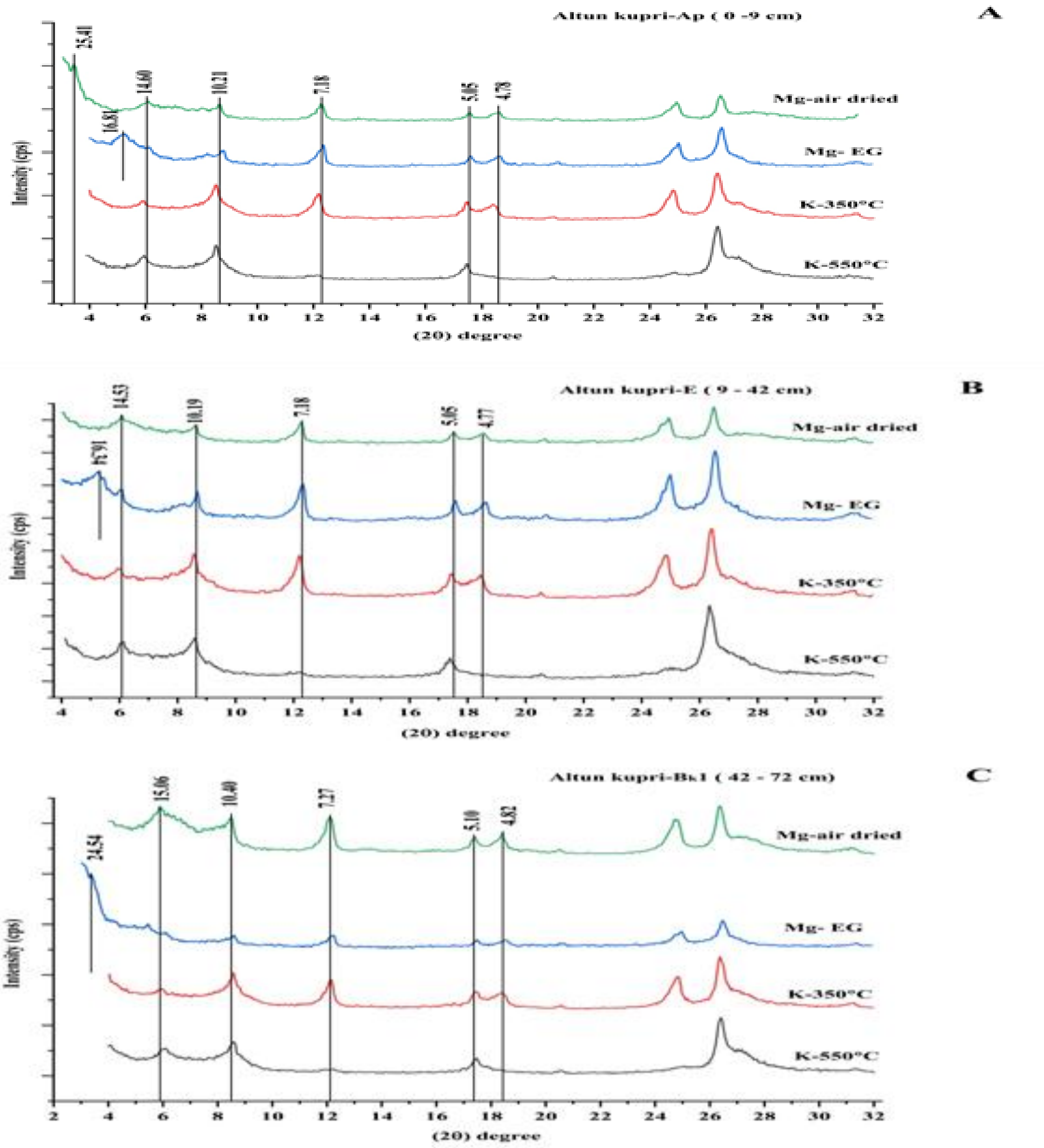


Fig. 4. X-ray diffraction curves of Altun Kupri soil. A. A_P horizon (0-9 cm), and B. E horizon (9-42 cm), and C. B_{K1} horizon (42-72 cm).

In Ap horizon of Aski-Kalak pedon, Fig (5A) show the presence of smectite minerals in the clay fraction, which indicated by 14.53 A^0 reflection in air-dried, Mg-saturated treatment and expanded to 16.81 A^0 reflection following ethylene-glycol salvation, and then shifts to an 10.26 A^0 reflection in K-saturated and heating to 350 and 550^0C. While the continued presence of 14.53 A^0 reflection in all treatments confirmed the presence of real chlorite in clay fraction of this horizon . Results in Fig (5C) representing the clay sample of B_{q2} horizon of Aski-Kalak pedon, and show that the presence of 14.56 A^0 reflection in air-dried, Mg-saturated treatment, and continued presence without changed in all treatments, reflecting the presence of real chlorite in this horizon. The presence of 21.34 A^0 reflection in ethylene glycol salvation treatment and shifted to 14.84 A^0 and 14.51 A^0 reflections in K-saturated with heat treatments to 350 and 550 ^{0}C respectively, combined with the diffraction peaks become shorter and broad, presumably due to presence of Mg-hydroxyl- interlayered between Smectite interlayer (4,7). Which confirms that this horizon was subjected to continuous fluctuation of water table, which encouraged a chloritization phenomenon to occur .

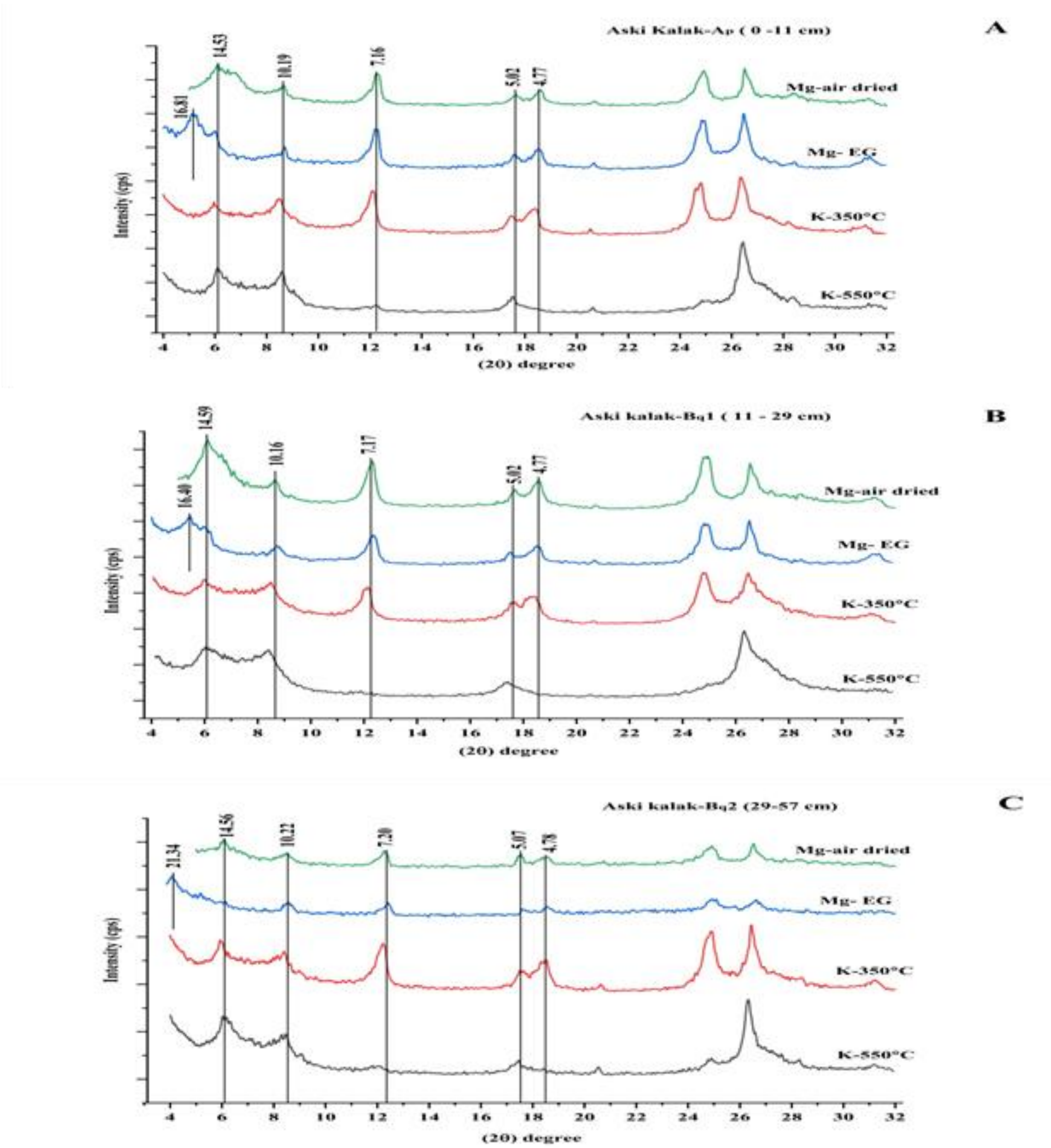


Fig. 5. X-ray diffraction curves of Aski Kalak soil. A. A_P horizon (0-11 cm), and B. B_{q1} horizon (11-29 cm), and C. B_{q2} horizon (29-57 cm).

CONCLUSION

From our point of view, the chloritization phenomenon was occurred in studied soils under the effect of two factors, one of them is organic acids content (Humic and Fulvic acids) resulting from the decomposition of organic residues (forest soil in Tawska Vally) . Also, the content and molecular weight of these organic acids, make them different in terms of their ability of impact on Mg-hydroxy- interlayer formation. While the second factor is the exposure of some of these soils (Altun-Kupri and Aski-Kalak pedons) to successive wetting and drying cycles, due to the fluctuation of water table level in some horizons. We assumed that Mg-hydroxide precipitated first and subsequently adsorbed in the interlayer space of montmorillonite through hydrogen bonding, and the whole process is happening by encouraging of subjected some soil horizons to continuous fluctuation of water table.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

DECLARATION OF FUND

The authors declare that they have not received a fund.

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