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Study Effect of Carbon: Nitrogen Ratio on the Minerals Weathering by Using Scanning Electron Microscope

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ABSTRACT

This study conducted to investigate the effect of soil C:N ratio under different tree types characterized by similarity in all soil forming factors (climate, parent material, topography, organisms ,time) located north of Iraq , difference between them was just in the composition rate of organic matter produce by different tree types which due to variation in c:n ratio, some clay fraction of studied pedons in surface and subsurface horizon has been tested under scanning electron microscope and x-ray diffraction, the result of SEM emages showed that the green grain forest was the higher effected soil through weathering signs which was very clear **,** clay samples showed breakness of mineral layers and edges also the minerals appear in different size and shapes and that correlated with decrement in C:N ratio in tree types , the results showed there is series of changes in mineral morphological features , then mineral particles surfaces in green grain and pine forest appear irregular and complicated especially in pine forest samples as well as the minerals in green grain forest appear spongy like shape which due to swelling and expansion sequence for mineral interlayer. images for wild pears and oak forests showed the mineral surfaces was in the exfoliation state where the exfoliation tracks appear very clear whereas some of them exposed to edge weathering indicated by appearance of edges in pale color which can recognize from surface zone which caused by bleaching process resulting from interlayer cation removal by the weathering process which probably be potassium or iron absence of complication state and restricted in exfoliation process associated with edge weathering of exfoliated surfaces explain weathering intensity reduction as compared with green grain and pine forest and less weathering intensity found in almond tree type which was more C:N ratio value. If we focused on the C:N ration results we can recognize the variation in this value between plant species and less value found in green grain and pine forests and greater value found in almond.

Keywords: C:N ratio, electron microscope , green grain forest , minerals weathering

1. INTRODUCTION

Similar to the inorganic components of soil, soil organic matter (SOM) plays a significant role in affecting the chemistry of soils. Despite extensive and important studies, the molecular structure and chemistry of SOM is still not well understood. Moreover, because of its variability and close relationship with clay minerals and metal oxides the chemistry and reactions it undergoes with metals and organic chemicals are complex. The SOM and soil mineral component together provide the structural matrix and the chemical environment for living organisms in the soil. The source of organic matter in the soil is litter. Litter is broadly defined as all that was recently living. This includes fallen leaves, woody debris and fallen bark, dead roots, cadavers, animal dung, insect frass and cuticles. It also includes secretions and excretions from living organisms, such as root exudates, Webster et. al, 2000. The decay of fresh litter accumulates on the surface and within the soil, as SOM. Fresh litter and the more decayed organic matter are sources of food for many species. They support the trophic interactions between interstitial species. The process of litter chemical decay caused by these trophic interactions is called decomposition. This is in contrast to the chemical degradation of litter and SOM not caused by living organisms. Degradation is caused by chemical reactions between SOM molecules, and of SOM with clays that lead to new molecular forms and to the aggregation of molecules into colloids and polymers. Thus degradation is caused by abiontic reactions. Aerts, (1997), Also none of these refer to a consistent degree of decomposition or chemical composition, but to size or density, the pedantic debates are unnecessary. With time, fresh litter is broken up into a range of increasingly small fragment sizes, down to microscopic debris and organic colloids and flocculants, as it is decomposed and degraded. A fraction of the SOM accumulates because it is difficult to digest or it is indigestible. His SOM can be referred to as humus. It is usually defined as all SOM exclusive of living biomass, litter and macrodetritus, i.e. the smaller and more decayed fractions of SOM Adl, 2003. Fractionation of SOM can provide an idea of its quality as food for decomposition. Size fractions are defined by how large the litter particles are, or by how quickly they sediment in a standard heavy liquid of known density (such as sucrose, sodium polytungstate or sodium iodide). The latter is called density fractionation and is very useful in estimating the amount of labile litter in the soil. It is based on differences between the density of the minerals (more dense) and the organic matter (least dense). The more biologically accessible fraction (for decomposition) is the light fraction. The light fraction is that which floats on top of the liquid and consists mainly of fine litter fragments, macrodetritus and microdetritus that are decomposed to varying degrees. The intermediate fraction consists of organic matter covering and attached to minerals. This SOM is more decayed than the light fraction and is mostly humus Adl, 2003. One important source of organic matter in the soil is released from soil living organisms as secretions. The sources of these secretions are numerous. They include bacterial cell wall components, protective (or defensive)

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mucopolysaccharides from protists, mucus from earthworms and secretions from root cap border cells. The plant root cell secretions are called root exudates (Hawes *et al.*, 1998). These consist of various sugars, amino acids, peptides and defensive molecules. The effect of these material on mineral weathering depend on its chemical composition and The ratio of carbon to nitrogen is the carbon: nitrogen ratio or the C:N ratio. The C:N ratio of the organic material in the soil influences the rate of decomposition of organic matter and this results in the release (mineralisation) or immobilization of soil nitrogen. If the organic material contains more nitrogen in proportion to the carbon, then nitrogen is released into the soil from the decomposing organic material. On the other hand, if the organic material has a less amount of nitrogen in relation to the carbon then the microorganisms will utilize the soil nitrogen for further decomposition and the soil nitrogen will be immobilized and will not be available and this depend on organic the source of organic compound (tree types) Berg and Ekbohm ,1991 . The chemical and physical weathering of minerals is the fundamental process giving rise to much of the regolith and affects critical processes of the regolith such as metal release and retardation (dissolution-precipitation) and adsorption. Although our understanding of mineral weathering reactions for most primary minerals is extensive from a unit cell scale (Hochella & Banfield 1995), knowledge of micro environments mineral weathering remains limited. This researched aid to investigate the effect of c:n ratio for different tree species on minerals weathering as showed by SEM

2. MATERIALS AND METHODS

This study was conducted to investigate the effect of carbon: nitrogen ratio of forest tree types on minerals weathering and their morphological features in some selected forest soils located in northern Iraq. Five forest soil sites were chosen, characterized by similarity in parent material, topography and annual rainfall. Five pedons under different tree species were chosen from different sites located on same rain line north of Iraq figure 1. The sites were Mergasur (Arbil province) included two pedons, the first one was wild pears forest, and the second was green grain forest. Zawita site (Dohok province) included one pedon for pine forest, and Sarsang sites (Dohok province) included two pedons, oak and almond forests. Mineralogical properties were determined according to pansu 2006, as well as determination of organic carbon and nitrogen in both soil samples and plant residues to use it in calculation of Carbon:Nitrogen ratio. Scanning electron microscope was used in examining a selected clay samples from studied soils.

Soil Locations

Fig-1: Iraq map show studied soil pedons location (Sarsang, Zawita, Mergasur)

3. RESULTS AND DISCUSSION

3.1 *C:N ratio and biological weathering intensity*

By taking a look on the results showed in Table-1 we can easily recognize the difference in C:N ration between the soils under different tree types. also we can conclude that the differences in C:N ratio make the organic matter differ in decomposition rate by microorganisms ,decomposition rate increase by C:N ratio decrease, in the other hand

Table-1: Soil Classification and Organic Carbon and Organic Nitrogen and C:N ratio

Pedon Number	Soil Classification	Location	Tree Type	Horizon	Depth (cm)	Organic Carbon gm/kg	Organic Nitrogen gm/kg	C:N ratio
1	Haploxerolls	Merga sur	Green grain	A	0-15	77.91	6.89	11.3
				E	15-35	26.25	0.75	34.8
				Bt	35-70	25.40	0.80	31.7
				C	100-70	14.82	0.53	27.8
2	Argixerolls	Zawita	Pine	A	0-15	82.99	5.56	15.0
				E	15-30	25.40	1.54	16.4
				B_t	30-60	10.16	0.43	23.5
				C_K	60-80	7.19	0.42	17.0
3	Haploxerolls	Merga sur	Wild pears	A	0-20	42.34	2.17	20.1
				Bt	20-50	19.90	1.00	19.8
				C_{K1}	50-90	10.58	0.43	24.5
				C_{K2}	90+	10.58	0.38	27.2
4	Haploxerolls	Sarsang	Oak	A	0-25	40.22	1.99	20.2
				B_K	25-48	10.58	0.34	30.6
				C_{K1}	48-78	12.70	0.38	32.6
				C_{K2}	78+	12.27	0.36	33.3
5	Haploxerolls	Sarsang	Almond	A	0-30	13.97	0.40	34.6
				Bt	30-70	12.27	0.39	30.7
				C	70+	15.24	0.32	47.4

abundance of organic materials decomposition products in the lowerest C:N ratio tree type (organic and amino acids, polysaccharides, enzymes and other compounds) will attach minerals surfaces and will push the weathering rates to increase, beside appearance new morphological features for the minerals in weathering media, in contrast the highest C:N ratio tree types will have no effect on the minerals morphological features because the weathering media poor in organic matter decomposition products due to decrease in decomposition rate, many researches had been carried out to study effect of plant species on the weathering clay minerals, several of them focused on the interaction of organic material and compounds with different clay minerals, we here tried to focus on the effect of soil C:N ratio of organic materials produced by different tree types on the weathering intensity by taking a look on the morphological features of most abundant clay minerals in study area by using scanning electron microscope at the university of Aiwa, USA, Scanning electron microscopy (SEM) imaging was used as a supplemental analysis. Since identification via SEM can be ambiguous at the clay size fraction and quantification only subjective, SEM images were only used to support the information derived from XRD. Images of one replicate from each horizon of five sites were taken at same soil forming factors to illustrate any visual differences between like horizons at different tree types. Both samples exhibit some platy minerals and some halloysite. The halloysite was not identified by x-ray because there was such a small amount that there was no x-ray reinforcement to create a peak. The resolution of the magnification did not allow further inspection. These could be montmorillonite that appear in the x-ray patterns. Mineralogical changes in micaceous minerals and the effect of plant have been reported (e.g., Robert and Berthelin, 1986; Hinsinger et al., 1992; Velde and Peck, 2002; Norouzi and Khademi, 2010). Plants can promote both the release of K from illite and the formation of 1.4 nm vermiculite layers (Mojallali and Weed, 1978; Hinsinger and Jaillard, 1993; Kodama et al., 1994; Surapaneni et al., 2002).

3.2 *X-Ray Diffraction Analysis*

The result of x-ray diffraction showed existence of smectite minerals and vermiculite Fig-2 and that maybe belong to smectitization of interstratified illite/smectite clay domains in K depleted conditions (Tributh et al., 1987; Velde and Peck, 2002). Hinsinger et al. (1992, 1993) demonstrated that in the rhizosphere of rape (Brassica napus) and ryegrass (Lolium multiflorum Lam.), trioctahedral mica (phlogopite), as the sole source of K, rapidly weathered and vermiculitized after root-induced release of interlayer K, which implies that K in solid framework forms could be a source of K for plants. Formation of complexes and production of acid compounds may promote the vermiculite formation mainly by a proton exchange process (Robert and Berthelin, 1986). Also, K uptake by plant roots may decrease K concentration in the soil solution at the root surface, which leads to mineralogical changes, as shown by Hinsinger and Jaillard (1993), Al-Dhahi (2009). Some soil microorganisms are able to solubilize unavailable forms of K-bearing minerals, such as micas and orthoclase, by excreting organic acids which either directly dissolve K-bearing minerals and the activity of microorganisms depend on C:N ratio of organic materials and this process inhance formation of smectite minerals from mica as show in x-ray Fig-2.

3.3 *Scanning electron microscope images*

The result of SEM images showed that the green grain forest characterized by higher effectiveness by weathering figure 3 A,B, the clay samples showed breakness of smectite and mica mineral layers and edges also the minerals appear in different size and shapes and that correlated with decrement in C:N ratio in tree types , the images A,B, in figure 2 showed there is series of changes in mineral morphological features , then mineral particles surfaces in green grain and pine forest appear irregular and complicated especially in pine forest samples as well as the minerals in green grain forest appear spongy like shape which due to swelling and expansion sequence for mineral interlayer (Tarzi & Portz,1978) , many researchers indicate that these changes due to exposed mineral surfaces to many weathering processes starting with splitting of surfaces passing through exfoliation then diphole and other shallow hole depending on weathering intensity which the Silicate mineral exposed to Bennet et. al, 2001. This swelling and expansion which cause Retile or cracking ending by crumbling same images showed low and high zones which represent Retiles appearance on these surfaces, this trend indicate reach of weathering process tom advance stage in same mineral parts , so we can coclude that some of mineral particles within weathering stage and the others in final stage, this state existence due to variation in mineral particles sizes, where the smaller particle size was more influenced by weathering as compared with bigger particle size in same conditions, April & Keller,1990, some aspects showed in pine forest images such as exist of different size holes , some of them moderate holes may be due to impurity coming from petrifying plant materials through mineral creation or from other minerals differ in geological age and weathering resistance degree which called Fission particles tracks (Price & Wallker, 1967).

The most important evidence for the effect of organic materials and its chemical composition and characteristics such as C:N ratio on the mineral weather in is the difference in weathering intensity for the minerals between surface horizons which domiatly rich in organic substances and subsurface horizons which is poor in organic substances as well as the effect of organic material on soil acidity which could enhance soil acidification Augusto et. al, 1998, by taking a look for the images and comparison the morphological features for the minerals.

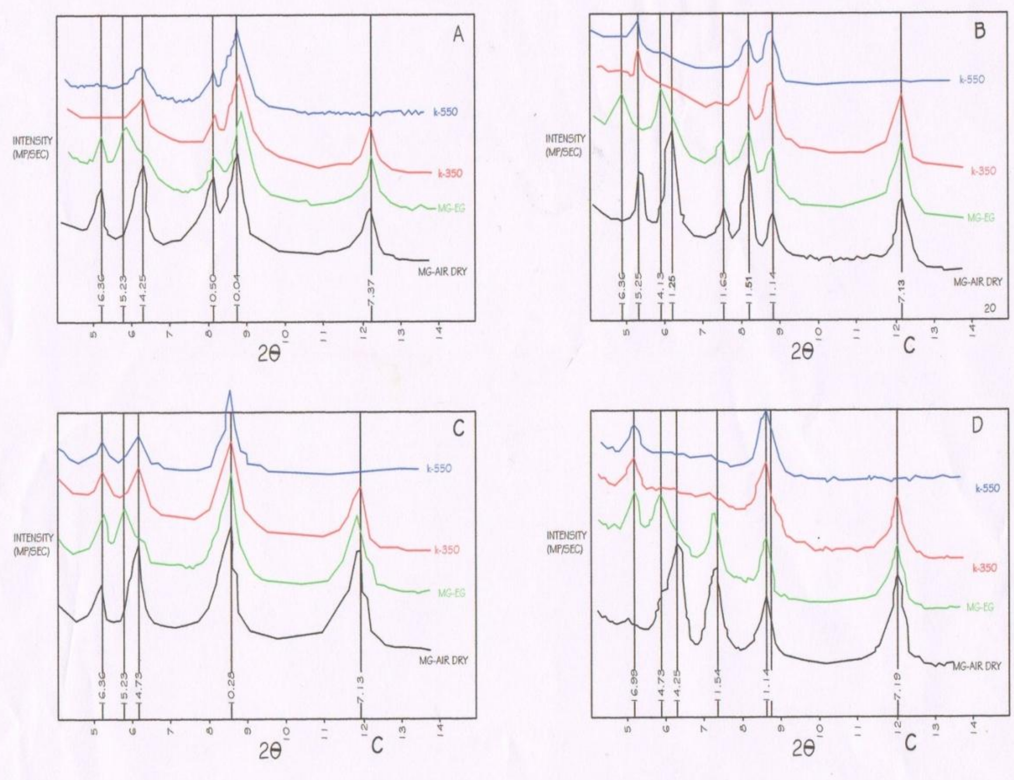

Figure (2) X-ray diffraction on studied soil pedonnd
A:-oak forest B:- green grain forest
C:- almondforest D:- pine forest

we found very clear difference from the dark color for surface horizons and light color for subsurface horizons and the weathering sighs appear more clear in in the surface horizons figure 3,4 beside clearing of edges and layer weathering for single layers while montmorilonite appear like pale and dark cloud according to effective degree of weathering process some complete layers has been removed from montmorillonite crystals by weathering, Bisdom et. al, 1982,
SEM images in Fig-3 E,F, for wild pears and oak forests showed the mineral surfaces was in the exfoliation stgte where the exfoliation tracks appear very clear whereas some of them exposed the edge weathering indicated by appearance of edges in pale color which can recognize from surface zone which caused by bleaching process resulting from interelayer cation removal by the weathering process which probably be potassium or iron Augusto et al 2000. The absence of complication state and restricted in exfoliation process associated with edge weathering of exfoliated surfaces explain weathering intensity reduction as compared with green grain and pine forest.

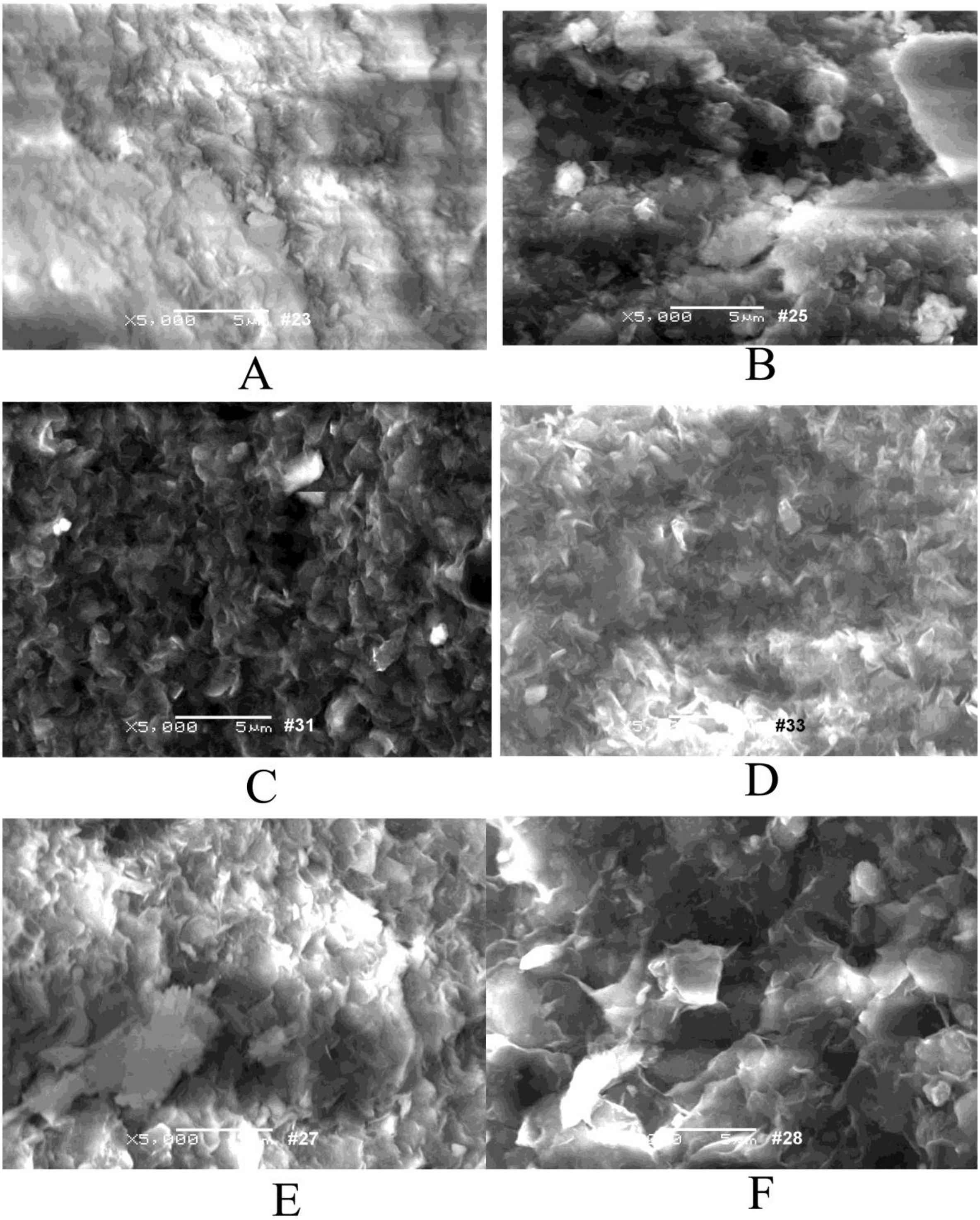

Fig-3: Scanning Electron Microscope images for clay samples of studied soils
A: Surface horizon for pine forest, **B:** subsurface horizon for pine forest
C: Surface Horizon for green grain forest, **D:** Subsurface horizon for green grain forest
E: surface horizon for oak forest, **F:** subsurface horizon for oak forest

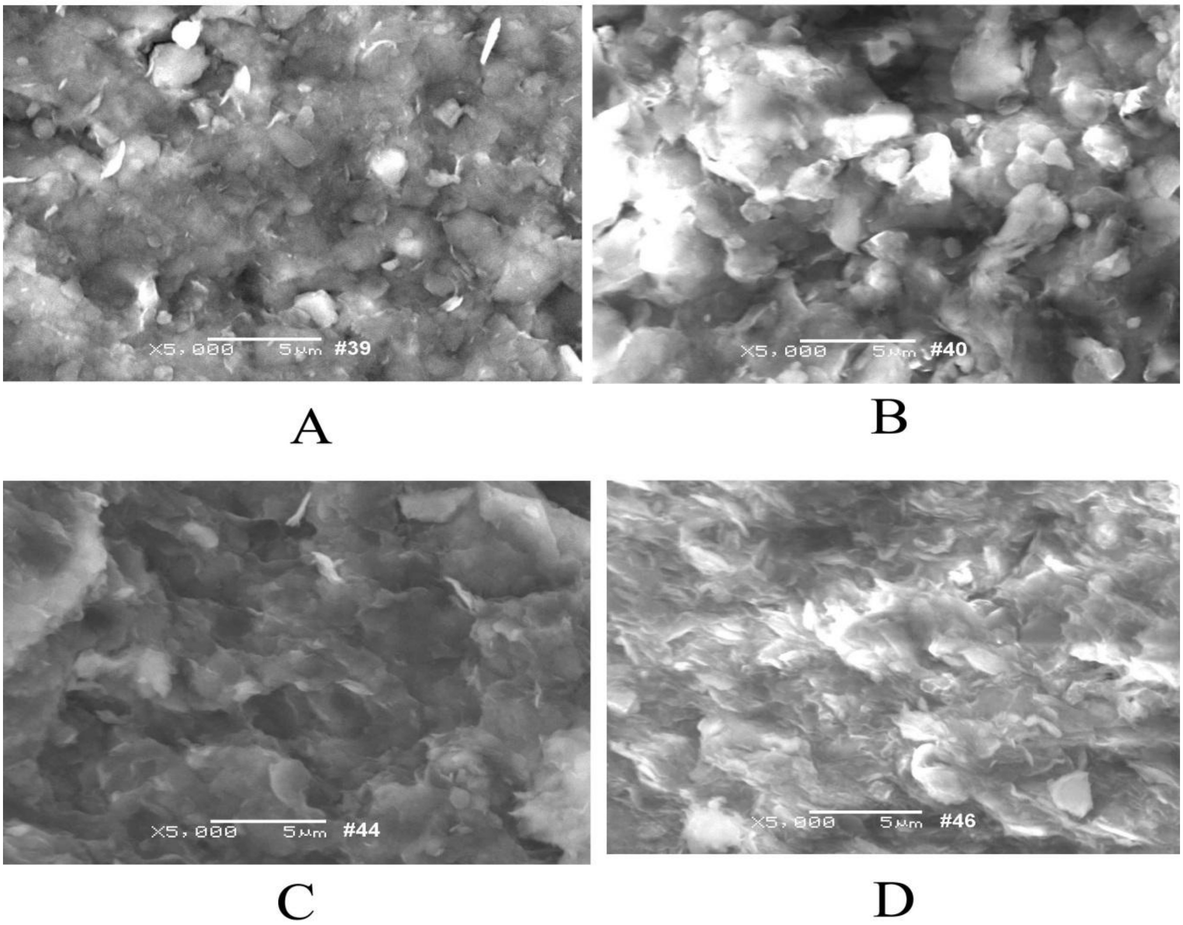

Fig-4: Scanning Electron Microscope images for clay samples of studied soils
A: Surface Horizon for almond forest, **B:** Subsurface Horizon for almond forest
C: Surface Horizon for wild pear forest, **D:** Subsurface Horizon for wild pear forest

If we focused on the C:N ration results in table 1 we can recognize the variation in this value between plant species and less value found in green grain and pine forests (11.30,15.07) respectively Cheshire etal, (2000) While the samples for almond forst showed appearance of exfoliation but with weaker effect compard with wild pears and oak forest whereas the exfoliated parts was unharmed edges with clear boundaries associated with appear the surface with less complication and some of them wavy like shape , this indicate the chemical weathering was weak which usualy create complicated surfaces and unclear signs edges (Gilkes &Suddniprakarn1979a).

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