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Supergene Alteration of Amphibole in Suryun Kaolin Deposits: Mineralogical and Morphological Studies

수륜 고령토광산에서 산출되는 각섬석의 표성 변질작용: 광물학적 및 형태적 연구

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ABSTRACT: X-ray, optical and electron microscope studies exhibit that the amphiboles in anorthositic saprolite from kaolin deposits, located in Suryun-myeon, Seongju-gun, Kyungsangbuk-do, have altered under weathering conditions to smectite, mixed-layer mineral, vermiculite and goethite. In early supergene alteration stage when rock structure is still preserved, smectite occurs as initial weathering product of amphibole. Further weathering leads to the formation of mixed-layer mineral, vermiculite and goethite as indicated by XRD and SEM studies.

Scanning electron microscopy studies of amphibole show that the dissolution of amphibole proceeds by selective etching at the surface along weaker zones producing distinct etch pattern. The calcic amphiboles according to electron microprobe analyses, show leaching of the most mobile elements (Mg, Ca and Fe) during alteration.

요약 : 경상북도 성주군 수륜면에 위치한 고령토 광산의 회상암질 사프롤라이트내 각섬석의 X-선 회절분석, 광학현미경 및 전자현미경 관찰결과 각섬석은 풍화에 의하여 스멕타이트, 혼합층 광물, 버미큘라이트 및 침철석으로 변질되었음을 보여준다. 모암 구조가 아직 보존되어 있는 초기 표성 변질 단계에서는 스멕타이트가 각섬석의 초기 풍화산물로 나타나며 풍화작용이 진행됨에 따라 혼합층 광물, 버미큘라이트, 침철석이 생성됨이 X-선회절 분석 및 SEM 연구에 의하여 관찰된다. 각섬석의 주사 전자 현미경 연구에 의하면 각섬석의 용해는 표면의 약대를 따라 선택적으로 진행되며 특징적인 용식 모양을 나타낸다. 전자현미 분석에 의하면 칼슘 각섬석은 변질중 Mg, Ca, Fe 등의 이동성이 강한원소들이 용낟된다.

INTRODUCTION

Amphiboles, due to their relative unstability on the earth's surface (Goldich, 1938; McClelland, 1950; Nickel, 1973), are highly susceptible to weathering and form a variety of secondary minerals. Early studies of chemical weathering of amphiboles have demonstrated a sequence of alteration phases. Ildefonce(1980) and Proust (1982) described talc, nontronite, saponite, di- and trioctahedral vermiculite and iron oxide minerals as secondary phases. Proust (1985) studied the two kinds of amphiboles in glaucophane schist and observed that the chemical composition of alteration product is controlled by the chemistry of amphibole precursor. Walker, *et al.* (1967) studied the geochemical changes in hornblende during intrastratal alteration to Fe-rich montmorillonite. The alteration involve loss of iron, alkalies, alkaline earth elements and relative increase in Si and Al.

Jeong (1987) and Park (1988) observed the weathering of amphibole in anorthositic rocks into vermiculite, mixed layr chlorite/vermiculite and goethite. The weathering of amphiboles in anorthositic rocks in the study area was expected to have produced pronounced chemical and mineralogical changes. XRD, SEM and optical microscopy studies show excellent examples of supergene transformation of amphibole to phyllosilicate minerals. This paper describes some mineralogical, morphological, and chemical changes during supergene alteration of amphiboles in anorthositic rocks of Suryun area, Korea.

MATERIALS AND METHODS

A weathered profile is developed on age unknown (Perhaps Precambrian) anorthositic rocks in Suryun area as shown in the geological map including kaolin deposits (Fig. 1). Anorthositic rocks are the main host of kaolin deposits in the area and shows textural and compositional gradation, indicating comagmatic origin (Jeong & Lee, 1986). Fresh and altered rock samples were collected (Table 1).

Amphibole grains were hand picked from fresh rock and saprolite under stereomicroscope

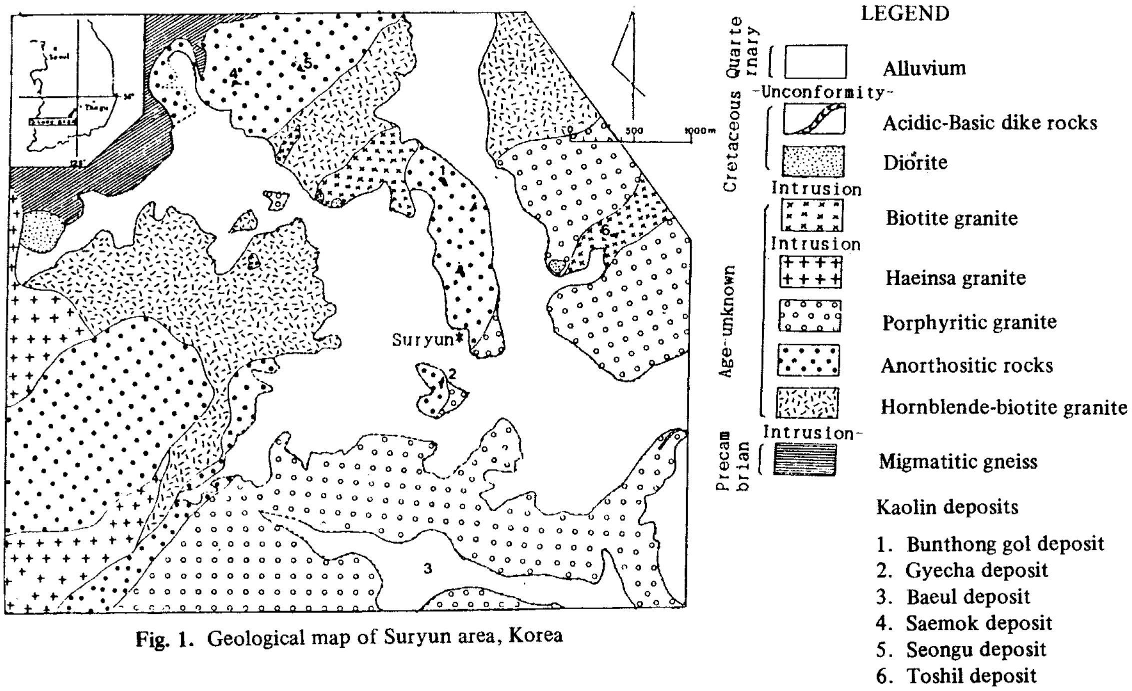

Fig. 1. Geological map of Suryun area, Korea

Table 1. Description of amphibole samples from weathering profile.

Sample	Size fraction	Description	Parent rock
A3	2 – 16 um	brownish green, highly weathered amphibole grains, occuring as spots in the saprolite.	Anorthosite
A4	macroscopic grains	brownish green, similar to sample A3	Anorthosite
TS4	macroscopic grains	yellowish green. weathered amphivole grains. occuring as irregular mass in kaolin	Amphibole-rich anorthosite
HBA4	macroscopic grains.	green amphibole grains with golden yellow flakes, highly weathered.	Amphibole rich anorthosite

and were treated with heavy liquid and magnetic separator for removal of impurities including quartz, feldspar, magnetite, and limenite. Clay size (< 2μm) particles were separated by sedimentation and were disaggregated by ultrasonic treatment. K, Mg-saturated, glycolated, heat treated, and untreated samples were prepared as preferred oriented and random powders. A JEOL Model JDX-5P diffractometer employing Ni-filtered Cu/Kα radiation at scanning speed of 1°2θ/min and at 20mA, 45kV condition, was used for taking XRD patterns.

Altered amphiboles associated with kaolin were impregenated with low-viscosity epoxy in vaccum and polished thin sections were made for optical study and electron microprobe analyses. The instrument used was JEOL Model JXA-733, electron microprobe analyser operated at 15kV with beam current of 10nA and beam diameter of 10μ. Average spectrum counts (10x5 sec) were compared with the natural silicate standard. Bense and Albee's method (1968) was used for the calibration.

Fresh surface of amphibole grains were coated with gold and observed under scanning electron microscope for morphological study and qualitative chemical analyses using PHILIP SEM-505 equipped with X-ray energy dispersive spectrum analyser.

RESULTS AND DISCUSSION

Mineralogical Characteristics

The amphibole in anorthositic rocks have been subjected to two distinct alteration processes; the first of retrogressive type (Jeong, 1986) which developed chlorite, muscovite and epidote (Fig. 2a) and the second of weathering type that has formed 14A trioctahedral phases, mixed -layer mineral (hydrobiotite) and goethite (Fig. 2b) along microfractures and cleavages. The mineralogy of anorthositic rocks in the study area varies slightly as determined by thin section. The relative mineral composition of altered amphibole was estimated through XRD (Table 2). Small amount of quartz, feldspar, chlorite and kaolinite/halloysite are associated with amphibole. Smectite, vermiculite, mixed-layer mineral hydrobiotite and goethite are major alteration products of amphibole in every sample. Goethite is present as abundant mineral in sample A3 and A4, while gibbsite occurs in trace (Table 2).

X-ray Power Diffraction Analyses

The d-values of the (001) reflection used for identification of the layer silicates are shown in table 3. With increasing alteration, the sharp 8.50Å reflection of amphibole is reduced and 14 & 24Å reflections appears (Fig. 3). It has been revealed by XRD that 14.7Å reflection is attributed to both smetite and vermiculite as evidenced by glycolation experiment (Fig. 4) during which the smectite expanded to 16.7Å while the vermiculite remains at 14.2Å. The (001) reflection of vermiculite completely collapses on K saturation and heat treatment (Fig. 4 & 5). Both smectite and vermiculite are trioctahedral as shown by (060) d-spacing (1.52 – 1.54Å).

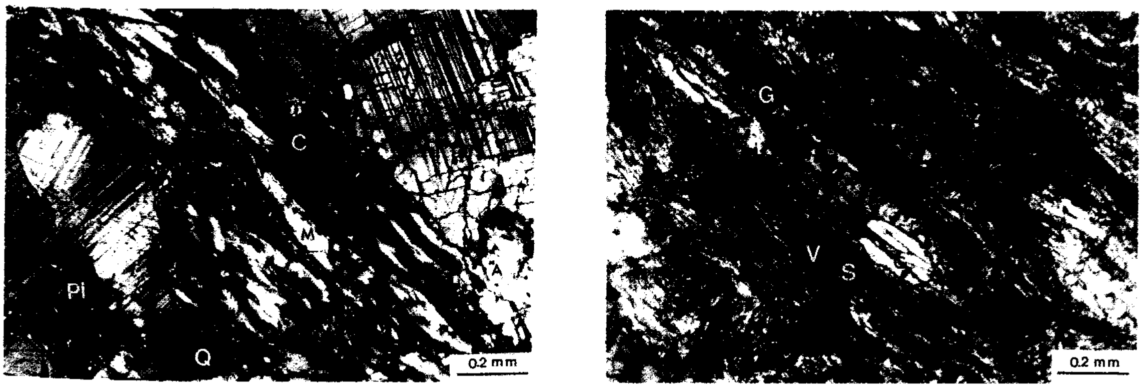

Fig. 2a) Photomicrograph showing alteration of amphibole (A) to chlorite (C) and muscovite. (M) Pl: Plagioclase, Q: Quartz.

2b) Photomicrograph showing alteration of amphibole (A) to vermiculite (V), smectite (S) and goethite (G) by weathering along fracture and cleavage.

Table 2. Mineralogical composition of amphibole samples from Saprolite.*

Sample	Minerals									
	Amp	Ch	Mx	Vm	Sm	Gt	Gb	K/H	Qtz	Fld
A3	+	.	+++	++	+	++	.	+	.	.
A4	+	.	+++	++	+	++	.	+	.	.
TS4	+	.	+	+++	+++	+	.	.	.	.
HBA4	+	.	+	+++	+++	+	.	.	.	.

* Mineralogy by X-ray powder diffraction; Amp = amphibole, CH = Chlorite, Mx = mixed layered mineral, Vm = vermiculite, Sm = smectite, Gt = goethite, Gb = gibbsite, K/H = kaolinite/halloysite, Qtz = quartz, Fld = feldspar. Mineral content ranges from traces (-) to predominant (+++)

Table 3. The d-values (Å) of the (001) reflections used for identification of layer silicates.

Mineral	Treatments					
	Unt 1)	Mg 2)	Eg 3)	K 4)	300°C 5)	500°C 5)
Smectite	14.7	14.9	16.7	10.2	10.2	9.3
Vermiculite	14.2	14.2	14.2	10.2	10.2	9.3
Mixed layered mineral (hydrobiotite)	24.5	24.5	24.5	22.5	–	–
Kaolinite/Halloysite	7.3	7.3	7.3	7.3	7.3	Suppressed

1) Untreated sample.
2) Mg saturated.
3) Ethylene glycol treatment.
4) K saturated.
5) Heating treatment.

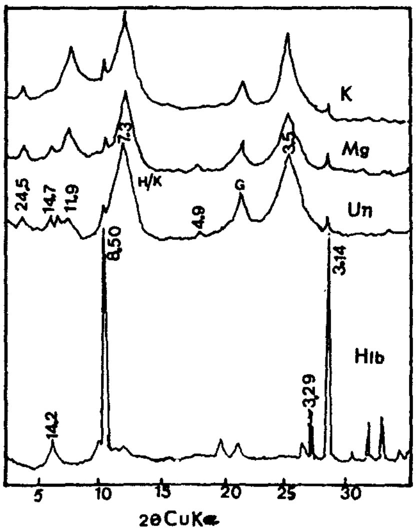

Fig. 3. X-ray diffraction pattern showing alteration product of hornblende in supergene weathering of anorthositic rock. Hlb: hornblende in fresh rock, G: goethite, H/K: halloysite/kaolinite, Mg: Mg-saturated, K: K-saturated, Un: untreated.

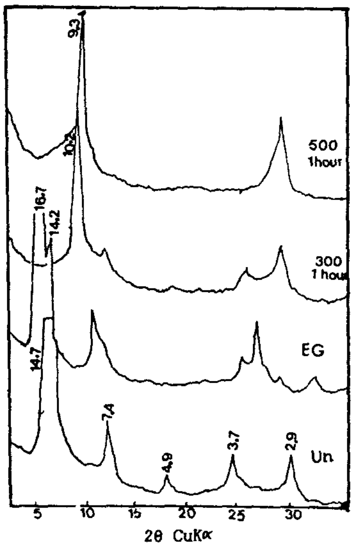

Fig. 4. X-ray diffraction pattern of glycolated and heat treated smectite, vermiculite mixture. Un: untreated sample.

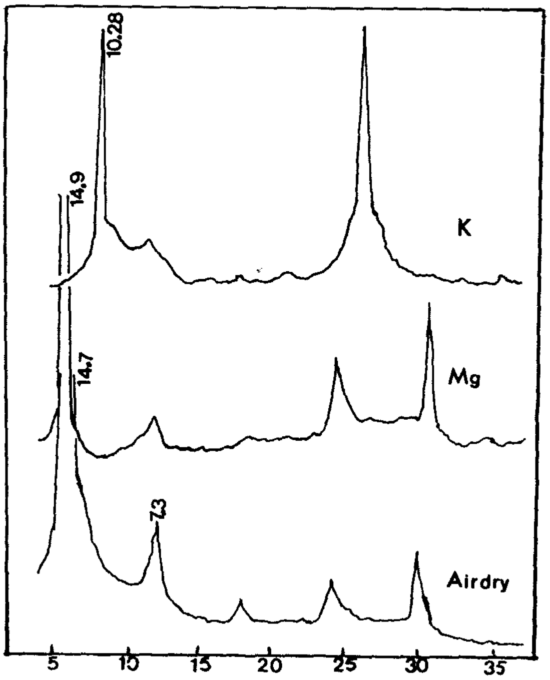

Fig. 5. X-ray diffraction pattern of saturated sample.

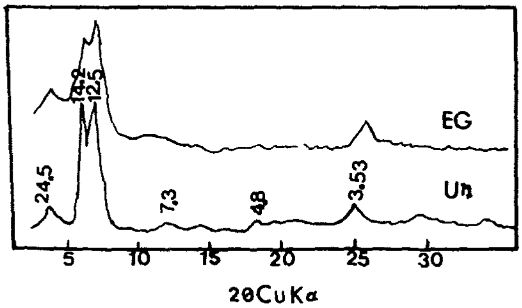

Fig. 6. X-ray diffraction pattern of poorly ordered mixed layered mineral. EG: ethylene glycolated, Un: untreated sample.

A poorly ordered hydrobiotite-like phase with reflections of 24 and 12Å is present in the altered amphibole (Fig. 6) and shows no change in the d-spacing on various treatments. Major XRD peaks of goethite and kaolinite/halloysite show reflections at 4.8Å and 7Å, respectively (Fig. 5 and 6).

Chemical Characteristics

Microprobe analyses of fresh amphiboles in anorthositic rocks are given in table 4. According to the nomenclature of amphiboles by Leake (1978), and as shown in Fig. 7, the amphiboles belongs to the Ca-amphibole group with $(Ca+Na)_B > 1.34$ and $(Na)_B < 0.05$. It has relatively constant Mg/Mg+Fe ratios (0.53–0.72) (Table 4), and grade from actionlite to actinolitic hornblende to magnesio hornblende in terms of the Si-Al substitution (Fig. 7). The microprobe analyses of altered products of amphiboles (Table 5) show that the composition becomes more and more aluminum rich (Al_2O_3: 17.47-19.35%) as compared to fresh amphiboles (Al_2O_3: 3.51-5.21%). Also the concentration of Fe, Mg, and Ca decrease with the alteration of amphiboles. These results suggest the leaching out of most mobile elements (Mg, Fe and Ca) from the weaker zones such as cleavage and micro fractures, in the grain. Optical study of thin section (Fig. 2b) shows that the iron oxide, which is mainly goethite, as shown by XRD pattern, have precipitated interstitially and is responsible for the coloration (Walker, *et al.* 1967). Microprobe and XRD analyses suggest that the amphibole with low aluminium and high calcium would have been weathered to trioctahedral mineral phases (smectite and vermiculite) as shown by Proust (1985).

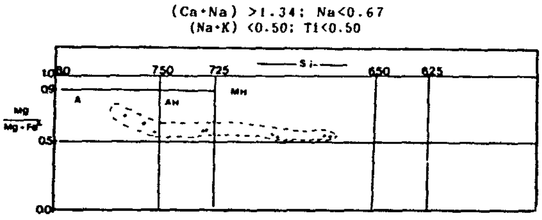

Fig. 7. The composition of amphibole in anorthositic rocks plotted on the nomenclature diagram by Leake (1978). A: Actinolite, AH: Actinolitic hornblende, MH: Magnesio hornblende

Morphological Characteristics

Scanning electron miroscopy observation with EDS analyses shows that amphibole has weathered into two different type of minerals with distinct morphologies (Fig. 8). The first type of mineral show honey-comb structure and has crystallizes at grain surface and edges of amphibole (Fig. 9), where as the second type of mineral show flaky morphology, and is associated with the amphibole grain (Fig. 8).

EDS patterns of these two minerals also show variation in peak ratios as compared to amphibole (Fig. 10A) In case of mineral with honeycomb structure, the EDS pattern show high Al and low Ca peak ratio (Fig. 10B), while in case of mineral with flaky morphology (Fig. 10C), high Fe peak ratio was displayed, as compared to EDS pattern of amphibole.

Table 4. Chemical analyses of amphiboles by EPMA.

	1	2	3	4	5	6	7	8	9
Na_2O	.363	.729	.123	.826	1.100	.958	.328	.551	.573
SiO_2	51.934	47.176	52.868	46.680	45.080	45.177	52.038	50.187	50.487
TiO_2	.172	.340	.122	.278	.915	.824	.130	.373	.248
Al_2O_3	4.348	7.228	2.492	8.093	10.197	10.404	3.982	6.331	7.033
Cr_2O_3	.149	.089	.193	.205	.150	.126	.169	.088	.066
FeO	11.845	15.374	10.648	16.806	16.047	15.672	13.440	13.491	13.078
MgO	15.288	12.033	15.911	10.746	10.376	10.250	14.240	13.563	13.049
MnO	.451	.344	.132	.464	.364	.391	.269	.302	.360
CaO	12.496	12.808	13.037	12.449	12.252	12.072	11.978	11.642	11.859
K_2O	.258	.220	.106	.451	.973	.972	.102	.170	.198
BaO	0.000	0.000	0.000	0.000	0.000	0.000	.053	.073	.323
Total	97.303	96.341	95.630	96.999	97.455	96.786	96.729	96.771	97.275
Total number of ions on the basis of 23 oxygens									
Si	7.513	7.073	7.720	7.007	6.743	6.772	7.601	7.345	7.346
Al(IV)	.487	.927	.277	.993	1.257	1.228	.933	.655	.654
Al(VI)	.255	.350	.152	.438	.540	.612	.286	.437	.552
Cr	.017	.010	.022	.196	.018	.015	.019	.010	.007
Ti	.019	.038	.013	.031	.102	.092	.014	.041	.026
Fe*	1.433	1.928	1.300	2.110	2.007	1.967	1.641	1.651	1.591
Mg	3.276	2.674	3.465	2.225	2.313	2.293	3.040	2.861	2.824
Mn	0.000	0.000	.016	.059	.020	.021	0.000	0.000	0.000
Mn	.055	.044	0.000	0.000	.026	.028	.033	.037	.044
Mg	.020	.015	0.000	.179	0.000	0.000	.061	.098	.005
Ca	1.936	2.057	2.040	2.001	1.963	1.941	1.874	1.625	1.848
Na	0.000	0.000	0.000	0.000	.011	.031	.030	.037	.085
Ba	0.000	0.000	0.000	0.000	0.000	0.000	.002	.003	.018
Na	.101	.211	.034	.240	.308	.247	.062	.119	.076
K	.047	.038	.020	.086	.185	.184	.019	.031	.036
Mg/ Mg+Fe	.697	.582	.727	.532	.535	.538	.653	.641	.640

*Total Fe = FeO

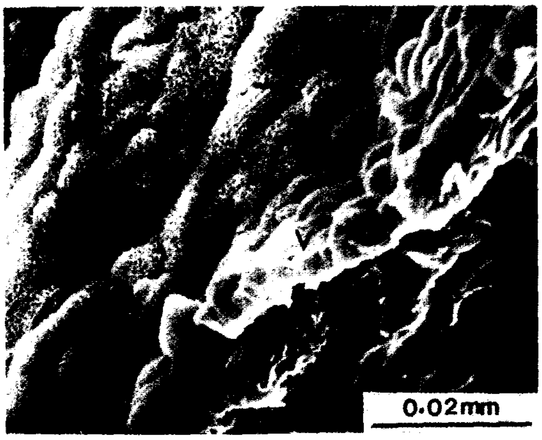

Fig. 8. SEM photograph of amphibole (A), vermiculite (V), and smectite (S).

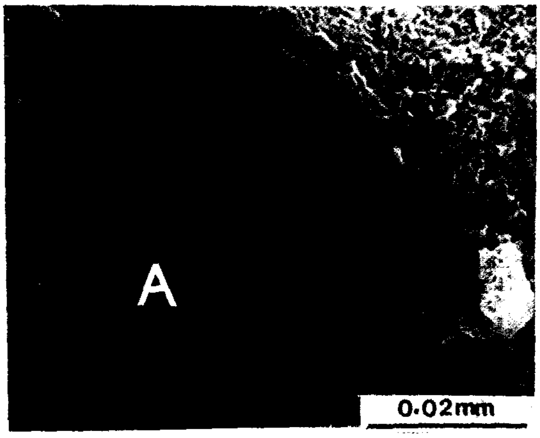

Fig. 9. SEM photograph of amphibole (A) and smectite (S). Note smectite forming from the surface of amphibole.

XRD analysis, EDS patterns, and morphological characteristics strongly suggest that the mineral representing honey-comb structure is smectite, and the mineral showing flaky morphology is vermiculite. The smectite crystallizes at the early stage of amphibole alteration at its grain surface and edges. Further weathering leads to the formation of mixed layer mineral, hydrobiotite and vermiculite.

SEM study also revealed dissolution mechanism in amphiboles (Fig. 11). The study shows the development of oval, lense and elongated pyramid shaped structures on grain surface. The small (1-2μm) oval and lense shaped etch pits (Fig. 11A and 11B), are developed along weaker zones, where as the elongated pyramid like structures are associated with enlarged fractures (Fig. 11C and D). The nature of their occurences suggest that their formation is effectively controlled by the weathering conditions. In the early stage of weathering, the dissolution in amphibole is initiated along cleavage planes (110), forming oval and lense shaped etch pits. On further weathering, these etch pits are enlarged to form fractures (Fig. 11B). As weathering proceeds, these fractures lead to the formation of elongated pyramids with sharp edges and pointed ends (Fig. 11C and D). It is inter-

Table 5. Chemical analyses of amphibole and its altered products by EPMA

	Amphibole		Altered products*				
Na_2O	.343	.549	.052	.027	.057	.017	.050
SiO_2	52.249	50.752	36.366	35.001	35.307	33.799	33.580
TiO_2	.101	.075	.209	.036	.052	.008	.020
Al_2O_3	3.511	5.121	17.470	18.613	18.677	19.712	19.355
Cr_2O_3	.062	.188	.279	.149	.205	.146	206
FeO	10.970	11.391	12.728	14.026	13.860	12.989	12.400
MgO	15.945	14.858	11.807	15.297	15.445	16.743	17.290
MnO	.414	.319	.141	.166	.125	.088	.140
CaO	12.551	12.489	1.195	1.026	.625	.646	.550
K_2O	.158	2.89	.744	.316	.155	.093	.093
SrO	0.000	.286	.120	0.000	0.000	.334	.080
Total	96.304	96.027	81.111	84.657	84.509	84.572	83.764

* Altered products consist of very fine-grained mixture of smectite and vermiculite.

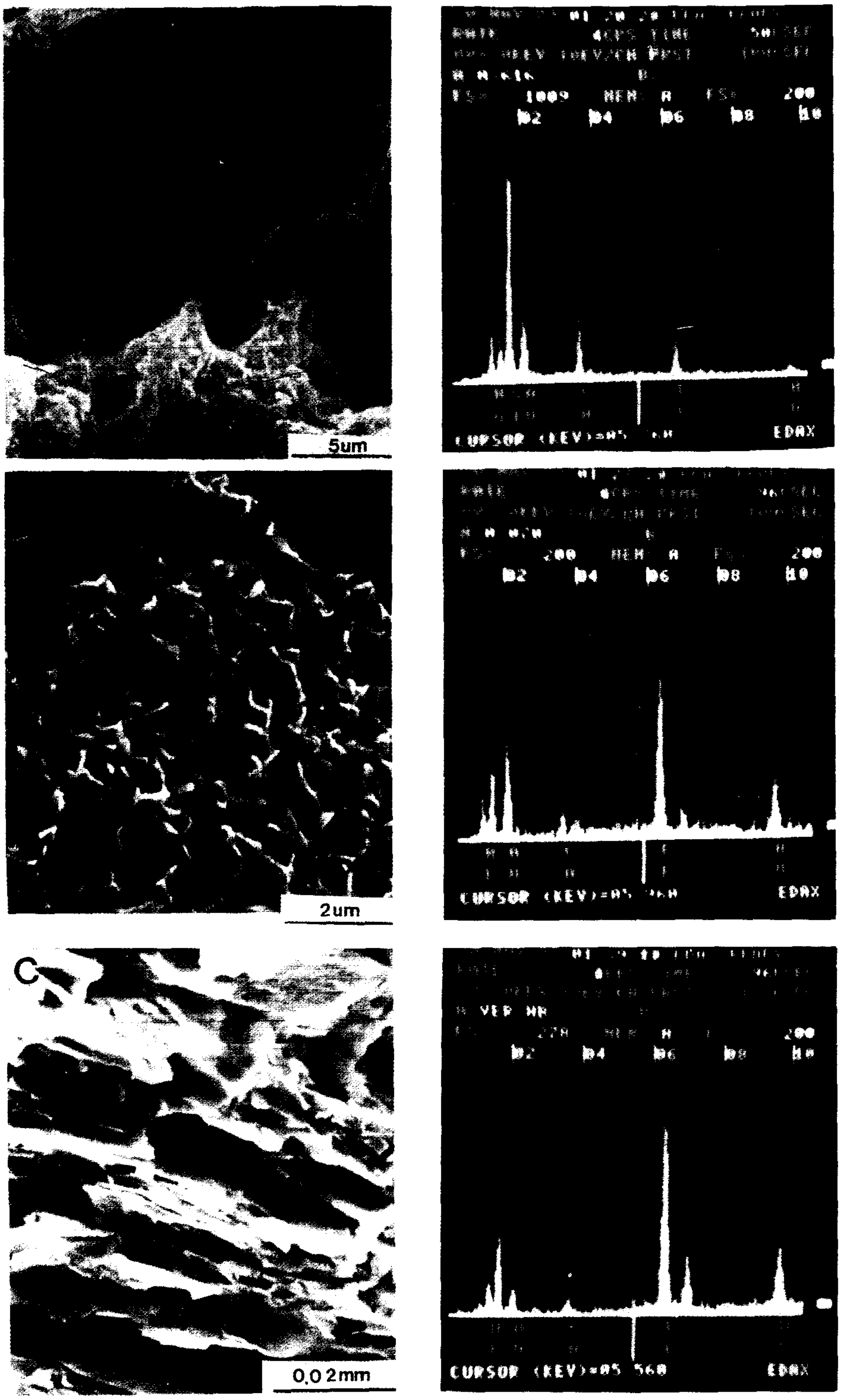

Fig. 10. Scanning electron microscope photographs and EDS patterns of a Amphibole (A), smectite (S) and vermiculite (V).

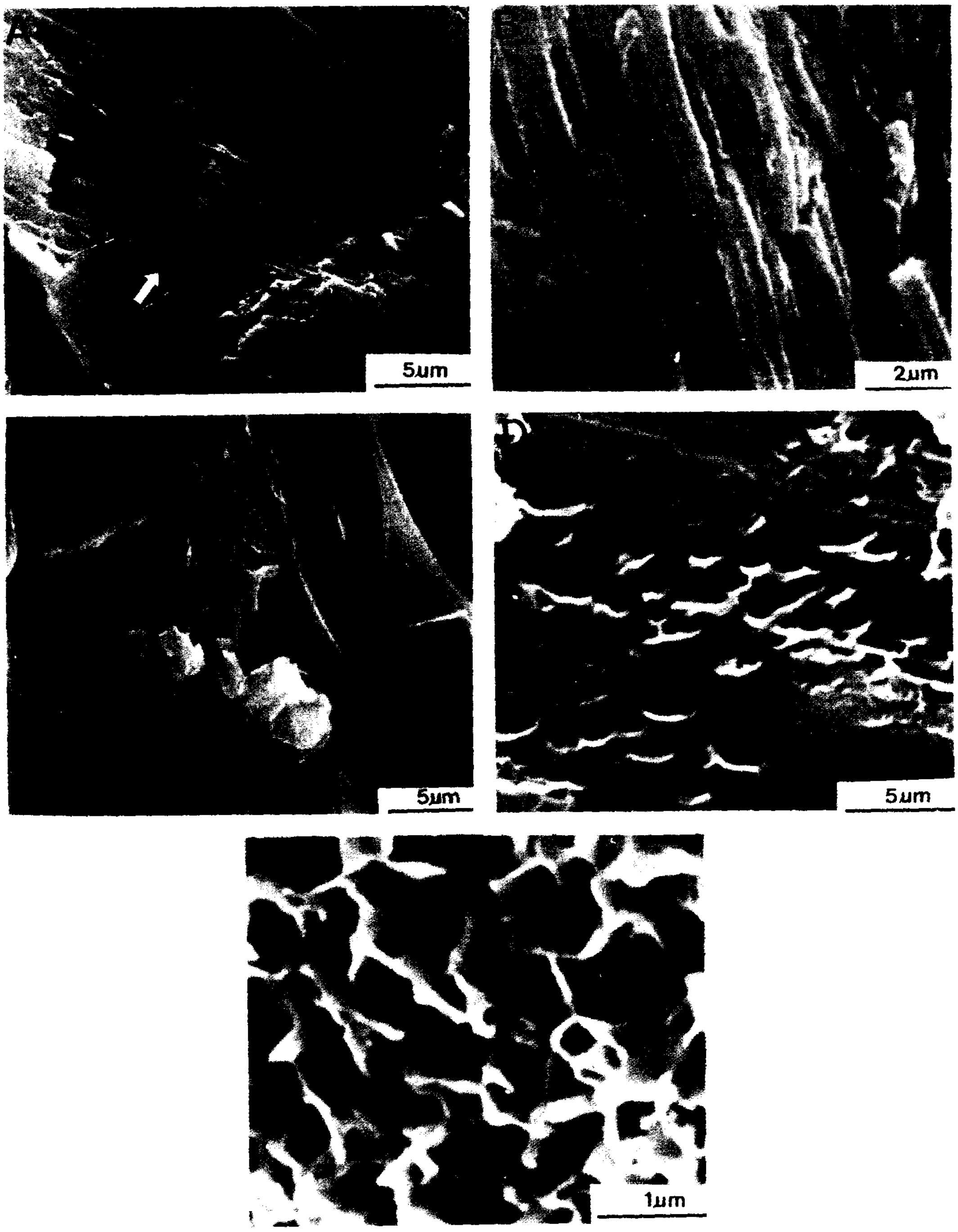

Fig. 11. Scanning electron microscope photographs, showing dissolution mechanism of amphibole. A: formation of narrow lens-shaped pits (arrow), B: enlargement of cleavage and fracture, C: amphibole forming sharp edges, D: advanced dissolution etch pits, E: smectite showing honey-comb structure.

pretated on the basis of morphological characteristics that smectite (Fig. 11E) form predominantly on sharp dissolution edges of amphibole.

CONCLUSION

The amphiboles have been subjected to two distinct alteration process, the first of retrogressive metamorphism which developed chlorite, muscovite, and epidote along cracks, and the second of weathering that has developed 14Å trioctahedral phases, mixed layer mineral and goethite. Supergene alteration of smectite showing honeycomb structure. Further weathering leads to the formation of mixed layer mineral hydrobiotite, flaky vermiculite, and goethite. Both smectite and vermiculite occur as intimate mixture. Their presence is attested by XRD and SEM analyses. The mixed layered mineral shows poor order and its basal reflection (24Å and 12Å) correspond to hydrobiotite. Goethite appears to precipitate along the fractures and forms secondary texture in more altered grains.

The amphiboles are calcic type and show compositional gradation in the range of actionlite – actinolitic hornblende – magnesio-hornblende. Microprobe analyses of altered amphibole show leaching of elements. The most mobile elements such as Mg, Ca, and Fe are leached out from the weaker zones (cleavages and microfractures). Iron oxide is precipitated interstitially and is responsible for coloration.

A mechanism of dissolution in amphibole grains has been traced. The dissolution process is initiated with formation of small (1-2μm) lens and oval shaped etch pits along cleavage planes. These etch pits are enlarged to form fractures which are further dissolved forming elongated pyramids with sharp edges and pointed ends. Smectite have formed predominantly on the sharp edges of amphibole grains.

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