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PETROLOGIC AND CHEMICAL INVESTIGATION OF CHEMICAL WEATHERING IN MAFIC ROCKS, EASTERN PIEDMONT OF MARYLAND

by Emery T. Cleaves



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CONTENTS

Abstract	.]
Introduction	. 3
Analytical Methods	. {
Mineralogic and chemical evaluation of weathering profiles	
Well-drained domains	. [
Profile 64-95 Profile 64-79 Profile 64-149 Profile 64-107	. 10 . 14
Well-drained domains, conclusions and observations	. 18
Poorly-drained domains	. 19
Profile 63-120 Profile 64-138 Profile 64-111 Profile 64-33	. 22 . 23
Poorly-drained domains, conclusions and observations	. 25
Drainage domains compared — a summing up	. 26
References cited	. 27

ILLUSTRATIONS

Figure	1.	Area of investigation and general location of rock weathering profiles	2
0	2.	Map showing location of Profiles 64-95, 64-107 and 64-111	7
	3.	Cross-section of trench showing location of samples of Profile 64-95	8
		Profile 64-95, mineralogical, porosity, and density changes	
		accompanying weathering	9
	5.	Map showing location of Profiles 64-79, 64-138, and 64-149	10
	6.	Cross-section of trench showing location of samples of Profile 64-79	11
		Profile 64-79, mineralogical, porosity, and density changes	
		accompanying weathering	12
	8.	Diagram portraying mineral changes in sample 64-81	13
	9.	Sketches showing mineral weathering in amphibolite (No. 64-81 and No. 64-149b)	14
	10.	Cross-section of trench showing the location of samples of Profile 64-149	15
		Profile 64-149, mineralogical, porosity, and density changes	
		accompanying weathering	
	12.	Cross-section of trench showing the location of samples of Profile 64-107 and 64-111	18
	13.	Map showing location of Profiles 63-120 and 63-33	20
	14.	Cross-section of trench showing the location of samples of Profile 63-120	20
	15.	Profile 63-120, mineralogic, porosity, and density changes	
		accompanying weathering	21
	16.	Cross-section of trench illustrating the geologic setting of Profile 64-138	23
	17.	Cross-section of trench showing the location of samples of Profile 63-33	24
		Schematic cross-section comparing secondary mineral assemblages in	
		saprolite to drainage domains	26

TABLES

Table	1.	X-ray analyses of weathering sequences	. 4
		DTA determinations of kaolinite in nine samples	
	3.	Chemical analyses of the weathering profiles	. 5
		Mineral densities used for calculation of porosity	
	5.	Profile 64-95, Mineralogy by weight %	. 8
		Geochemical balance by isovolumetric method, quartz-plagioclase-hornblende gneiss	
		(Profile 64-95)	. 8
	7.	Profile 64-79, Mineralogy by weight %	
		Geochemical balance by isovolumetric method, amphibolite (Profile 64-79)	
	9.	Profile 64-149, Mineralogy by weight %	. 15
		Geochemical balance by isovolumetric method, amphibolite (Profile 64-149)	
		Sample No. 64-107a, Mineralogy by weight %	
		Profile 63-120, Mineralogy by weight %	
		Geochemical balance by isovolumetric method, amphibolite, (Profile 63-120)	
		Profile 64-138, Mineralogy by volume %	
		Geochemical balance by isovolumetric method, hornblende-plagioclase-quartz gneiss	
		(Profile 64-111)	. 24

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ABSTRACT

Microenvironments of chemical weathering were investigated for eight mafic rock weathering profiles by petrologic and chemical methods in the eastern Piedmont of Baltimore and Harford Counties, Maryland. The chemical weathering is a constant volume process, whereby 30 to 60 precent of the original rock mass is removed as dissolved solids in percolating groundwater. In the transition from rock to saprolite, original rock minerals are replaced by secondary minerals of lesser density, bulk density decreases and porosity increases. Mineralogically, the transition is accompanied by the replacement of alumina-poor minerals like hornblende and plagioclase by more aluminous ones such as montmorillonite, kaolinite, and gibbsite. The mineral changes reflect the relative enrichment of alumina contrasted to silica, although silica, alumina, and alkali and alkaline earth cations are all leached out of the system.

In poorly-drained domains, the environment is weakly acid to alkaline and reducing. Alteration of the alumino silicate rock minerals yields montmorillonite, kaolinite, aqueous silica and various cations. In contrast chemical weathering in well-drained domains proceeds in an acidic, oxidizing environment and yields kaolinite, gibbsite, hydrous ferric oxides, amorphous matter plus aqueous silica and various cations.

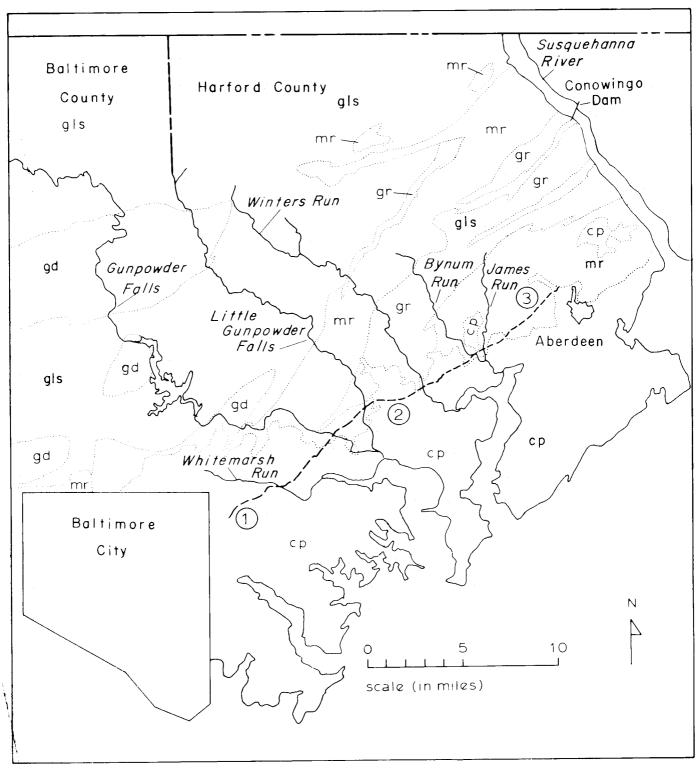


Figure 1.—Area of investigation and general location of rock weathering profiles.

Susquehanna Aqueduct, dashed line. (1) Location of Profiles 64-95, 64-107, and 64-111. (2) Location of Profiles 63-33 and 63-120. (3) Location of Profiles 64-79, 64-138, and 64-149. Rock units generalized from Geologic Map of Maryland (1968). cp - coastal plain sediments; gd - granitic rocks; gls - Glenarm Series; mr - mafic rocks.

INTRODUCTION

As part of a continuing study of chemical weathering in the Piedmont of Maryland, this paper concerns microenvironments of chemical weathering of mafic rocks in the Baltimore area, (Figure 1). Earlier studies include a survey of saprolite stratigraphy, age, and heavy mineral and clay mineral content of felsic and mafic rocks (Cleaves, 1968), and chemical weathering of a felsic rock (Cleaves, Godfrey, and Bricker, 1970).

The clay mineral survey of the mafic rocks brought out the apparently paradoxical occurrence together of kaolinite and montmorillonite (Cleaves, 1968). Generally, genesis of kaolinite is favored by a leaching environment whereby cations are removed and the pH is acid (Millot, 1970, p. 350; Reiche, 1950, p. 50; Grim, 1968, p. 517-518; and Keller, 1957). Montmorillonitic clay minerals generally are formed in a confined environment in which pH is alkaline and cations such as Mg++, Ca++, and Fe++ are present (Millot, 1970, p. 351; Grim, 1968, p. 517-518, and Keller, 1957). Contrarywise, geochemical stability diagrams suggest that the two clay minerals may occur together (Kittrick, 1969).

The inception of this study stems from the seemingly incompatible occurrence together of kaolinite and montmorillonite. Furthermore, I wanted to analyze the transition of rock to saprolite on a microenvironmental scale on generally the same type of rock and in the same general macroclimate. The rock weathering profiles analyzed below each occur in an open environment, one in which through going meteoric waters create a leached environment, or "the environment of lessivage" as Millot (1970, p. 330) terms it. In this environment of lessivage, the local or microenvironmental concentration of ions generally control formation of the clay minerals and gibbsite. The ionic concentrations depend upon the parent minerals, the rate of reaction between various alumino silicate minerals and the water bathing them, and the rate of movement of the solutions through the local environment. Water movement as a controlling factor in chemical weathering has been indicated by Berner (1971, p. 173) and is implicit in examples cited by Mohr and Van Baren (1954) and in the study of Nettleton, et al., (1968), and that of Cleaves, et al., (1970, p. 3021). The water bathing the

alumino silicate minerals appears to react quite rapidly with them (Bricker, et al., 1968, p. 136) with equilibrium being attained within a matter of days. Consequently, for continued chemical weathering of a rock, movement of groundwater solutions is imperative. And, coming full circle, the rate of movement will strongly control ionic concentrations, with a well-drained environment having a more acid and lower cation concentration than a poorly drained one.

With this in mind, weathering profiles in what I term well-drained domains are those on hillslopes and above the water table and those termed poorly drained are in topographically low, flat areas and beneath the water table. In these domains, the transition by chemical weathering of rock to saprolite will be examined.

The weathering profiles selected for study have as their parent rock, either a plagioclase-hornblende-quartz gneiss or amphibolite in which hornblende, plagioclase, and epidote are major rock forming minerals. In either case, the major weatherable alumino silicate minerals are plagioclase and hornblende. The area from which the profiles were collected lies between Baltimore and Aberdeen, Maryland, (Figure 1) essentially parallel to and within the Fall Zone.

The climate of the area is classified as temperate, rainy (Strahler, 1960, p. 186, 190). The average annual temperature is 54° to 55° F., with an average of 90 to 100 days with temperatures below freezing. Average annual precipitation is between 40 and 44 inches, with the greatest average precipitation occurring in July, and the least in December. (Climatological data comes from Vokes, 1957, p. 19-33.)

Physiograpically the weathering profiles are located in the Fall Zone, the boundary area between the Piedmont Province and the Coastal Plain. In the vicinity of the profiles the local relief varies from 60 to 140 feet (Figure 2, 5 and 13).

I wish to acknowledge Dr. John G. Cady and Professor Charles B. Hunt whose critical reviews of the manscript have materially improved the report. The petrographic phase of the investigation was greatly enhanced by Dr. Cady. The thoughtful comments and observations of Dr. John E. Costa and Professor Owen P. Bricker are also gratefully acknowledged.

Table 1-X-ray analyses of weathering sequences.

Sample No.	quartz	hornblende	plagioclase	chlorite	biotite	kaolinite	halloysite	vermiculite	montmorillonite	gibbsite	goethite	Comments
63-33c	-	-	-	-	-	x	-	-	x	-	-	
63-33b	x	x	-	-	-	x	?	-	X	-	•	
63-33a	?	x	x	-	-	-	-	-	-	-	-	
63-118	-	x	x	-	-	x		-	x	-	-	magnetite (2.53Å)
63-119	-	x	x	x	x	x	-	x	x	-	-	magnetite (2.53Å); chlorite is a rock mineral and not a weathering product
63-120	-	x	x	-	-	1	-	-	•	-	_	
64-80a	x	-	_	-	-	x	-	-	-	-	x	
-	x	-	-	-	-	х	?	-	-	-	x	outer zone
64-81	?	x	-	-	-	-	-	-	-	x	х	intermediate zone
04-01	-	x	X	-	-	-	-	=	-	х	-	inner zone
64-79a	-	x	x	-	-		-	-	-	-	-	
64-97	x		-	-	-	x	-	-	-	-	x	biotite-vermiculite mixed layer clay (11.5Å)
64-96	x	-	-	-	-	x	-	-	x	-	?	
64-95	x	x	x		•	x	-	-	-	-	-	
64-107c	x	-	х	-	x	x	-	x	-	x	-	biotite-vermiculite mixed layer clay; gibbsite peaks strong
64-107b	x	x	x	-	-	?	x	-	-	x		
64-107a	x	x	x	-	x	,	•	-	-	-	-	
64-114	-	-	-	-	-	x	-	-	x	-	-	
64-112	x	x	x	-	-	x	-	-	-	-	-	7Å very weak
64-139	-	x	-	x	-	x	-	-	x	-	-	
64-138	-	x	x	-	-	-	-	-	-	-	-	
64-149c	-	-	-	-	-	?	x	-	-	-	х	
64-149b	-	x	-	-	-	x	x	-	-	-	x	kaolinite and halloysite peaks are weak
64-149a	-	x	-	-	-	-	-	-	-	-	-	weak epidote peak (2.90Å)

x equals present; - equals absent; ? equals possibly present

ANALYTICAL METHODS

Weathering profile samples were collected between July, 1963 and August, 1964 during construction of an aqueduct between Baltimore and Aberdeen, Maryland. For each profile representative samples were collected between 200 and 500 grams in weight. Weathered rock and saprolite samples were stored in sealed glass bottles. Duplicate samples were collected specifically for measurement of density and for thin sectioning and in such a manner that disturbance of the sample was minimized.

Minerals in the weathering profiles were identified by optical (petrographic microscope), X-ray, and DTA methods. Minerals in the unweathered rock were identified by standard petrographic methods. In the weathered rock and saprolite secondary minerals were identified by their optical properties, with the assistance of Professor John Cady. Mineral weathering products were also identified by standard X-ray diffraction techniques (Brown, 1961) and were tabulated (Table 1). On the basis of data cited by Brindley and others (1963) halloysite was differentiated from kaolinite.

Differential thermal analyses of nine samples were made to determine the weight percent of kaolinite (Table 2). The analyses were kindly performed by Mr. C. Steven Holzhey, Research Soil Scientist, U.S. Soil Survey Laboratory, Beltsville, Maryland. Percentages were derived by crediting the entire 500°-600°C endotherms to kaolinite. These results served as an independent check of weight percent of kaolinite determined from four modal analyses of thin

sections (Table 2). The agreement is excellent, and provides additional confidence in the optical identification and tabulation of the weathering products seen in thin section.

Table 2-DTA determination of kaolinite in nine samples.

Sample No.	Weight % (DTA)	Weight % (calculated from modal analyses
63-33c	38%	******
63-118	14	11.5
64- 80a	31	
64-96	30	34.4
64-97	58	56.8
64 - 107c	4	
64 - 114	19	
64-139	2	3.5
64-149c	48	

Bulk density, in grams per cubic centimeter, was determined as follows. Each sample was thoroughly air dried, and weighed to the nearest centigram in a low humidity environment. Krylon was sprayed on the sample to seal surface pores. Sample volume was determined by displacement in water.

Standard wet chemical analyses on rock and saprolite samples were performed by Penniman and Browne, Inc., Baltimore, Maryland for SiO_2 , Al_2O_3 , CaO, MgO, Na_2O , total iron (reported as Fe_2O_3) and loss on ignition (Table 3). Analyses of these seven constituents accounts for more than 97 weight percent of each sample.

Table 3—Chemical analyses of the weathering profiles (weight %).

Sample Number	${ m SiO}_2$	${ m Al}_2{ m O}_3$	CaO	MgO	Na ₂ O	Total Fe	Loss on Ignition	Total
63-118 63-119 63-120	46.77 49.94 46.62	18.96 22.07 15.81	$5.55 \\ 3.01 \\ 12.86$	2.69 3.55 8.10	$\frac{2.83}{4.48}$ $\frac{0.81}{0.81}$	15.83 11.13 12.44	5.76 3.49 0.79	98.39 97.76 97.43
64-80a 64-81 64-79a	38.26 35.52 49.25	22.19 18.29 14.17	$0.06 \\ 4.42 \\ 13.43$	$0.90 \\ 2.63 \\ 7.34$	$0.06 \\ 0.49 \\ 1.35$	$21.32 \\ 28.39 \\ 12.97$	$15.80 \\ 9.34 \\ 0.10$	98.59 99.08 98.61
64-97 64-96 64-95	61.11 52.92 53.87	$25.00 \\ 24.90 \\ 18.74$	$0.03 \\ 0.03 \\ 6.68$	$0.26 \\ 0.24 \\ 2.18$	$0.04 \\ 0.01 \\ 2.12$	$\begin{array}{c} 2.60 \\ 7.11 \\ 10.60 \end{array}$	$10.19 \\ 14.24 \\ 3.61$	99.23 99.45 97.80
64-114 64-112 64-111	67.90 58.25 70.13	$\begin{array}{c} 16.31 \\ 17.83 \\ 14.97 \end{array}$	$0.63 \\ 6.66 \\ 4.55$	$0.58 \\ 2.07 \\ 0.38$	$0.28 \\ 2.79 \\ 3.85$	3.99 7.65 1.88	$8.55 \\ 2.22 \\ 2.17$	98.24 97.47 97.93
64-149c 64-149b 64-149a	34.77 47.42 48.02	28.89 21.67 16.30	$0.08 \\ 7.33 \\ 16.15$	$0.40 \\ 5.62 \\ 8.52$	$0.05 \\ 0.51 \\ 0.82$	20.05 8.75 7.79	$14.68 \\ 7.71 \\ 1.30$	98.92 99.01 98.90

Table 4—Mineral densities used for calculation of porosity.

Mineral	Density	Reference and Comments
hornblende	3.20	D variable, 3.02-3.45 (Deer, et al, 1963b, p. 262). Comparison of calculated chemical composition of hornblendes in samples with those in Deer, et al, (1963), suggests density of about 3.20 as appropriate.
plagioclase		determined from Wahlstrom, 1955, p. 118, Figure 20, curve E.
quartz	2.65	Deer, et al, 1963a, p. 179.
biotite	3.00	variable D, 2.7-3.3; Deer, et al, 1962a, p. 55.
apatite	3.20	variable D, 3.10-3.35; Deer, et al, 1962b.
garnet	4.10	In hand specimens garnets are red, suggesting almandite. D range for almandite is cited as 4.32-3.81 (Wahlstrom, 1955, p. 195).
opaque	5.20	Mostly magnetite, consequently D for magnetite used. Deer, et al, 1962b, p. 56.
montmorillonite	2.30	variable D, 2-3; Deer, et al, 1962a, p. 226.
kaolinite	2.65	D, 2.61-2.68; Deer, et al, 1962a, p. 194.
vermiculite	2.30	Deer, et al, 1962a, p. 246.
epidote	2.40	Deer, et al, 1962b, p. 93.
ferric oxides	3.50	In weathered rock and saprolite, iron oxides may be present, but goethite x-ray line absent. Therefore, mean value of limonite used. (Deer, et al, 1962b, p. 124).
goethite	4.30	Deer, et al, 1962b, p. 118.
amorphous	2.00	Adapted as a compromise between allophane (D of 1.85-1.89; Winchell and Winchell, 1951, p. 531) and limonite, with bias towards low iron material
gibbsite	2.40	Deer, et al, 1962b, p. 93.

Using the chemical and density data it is possible to evaluate chemical weathering within an individual rock profile by comparison to a constant volume. Such a method, termed the isovolumetric method by Millot and Bonifas (cited in Millot, 1970, p. 119), is herein applied to five rock weathering profiles (Tables 6, 8, 10, 13, and 15). Application of this method seems reasonable because of the excellent preservation of parent rock textures in much of the saprolite. Preservation of the textures suggests that the weathering is a constant volume process, which is generally confirmed by microscopic study of thin sections of the rock profiles. Isovolumetric weathering also appears reasonable for the massive saprolite associated with two of the rock weathering profiles, although such an assumption certainly cannot be made for all occurrences of massive saprolite. Once the parent rock texture is lost, the isovolumetric method cannot be applied unless equal volume weathering can be inferred from other evidence.

The porosity, percent of pore space, was calculated for samples for which density data and mineralogical analyses were available, using the formula:

Bulk density for each sample was determined as cited above, and particle density was determined as weight percent of the mineral times its density (Table 4).

MINERALOGIC AND CHEMICAL EVALUATIONS OF WEATHERING PROFILES

Well-Drained Domains

In areas classified as well-drained four weathering profiles have been studied. Three of them, 64-95, 64-79, and 64-149, have been evaluated by means of chemistry, petrography, density, X-ray, and DTA methods. The fourth, 64-107, has been evaluated by means of petrography, X-ray and DTA.

Profile 64-95: Profile 64-95 represents a weathering sequence on a mafic gneiss comprised mainly of plagioclase and hornblende, with subordinate amounts of quartz and garnet (Table 5). The site of the profile is a well drained hillslope (Figure 2). Each sample comes from above the water table, and a cross-section (Figure 3) portrays their location relative to each other. The fresh rock (No. 64-95) is a medium grained garnetiferous quartz-plagioclase-hornblende gneiss. The gneiss is comprised of interdigitated bluish black and white layers. The structured saprolite (No. 64-96) consists of interdigitated whitish blue and yellowish brown layers. Circular voids mark former sites of garnets, and reddish brown circular areas are occupied by ferric oxide pseudomorphs after garnet. The massive saprolite (No. 64-97) is mottled pink, yellow, and white. No macroscopic evidence of gneiss texture remains.

The marked change from plagioclasehornblende gneiss to a quartz vermiculitekaolinite saprolite is strikingly reflected in the geochemical balance calculations (Table 6). The calculations show:

- (1) moderate removal of silica
- (2) moderate removal of alumina
- (3) major removal of calcium, magnesium, and sodium
- (4) major removal of iron
- (5) a moderate increase in water, with more water present in the montmorillonitic structured saprolite than in the kaolinitic massive saprolite. The large amount of water in "fresh rock" is due to presence of kaolinite.
- (6) approximately 40 percent of the original rock mass lost

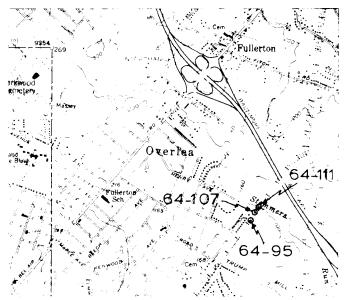


Figure 2.—Map showing location of Profiles 64-95, 64-107 and 64-111.

Contour interval 20 feet. Baltimore East 7½ minute quadrangle, U.S. Geological Survey, 1966.

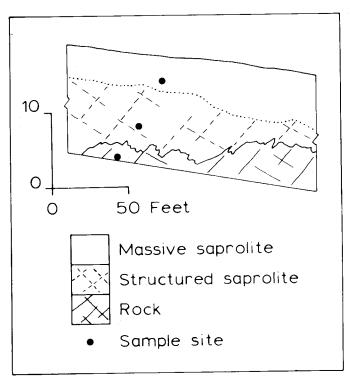


Figure 3.—Cross-section of trench showing location of samples of Profile 64-95

Table 5-Profile 64-96, Mineralogy by weight %.

Sample No.	64-95 (fresh rock)	64-96 structured saprolite	64-97 massive saprolite
hornblende	45.1	Т	
plagioclase Ab ₅₄ An ₄₆	21.8		
quartz	14.6	11.5	17.7
garnet	3.4	T	
apatite	0.8		
magnetite	1.6	2.6	1.1
montmorillonite		42.9	
kaolinite	12.9	$34.4^{(1)}$	56.8 ⁽²⁾
vermiculite-biotite		T	19.2
ferric oxides		7.6	5.2
amorphous		0.9	T
TOTAL	100.2	99.9	100.00
No. of points	1264	1316	1243

Notes: (1) Kaolinite equals 30%, by DTA analysis

(2) Kaolinite equals 58%, by DTA analysis

The layered character of the gneiss which is not readily apparent from the chemistry is indicated by the variable amount of quartz (11.5 to 17.7%) (Table 5) and the presence of vermiculite (after biotite) in the massive saprolite. Just like the chemistry, marked changes take place in mineralogy, porosity, and density as weathering alters the rock to saprolite (Figure 4).

In this Profile, as well as the others, it is generally assumed that the weathering processes that effected the upper zones are the same as those effecting the lower zones although the intensity of the processes and mineral-water reaction rates may have varied. That is, in Profile 64-95, the massive saprolite, when it was structured saprolite, was effected by the same processes that currently affect the structured saprolite. It should be noted, especially in a gneissic rock with contrasting mineral layers, the processes by which a quartz-plagioclase-horneblende assemblage will be replaced by a quartz-kaolinite one may also result in a quartz-plagioclase-biotite assemblage being replaced by a quartz-kaolinite-vermiculite one. The microenvironment of the contrasting primary mineral layers is reflected in their secondary mineral replacements, and the new microenvironmental conditions influence subsequent weathering processes.

Both chemical and physical alteration are evident in the "fresh rock" (64-95). About one-third to one-half of the plagioclase has been replaced by kaolinite which is pale green with first order grey birefringence. The other minerals are unaffected by chemical weathering. In places, hornblende, garnet, magnetite,

Table 6-Geochemical balance by isovolumetric method, quartz-plagioclase-hornblende gneiss (Profile 64-95).

weight of 1 cubic centimeter in centigrams	fresh rock	structured saprolite	massive saprolite
total sample	260	190	160
SiO_2	140.0	100.5	97.8
Al_2O_3	48.7	47.3	40.0
CaO	17.4	< 0.1	< 0.1
MgO	5.7	0.5	0.4
Na ₂ O	5.5	< 0.1	< 0.1
Fe (total)	27.6	13.5	4.2
loss on ignition	9.4	27.1	16.3
sum of constituents	254.3	188.9	158.7

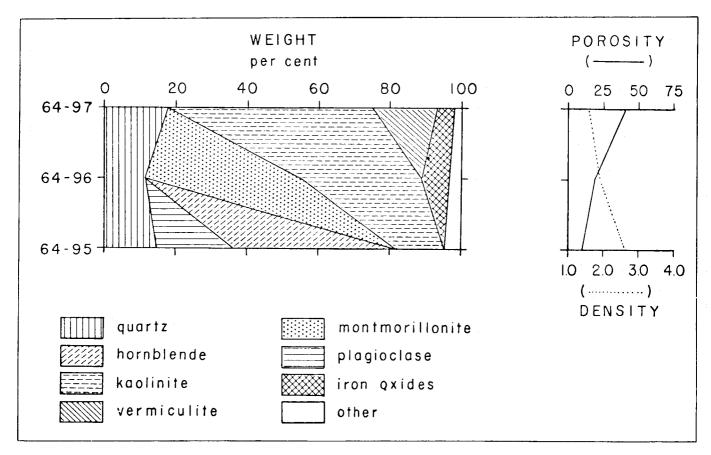


Figure 4.—Profile 64-95, mineralogical, porosity, and density changes accompanying weathering

and quartz grains are fractured, with the fractures filled by a very pale green, low birefringent material (presumably kaolinite). Fracturing probably is concurrent with alteration of plagioclase to kaolinite. None of the fractured grains, however, show measurable offsets along the fractures.

The replacement of plagioclase by kaolinite appears to involve a liquid phase (rather than be a solid-solid reaction) as evidenced by general lack of preservation of plagioclase twin planes and by kaolinite fillings in fracture openings in hornblende, magnetite, quartz, and garnet. However, plagioclase grain boundaries are maintained, a consequence of adjacent minerals being chemically inert at this stage of weathering.

In the structured saprolite (64-96) essentially all of the hornblende and plagioclase has been replaced. The original gneissic rock texture is preserved by septa of quartz grains. The quartz grains commonly are fractured, with the fractures filled by ferric oxides, and many quartz grains are rimmed by ferric oxides. Despite fracturing, individual grains extinguish simultaneously in polarized light, indicating no significant displacement.

The distribution of the montmorillonite and kaolinite mimic the distribution of the horn-blende and plagioclase in the fresh rock. Montmotillonite has generally replaced horn-blende, as outlines of hornblende crystals and cleavage fragments are common. The montmorillonite is white to pale brown; with crossed nicols it has a speckly bright second order birefringence. The kaolinite commonly pseudomorphs plagioclase, although no twin planes and cleavage are preserved. The kaolinite is white to very pale green, with first order grey to white birefringence.

Garnet is present in trace amounts as fresh garnet cores surrounded by ferric oxides and minor amounts of montmorillonite. Commonly, garnet has weathered completely, its former presence evidenced only by dodecahedrally shaped voids lined by ferric oxides.

Pores and fracture openings as seen in thin section comprise 8.3 percent, by volume. Some are filled with ferric oxides, others have ferric oxide linings, but most are empty. No clay skins are present.

In this sample extensive reconstitution of clays minerals on a very local basis appears to

have occurred from solution. The local microenvironment within a plagioclase or hornblende domain controls development of montmorillonite (after hornblende) and kaolinite (after plagioclase). Some migration of solutions is suggested by ferric oxides in fractures and montmorillonite occupying former garnet areas.

In the massive saprolite (64-97), the original rock minerals except quartz have been destroyed. In outcrop, the saprolite has a featureless appearance, but in thin section quartz septa, and 11 Å clay mineral pseudomorphs after biotite mimic the gneissic texture of the parent rock. One mineral layer, reddish in color, consists of kaolinite, quartz, and ferric oxides, and a second yellowish layer of 11 Å clay mineral, kaolinite, and quartz. Quartz grains show no unequivocal evidence of solution. Most of the grains, however, are fractured, but the fractures are tight.

The 11 Å clay mineral is identified (by X-ray) as a mixed layer biotite-vermiculite. Some crystals still exhibit brown to yellowish brown pleochroism. Commonly, the ends of 001 plates are frayed, and some plates show interdigitation of pleochroic and non-pleochroic segments.

The magnetite present is altering to ferric oxides along grain boundaries and fractures. Octahedrally shaped areas, partly void space and partly filled with ferric oxides, indicate former magnetite grains.

Kaolinite exhibits four habits: "books", fine grained granular mosaics, fracture fillings, and clay skins. The clay skins indicate translocation of kaolinite particles and their deposition on pore walls. The books, granular mosaics, and fracture fillings evidence crystallization from solution.

Montmorillonite which is so abundant in the structured saprolite is completely missing in the massive saprolite. Either the montmorillonite has been replaced by kaolinite or montmorillonite was never present. I favor the former hypothesis. Complete destruction of preexisting textures and minerals and formation of entirely new ones are known from Profile 64-79. In addition, the mineralogic layering of the mafic gneisses in the area indicates that weathering can be expected to generate the magnesium cations as well as silica and alumina necessary to form montmorillonite (Southwick, 1969, and Crowley [Unpublished data]). Consequently, I believe that the local microenvironmental conditions were unfavorable for montmorillonite, and that in the transformation of the structured saprolite to massive saprolite, montmorillonite has been destroyed.

Profile 64-79: Profile 64-79 represents a weathering sequence on an epidote amphibolite comprised primarily of hornblende and plagioclase with very subordinate amounts of quartz, epidote, and magnetite (Table 7). The profile is located on a well-drained hillslope (Figure 5). Each of the samples in the Profile comes from above the water table, and a cross-section (Figure 6) shows their location relative one to the other. The "fresh rock", No. 64-79a is a medium grained, bluish black epidote amphibolite. Sample No. 64-81 consists of an inner core of bluish black amphibolite, an intermediate zone of yellowish white and yellowish brown weathered amphibolite and structured saprolite. and an outer zone of reddish brown massive saprolite. The third sample. No. 64-80a is massive saprolite. It is vari-colored, yellow, reddish brown, and maroon.

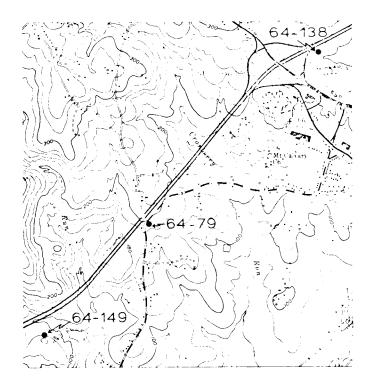


Figure 5.—Map showing location of Profiles 64-79, 64-138, and 64-149.

Contour interval 20 feet. Aberdeen 7½ minute quadrangle, U.S. Geol. Survey, 1970.

The transition from amphibolite to kaolinitic saprolite is accompanied by extensive chemical changes (Table 8). The geochemical balance calculations for Profile 64-79 show:

- (1) major removal of silica
- (2) moderate removal of alumina
- (3) major removal of calcium, magnesium, and sodium
- (4) moderate decrease of iron comparing fresh rock to massive saprolite; iron increases from fresh rock to weathered rock, apparently due to presence of both hornblende and geothite
- (5) major increase in water
- (6) approximately 60 percent of the original rock mass lost

Evidence from petrographic investigation and X-ray analyses show that weathering of the rock minerals produce kaolinite, gibbsite, iron oxides, and amorphous material as secondary products (Table 7, Columns 64-81, 64-80a). Accompanying the mineralogical changes, there is a substantial increase in porosity which, in turn, is the main factor in a drastic decrease in density (Figure 7).

The transition from fresh rock to massive saprolite occurs abruptly, over a distance of 2 to 12 inches. Sample 64-81 from the transition zone documents unusually well the mineralogical

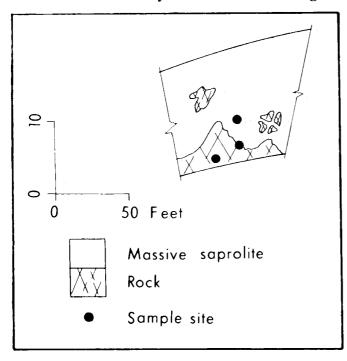


Figure 6.—Cross-section of trench showing location of samples of Profile 64-79

changes (Figure 8). In the interval from the fresh rock inner zone to the massive saprolite outer zone, the rock minerals hornblende, plagioclase, magnetite, and epidote are destroyed. Although quartz remains, etched and embayed areas on the grains evidence their partial chemical alteration. As the rock minerals are destroyed, they are replaced by the secondary minerals kaolinite, gibbsite and

Table 7—Profile 64-79, Mineralogy by weight %.

Sample No.	64-79a (fresh rock)	64-81 weathered rock plus saprolite	64-80a ⁽¹⁾ massive saprolite
hornblende	79.8	38.9	
plagioclase	14.1	4.0	
quartz	2.2	1.7	2.0
apatite		T	
epidote	1.7	T	
magnetite	2.2	3.0	
kaolinite		12.1	31.0
gibbsite		6.0	
ferric oxides (mostly goethite)	*****	24.8	23.9
amorphous		9.5	41.2
TOTAL	100.0	100.0	98.1
No. of points	1052	807	(1)

⁽¹⁾ Extensive ferric oxide staining precluded accurate modal analysis. Mineral identifications made by petrography and X-ray. Using chemical and DTA analyses, weight percent or secondary minerals assigned as follows: kaolinite, weight % from DTA; goethite, all Fe₂O₃ assigned to mineral, and weight % calculated using formula from Deer, et al, 1962b, v. 5, Table 19, No. 2 (constitutes maximum value for ferric oxide, and assumes none in amorphous material); quartz, average value of .79a and .81, assumes rock is homogeneous; amorphous, remainder of material

Table 8—Geochemical balance by isovolumetric method, amphibolite (Profile 64-79).

weight of 1 cubic centimeter in centigrams	fresh rock	weathered rock	massive saprolite
total sample	300	180	120
SiO_2	147.8	63.9	45.9
Al ₂ O ₃	42.5	32.9	26.6
CaO	40.3	8.0	< 0.1
MgO	22.0	4.7	1.1
Na ₂ O	4.1	0.9	< 0.1
Fe (total)	38.9	51.1	25.6
loss on ignition	0.3	16.8	19.0
sum of constituents	295.9	178.3	118.3

geothite. In the process a substantial volume of microscopic pore space develops.

Initial evidence of weathering occurs along fractures traversing the fresh rock zone. In places both hornblende and plagioclase grains adjacent to the fractures are corroded. The fractures, themselves, are filled with yellowish brown, brown, and black, granular textured material. Some of the material has a first order birefringence (gibbsite?, kaolinite?), some has a second order, speckly, birefringence (montmorillonite?), and some is reddish in reflected light (ferric oxide). Presumably, the fracture filling represent both alteration products of the adjacent grains, and matter originating from higher up in the profile which was transported downward in solution and crystallized out in the fractures.

With the exception of the fractures, the fresh rock abruptly changes to structured saprolite. In this intermediate zone both plagioclase and epidote are completely destroyed; hornblende exhibits significant alteration only after alteration of the plagioclase is completed. Alteration of feldspar prior to that of hornblende has also been described by Cady (1951, p. 339).

Alteration of plagioclase proceeds along cleavage and fracture traces, with secondary weathering locii along twin planes. Weathering of the plagioclase initially appears as speckly, very, very fine grained granular material I interpret to be gibbsite. With crossed nicols and a crystal at extinction position the altered areas have a first order white birefringence. Where replacement has progressed further plagioclase crystals are in contact with both gibbsite and a glassy isotropic substance with an index of refraction less than plagioclase and gibbsite (Figure 9). In places gibbsite occurs within the isotropic substance. No high index or high birefringent material, such as sercite, is present. Rarely, cleavage traces are present in the isotropic material (Figure 9), but where alteration has proceeded completely to gibbsite relict plagioclase structures are absent. Former grain boundaries of plagioclase are mimicked by the secondary products because the enclosing hornblende commonly remains unaltered at this stage.

Like plagioclase, the epidote also alters prior to weathering of the hornblende. Both isotropic material and gibbsite are observed replacing epidote. No high birefringent material is present.

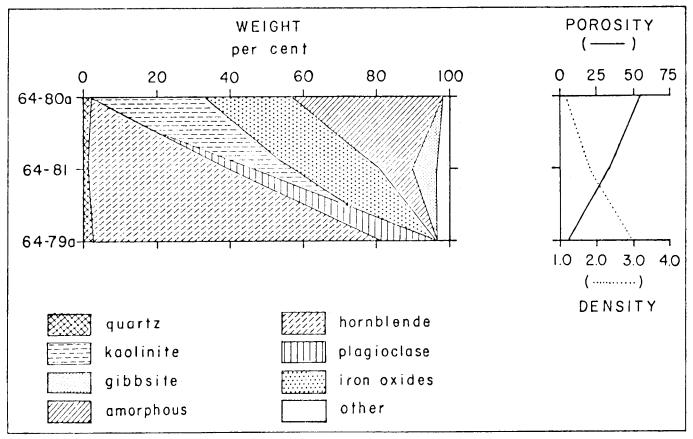


Figure 7.—Profile 64-79, mineralogical, porosity, and density changes accompanying weathering

In both the plagioclase and hornblende spheres of alteration, magnetite is altering to ferric oxides.

Weathering of the hornblende takes place mainly in the intermediate zone after the plagioclase and epidote are altered. Focii of hornblende weathering are grain boundaries, cleavage traces, and fracture traces. Initial evidence of weathering is ferric oxide staining of hornblende crystals and accumulations of fine grained granular aggregates of ferric oxides along grain boundaries, cleavages, and fractures. As alteration progresses, ferric oxides are concentrated along these traces, and stain isotropic (amorphous) and clay mineral products replacing the hornblende. This process develops a "boxwork texture", which is characteristic of the outer layer. Similar textures have been described by Cady (1951, p. 340). The chemical weathering character of the process is suggested by the etched appearance and ragged, sawtooth terminations of fresh hornblende crystals (Figure 9) where they abut against pores, isotropic material, or gibbsite.

From the petrographic evidence it is not clear if gibbsite crystallizes from solution. However, gibbsite certainly is crystallizing from the isotropic, amorphous, matter. Presumably, both processes are operative.

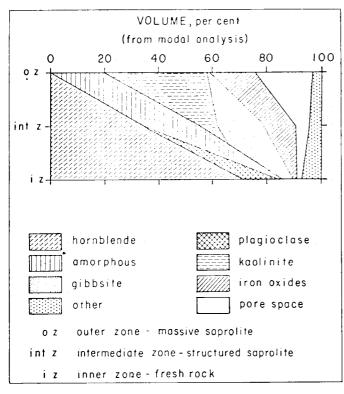


Figure 8.—Diagram portraying mineral changes in sample 64-81.

Kaolinite apparently does not form directly from the hornblende microenvironment. Instead, there is an amorphous intermediary (Figure 9).

Numerous macroscopic pores, over and above those caused by plucking during thin sectioning, indicate extensive removal of matetial, and indicate the existence of channelways for rapid passage of solutions. The volume of macroscopic pores increases from 2 percent in the inner zone to 5 percent in the intermediate and to 21 percent in the outer zone. If gibbsite is considered an indicator of intensive leaching (Millot, 1970, p. 324), then the pore spaces in the intermediate zone presumably act as a better conduit for solutions than those in the outer zone.

In the outer layer (Figure 8) the major rock forming minerals have been completely replaced, gibbsite has decreased drastically, and the "boxwork" texture initially developed in the intermediate layer becomes fully developed. The individual septum of the boxes are a mixture of ferric oxides, isotropic material, and kaolinite. The septa, in part, mimic cleavage traces of former hornblende grains, but generally mimic none of the original rock textures. Ferric oxide staining is intense. Individual boxes may be devoid of any filling. Many, however, are partly to completely filled with various combinations of 1) isotropic to weakly birefringent material, 2) yellowish to yellowish brown first order birefringent material with platy to granular textures (kaolinite), and 3) minor amounts of white to yellowish feathery aggregates (gibbsite). The amount of gibbsite is less than that that could be detected by X-ray.

Both petrographic and X-ray evidence indicate that gibbsite decreases and the kaolinite increases in amount from the intermediate to the outer zone. I interpret this to mean that gibbsite is being dissolved, thereby providing alumina for the kaolinite. The silica source presumably is the overlying massive saprolite from which the isovolumetric data (Table 8, 64-80a) indicate considerable silica has been removed. Alternatively, the gibbsite is being resilicated to form kaolinite. Gibbsite as an intermediate product of weathering has been described from North Carolina (Cady, 1951, p. 340, 342).

In the massive saprolite (No. 64-80a) original rock minerals and textures are completely gone as chemical and physical rearrangement of various constituents is complete. Pervasive ferric oxide staining makes

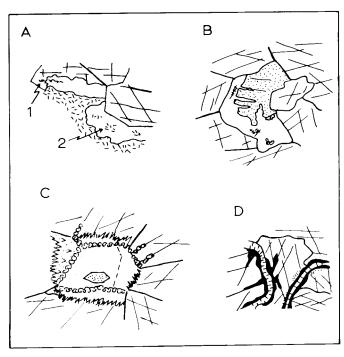


Figure 9.—Sketches showing mineral weathering in amphibolite [No. 64-81 and No. 64-149b].

(A) Plagioclase alteration (No. 64-81): plagioclase with right angle cleavage traces; hornblende, with inclined cleavage traces; gibbsite, hatchured areas; isotropic substance, clear areas between gibbsite and hornblende, and gibbsite and plagioclase. All sketches drawn with magnification of 160X.

Plagioclase being replaced by isotropic substance and gibbsite. Hornblende not altered. Gibbsite crystallizing within isotropic material (2), and occupying cleavage trace (1) which extends from plagioclase into the isotropic.

- (B) Plagioclase alteration (No. 64-81): plagioclase, stippled; hornblende, with inclined cleavage traces; isotropic material, clear; gibbsite, hatchured; iron oxides, granular. Plagioclase replaced by isotropic material in which gibbsite has crystallized. Replacement, in part, along cleavage traces. Hornblende unaltered.
- (C) Hornblende alteration (No. 64-81): hornblende, with inclined cleavage traces; isotropic substance, clear; kaolinite crystal, stippled; iron oxide, granular; intermixed hornblende, iron oxide, and isotropic, stipple and "sawtooth" terminations intermixed. Hornblende alteration indicated by ragged, etched, sawtooth terminations, by ferric oxide replacing hornblende along cleavage, and by ferric oxide "outline" of hornblende that has been replaced by isotropic material. Within the isotropic pseudomorph a kaolinite crystal has grown and an apparent fracture trace or hornblende grain boundary is faintly preserved.
- D) Fracture filling and hornblende alteration (No. 64-149b): hornblende, with inclined cleavage traces; intermixed kaolinite and iron oxides, black; white kaolinite, hatchured; iron oxides, stippled. See text for explanation.

possible only general observations. Most of the identifiable kaolinite is very fine grained and appears white or gray in crossed nicols. Accordian pleated "worms" of kaolinite are present in minor amounts. A number of pores and fractures are lined with blood red to yellowish brown clay skins presumably composed mainly of kaolinite. Kaolinite is the only clay mineral identified by X-ray and constitutes 31 percent by weight (DTA analysis). The "boxwork" texture remains in places but the septa generally form an irregular lattice work arrangement. Observable pore and open space I estimate at less than 10 percent of the thin section. Porosity is high, however, 55.8 percent (Figure 7). Consequently, most of the pore space is in the submicroscopic range. Amorphous material constitutes 41.2 percent, by weight, of the sample (Table 7) the highest determined in any of the profiles.

The massive saprolite of this sample differs from the outer zone of 64-81 and that of Profile 64-95 in the occurrence of pervasive ferric oxide staining and presence of clay skins. Although the "boxwork" texture suggests that sample 64-80a has been subjected to the same processes presently operative at the weathering front (No.64-81), the absence of gibbsite suggests some caution in assuming this fact. The lack of gibbsite may result from the chemical weathering accompanying the transition from structured to massive saprolite, as certainly seems reasonable from the transition represented in No. 64-81. Alternatively, the processes now active at the weathering front may not be the same as those operative when the weathering front passed through the area now occupied by sample No. 64-80a.

Profile 64-149: Profile 64-149 represents a weathering sequence on an epidote amphibolite consisting mainly of hornblende and epidote with subordinate plagioclase and magnetite (Table 9). The profile is located on a welldrained hillslope (Figure 5). The three samples come from above the water table, and a cross-section (Figure 10) shows their location relative one to the other. This locality excellently demonstrates saprolitization along joints which is characteristic of the poorly foliated to massive rocks in this area. Note also that the adjacent quartz monzonite (Figure 10) has completely altered to saprolite indicating the deeper chemical weathering of the coarser grained quartz rich felsic type rock in this area.

Table 9—Profile 64-149, Mineralogy by weight %.

Sample No.	fresh rock (64-149a) ¹	weathered rock plus structured saprolite (64-149c) ²	structured saprolite (64-149c) ³
hornblende	78.6	26.7	
$_{\rm (Ab_{35}An_{65})}^{\rm plagioclase}$	6.7		
epidote	13.8	T	
magnetite	0.9		
chlorite	\mathbf{T}^{-1}		
apatite	Т		
kaolinite gp ⁴		54.0	48.0
montmorillonite		Т	
amorphous		12.2	29.4
ferric oxides (mostly goethite)		7.1	22.6
TOTAL	100.0	100.0	100.0

(1) calculated from modal analysis

(2) calculated from modal analysis and chemical analysis

(4) identified as kaolinite and halloysite by X-ray

The fresh rock (No. 64-149a) is a medium grained bluish black amphibolite. Sample No. 64-149b contains both weathered amphibolite and structured saprolite. The material is vari-colored, yellowish white, reddish brown, and brown. No. 64-149c is structured saprolite and is vari-colored, yellowish white, reddish brown, and brown.

Major chemical changes accompany the change from amphibolite to kaolinitic saprolite (Table 10). The geochemical balance for Profile 64-149 shows:

- (1) major removal of silica
- (2) moderate removal of alumina
- (3) major removal of calcium, magnesium, and sodium
- (4) overall essentially no loss of iron comparing fresh rock to structured saprolite; moderate loss comparing fresh rock to weathered rock-structured saprolite, apparently due to extensive alteration of hornblende and relatively moderate formation of goethite
- (5) major increase in water
- (6) approximately 60 percent of original rock mass lost

Table 10—Geochemical balance by isovolumetric method, amphibolite (Profile 64-149).

weight of 1 cubic centimeter in centigrams	fresh rock	weathered rock plus structured saprolite	structured saprolite
total sample	315	176	122
SiO_2	151	83	42
$\mathrm{Al}_2\mathrm{O}_3$	51	38	35
CaO	51	13	< 0.1
MgO	27	10	< 0.1
Na ₂ O	3	1	< 0.1
Fe(total)	25	15	24
loss on ignition	4	14	18
sum constituents	312	174	119

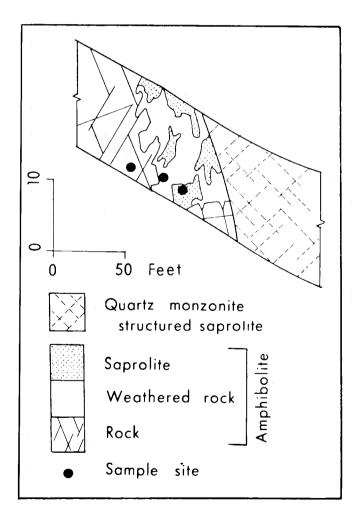


Figure 10.—Cross-section of trench showing the location of samples of Profile 64-149.

⁽³⁾ calculated from chemical analysis and DTA data. From DTA, kaolinite equals 48.0%; goethite, all Fe₂O₃ assigned to mineral, and weight % calculated using formula from Deer, et al, 1962b, Table 19, No. 2; amorphous, remainder of material

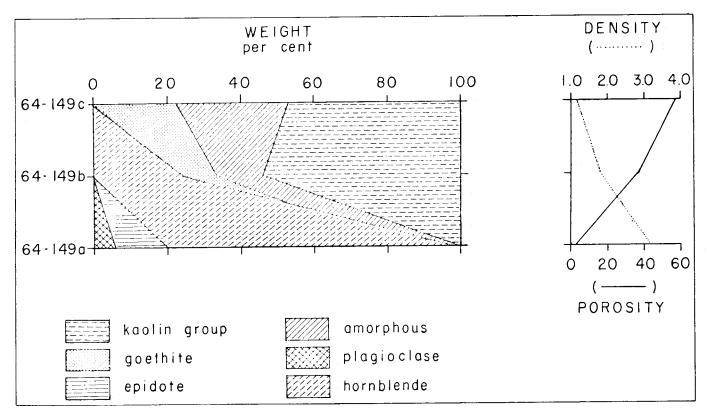


Figure 11.—Profile 64-149, mineralogical, porosity, and density changes accompanying weathering.

Mineralogic evidence from petrographic investigation and X-ray analyses indicate that weathering of the amphibolite results in the replacement of the rock minerals by kaolin clay minerals, geothite, and amorphous material, a very substantial increase in porosity, which is accompanied by reduction of the density by over one-half of the original rock mass (Figure 11).

In the weathering environment represented by sample 64-149b, plagioclase and epidote have been destroyed. Former epidote areas cannot be recognized. A few pseudomorphes after plagioclase are apparent where ferric oxide lineaments trace out a grain boundary or cleavage trace.

In the hornblende grains, cleavage and fracture traces are the locii of weathering. As weathering of individual grains progresses some traces may be preserved by lineaments of very fine grained, granular kaolin and ferric oxide. Secondary mineral products that replace the hornblende include kaolin (both halloysite and kaolinite identified by X-ray) and ferric oxide plus isotropic, amorphous material. The kaolinite is white, with first order grey to white birefringence. Halloysite appears as white to brownish yellow with a very weak grey birefringence. The two could not be consistently

separated in thin section and are collectively tabulated as kaolin. That alteration of the hornblende involves a solutional phase is indicated by etched and frayed hornblende grain boundaries, concentrations of ferric oxides along grain boundaries, cleavage traces, and fracture traces, and development of microscopic pore space within crystal boundaries of hornblende. (In Sample No. 64-149b, pore space constitutes 7.4 percent, by volume, as determined by point count.)

Kaolin, the main secondary mineral, exhibits four habits. Oriented aggregrates line pores and fractures (suggesting migration of the clay mineral as particulate matter). Unoriented aggregates occur in some fractures and as pseudomorphs after plagioclase (suggesting nucleation and growth from solution). Accordian-like books are sparingly present (indicating growth from a solutional phase). Crystal plates occupy some former pore spaces and segments of former hornblende crystals (evidencing nucleation and growth from solution).

Mobilization, movement, and crystallization of ferric oxides, silica, and alumina also is indicated by the pattern of filling in fractures (figure 9d) and between individual grains of hornblende. This pattern suggests mobilization and crystallization of ferric oxides prior to and in

part concordant with that of the silica and alumina constituents of kaolin. Mobilization of ferric oxides prior to that of silica and alumina also is indicated by iron staining between hornblende crystal boundaries, along cleavage, and in fracture traces prior to any other observable alteration.

Isotropic material with low index of refraction, interpreted as amorphous matter, constitutes 12.2 percent, by weight of the sample. The material is colorless in places and iron stained elsewhere. Commonly, kaolin crystals are present within the material, which suggests that the amorphous matter represents a "frozen" gel stage in the replacement of hornblende and plagioclase by secondary products.

In the structured saprolite, Sample No. 64-149c, the original rock minerals are completely replaced by secondary minerals, kaolin and ferric oxides, and amorphous matter (Table 9). Many large pores and openings are present, the voids, altogether, comprising 22.6 percent by volume. Primary rock textures, mainly cleavage and fracture traces preserved as ferric oxide-kaolin lineaments, mimic original hornblende in some places. Elsewhere, delicate septa of ferric oxides and kaolin form an irregular boxwork-like texture.

The various habits in which the kaolin minerals occur indicate both precipitation from solution and illuviation of clay particles. Illuviation is indicated by clay skins, yellow to yellowish brown particles oriented parallel to pore walls. Precipitation from solution is indicated by feathery white aggregates which occur in amorphous matter, fillings in some pores, and in pore walls, by accordian-like books, and by mixtures with goethite and other ferric oxides forming septa of "boxes" and mixtures forming granular aggregates along pore walls and in amorphous matter.

Profile 64-107: Profile 64-107 represents a weathering sequence on a hornblende-quartz-plagioclase gneiss (Table 11). The profile is located on a well-drained, short, steep hillslope (Figure 2). The three samples in the sequence come from above the water table, and Figure 12 shows their location relative to one another. The hornblende-quartz-plagioclase gneiss is interdigitated with dense, massive amphibolite. Sample No. 64-107a is a fine to medium grained, grey and black gneiss. No. 64-107b is weathered gneiss, colored white, yellowish brown, and bluish black. No. 64-107c is a yellowish brown,

reddish brown, and grey structured saprolite.

Mineralogic evidence from petrography, X-ray, and DTA analyses indicate that weathering of the rock forming minerals, except quartz, results in their replacement by gibbsite, ferric oxides, and the clay minerals vermiculite, kaolinite, and halloysite. Because of pervasive ferric oxide staining and the fine-grained texture of the partially weathered minerals and the secondary minerals, it is possible only to make general observations. In the weathered rock (No. 64-107b), plagioclase, hornblende, and epidote are being replaced by clay minerals kaolinite and halloysite, by gibbsite, and by ferric oxides. Garnet is partly pseudomorphed by ferric oxides. Neither biotite nor quartz has been significantly altered.

In the structured saprolite, quartz and plagioclase remain of the rock-forming minerals. However, the plagioclase exists as remnants of larger crystals. X-ray analyses of the saprolite indicate very strong gibbsite peaks, and very weak 7Å, 10.1Å, 12.1Å and 14.2Å peaks. DTA analysis indicates 4 weight percent kaolinite, accounting for the weak 7Å peak, and the presence of minor numbers of low birefringent (grey and white) accordian-like books in thin section further confirms the identification of kaolinite. Weakly birefringent, bleached, brownish platy textured material is identified as mixed layered biotite-vermiculite. This petrographic identification is substantiated by the presence of weak 10.1 Å, 12.1 Å, and 14.2 Å peaks on the X-ray pattern. Of the original rock minerals, only quartz remains essentially intact. However, embayed and etched areas on the quartz suggest that chemical weathering has also effected it.

Table 11—Sample No. 64-107a, Mineralogy by weight %.

No. of points	1046
TOTAL	99.8
opaque	1.1
epidote group	2.8
garnet	0.5
apatite	< 0.1
biotite	4.6
quartz	26.9
plagioclase (Ab ₆₅ An ₃₅)	47.2
hornblende	16.7

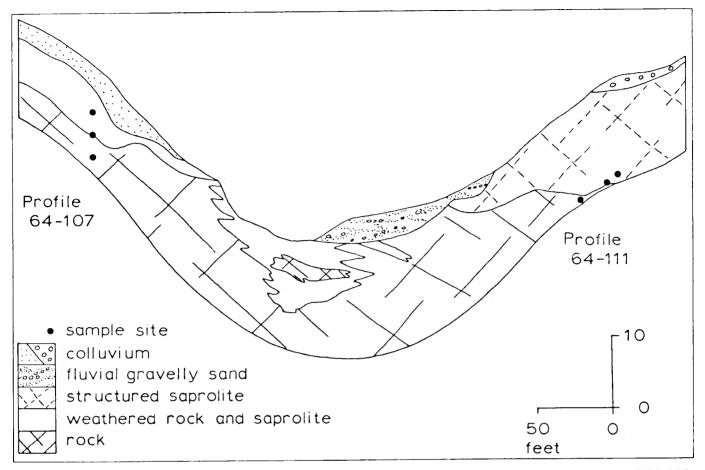


Figure 12.—Cross-section of trench showing the location of samples of Profile 64-107 and 64-111.

Well Drained Domains, Conclusions and Observations

Chemical weathering of the mafic rock in well drained areas is by leaching, or subtraction of mass from the parent rock. In Profiles 64-79, 64-95, and 64-149 from 40 to 60 percent of the original rock mass has been removed as dissolved solids in percolating groundwater. Accompanying the loss of mass, the major rock minerals hornblende and plagioclase are replaced by secondary minerals. Where present minor minerals such as epidote, garnet, biotite, and magnetite are also destroyed, and their places occupied by secondary minerals. Quartz, however, remains relatively unaltered, although etched and embayed surfaces indicate that it also is affected. Although the secondary minerals are of lesser density than the rock minerals, the very substantial decrease in density is directly related to major increases in porosity. For example, in Profile 64-79, as density decreases from 3.0 to 1.2 gm/cc, porosity increases from 5.1 to 55.8 percent. Despite these changes, however, there is no significant change in volume. The chemical weathering in these profiles is a constant volume process.

The secondary minerals kaolinite, halloysite, montmorillonite and gibbsite form by crystallization from solution or from a "gel" stage represented by amorphous matter. The clay minerals and gibbsite do not inherit their crystalline structure from plagioclase, hornblende or any of the other minerals in the parent rock. Contrarywise, vermiculite occurs as an alteration product of biotite, and the vermiculite structure is apparently inherited from the biotite.

The structure of the structured saprolite results from: a) preservation of quartz layers and septa originally present in the fresh rock; b) ferric oxide-kaolinite lineaments preserving cleavage traces and grain boundaries, especially of hornblende; and c) secondary minerals and amorphous matter replacing and filling the space formerly occupied by plagioclase and hornblende. This feature is enhanced by the

extensive alteration of plagioclase prior to significant chemical weathering of hornblende, a relationship well displayed in No. 64-81.

Considering the three profiles for which both chemical and petrologic data are available (64-95, 64-79, and 64-149), four minerals, hornblende, plagioclase, epidote, and quartz are the main rock-forming minerals. However, chemical weathering of the hornblende, plagioclase, and epidote provides the main supply of cations and silica to solution that is eventually removed by surface streams draining the area. Isovolumetric calculations indicate that almost all of the calcium, magnesium, and sodium are removed. Silica is lost in varying amounts from each profile: 72 percent from 64-149, 69 percent from 64-79, and 30 percent from 64-95.

Moderate amounts of alumina are lost from each profile, although relative to the other elements alumina is enriched. For example, in Profile 64-149, 16 centigrams of the original 51 cg are lost, but the weight percent of alumina increases from 16.2 percent in the fresh rock to 28.7 percent in the structured saprolite. The alumina retained in the weathering profiles is removed from the rock-forming minerals and reconstituted into gibbsite and clay minerals. In the process of forming the clay minerals some of the silica is also "fixed", and where montmorillonite and vermiculite are formed some of the cations are also retained.

Iron is lost, the amount depending upon the hornblende remaining in the system and the geothite and ferric oxides being formed. (Hornblende is the major iron bearing mineral present in the parent rocks.) Of the oxides considered, iron has the greatest variability.

The water content generally shows a major increase; variations within individual profiles depend upon the secondary minerals present.

In each of the four well-drained profiles apatite occurs in the fresh rock but is absent in the structured and massive saprolite. Apparently the apatite has been destroyed by chemical weathering. Because apatite dissolves below pH 5.6-5.8 (John Cady, personal communication), I infer that the saprolite of Profiles 64-95, 64-79, and 64-149 has been subjected to an acid environment below pH 5.6. The same acid environment presumably affected Profile 64-107. In the same manner, magnetite is

unaltered in the fresh rock of each profile, but has been replaced, or is partly replaced by geothite and ferric oxides. Taken together the evidence from apatite and magnetite indicate that saprolite in the well-drained sites has been subjected to an oxidizing and acid environment, and apparently has a similar environment at present.

Even though each profile appears to have an acid, oxidizing, well-drained environment, differences in the surface topography seem to reflect differences in the secondary mineral assemblages. Profile 64-95 is located on a moderate slope at the edge of an upland. A rock buttress rises up towards the surface between the Profile and the steep slope down to Stemmers Run (Figure 3 and 14) similar to one on the south side of Gunpowder Falls (Cleaves, 1968, Figure 10, p. 11). The buttress may serve as partial barrier to migration of ground-water such that a sufficient concentration of cations is achieved from which montmorillonite may crystallize in the lower part of the Profile. In particular, magnesium, an essential ion for formation of montmorillonite (Millot, 1970, p. 351) is retained in the microenvironment. In contrast to Profile 64-95, Profiles 64-79 and 64-149 are located on well-drained hillslopes with no apparent subsurface drainage barriers. The secondary mineral assemblages are composed of kaolinite, ferric oxides, and amorphous matter. Profile 64-107 underlies a very steep slope. It contains substantial amounts of gibbsite. If these four profiles are at all representative, it appears that topography may be used as a general guide to predict the clay minerals in the saprolite. Where internal drainage may be partly obstructed by rock buttresses or other features, montmorillonite may be anticipated.

Poorly-Drained Domains

Four weathering profiles have been studied in areas classified as poorly-drained domains. Petrographic, chemical, density, X-ray, and DTA methods have been applied to Profile 63-120. Various combinations of petrographic, chemical, X-ray, and DTA methods have been used to evaluate chemical weathering in Profiles 63-33, 64-111, and 64-138.

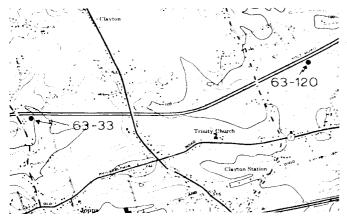


Figure 13.—Map showing location of Profiles 63-120 and 63-33.

Contour interval 20 feet. Edgewood 7½ minute quadrangle, U.S. Geol. Survey, 1970.

Profile 63-120: Profile 63-120 represents a weathering sequence on an amphibolite comprised of plagioclase and hornblende with lesser amounts of quartz and opaque minerals (Table 12). The profile is located in a poorly-drained lowland adjacent to a stream (Figure 13), and each of the three samples comes from below the water table (Figure 14). The amphibolite exhibits pinnacle weathering, a feature common in many of the Baltimore Piedmont areas underlain by well jointed but weakly lineated to equigranular rocks. The profile is overlain by sediments of Cretaceous age. Sample No.

Table 12-Profile 63-120, Mineralogy by weight %.

Sample No.	63-120 (fresh rock)	63-119 (weathered rock)	63-118 (saprolite)
hornblende	84.9	12.0	27.5
plagioclase ¹	11.3	42.3	20.6
quartz	1.7		
biotite		1.2	
chlorite		T	•
opaques (mainly magnetite)	2.1	11.2	7.9
montmorillonite		11.2	32.0
kaolinite	*******	3.0	11.5^{2}
vermiculite		17.7	T
apatite		1.3	0.4
TOTAL	100.0	99.9	99.9
No. of points	1482	1821	1921

Notes: (1) plagioclase composition: No. 63-120, ${\rm Ab_{49}An_{51}}$; No. 63-119, ${\rm Ab_{80}An_{20}}$; No. 63-118, ${\rm Ab_{68}An_{32}}$.

(2) weight % by DTA equals 14%.

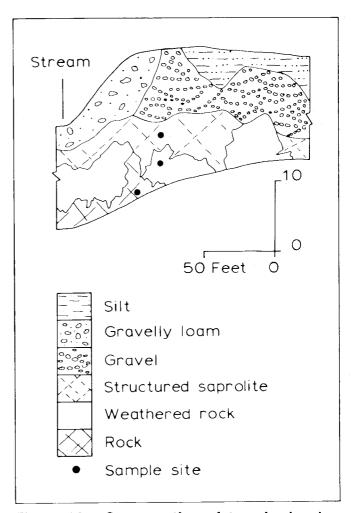


Figure 14.—Cross-section of trench showing the location of samples of Profile 63-120.

63-120 is a weakly lineated, greenish black, fine grained weathered amphibolite. No. 63-118 is bluish green structured saprolite.

Microscopic examination of thin sections indicates a distinct mineral layering that was not evident in outcrop. The layering is indicated by the contrast in weight percent of plagioclase and hornblende from one sample to another (despite replacement of some of the feldspar and hornblende), by the variation in composition of the plagioclase from Ab_{49} (fresh rock) to Ab_{80} (weathered rock) to Ab_{68} (saprolite), and by the occurrence of biotite, and vermiculite after biotite, in No. 63-119.

Weathering of the amphibolite results in the replacement of the rock minerals by kaolinite, montmorillonite, and vermiculite, a reduction of rock mass from 2.8 gm/cc to 1.7 gm/cc, and a substantial increase in porosity from 12.3 percent to 40 percent (Figure 15). Petrographic investigation and X-ray analyses of No. 63-119 indicate that montmotillonite is

replacing hornblende, kaolinite is replacing plagioclase, and vermiculite is replacing biotite. Neither apatite nor magnetite are altered. Weathering of hornblende crystals and their replacement by montmorillonite proceed along the cleavage traces, fractures and at grain boundaries. The montmorillonite is brownish yellow, has speckly extinction, and bright blue to yellow second order birefringence. Montmorillonite also occurs in fractures leading away from hornblende grains through adjacent plagioclase crystals, in fractures through magnetite and apatite, and as a filling in pores.

In plagioclase crystals, kaolinite occurs along cleavage and fracture planes. Twin planes are subordinate locii of weathering. The kaolinite has a pale green color and first order grey birefringence. Some plagioclase crystals exhibit zonation, with a calcic rich core and a sodic rich rim. Weathering effects the calcic core first; commonly the core will be replaced by kaolinite but the sodic rim will be unaltered. However, as alteration continues, internal features of plagioclase crystals, albite twinning, cleavage, and Ca-Na zonation, are not mimicked in the kaolinite.

Biotite has partly been replaced by vermic-

ulite. Alteration proceeds irregularly along (001) surfaces. Fresh biotite is colorless to green; the vermiculite is pale yellow to black in color. Overall, more biotite has altered than either hornblende or plagioclase.

Even though both the apatite and magnetite are unaltered, some crystals of both minerals are fractured, with montmorillonite filling the cracks. In other places the minerals are surrounded by montmorillonite.

In Sample No. 63-118, chemical weathering affects more of the original rock than in No. 63-119. Both hornblende and plagioclase are more completely altered although 48 percent of the sample still consists of identifiable fresh rock minerals. Focii of mineral weathering are the same as in No. 63-119. Montmorillonite replaces hornblende, as in No. 63-119, but plagioclase is replaced by both kaolinite and montmorillonite. Magnetite and apatite remain unaltered. The apatite occurs as small egg shaped grains, some of which exhibit crystal faces. Some grains are surrounded by montmorillonite, and others by kaolinite. Unlike the well-drained sites, neither No. 63-118 nor No. 63-119 contains amorphous matter or ferric iron concretions.

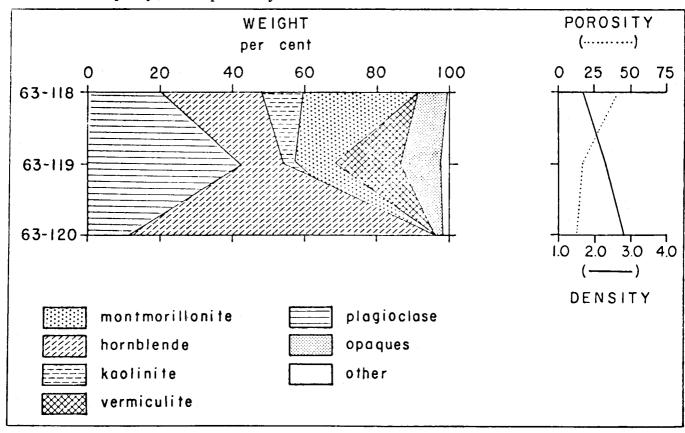


Figure 15.—Profile 63-120, mineralogical, porosity, and density changes accompanying weathering.

In both Samples No. 63-119 and 63-118 physical readjustment of crystals related to weathering is seemingly minor in extent. Rarely albite twinning in plagioclase is offset along fractures. Commonly, where two or more "fragments" of plagioclase or hornblende remain of an otherwise altered crystal, the fragments extinguish together in polarized light, indicating no relative movement of the fragments during weathering.

The minor physical disruption of the rock, however, contrasts greatly with the major chemical alterations that have taken place. Primary rock minerals have been extensively replaced by secondary minerals. Where horn-blende crystals are replaced by montmorillonite, no traces remain of the amphibole cleavage. Rearrangement of ions to form montmorillonite has destroyed the original internal structure of the hornblende. Apparently the change involves a solutional phase and is not a solid--solid reaction although there is no direct evidence of this in the thin sections.

However, there is substantial evidence of movement of solutions. Both montmorillonite and kaolinite occur as fillings in pores. Montmorillonite replaces plagioclase in 63-118. Montmorillonite fills fractures radiating from hornblende through plagioclase. Montmorillonite also fills cracks and fractures in magnetite and apatite. Altogether, such occurrences indicate migration and precipitation of magnesium, iron, aluminum, silica, and other ions.

Accompanying the extensive mineralogical alterations, geochemical balance calculations indicate extensive chemical changes. Although the rock sequence is layered, the geochemical balance for Profile 63-120, (Table 13) shows:

- (1) major removal of silica
- (2) moderate removal of alumina
- (3) major removal of calcium and magnesium. However, significant amounts remain. In the weathered rock calcium can be accounted for in the plagioclase and hornblende. Magnesium, however, is present not only in biotite and hornblende, but also apparently in significant amounts in either the vermiculite or montmorillonite or both. In the structured saprolite, calcium and magnesium present in excess of that required for plagioclase and hornblende probably is in the montmorillonite.
- (4) sodium increases. Both in the weathered rock and structured saprolite, sodium in excess of that required for

Table 13—Geochemical balance by isovolumetric method, amphibolite (Profile 63-120).

weight of 1 cubic centimeter in centimeters	fresh rock	weathered rock	structured saprolite
total sample	280	230	170
SiO_2	130.5	114.9	79.5
Al_2O_3	44.3	50.8	32.2
CaO	36.0	6.9	9.4
MgO	22.3	8.2	4.6
Na ₂ O	2.3	10.3	4.8
Fe (total)	34.8	25.6	26.9
loss on ignition	2.2	8.0	9.8
sum of constituents	272.4	224.7	167.2

plagioclase (the major sodium mineral) is presumably tied up in the clay minerals.

- (5) moderate removal of iron
- (6) major increase in water
- (7) approximately 40 percent of original rock mass is lost.

Profile 64-138: Profile 64-138 represents a weathering sequence on amphibolite in which epidote, plagioclase, and hornblende are the major rock forming minerals (Table 14). The profile is in a very swampy, poorly-drained floodplain (Figure 5). In excess of six feet of structured saprolite has been formed by chemical weathering of the amphibolite. However, the rock has not been completely destroyed, as corestones remain in the saprolite and a pinnacle (extreme right, Figure 16) reaches almost to the surface. In the rock, itself, an early stage in weathering is indicated by saprolite along joints. Commonly a weathered rock "skin", 1/8 to 1/4 inch thick is present between the rock and structured saprolite. The saprolite profile is truncated by sedimentary deposits of Cretaceous age (Cleaves, 1968, p. 5, Figure 3). The basal one to two feet of gravelly sand contains saprolite clasts. Sample No. 64-138 is an equigranular to weakly lineated bluish black medium-grained amphibolite. Sample No. 64-139 is an intense greenish blue structured saprolite. Although approximately 75 percent of the sample contains the original rock-forming minerals, sufficient weathering and development of secondary clay minerals has taken place so that the material may be cut with a penknife. Hence, its classification as structured saprolite rather than weathered rock.

Table 14-Profile 64-138, Mineralogy by volume %.

Sample No.	64-138 (fresh rock)	64-139 (structured saprolite)
hornblende	62.6	48.6
plagioclase (Ab ₅₆ An ₄₄)	33.4	0.5
epidote group	3.7	28.1
chlorite		4.1^{1}
quartz		0.1
opaque	0.2	Т
apatite	T	
montmorillonite		15.1
kaolinite		3.5^2
TOTAL	99.9	100.0
No. of points	1133	1144 ³

- Primary rock mineral; intergrown with hornblende and epidote.
- (2) Kaolinite, by DTA, equals 2% by weight.
- (3) Void space equals 60 additional points; some voids are original pore space and others caused by plucking during thin section preparation.

Weathering of the amphibolite results in the replacement of hornblende, plagioclase and epidote by montmorillonite and kaolinite. In Sample No. 64-139 montmorillonite replaces hornblende along cleavage planes, fractures, and grain edges. The montmorillonite is generally yellowish to deep reddish brown, but in places is pale yellowish white to pale yellow. It has a yellowish red to pale yellowish green birefringence. Due to the very fine grained crystals, the montmorillonite exhibits a speckly aspect. Commonly, montmorillonite fills fractures between epidote grains. The fracture margins are not etched or frayed, indicating that differential physical displacement broke the grain and opened the fracture. Subsequently montmorillonite was precipitated from solution. Precipitation is suggested because of the speckly, unoriented, non-clay skin, appearance of the material. Rarely, montmorillonite fills pores.

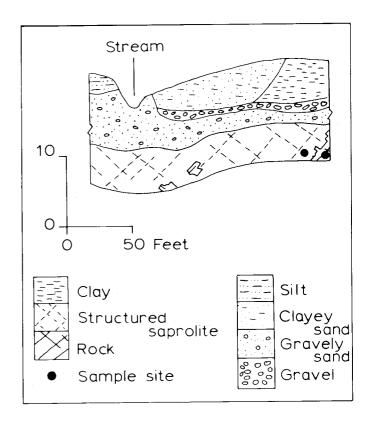


Figure 16.—Cross-section of trench illustrating the geologic setting of Profile 64-138.

Unlike montmorillonite, kaolinite replaces epidote and plagioclase. In thin section the kaolinite appears colorless, and has a first order grey to white birefringence. Where present, kaolinite surrounds small fragments of epidote, and appears to be replacing them. Kaolinite also is replacing plagioclase along crystal margins and cleavage traces.

Profile 64-111: Profile 64-111 represents a weathering profile on a hornblende-plagioclase-quartz gneiss adjacent to Profiles 64-95 and 64-107 (Figure 12). Unlike those two profiles, Profile 64-111 is located adjacent to a floodplain and beneath the water table (Figure 12). The fresh rock (No. 64-111) is a medium to fine grained grey and black gneiss. Its composition by modal analysis is quartz 50.2 percent, plagioclase 42.3 percent, hornblende 4.6 percent, epidote 0.4 percent, garnet 0.5 percent, and opaques 2.0 percent.

Table 15—Geochemical balance by isovolumetric method, hornblende-plagioclase-quartz gneiss (Profile 64-111).

weight of 1 cubic centimeter in centigrams	fresh rock	weathered rock	structured saprolite
total sample	256	263	159
SiO_2	180	155	108
Al_2O_3	38	47	26
CaO	12	16	1
MgO	1 .	5	1
Na ₂ O	10	7	< 0.5
Fe (total)	5	20	6
loss on ignition	6	6	14
sum of constituents	252	256	156

The weathered rock (No. 64-112) is a white, bluish black, and yellowish brown gneiss. The white and yellowish brown colors visually reflect initial chemical weathering of the rock. This effect is also indicated by weak 7Å kaolinite peaks on the X-ray pattern. However, comparison of the fresh rock - weathered rock chemical analyses (Table 15) shows no changes that can be readily attributed to weathering.

The structured saprolite (No. 64-114) is multicolored in white, brown, maroon, green, and vellowish brown and retains its gneissic texture due to preservation of quartz septa. X-ray analyses of non-quartz areas indicate that no X-ray detectable plagioclase, hornblende, or epidote remain. These minerals have been replaced by montmorillonite and kaolinite, with the kaolinite comprising 19 weight percent (DTA analysis). With only 19 percent kaolinite, there apparently is a substantial amount of montmorillonite present. Because of the layered character of the gneiss, it is uncertain whether montmorillonite is replacing hornblende. Alternativley, plagioclase may be the dominant rock mineral as it is in No. 64-111, which would indicate excellent conservation of Mg++ and possibly iron in order to form montmorillonite from the decomposition products of plagioclase and hornblende.

Overall geochemical balance calculations indicate (Table 15):

- (1) no identifiable loss of constituents in the weathered rock
- (2) overall moderate loss of silica, alumina
- (3) overall major loss of calcium and sodium

- (4) no loss of magnesium or iron
- (5) major increase in water
- (6) 38 percent of the original rock mass has been lost.

Profile 64-33: Profile 63-33 represents a weathering sequence on a quartz amphibolite. The profile is located beneath a poorly-drained flat adjacent to a floodplain (Figure 13). The samples in the sequence come from below the water table, and Figure 17 shows their location one to the other. Sample No. 63-33a is a well lineated, dense, black, medium to fine grained amphibolite. No. 63-33b is a bluish green weathered amphibolite. And No. 63-33c is a bluish green structured saprolite. Modal analyses of a similar nearby amphibolite indicates that the major minerals are hornblende 42.9 percent, plagioclase 31.4 percent, quartz 20.5 percent, epidote 2.7 percent, opaques 2.1 percent, others 0.4 percent, (Southwick, 1969, Table 9 Column 10).

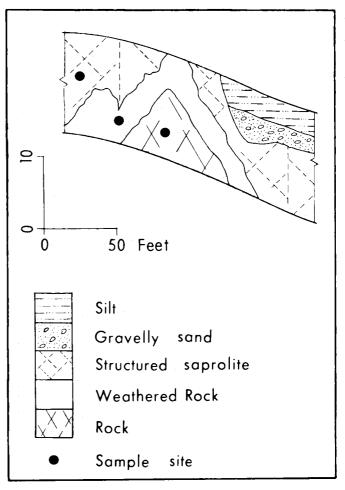


Figure 17.—Cross-section of trench showing the location of samples of Profile 63-33.

X-ray analysis of the weathered rock, No. 63-33b, indicates that montmorillonite, kaolinite, and possibly halloysite are present, as well as quartz and hornblende. In the structured saprolite (63-33c) X-ray analysis detected only kaolinite and montmorillonite. DTA analysis of No. 63-33c indicates 38 weight percent kaolinite.

Poorly-Drained Domain, Conclusions and Observations

In the poorly-drained areas, just as in the well-drained ones, chemical weathering is by leaching. Geochemical data indicates that approximately 40 percent of the original mass has been removed. The loss of mass is accompanied by increase in porosity and replacement of the major rock-forming minerals by the secondary minerals, kaolinite and montmorillonite. In Profile 63-120, for example, kaolinite and montmorillonite replace plagioclase and hornblende. Density decreases from 2.8 gm/cc to 1.7 gm/cc, primarily as a result of porosity increasing from 12.3 percent to 40 percent.

Unlike the well-drained sites, plagioclase and hornblende apparently are weathering simultaneously. However, because the rockforming minerals are initially replaced by specific clay minerals (hornblende by montmorillonite and plagioclase by kaolinite), the rock textures are mimicked in the saprolite. The presence of unaltered apatite and magnetite and lack of ferric oxides indicates that the minerals weather in a reducing and weakly acid or alkaline environment.

Although alumina is generally conserved within the weathering system, isovolumetric

calculations (Table 13 and 15) indicate that in absolute amount alumina is removed from the two profiles. Even though the geochemical picture is complicated by mineral layering inherited from the rock in Profiles 63-120 and 64-111, it also is apparent that large amounts of silica are removed. Calcium, magnesium, and sodium are all partly leached out of the saprolite. Significant amounts, however, are retained in the saprolite as well as in the unweathered minerals still present.

From the thin sections of Profiles 63-120 and 64-111, it is evident that chemical changes predominate over physical disruption. Even though apatite and magnetite grains are fractured and some albite twin planes in plagioclase are offset, unaltered plagioclase or hornblende "relics" in otherwise altered crystals extinguish together in polarized light. This indicates no distortion or displacement. On the other hand, extensive replacement of rockforming alumino silicate minerals by clay minerals, increase in porosity, and decrease in density attest to the pervasive affect of chemical weathering.

As chemical weathering proceeds, destruction of the rock minerals is accompanied by precipitation of kaolinite and montmorillonite. The common association of montmorillonite after hornblende and kaolinite after plagioclase suggests significant microenvironmental control by the rock-forming minerals of the solution from which the initial clay mineral precipitates. Precipitation from solution is suggested by lack of amphibole cleavage where montmorillonite replaces hornblende, by the speckly, unoriented, non-clay skin appearance of montmorillonite, by kaolinite replacement of plagioclase without replication of albite twinning or plagioclase cleavage, and by clay mineral filled fractures.

DRAINAGE DOMAINS COMPARED—A SUMMING UP

The primary aim of this report is evaluation of the affects of chemical weathering on mafic rocks in which the major variable is internal drainage through the weathering profile. Comparison of geochemical balances computed by the isovolumetric method (Profiles 64-95, 64-79. 64-149, 63-120, and 64-111) indicate that chemical weathering subtracts mass from the parent rock irrespective of drainage domain. The rock-forming minerals are replaced by secondary minerals of lower density concurrently with extensive removal of mass in groundwater. The transition from rock to saprolite is also accompanied physically by increase in porosity and decrease in density. Of the rock constituents, silica is removed in the greatest quantity. Alumina also is removed from the weathering profiles, and the relative rates of removal are such that alumina is enriched compared to silica. Mineralogically, this process is reflected in the replacement of relatively alumina poor minerals like hornblende, plagioclase, and epidote by more aluminous ones like kaolinite and gibbsite.

Calcium, magnesium, and sodium are quite thoroughly leached from the well-draind profiles (64-95, 64-79, 64-149) in contrast to the poorly drained ones. Likewise, iron is lost from the well-drained domains, even though significant amounts remain in both. However, in the poorly-drained domains the iron released during the breakdown of hornblende and epidote goes into solution as ferrous ion. The iron released from hornblende, epidote, and magnetite in well-drained profiles is oxidized to ferric ion and precipitated from solution as goethite and X-ray amorphous hydrous oxides of iron. All five profiles in both domains increase in water content in the transition from rock to saprolite, reflecting the formation of secondary minerals such as kaolinite, goethite, montmorillonite, and gibbsite.

The secondary mineral assemblages which replace the rock-forming alumino silicate ones may be directly correlated with drainage domains. In the poorly-drained domains montmorillonite and kaolinite are the only secondary minerals resulting from alteration of plagioclase and hornblende. Where present biotite alters to vermiculite. In the well-drained domains, too, biotite alters to vermiculite. However, plagioclase and hornblende are replaced by kaolinite, and in very well drained areas, by gibbsite as

well. X-ray amorphous hydrated iron oxides and goethite also are weathering products of the well-drained domain. Where it occurs, montmorillonite is a transitory product. Profiles 64-95, 64-107, and 64-111 illustrate the transition in weathering products from well to poorly-drained domains (Figure 18).

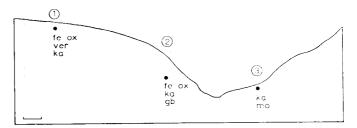


Figure 18.—Schematic cross-section comparing secondary mineral assemblages in saprolite to drainage domains.

From left to right: (1) well drained domain, Profile 64-95, fe ox equals iron oxides, ver equals vermiculite, ka equals kaolinite; (2) very well drained domain, Profile 64-107, gb equals gibbsite; (3) poorly drained domain, Profile 64-111, mo equals montmorillonite. Scale bar at lower left equals 50 feet horizontally; vertical exaggeration is 5X.

The influence of the rock-forming alumino silicate minerals on the clay mineral secondary products which replace them I interpret to be primarily a consequence of the geochemical microenvironment associated with weathering of the parent mineral rather than structure of the rock-forming mineral. The alumino silicate structures of plagioclase and hornblende are destroyed. The clay minerals which replace them do not inherit their structure from the original mineral. Secondary minerals such as montmorillonite and gibbsite either are precipitated from solution or crystallize from amorphous material (gels). Biotite is the only exception in the profiles studied. Vermiculite replaces biotite (Profiles 64-95, 64-149), inheriting much of the parent mineral's structure. The general case for precipitation of clay minerals from solution is succintly stated by Millot (1970, p. 349-351) and that for influence of parent mineral structure on clay minerals by Loughnan (1969, p. 29-31).

The structured saprolite investigated in this study results from the varied susceptibility of the rock-forming minerals to chemical weathering and the microenvironmental influence of rock-forming minerals on clay mineral products. In Profiles 64-79 and 64-149 plagioclase is replaced by kaolinite, and mimics the plagioclase grain boundary because the adjacent hornblende is chemically inert. After the plagioclase is almost entirely replaced, hornblende alteration commences and montmorillonite is preferentially precipitated in former hornblende areas (64-95). Mimicking of the former hornblende crystal is enhanced by precipitation of ferric oxide in lineaments replicating former cleavage traces and crystal boundaries. In Profile 63-120, because the iron remains in solution as ferrous ion, the mimicking of the amphibolite mineral texture results from the replacement of plagioclase by kaolinite and hornblende by montmorillonite. In Profile 64-95, unaltered quartz septa as well as replacement of parent rock minerals by clay minerals preserves the rock texture.

Two general weathering equations can be formulated for chemical weathering in the environment of lessivage on mafic rock terrain in the Baltimore area. In the acidic, oxidizing well-drained environments, rock-forming alumino silicate minerals plus water plus carbon dioxide react to yield aluminum rich solids (kaolinite, gibbsite) plus ferric oxides (goethite, ''limonite'') plus Ca⁺⁺, Mg ⁺⁺, Na⁺, HCO₃, and aqueous silica. Substantial volumes of amorphous matter may also be formed. Biotite, where present, alters to vermiculite. Montmoril-

lonite may form as a transitory weathering product. In weakly acid to alkaline, reducing, poorly-drained environments, the rock-forming alumino silicate minerals react with water and carbon dioxide to form aluminum rich solids (montmorillonite, kaolinite) with the release to solution of Ca⁺⁺, Mg⁺⁺, Fe⁺⁺, Na⁺, HCO₃ and aqueous silica. Biotite, where present, alters to vermiculite. In both domains, alumina has a transitory mobility, being released into solution by weathering of the alumino silicate minerals, and then quite rapidly recombining with other elements into secondary minerals.

As indicated by the general weathering reactions identifiable amorphous matter is absent from the wet sites in contrast to the well-drained ones. Although it is dangerous to generalize from so few sites, some speculations seem in order. The poorly-drained sites appear to be continuously wet. In effect, the rock and saprolite are continuously immersed in water. and relatively high concentrations of ionic constituents can be reached and maintained in the solution bathing the minerals. Such an environment appears very conducive to precipitation of clay minerals from solution with the kind of mineral and amount depending upon the concentrations of the constituents in solution in a given place.

In contrast, the well-drained sites are alternately wet and dry. The amorphous matter may represent those soluble constituents that did not precipitate from solution prior to the solution's stagnation and eventual evaporation in that part of the profile. Subsequently, aging of the gel results in formation of gibbsite or kaolinite.

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