

ROLE OF FERROUS IRON OXIDATION IN THE ALTERATION OF BIOTITE AND ITS EFFECT ON THE TYPE OF CLAY MINERALS FORMED IN SOILS OF ARID AND HUMID REGIONS¹

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ABSTRACT

Artificial weathering of biotites in the laboratory indicates that ferrous iron is oxidized to the same extent under acid, neutral and alkaline conditions, contrary to theoretical assumptions. Under neutral and alkaline conditions, the ferrous iron oxidation causes a large decrease in surface charge and the expanded crystal lattices of montmorillonite are formed. Under acid conditions the oxidation of ferrous iron is balanced mainly by a decrease in total octahedral layer charge through loss of octahedral iron and magnesium. Accordingly, the total surface charge remains high and vermiculites are formed. This experimental work explains the field occurrence of different clay minerals formed from granitic rocks under differing climatic conditions and emphasizes the importance of the pH of the weathering environment in biotite alteration.

INTRODUCTION

Since the discovery of the crystal structure and chemical composition of coarse-grained vermiculite, and the development of methodology for its identification, many investigators have found that vermiculites occur in many soils over the earth's surface. Vermiculite occurs most commonly in soils with pH values of less than 7.0. Very rarely, if at all, has a vermiculite been reported in calcareous or alkaline soils. When mica clays are present in large amounts in calcareous or alkaline soils, the predominant clay mineral other than mica clays is montmorillonite (McNeal *et al.*, 1965).

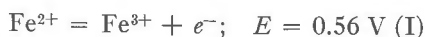
In order to discover whether there is any relation between vermiculite and montmorillonite occurrence and the weathering environment, a study was conducted by Barshad (1966) on the frequency distribution of clay minerals in residual soils developed from biotite-rich granitic rocks under mean annual precipitations ranging from five inches to eighty inches. Barshad showed the existence of a relationship between the frequency distribution of different clay minerals and the mean annual rainfall. For example, montmorillonite clays were developed only in calcareous soils with less than 15 inches of annual precipitation, whereas vermiculite clays were only developed in acidic soils with more than 40

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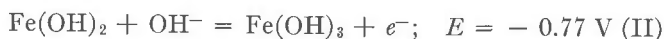
inches of annual precipitation. It was concluded that the pH of the soil was responsible for the different pedogenic formation of clays in these weathering systems.

Theoretical considerations suggest that biotite could weather to vermiculite under acid conditions and to vermiculite plus montmorillonite under neutral and alkaline conditions. The oxidation of ferrous iron to ferric can take place under acid or alkaline conditions as follows (Latimer 1952):

Under acid conditions



Under alkaline conditions



The oxidation-reduction potential indicates that the oxidation of ferrous iron to ferric takes place much more readily in alkaline solutions than in acid solutions.

EXPERIMENTAL

The experiment was designed to demonstrate the effect of the weathering environment pH on the type of clay minerals formed. Three biotite samples were chosen for the oxidation experiment. These samples were dry ground in a ball mill and the 2–10 micron size fraction was used for the oxidation experiment. The origin and chemical analyses of these samples are presented in table 1. The principal difference between these samples is the degree of isomorphous substitution of Fe^{2+} for Mg^{2+} in the octahedral layer.

Oxidizing solutions were selected to represent natural weathering conditions in soils of humid, semi-arid and arid regions (Barshad 1960, 1960a; Chernov 1947; Jenny 1961). The acid oxidizing solution consisted of 50 parts of 1M solution of $\text{AlCl}_{1.5}(\text{OH})_{1.5}$ and 25 parts 20% H_2O_2 . The neutral one consisted of 50 parts distilled water and 25 parts 20% H_2O_2 with the pH adjusted to 7.0 using saturated solution of Ca(OH)_2 . The alkaline one consisted of 25 parts of saturated CaCO_3 solution and 25 parts of 20% H_2O_2 with the pH adjusted to 8.8 using saturated solution of Ca(OH)_2 .

TABLE 1. CHEMICAL ANALYSIS OF MINERAL SAMPLES (MMOLES/100 G IGNITED WEIGHT)

Sample	Fe^{2+}	Fe^{3+}	Mg^{2+}	Ca^{2+}	K ⁺	Na^{2+}	$\text{Fe}^{2+} + \text{Fe}^{3+}$
							Mg^{2+}
Vermiculite-biotite #16 ^a	139.00	25.00	450.00	0.38	172.60	25.00	0.28
Vermiculite-biotite #19 ^b	123.00	27.00	469.00	1.06	204.00	12.30	0.24
N. Y. Biotite ^c	380.50	64.50	141.00	—	225.00	7.20	3.15

^a Gold Butte District, Clark County, Southern Nevada.

^b Bramaville-Millbury, Massachusetts.

^c Biotite complex silicate from Adirondack Mountains, New York.

The experimental procedures were as follows:

1. Each sample was leached three times with 1N Na₂EDTA solution at pH 11.4 and then treated with 1N NaCl solution to replace the interlayer cations with Na ions. The excess salt was leached out using neutral methanol.
2. About 2-3 gm of each Na-saturated mineral sample plus 75 ml of its respective oxidizing solution were placed in a 250 ml beaker covered with a watch glass. The total volume of each sample was brought up to a 200 ml using distilled water.
3. Samples were placed in an oven at 40°C. The suspensions were stirred occasionally and 25 ml of 20% H₂O₂ was added every 5 days. The pH of the suspensions were continually adjusted and the total volume of each suspension was maintained at 200 ml.
4. After 30 days of treatment, the temperature was raised to 90°C to accelerate the oxidation process.
5. After 45 days the oxidizing solutions were replaced by centrifugation and were analyzed for the diffused ions. At the end of 60 days, the solutions in contact with the samples were removed by centrifugation and were analyzed for Na, K, Fe and Mg to establish the material balance.

The mineralogical changes were evaluated by X-ray and chemical analysis. Part of each sample was X-rayed using the salted paste technique of Barshad (1959) to detect any newly formed minerals. This technique consisted of flocculating each clay sample from a suspension with sodium chloride. The salted clay suspensions were centrifuged and then each clay paste glycerated and intruded through a hypodermic needle to produce capillary rods for X-ray analysis using flat cassette camera film. This method of X-ray analysis was designed to measure primarily the difference in interlayer expansion as affected by the interlayer charge. The purpose of the chemical analysis was to determine the change in external surface charge and octahedral layer charge of the biotite samples upon oxidation. At the end of the oxidation experiment samples were saturated with Na using 1N NaCl solution and washed free of excess salt using neutral methanol. To insure the complete removal of CaCO₃ from samples that were oxidized in CaCO₃ buffer, they were treated repeatedly with 1N Na₂EDTA at pH 11.4 until there was no Ca detected in the extract. To insure the removal of adsorbed Al from samples oxidized in Al(OH)_{1.5}Cl_{1.5} buffer, they were first treated with 1N NaCl solution, then heated at 90°C for three hours in 2% Na₂CO₃ solution and again treated with 1N NaCl solution.

The change in the total surface charge of each mineral sample was determined as the difference in the amount of interlayer Na and K in a sodium saturated sample before and after oxidation. The change in surface charge was measured by the amount of Na and K that diffused to the oxidizing solutions. The change in the octahedral charge was determined by the amount of ferrous iron oxidized to ferric and the amount of iron and magnesium ions that diffused to the oxidizing solution. The Na⁺ and K⁺ ion were determined using the flame photometric techniques. It was found that the atomic absorption technique of Prince (1965) was the most adequate for the determination of Fe²⁺ and Mg²⁺ released to the oxidizing solutions. To determine the Fe²⁺ oxidized, samples were analyzed before and after oxidation for their total Fe content. The method of Wilson (1955, 1960) was adopted as it proved to be adequate for samples with low ferrous content.

RESULTS AND DISCUSSION

Since the crystal lattices of weathered minerals have to maintain electric neutrality at all times, the following conditions must be met at the

end of the oxidation experiment:

$$\text{Changes in the internal charges} = \text{Changes in the external charges or} \quad (1)$$

$$\text{Changes in the octahedral charges} = \text{Changes in the surface charges}$$

$$\text{Fe}^{2+} \text{ oxidized} - (\text{Fe}^{2+} + \text{Mg}^{2+}) \text{ released} = (\text{Na}^+ + \text{K}^+) \text{ released} \quad (2)$$

$$\text{Fe}^{2+} \text{ oxidized} = (\text{Na}^+ + \text{K}^+ + \text{Fe}^{2+} + \text{Mg}^{2+}) \text{ released} \quad (3)$$

The X-ray analysis (table 2) showed that montmorillonite and montmorillonite-biotite interleaves appeared in samples oxidized under neutral and alkaline conditions. In samples weathered under acid conditions only vermiculite and vermiculite-biotite interleaves were formed. In contrast with the samples weathered under acid conditions, the samples weathered under neutral and alkaline conditions showed a substantial decrease in surface charge. The high loss of surface charge accompanied the formation of wide montmorillonite spacing in these samples (table 3).

It was assumed that upon treatment of the mineral samples with oxidizing agents, octahedral ferrous iron was oxidized to ferric, while no

TABLE 2. X-RAY DIFFRACTION SPACING LINES FOR MINERAL SAMPLES AT THE END OF THE OXIDATION EXPERIMENT

Samples	Oxidized in acid solution	Oxidized in neutral solution	Oxidized in alkaline solution
Vermiculite-biotite #16	13.35 (vs)	18.02 (vw)	(vw)
	10.16 (m)	16.67 (vw)	14.23 (vw)
		14.24 (m)	12.23 (vw)
		10.36 (vs)	10.97 (vs)
Vermiculite-biotite #19	11.77 (s)	20.06 (vw)	20.06 (vw)
	10.39 (w)	19.19 (vw)	18.78 (vw)
		16.35 (vw)	16.06 (vw)
		14.24 (m)	14.24 (m)
		12.99 (m)	10.30 (s)
		10.56 (s)	
New York biotite	14.24 (vw)	13.79 (vw)	14.24 (vw)
	10.22 (vs)	12.80 (vw)	10.29 (vs)
		10.29 (vs)	

(vs) very strong intensity.

(vw) very weak intensity.

(m) medium intensity.

(w) weak intensity.

(s) strong intensity.

TABLE 3. INTERNAL AND EXTERNAL CHARGE BALANCE OF THE CRYSTAL LATTICES OF BIOTITE-VERMICULITE MINERALS AT THE END OF THE OXIDATION EXPERIMENT

Sample	Loss in surface charge (m.e./100 gm) ^a	Fe ²⁺ Oxidized (mmole/100 gm) ^a	Interlayer Na ⁺ +K ⁺ released to solution (m.e./100 gm) ^a	Octahedral ions released to solution (m.e./100 gm) ^a		Total ions released to solution a ⁺ +K ⁺ +Fe ²⁺ +Mg ²⁺ (m.e./100 gm) ^a *	Net charge balance Fe ²⁺ oxidized-total ion released
				Fe ²⁺	Mg ²⁺		
Vermiculite-biotite							
16-Ca	42.12	70.90	44.25	26.20	---	70.45	0.45
16-H ₂ O	33.55	66.90	30.92	31.40	1.92	64.24	2.66
16-Al	-7.50	86.36	107.13	40.28	43.25	190.66	-104.30
Vermiculite-biotite							
19-Ca	49.48	63.30	52.05	13.40	---	65.45	-2.15
19-H ₂ O	46.57	70.40	49.04	18.00	1.80	68.84	1.56
19-Al	0.40	90.58	62.64	24.00	39.30	125.94	-36.36
New York biotite							
N.Y.-Ca	23.21	110.40	24.52	86.40	1.62	112.54	-2.14
N.Y.-H ₂ O	11.03	103.30	9.26	92.80	1.35	103.41	-0.11
N.Y.-Al	1.62	121.20	64.61	69.20	17.90	151.71	-30.51

^a Based on weight after ignition.

Ca Denotes samples oxidized under alkaline solution.

H₂O Denotes samples oxidized under neutral conditions.

Al Denotes samples oxidized under acid conditions.

changes took place in the tetrahedral sheets. In the case of neutral and alkaline oxidizing environments the ions in the solutions were Ca, Na and K. All of these ions were too large in size to enter the tetrahedral positions. In the case of an acid oxidizing environment the presence of a large amount of Al ions presents a problem. Some of the Al ions may enter the tetrahedral sheets and balance the effect of ferrous iron oxidation on the surface charge. According to Mitsuda (1960) the percolation of granitic rocks with ground water at pH 5.0–6.0 caused a release of tetrahedral silica and changed the coordination of Al in the tetrahedral positions from 6 to 4 which caused a loss in volume. This mechanism may explain the high release of tetrahedral and octahedral cations in the acid solutions during oxidation (table 3). The high Na and K release under these conditions may be partially due to the complete destruction of the crystal structure of part of the sample.

The numerical solution of equation (3) for all samples used is shown in table 3. The two sides of the identity are balanced within 4% for all the samples which were altered in alkaline or neutral solutions. This 4% error is due to the Ca^{2+} ion effect in the buffer solutions and to the other experimental errors. Acid samples released much more internal and external ions than can be accounted for by ferrous iron oxidation. This condition can be explained by the role of aluminum ion in penetrating the crystal structure and occupying some octahedral and tetrahedral positions.

The magnesium content of the samples is important in the ease of transformation to vermiculite and biotite during oxidation. These unexpected results could be explained by the differential loss of ferrous and magnesium ions under neutral and alkaline conditions. Under these conditions some of the octahedral iron was released to the solution but almost none of the octahedral magnesium was (table 3). The differential release of iron under these conditions is greater in samples with high $\text{Fe}^{2+}/\text{Mg}^{2+}$ ratios. The process of high iron loss kept the surface charge of the minerals high enough to slow the formation of expanded lattices of vermiculites and montmorillonite in the N. Y. samples oxidized under acid conditions.

The oxidation of ferrous iron in biotites weathered under neutral and alkaline conditions was balanced by a substantial decrease in the surface charge producing expanded lattices of vermiculites and montmorillonite-biotites interleaves. While under acid conditions, the ferrous iron oxidation was balanced mainly by a release of the octahedral ions, which kept the surface charge high and prevented the formation of montmorillonite spacing. Under these conditions the vermiculite spacing is the maximum expanded lattices produced. These results and mechanisms explain the

formation of montmorillonite in soils of arid regions and the formation of vermiculites in humid areas.

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