

## NONTRONITE IN THE COLUMBIA RIVER REGION\*

VICTOR T. ALLEN AND VERNON E. SCHEID,

*Geological Survey, U. S. Department of the Interior, Washington, D. C.*

### ABSTRACT

New occurrences of nontronite have been discovered in Washington, Idaho, and Oregon. The nontronite has formed by the weathering of basaltic glass, palagonite, iddingsite, and augite under conditions of poor drainage in the presence of alkalis, magnesium and probably ferrous iron. Under conditions of thorough drainage in the presence of neutral or slightly acid solutions kaolinite and halloysite are formed from plagioclase feldspar, while nontronite migrates and fills vesicles as well as cracks ranging from a fraction of an inch to six inches in width. Chemical analyses and optical data are given for three new nontronites and for two materials connected with the formation of nontronite.

### INTRODUCTION

Several new occurrences of nontronite in Washington, Idaho, and Oregon have been studied during the investigation of high-alumina clays by the Geological Survey, U. S. Department of the Interior. In the Columbia River region nontronite is associated with altered basaltic rocks, pillow lavas, tuffs and palagonite, indicating a genetic connection between the weathering of these materials and the formation of nontronite. In the Excelsior district the study of cores obtained during a cooperative drilling project with the Bureau of Mines, U. S. Department of the Interior, revealed a significant variation in the weathering products of basaltic rocks with depth. At Excelsior, Colfax and Garfield, Washington, nontronite of exceptional purity was collected from veins, ranging from a fraction of an inch to six inches in width. Petrographic and chemical studies of nontronite and the associated rocks indicated that the nontronite is formed chiefly by the weathering of basaltic glass and that palagonite is an intermediate product in its alteration. This observation led the writers to examine the published information on palagonite.

### PREVIOUS WORK ON PALAGONITE

The selected references that are reviewed here summarize the previous studies of palagonite and its alteration.

Von Waltershausen (1845) applied the name palagonite to the material forming the brown groundmass of a tuff from Palagonia, Val di Noto, Sicily. He (1847) found palagonite typically developed in the massive tuffs of Iceland.

\* Published by permission of the Director, Geological Survey, U. S. Department of the Interior.

Fermor (1925) concluded that the brown and orange varieties of palagonite in the Deccan trap of Bhusawal, Bombay Presidency, are identical with chlorophaeite and that the green variety, when anisotropic, is probably delessite or celadonite.

Peacock (1926) recorded the chemical composition of basaltic glass from Iceland, for which he used the term "sideromelane," and gave the index of refraction of eight Icelandic "sideromelanes" ranging from 1.604 to 1.615. He considered that the "sideromelane" resulted from chilling by Pleistocene ice sheets on the products of sub-glacial volcanoes. By hydration, oxidation of iron and partial loss of lime and soda, "sideromelane" changed to a yellow material that is isotropic (gel-palagonite) or obscurely fibrous and birefracting (fibro-palagonite). The index of refraction of his palagonites ranged from 1.48 to 1.52 and the water content of five palagonite rocks from 14.20 to 24.40 per cent. He concluded that palagonite is unstable and tends to crystallize with a partial loss of water into chlorite and zeolites.

Peacock and Fuller (1928) described chlorophaeite, "sideromelane" and palagonite from the Columbia River plateau. They urged that the name chlorophaeite be extended to cover all hydrous, amorphous, pitch-like materials of deuteric origin in basalts and dolerites; that "sideromelane" be continued as a specific name for ideal basaltic glass formed under conditions of specially rapid cooling; and that palagonite should be restricted to its original significance, namely the hydration product of sideromelane by water or water vapor of exotic origin. Rapid cooling that would produce sideromelane results when a lava is extruded into the sea or a lake. Palagonitization of tuffs which involves hydration of sideromelane, extensive oxidation of its iron and loss of some lime and soda is here attributed to the steam generated in the quenching of the extruded material. At the vents steam charged with acidic volatiles is considered responsible for the alteration of sideromelane fragments to a turgid-gray iron-free material with an index of refraction of 1.45. This material which is considered to have lost iron and perhaps other bases by solution would be included under the term palagonite as used by these writers.

Powers (1932) observed that the chemical decomposition of basaltic ash in Hawaii proceeds more rapidly than that of basaltic lava. He believes this is connected with the unstable nature of the glass particles composing the ash and with the rapidity with which basaltic glass changes to palagonite. He was unable to determine all the secondary decomposition products of the glass, but he recognized the presence of palagonite and undetermined materials of colloidal dimensions. Pertinent quotations

from this significant paper seem advisable, since it is not widely available for reference:

"The fundamental cause for the difference in the amount of chemical decomposition of the ash and lava lies in the fact that the former is an unstable glass and the latter an aggregate of crystals. The ash particles are in reality a liquid, undercooled far below the crystallization temperatures of the constituent compounds. The glass thus is in a highly unstable physical state and will rapidly break down to more stable forms under atmospheric conditions of temperature, pressure and moisture. The first stage in this breakdown is a complete alteration of the original glass to palagonite. This is a yellow isotropic substance which has essentially the same chemical composition as the primary basaltic glass, that is, the total composition of the basaltic magma—except that most of the iron is oxidized and water of hydration is added. Insufficient work has been done to determine the exact identity of all the secondary products resulting from the decomposition of the original glass. Much of the material large enough in particle size to be microscopically identified is definitely palagonite. On the other hand, a very considerable portion is of colloidal dimension and highly hydrated and can not be identified by ordinary petrographic methods. It is significant in this connection, that in the various localities where ash deposits exist in the Hawaiian Islands the decomposition products are always of the same general character as to color and physical properties. This would seem to indicate that this yellow-brown alteration product is fairly definite in composition and also rather stable in character.

"The slow cooling of lava gives an opportunity for the constituents of the liquid to crystallize as minerals of fairly definite chemical composition. The bulk of the crystalline constituents consists of pyroxene, a metasilicate of calcium, iron, and magnesium; plagioclase feldspar, a polysilicate of aluminum, calcium and sodium (and a trace of potassium); and olivine, an orthosilicate of magnesium and iron. Although much of the surface lava in Kona is older than the ash, it shows practically no decomposition. Even the very permeable scoria of an aa flow, which is largely crystalline material, yields very slowly to the alteration processes. A striking example of the differences in weathering of glassy and crystalline material under equal climatic conditions is found in the ash beds of Tantalus and Punchbowl on Oahu. Some layers are completely altered to yellow, but other layers and pockets are black and untouched by weathering. The altered beds were made up of fine particles of basaltic glass whereas the black unaltered material consists of coarse particles of partly crystalline basaltic rock. . . .

"Microscopic examination of the very fine sand and silt fractions of the pure ash samples shows that they are composed of three chief types of material—black particles of magnetite which formed within the basaltic glass and remained unaltered during its decomposition; rounded yellow particles of palagonite, the decomposition product of basaltic glass; and undecomposed, angular fragments of minerals, chiefly olivine and feldspar, which were present as crystals in the magma from which the ash was formed. The absence of any undecomposed particles of glass and the lack of decomposition of the mineral fragments bear out the conclusion that the soils of Kona are in the main the result of decomposition of basaltic glass, although it is probable that in the wetter belts the very fine particles of scoria have undergone a certain amount of decomposition."

Hoppe (1941) carried on experiments on the decomposition of basaltic glass by waters of varying pH values to determine the conditions of formation of palagonite. He concluded that decomposition was probably

due to the action of water vapor at elevated temperature, perhaps approximately 200°.

In a study of some altered palagonite tuffs from Jamaica, Raw (1943) recognized that the palagonite originated from basaltic glass, that "sideromelane" is inherently unstable, and that palagonite, which is the product of the action of water on it, is essentially chlorite. He considered that palagonitization is a slow process, and before it is much advanced, the rock spaces are filled with low-grade chlorite followed by a zeolite. Two types of chlorite, belonging to two stages and differing in orientation, are described. Deformation may raise the grade of both these chlorites and change palagonite tuffs to chlorite schists and chlorite-albite schists.

Ross and Hendricks (1945) suggested that the beidellite-nontronite collected by Edward Sampson from material lying between two basalt flows near Spokane, Washington, is an alteration product of basaltic volcanic glass. They remark that it would be interesting to know if the volcanic glass first altered to palagonite as observed by Powers in Hawaii and later assumed the crystalline form.

#### COMPOSITION AND OPTICAL PROPERTIES OF NONTRONITE

Analyses of the nontronites, which were collected from the veins at Excelsior, Colfax, and Garfield are shown in Table 1 along with an un-

TABLE 1. NONTRONITE ANALYSES

	1 Excelsior, Wash.	2 Colfax, Wash.	3 Garfield, Wash.	4 Dale Co., Ala.	5 Sandy Ridge, N. C.	6 Spokane, Wash.	7 Spokane, Wash.
SiO <sub>2</sub>	41.63	40.25	40.24	40.93	41.38	40.72	46.06
Al <sub>2</sub> O <sub>3</sub>	8.69	5.50	4.94	6.33	9.84	4.96	12.22
Fe <sub>2</sub> O <sub>3</sub>	25.99	29.44	30.17	30.07	27.47	29.57	18.54
FeO		none	none	.11	tr.?	.71	.28
MgO	.33	.53	.39	.80	tr.?	.74	1.62
CaO	1.78	2.29	2.36	.23	tr.?	1.98	1.66
Na <sub>2</sub> O	.22	none	none	none	tr.?		
K <sub>2</sub> O	.32	none	none	none			
H <sub>2</sub> O—	10.67	15.09	15.29	14.04	12.10	15.46	} 17.26
H <sub>2</sub> O+	9.91	7.25	6.79	7.76	9.25	6.66	
TiO <sub>2</sub>	tr.	.03	.02	.04	tr.?	.02	.84
Total	99.54	100.38	100.20	100.31	100.04	100.82	98.48
Analyst	J. Husted	N. Davidson	N. Davidson	W. Brannock	R. C. Wells	J. Fairchild	E. Shannon
Collector	Allen and Scheid			F. MacNeil	J. Shaffer	—	E. Sampson

published analysis of nontronite from Dale County, Alabama, and three published analyses. C. S. Ross (1927, p. 148), Larsen and Steiger (1928), and others (Ross and Kerr (1931) ) have recognized that nontronite is the

ferric oxide end member of an isomorphous series in which beidellite is the aluminous end member. Gruner (1935) has emphasized that the similarity in structure of nontronite, beidellite and montmorillonite as shown by *x*-ray patterns indicates an isomorphous series that is completely miscible.

LOCATION OF SAMPLES LISTED IN TABLES 1 AND 2

- (1) Excelsior clay deposit, Spokane County, about 12 miles southeast of Spokane, Washington, SE $\frac{1}{4}$  SE $\frac{1}{4}$  sec. 16, T. 24 N., R. 44 E. Veins of yellow green clay associated with weathered pillow lava.
- (2) Along road cut on U. S. Highway 195, north of Colfax, Whitman County, Washington, SE $\frac{1}{4}$  sec. 35, T. 17 N., R. 43 E. Veins of yellow green clay associated with weathered basalt.
- (3) Along road cut on Palouse Highway, 1 mile south of Garfield, Whitman County, Washington, sec. 4, T. 17 N., R. 45 E. Veins of yellow clay 1" to 6" wide associated with weathered basalts.
- (4) Along a road cut in the north center of sec. 18, T. 7 N., R. 24 E., about 3 miles southeast of Ariton, Dale County, Alabama. Unpublished analysis of a sample submitted by F. S. MacNeil. Nontronite occurs as nodules in a glauconite sand in the Hatchetigbee formation of Eocene age.
- (5) Sandy Ridge, N. C. Veinlets 5 to 10 mm. wide in schist. Collected by J. B. E. Shaffer of Sandy Ridge. Color, clear dull green. Wells (1937, p. 109).
- (6) About 17 miles southeast of Spokane, Washington, in SW $\frac{1}{4}$  sec. 5, T. 23 N., R. 45 E. Relations unknown. Color, clear dull yellowish green. (Ross and Hendricks (1945, p. 32).)
- (7) Spokane, Washington. Nontronite-beidellite of yellowish citrine color lying between two basalt flows. Collected by Edward Sampson. Ross and Shannon (1936, p. 94).

In the six nontronites listed in Table 1, the silica varies between 40.24 and 41.63 per cent; ferric oxide varies between 25.99 and 30.17 per cent. Alumina depends on the amount of the beidellite molecule present and varies between 4.94 and 9.84 per cent. No. 7 is the nontronite-beidellite of Ross and Shannon in which alumina is about equal molecularly to the ferric oxide.

TABLE 2. OPTICAL PROPERTIES OF NONTRONITE

Sample No.	Locality	Indices of Refraction		Birefringence $\gamma - \alpha$	Optical Character
		$\alpha$	$\gamma$		
1	Excelsior, Wash.	1.572	1.615	.043	negative
2	Colfax, Wash.	1.580	1.625	.045	negative
3	Garfield, Wash.	1.598	1.643	.045	negative
4	Dale County, Ala.	1.585	1.625	.040	negative
5	Sandy Ridge, N. C.	1.590	1.630	.040	negative
6	Spokane, Wash.	1.585	1.625	.040	negative
7	Spokane, Wash.	1.568	1.606	.038	negative

FORMULAS OF NONTRONITES

Sample No.	Octahedral Coordination	Tetrahedral Coordination
1	(Al <sub>.29</sub> Fe <sup>'''</sup> <sub>1.66</sub> Mg <sub>.03</sub> )	(Al <sub>.57</sub> Si <sub>3.49</sub> ) (Ca <sub>.32</sub> Na <sub>.02</sub> K <sub>.03</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
2	(Al <sub>.06</sub> Fe <sup>'''</sup> <sub>1.92</sub> Mg <sub>.70</sub> )	(Al <sub>.50</sub> Si <sub>3.50</sub> ) (Ca <sub>.43</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
3	(Al <sub>.02</sub> Fe <sup>'''</sup> <sub>1.97</sub> Mg <sub>.50</sub> )	(Al <sub>.50</sub> Si <sub>3.50</sub> ) (Ca <sub>.44</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
4	(Al <sub>.07</sub> Fe <sup>'''</sup> <sub>1.92</sub> Fe <sup>''</sup> <sub>.01</sub> Mg <sub>.20</sub> )	(Al <sub>.52</sub> Si <sub>3.48</sub> ) (Ca <sub>.03</sub> H <sub>.25</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
5	(Al <sub>.39</sub> Fe <sup>'''</sup> <sub>1.70</sub> )	(Al <sub>.58</sub> Si <sub>3.42</sub> ) (Ca <sub>.00</sub> H <sub>.26</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
6	(Al <sub>.06</sub> Fe <sup>'''</sup> <sub>1.94</sub> Fe <sup>''</sup> <sub>.05</sub> Mg <sub>.10</sub> )	(Al <sub>.46</sub> Si <sub>3.55</sub> ) (Ca <sub>.13</sub> ) O <sub>10</sub> (OH) <sub>2</sub>
7	(Al <sub>.77</sub> Fe <sup>'''</sup> <sub>1.10</sub> Fe <sup>''</sup> <sub>.02</sub> Mg <sub>.19</sub> )	(Al <sub>.37</sub> Si <sub>3.63</sub> ) (Ca <sub>.28</sub> ) O <sub>10</sub> (OH) <sub>2</sub>

In Table 2 a formula representing  $\frac{1}{2}$  the unit cell is given for each nontronite according to the method of Ross and Hendricks (1945, pp. 41-45) in which the aluminum+silicon ions in tetrahedral coordination must equal 4 and the O+(OH) ions must equal 12. In the nontronites from Washington the replaceable ion is Ca, and in those from Alabama and North Carolina, Nos. 4 and 5 respectively, hydrogen is present, making them acid clays. Small amounts of magnesium are significant, as magnesium plays an important role in the synthesis of beidellite, montmorillonite and possibly nontronite (Ewell and Insley, 1935; Noll, 1936).

In these samples the indices of refraction are highest for the nontronites with the highest ferric iron. No. 3 from Garfield has the highest indices of refraction and most nearly approximates a pure iron-end member, having 1.97 ferric iron and only .02 alumina proxying ferric iron in octahedral coordination. The values for the indices of refraction given in Table 2 were determined on prepared mineral strips that were immersed for several weeks in closed vials, each containing an oil of a known index of refraction (Ross and Hendricks, 1945, p. 54). The values determined on samples with occluded air, as they came from the field, are somewhat lower.

#### FIELD RELATIONS OF THE NONTRONITE

The field relations indicate that most of the nontronite in the Columbia River plateau has been produced by weathering of basaltic glass that originally composed basaltic vitric tuffs, the glassy skin of pillow lavas and the glassy groundmass of basaltic lavas. The nontronite from this source and from the weathering of augite and iddingsite migrated into cracks, ranging from a fraction of an inch to 6 inches wide, like those at Excelsior, Colfax, and Garfield. Other nontronite veins occur along the U.P.R.R. cut at the old Lockwood siding, 1 mile west of Manito, Wash-

ington. These were probably the source of the material submitted to Dr. C. S. Ross and listed as No. 6, Tables 1 and 2.

In the Excelsior district (NE.  $\frac{1}{4}$  sec. 8, T. 23 N., R. 45 E.) cores 5 inches in diameter and one foot long were composed wholly of massive yellow-green nontronite. Similar masses 1 to 4 inches in diameter were found in other drill holes at the Excelsior deposit and at the Olson clay deposit, about 8 miles northeast of Troy, Latah County, Idaho (secs. 19, 30, T. 40 N., R. 2 W.). The textures of this nontronite in thin section indicate that the original rock was a vitric tuff, in which some of the glassy fragments had a pumiceous texture. At Colfax the glassy material of a vitric crystal tuff is altered to nontronite and to palagonite (Fig. 6). The relations clearly indicate that large masses and perhaps beds of nontronite have been formed from the fragments of basaltic glass that are inter-layered with basalt flows.

The nontronite at Excelsior (No. 1, Tables 1 and 2) occurs at the margins of pillows and in veins cutting weathered pillow basalt. It was probably formed from the glassy skin and vesicular crust that was produced by rapid cooling of the lava induced by contact with water or a moisture-laden medium, or from the glassy fragments that were shattered from the outer rim of the pillows (Fenner 1910, p. 103; Lewis 1914, p. 650). Along a road-cut on highway 99 W. about 2 miles south of Portland, Oregon, brown nontronite-beidellite is associated with palagonite and opal at the rim of pillow lavas (Fig. 5). Yellow-green nontronite fills vesicles in the basaltic lava at this locality.

Along a road-cut about 800 feet west of Valleyford, Spokane County, Washington, nontronite has formed from the glassy groundmass of a basalt in which the plagioclase and augite have remained fresh (Fig. 2). Yellow green nontronite fills vesicles in the basalt. The combined effect of both types of nontronite is to give to the hand specimen of the rock a yellowish-green color.

At Marion, Oregon, palagonite (No. 1, Table 3) occurs in irregular veins around pillow lava in a manner similar to that of the nontronite at Excelsior, Washington. The change of basaltic glass, such as No. 3, Table 3, to palagonite involves extensive hydration, almost complete oxidation of iron, and loss of some silica, alumina, calcium, magnesium, and alkalis. According to Peacock and Fuller (1928, p. 376) this change is accomplished by the steam generated in the quenching of the extruded lava. Powers (1932, p. 9) in his study of Hawaiian soils attributed palagonitization to weathering of basaltic glass in the moist, warm climate of the Hawaiian Islands.

The "basaltic glass" found by Diller (No. 4, Table 3) at Rooster Rock, 25 miles east of Portland, Oregon, might well be termed palagonite, since almost all the iron is present as  $\text{Fe}_2\text{O}_3$  and the total water is 19.46 per cent. Diller recognized the relation of the material to palagonite and its altered condition. His description of the material and its occurrence follows:

"The whole mass of the cliffs when seen from the railroad is more or less distinctly stratified, but the layers are large and massive, so that the stratification is not conspicuous. When examined in detail the strata are found to be made up entirely of fragmental volcanic material forming what is technically called tuff, or, in this case, basalt tuff, on account of the basaltic character of the fragments. Such material is sometimes called palagonite tuff, from its occurrence in Palagonia, Sicily.

"The layers are composed chiefly and often wholly of a substance ranging in color from light to dark brown and black, and in luster from dull glassy to pitch like and resinous. For the most part the rock is decidedly fragmental. It contains fragments of dark basalt from the size of a pea to blocks several feet in diameter. When broken, these pieces are often seen to have a black pitchy border, as if once enveloped by a molten mass.

"Weathering brings out the fragmental structure on the surface of the glassy portions, but this is still more evident in a thin section of the rock where the dark brown completely isotropic glass fragments full of small lath-shaped crystals of plagioclase feldspar, with fewer crystals of augite and grains of olivine, like those of the basalt, are encompassed and bound together by a lighter brown matrix like gelatin, which has fibrous polarization.

"Locally among the distinctly fragmental layers are sheets of the yellowish-brown waxy-lustered material which in thin section is found to be an altered jellylike substance containing crystal fragments of plagioclase, augite, and olivine like those in the basalt of the large fragments and flows in the cliffs, and it is evident that the whole mass is from a volcano erupting basalt."

This locality was not visited by the writers, but the description of waxy-lustered material of various colors suggests the material at Marion and that occurring two miles south of Portland, which changed color with loss of water. J. M. Axelrod of the Geological Survey, U. S. Department of the Interior, could detect no difference in the  $x$ -ray patterns of different colored parts, all of which gave the  $x$ -ray patterns of nontronite and opal.

The change of palagonite to nontronite with 40 or 41 per cent silica and 26 to 30 per cent ferric oxide would generally require some further loss of silica, alumina, calcium, magnesium and alkalis. Opal associated with palagonite (No. 1, Table 3), with nontronite (No. 2, Table 3), with altered pillow lavas south of Portland (Fig. 5) and east of Pullman, Washington, is evidence that intensive chemical change has taken place.

Other occurrences of nontronite are known in the Columbia River region where the source material of the nontronite is not so definitely dis-



TABLE 3

	1 Palagonite Containing Opal. Marion, Ore.	2 Opal, White Earthy Veins in Nontronite. Colfax, Wash.	3 Basaltic Glass (Sidero- melane). Douglas county, Wash.	4 Palagonite Tuff 25 Miles East of Portland, Ore.	5 Palagonite Rock. South Pacific	6 Palagonite Rock. Iceland	7 Iddingsite. Average of 7 Analyses
SiO <sub>2</sub>	69.39	92.69	51.30	40.89	44.73	35.34	39.11
Al <sub>2</sub> O <sub>3</sub>	2.53	.64	18.54	10.41	16.26	11.15	3.29
Fe <sub>2</sub> O <sub>3</sub>	12.70	1.91	0.26	15.00	14.57	10.28	31.49
FeO	none	none	11.21	0.07	nd.	2.19	.96
MgO	.59	.05	4.03	3.76	2.23	6.52	8.05
CaO	1.09	.44	8.55	5.18	1.88	7.01	2.28
Na <sub>2</sub> O	none	none	2.83	0.47	4.50	0.16	
K <sub>2</sub> O	none	none	1.05	0.53	4.02	0.19	
H <sub>2</sub> O—	8.79	1.75	tr.	9.14		15.50	7.78
H <sub>2</sub> O+	4.67	2.72	0.30	10.32	9.56	8.90	8.49
TiO <sub>2</sub>	.04	.04	1.40	3.37		2.10	.18
MnO	tr.	none	0.35	0.90	2.89	0.22	
Others			0.05	.56		.31	
Total	99.80	100.24	99.87	100.60	100.64	99.87	101.63
Analyst	N. Davidson	N. Davidson	Herdsmen	G. Steiger	A. Renard	Herdsmen	Shannon
Collector	V. Allen	V. Scheid	Fuller	Diller	Murray	Peacock	Ross

## LOCATION OF SAMPLES LISTED IN TABLE 3

- (1) Palagonite containing opal occurs in veins around pillow lava along S.P.R.R. cut near station, Marion, Marion County, Oregon.
- (2) White, earthy opal in center of 2 inch nontronite vein (Tables 1 and 2, No. 2). Along road cut on U. S. Highway 195, north of Colfax, Whitman County, Washington, SE $\frac{1}{4}$  sec. 35, T. 17 N., R. 43 E.
- (3) Basaltic glass (sideromelane) from the lake-quenched nose of a flow at Columbia River, 3 miles south of Moses Coulee, Douglas County, Washington. Peacock and Fuller (1928, p. 371).
- (4) Palagonite tuff. Near Rooster Rock, about 25 miles east of Portland, Oregon, Diller (1905, p. 345).
- (5) Palagonite, South Pacific. Murray and Renard (1891, p. 307).
- (6) Palagonite rock, Iceland, Peacock (1926, p. 66).
- (7) Iddingsite, average of 7 analyses. Ross and Shannon (1925, p. 16).

played. In the Eola Hills, west of Salem, Oregon, nontronite and halloysite fill a vein  $\frac{3}{4}$  inch thick which cuts the Stayton lavas (Allen, 1945, p. 269). Green nontronite cements andesitic detritus occurring along the new Ostrander logging road, about three miles southeast of Molalla, Oregon (Allen, 1945, p. 269). The nontronite is cracked and pale-green nontronite fills the cracks in the sedimentary nontronite. This relationship at Molalla suggests that the cracks were formed when the clay dried

and that pale-green nontronite was deposited in the cracks when the clay was again saturated with water. In the clay deposit near Castle Rock, Cowlitz County, Washington, nontronite occurs in detrital sedimentary rocks (Allen and Nichols, 1943; Allen, 1946). At Salem, Molalla and Castle Rock basaltic lavas are present in the same section as the nontronite but a close relationship between the altered glass or ferromagnesian minerals of the basalts and the nontronite at these localities has not been demonstrated thus far.

#### PETROGRAPHIC OBSERVATIONS AND THEIR SIGNIFICANCE

Petrographic study has contributed additional information. The glassy groundmass of some basalts contains rod-like inclusions of augite or other ferromagnesian minerals that may have a fan-like arrangement (Fenner 1910, p. 100). In the Excelsior district basaltic glass alters to nontronite that retains rods of augite (Figs. 1, 2, 4). Basaltic glass is less stable than the augite-rods it encloses or the large grains of fresh augite in the same specimen.

In Fig. 1, iddingsite crystals are embayed by and partially altered to nontronite. As basaltic glass is also partially altered to nontronite in this specimen, iddingsite was almost as susceptible to alteration as was the basaltic glass. If one compares the composition of iddingsite (No. 7, Table 3) and nontronite (Table 1), it is evident that iddingsite needs only to lose some magnesium and to gain additional water to approach nontronite in composition. Iddingsite with a definite crystalline structure would be more apt to resist alteration and reorganization than amorphous material, such as a basaltic glass, having a similar composition.

In Fig. 2 nontronite has formed from basaltic glass, whereas augite, plagioclase and ilmenite have remained fresh. Nontronite fills vesicles and openings in the lava. Also, irregular masses of zoned nontronite have resulted from the alteration of the glassy groundmass, and small spherical nodules may have resulted from the resorption of olivine, as suggested by Fenner (1910, p. 102), and its subsequent alteration. Some of the nontronite varies in color with the amount of ferric oxide present and forms varied colored zones within a single area. If all the zones were composed of members of the nontronite-beidellite series one would expect the dark zones to have more ferric iron and higher indices of refraction than the light colored zones. In a thin section from Colfax a dark zone in the center had lower indices of refraction than those of the light colored material surrounding it, and this suggested the dark zone was composed of the magnesium member of the montmorillonite group, saponite (Ross, 1945). Numerous immersions were made of the clay minerals from the vesicles but the presence of saponite could not be substantiated. All the grains

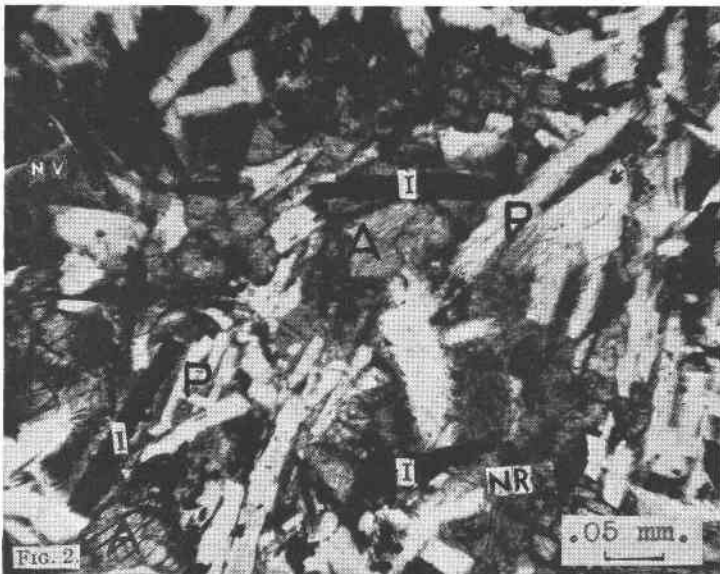
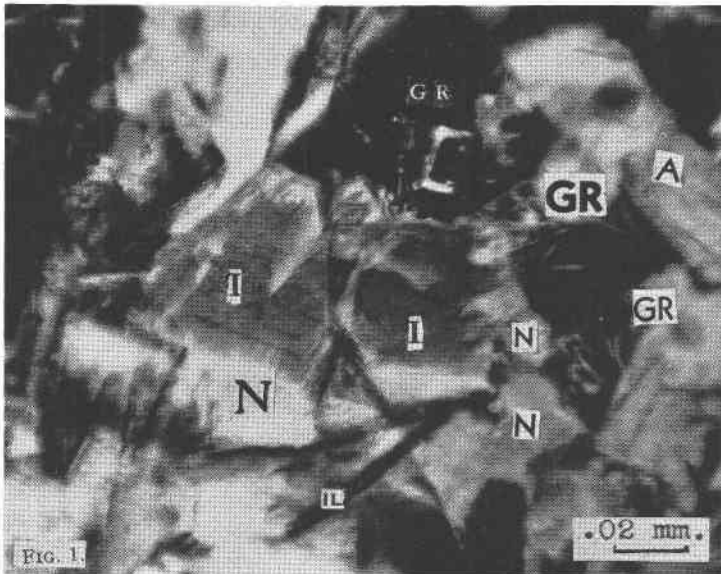


FIG. 1. Nontronite (N) has formed from the glassy groundmass and from iddingsite (I). Black (GR) is basaltic glass containing rods of augite. Augite (A) is fresh. IL is ilmenite. Excelsior, Spokane County, Washington.

FIG. 2. Nontronite (NR) contains rods of augite once present in basaltic glass. Nontronite fills vesicles (NV), some of which are zoned (left near center). Augite (A) is unaltered. Plagioclase (P) is unaltered. I is ilmenite. Valleyford, Spokane County, Washington.

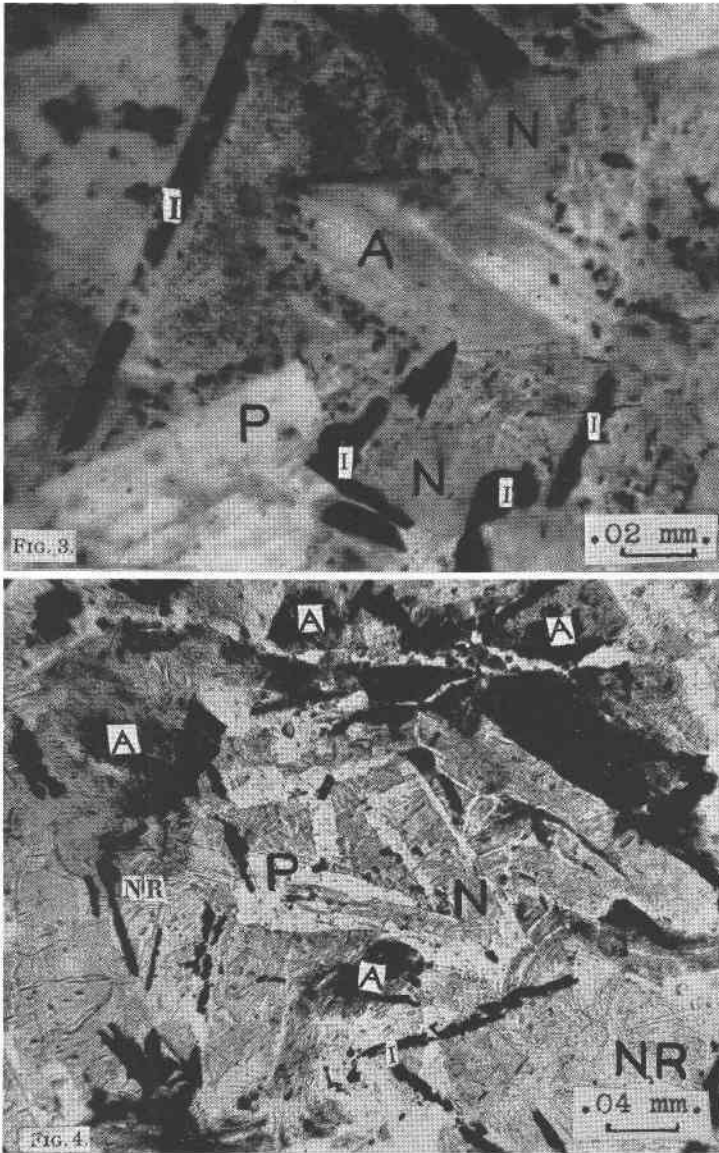


FIG. 3. Augite crystal (A) and glassy groundmass (N) are altered to nontronite. Plagioclase (P) is fresh. I is ilmenite. Excelsior, Spokane County, Washington.

FIG. 4. Nontronite (NR) contains rods of augite. Augite (A) is altered to nontronite. Calcic core of plagioclase (P) is altered to nontronite. I is ilmenite. Excelsior, Spokane County, Washington.

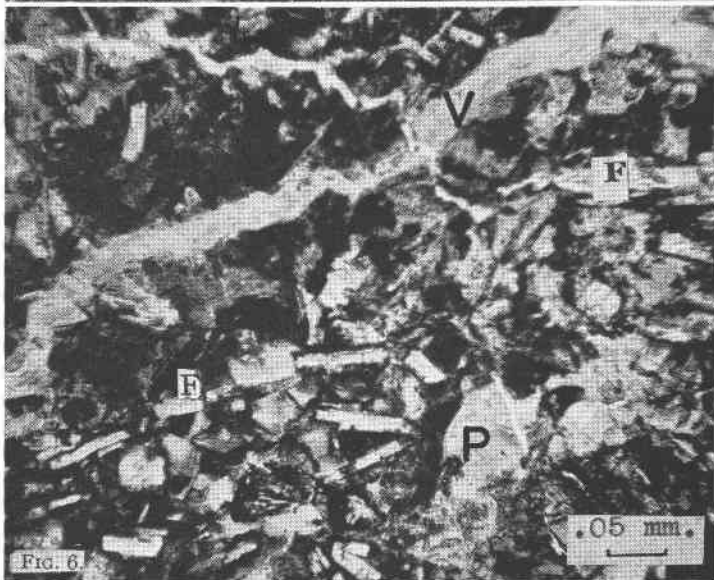
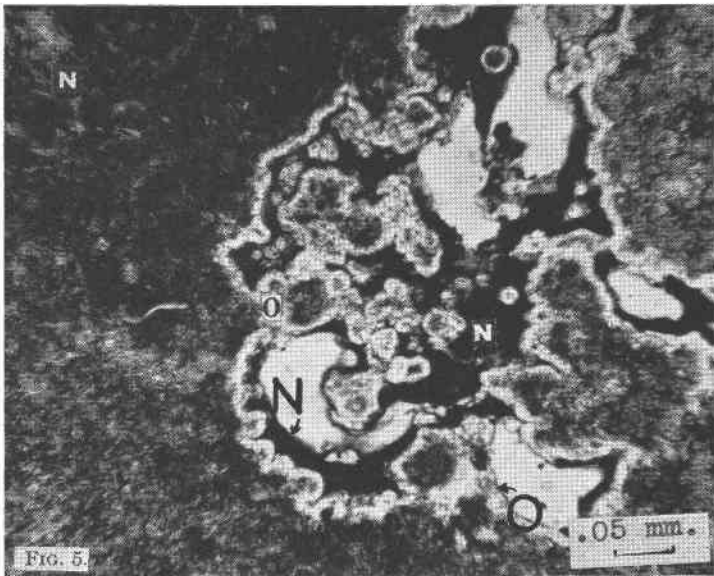


FIG. 5. Palagonite is altered to nontronite (N). Opal (O) and nontronite (N, black) fill an open cavity. Some nontronite has broken loose in making the thin section, leaving white areas. Around pillow lava, at a road cut on Highway 99 W, 2 miles south of Portland, Oregon.

FIG. 6. P is yellow palagonite; dark areas are altered and iron stained palagonite. V is a vein of nontronite. Lath shaped grains (F) are plagioclase altered to kaolinite. Colfax, Whitman County, Washington.

isolated and measured had indices of refraction within the range of those for the nontronite-beidellite series. The small amounts of magnesium in the nontronite analyses listed in Table 1 show that only limited amounts of saponite could be present in those samples and, it appears likely that magnesium ions proxy aluminum ions in octahedral positions in the analyzed samples.

In Fig. 3, a large crystal of augite and the glassy groundmass of a basalt have altered to nontronite, whereas plagioclase and ilmenite have remained fresh.

In Fig. 4, the glassy groundmass containing fan-like inclusions of augite and large augite grains are altered to nontronite. The calcic core of plagioclase is altered to nontronite, but not the sodic rim. The materials illustrated in Figs. 1 to 4 can be arranged in a series, each member of which has increased resistance to weathering, as: (1) basaltic glass, (2) iddingsite, (3) augite, (4) plagioclase, (5) ilmenite. Some residual basaltic clays in the Excelsior district contain 7 per cent  $\text{TiO}_2$ , which is present mainly as ilmenite.

The ease with which basaltic glass alters to nontronite depends first on its chemical composition. The curves of W. O. George (1924) can be used to estimate the composition of a volcanic glass from its index of refraction, which varies inversely as the silica content. Peacock (1926) recorded that the index of refraction of 8 Icelandic basaltic glasses varied between 1.604 and 1.615, and his analyzed specimen of Icelandic basaltic glass contained 46 per cent  $\text{SiO}_2$ . Fuller's determinations of the index of refraction of basaltic glasses from Washington (Peacock and Fuller, 1928) varied between 1.583 and 1.597. His analyzed sample (Table 3, No. 3) contained 51 per cent silica and had an index of refraction of 1.583. Thus, the composition of basaltic glass is known to vary. Other factors being equal, the basaltic glass with the lowest silica would be the most unstable.

Secondly, the ease of alteration of basaltic glass varies with its texture. A massive, glassy lava flow resists alteration, whereas the fragmental texture of a glassy tuff allows the ready percolation of reacting solutions. In the Excelsior district tuffs are more completely altered to nontronite than the associated lava flows at the same depth. Powers (1932) has observed that glassy tuffs in Hawaii weather more rapidly than lava flows characterized by crystalline materials.

Thirdly, the ease of alteration of basaltic glass to nontronite varies with the conditions and the composition of the reacting solutions. The formation of nontronite is favored by conditions of poor drainage and by the presence of alkalis, alkaline earths, magnesium, and probably ferrous iron.

Statements appear in the literature that palagonite is unstable and alters to chlorite. It was observed that heating certain specimens from Excelsior, Washington, during the preparation of thin sections caused some fragments with a glassy texture to turn green. Their mean index of refraction is within the range for chlorites, but also is within the range for intermediate members of the nontronite-beidellite series. X-ray patterns by J. M. Axelrod indicated the absence of chlorite and the presence of nontronite-beidellite. The apparent low birefringence of these fragments is probably caused by their fine-grained nature and incipient development of the nontronite. In the light of the experience with palagonite from Washington and Oregon it seems that reported occurrences of chlorite in palagonite at other localities should be reexamined using x-ray and other methods.

The x-ray pattern of the palagonite occurring around pillow lava at Marion, Oregon (Table 3, No. 1), is reported by J. M. Axelrod to indicate opal and nontronite. In thin section areas of opal are clearly visible, and there are also present materials with indices of refraction that vary in different parts of the section. Some of these have a mean index of refraction of 1.525, and others have moderate birefringence and a mean index of refraction (with occluded air) of 1.555 that may be nontronite-beidellite.

The massive palagonite around pillow lava, 2 miles south of Portland, Oregon, gave an x-ray pattern that indicated opal and a member of the nontronite-beidellite series. A green clay mineral that is probably nontronite-beidellite can be seen in the thin section of the massive portion (Fig. 5). Opal lines cavities in the massive portion and a brown nontronite-beidellite having a mean index of refraction of 1.565 (with occluded air) fills the center of the former openings. Reddish-brown common opal with an index of refraction of 1.445 forms lumps 1 to 3 inches across at this locality. Along a road cut on highway 3, at the east edge of Pullman, Washington, yellow common opal with an index of refraction of 1.455 forms similar lumps around pillow lava.

White earthy opal (Table 3, No. 2) forms a pod within a 2-inch nontronite vein at Colfax and the center of this pod is filled with nontronite. This earthy opal has an index of refraction of 1.455 and it gave no x-ray pattern, being truly amorphous.

The separation of silica from the glassy skin of pillow lava and from palagonite is indicated at these localities. The experiments of Lovering (1923) suggest that alkalis and magnesium bicarbonate are effective agents in removing silica. These agents were present in the original basaltic rocks and were partially or wholly removed along with silica during the weathering process.

Another locality where somewhat similar relations have been observed is Umnak Island, Alaska, which attracted the attention of scientists because volcanic activity was in progress during 1945 within 65 miles of Dutch Harbor. Lieutenant R. E. Wilcox collected volcanic material from the outer slopes of the unnamed caldera that occupies the northeastern part of Umnak Island. Dr. Clarence S. Ross, of the Geological Survey, U. S. Department of the Interior, studied the material and kindly prepared the following statement for inclusion in this paper:

"One specimen represented fresh unaltered basaltic glass, which is nearly colorless in thin section. Another specimen from the same eruption contains alteration products of the same type of glass. Part of it is a yellow-brown palagonite in which hydration and partial oxidation have produced an isotropic material with a lower index of refraction than that of the basaltic glass from which it was derived. Most of the material, however, has undergone further alteration to a very fine-grained aggregate that is dull green in color. This material is anisotropic under strong illumination, although it is so exceedingly fine grained that this evidence of its crystallinity would be recognizable only in a material with moderately high birefringence. These relations indicate that the dull green final product of the alteration of this basaltic glass is nontronite."

#### ORIGIN AND MIGRATION OF NONTRONITE

Several facts suggest that two different sets of weathering conditions have prevailed in the Columbia River region. In the Excelsior district nontronite is present in the lower poorly drained part of the profile of weathering, where the stagnant alkaline solutions contain magnesium. Here, plagioclase, basaltic glass and iddingsite are altered to nontronite. In the upper well-drained part of the profile revealed in the same drill-holes plagioclase is altered to kaolinite or halloysite and iddingsite resists alteration. Along a road cut on highway 8 near Nora, 3 miles east of Troy (NW.  $\frac{1}{4}$ , S. 1, T. 39 N., R. 3 W.), Latah County, Idaho, unaltered iddingsite occurs in a weathered basalt in which the plagioclase is completely altered to kaolinite. In the Mehama district, Marion County, Oregon, euhedral plagioclase phenocrysts with relict twinning are completely altered to kaolinite but the iddingsite in this volcanic rock is unaltered. Thorough leaching by neutral or slightly acid solutions that produces kaolinite from plagioclase did not favor the formation of nontronite from iddingsite at these localities.

Hosking (1940) found that montmorillonite clay minerals are formed in the basalts of Australia where waterlogging of the soils is apparent, but under conditions of good drainage kaolinite is formed from basalts. In the lower part of the profiles in the Excelsior district not only would the required conditions of poor drainage be present, but also all the elements needed in the synthesis of nontronite (Noll, 1936; Ewell and Insley, 1935) would be available for the formation of nontronite from basaltic



glass, palagonite, iddingsite and augite. Most of the nontronite was formed from basaltic glass, some of which was changed to palagonite by the steam generated in the quenching of the lava. The partial alteration of the glassy groundmass of some basalts to nontronite, with the adjacent glass of the groundmass unchanged, indicates that the action of steam is not always necessary but that weathering under conditions of poor drainage in the presence of magnesium can completely change basaltic glass to nontronite. The change of basaltic glass to palagonite requires the removal of the same constituents as those removed in the change of most palagonites to nontronite. Where glassy fragments were converted to palagonite by the steam action, the tuffs composed of them were already started on the way to nontronite and weathering processes completed the action.

In the upper part of the profiles of weathering in the Columbia River region kaolinization of plagioclase feldspars started as soon as good drainage conditions were established and when the chemical system changed from alkaline to neutral or slightly acid. Migration or movement of clay minerals was favored by the conditions of good drainage (Allen, 1945) and the presence of dispersing agents. The clays with the highest alumina in the Excelsior district are composed of kaolinite or halloysite and contain notable additions of kaolinite that fills cracks and former vesicles in the basaltic rocks. Some of the kaolinitic clay in the cavities contains tiny muscovite flakes and grains of quartz that were transported from the sedimentary clays in the area into the openings. The remainder may have been derived from altered basalts at higher elevations. When streams cut downward into the nontronite zones, increased relief, and improved the conditions of drainage, nontronite migrated into vesicles and into cracks. The concentration of the nontronite in the veins at Excelsior, Colfax, Garfield and Manito was accomplished under these conditions. Later, some kaolinite was carried downward and filled veins that transect the nontronite veins at some localities. As conditions of thorough drainage penetrated progressively downward, neutral or slightly acid solutions invaded lower depths and kaolinization of plagioclase took place at levels where nontronite had formed early in the cycle. In Fig. 6 is illustrated a basaltic vitric tuff, in which palagonite has altered to nontronite, nontronite has migrated in veins and plagioclase has altered to kaolinite.

#### CONCLUSIONS

Nontronite in the Columbia River region was formed chiefly from basaltic glass and to a minor extent from iddingsite and augite. Palagonite is an intermediate step in the alteration that may be accomplished by the

steam generated in quenching of the lava. The partial alteration of the glassy groundmass of basalts to nontronite indicates that the action of steam is not always necessary but that weathering under conditions of poor drainage is essential to the genesis of nontronite.

## REFERENCES

1. ALLEN, V. T., AND NICHOLS, R. L. (1943), Cowlitz high-alumina clay deposit near Castle Rock, Washington: *Bull. G.S.A.*, **54**, 1823.
2. ALLEN, V. T. (1945), Effect of migration of clay minerals and hydrous aluminum oxides on the complexity of clay: *Jour. Am. Ceramic Soc.*, **28**, 269.
3. ALLEN, V. T. (1946), Sedimentary and volcanic processes in the formation of high alumina clay: *Ec. Geol.*, **41**, 124-138.
4. DILLER, J. S. (1905), So-called "iron ore" near Portland, Oregon: *U. S. Geol. Survey, Bull.* **260**, 343-347.
5. EWELL, R. H., AND INSLEY, HERBERT (1935), Hydrothermal synthesis of kaolinite, dickite, beidellite, and nontronite: *Jour. Research Nat. Bur. Standards*, **15**, 173-186.
6. FENNER, C. N. (1910), The Watchung basalt and the paragenesis of its zeolites and other secondary minerals: *N. Y. Acad. Sci. An.*, **20**, 93-187.
7. FERMOR, L. I. (1925), On the basaltic lavas penetrated by a deep boring for coal at Bhusawal, Bombay Presidency: *Rec. Geol. Sur. India*, **58**, 125-133.
8. GEORGE, W. O. (1924), The relation of the physical properties of natural glasses to their chemical composition: *Jour. Geol.*, **32**, 352-372.
9. GRUNER, JOHN W. (1935), Structural relationships of nontronites and montmorillonite: *Am. Mineral.*, **20**, 475-483.
10. HOPPE, HANS-JÜRGEN (1941), Untersuchungen an Palagonittuffen und über ihre Bildungsbedingungen: *Chem. d. Erde*, **13**, 484-514; *Chem. Zentr.*, **II**, 1952. (Original is not available to the author.)
11. HOSKING, J. S. (1940), The soil clay mineralogy of some Australian soils developed on granitic and basaltic parent material: *Jour. Australian Counc. Sci. and Industr. Res.*, **13**, 206-216.
12. LARSEN, E. S., AND STEIGER, GEORGE (1928), Dehydration and optical studies of alunogen, nontronite and griffithite: *Am. Jour. Sci.*, 5th series, **25**, 14, 15.
13. LEWIS, J. V. (1914), Origin of pillow lavas: *Geol. Soc. Am., Bull.* **25**, 591-654.
14. LOVERING, T. S. (1923), The leaching of iron protores: solution and precipitation of silica in cold water: *Eco. Geol.*, **18**, 523-540.
15. MURRAY, J., AND RENARD, A. F. (1891), Report on deep-sea deposits, based on the specimens collected during the voyage of H.M.S. "Challenger" in the years 1872-76; *London*, 307.
16. NOLL, W. (1936), Synthese von Montmorilloniten: *Chem. Erde*, **10**, 129-154.
17. PEACOCK, M. A. (1926), The petrology of Iceland (Tyrrell and Peacock), Part I, The basic tuffs: *Trans. Roy. Soc. Edinburgh*, **55**, 51-76.
18. PEACOCK, M. A., and FULLER, R. E. (1928), Chlorophaeite, sideromelane and palagonite from the Columbia River plateau: *Am. Mineral.*, **13**(7), 360-382.
19. POWERS, H. A., RIPPERTON, J. C., and GORO, Y. B. (1932), Survey of the physical features that affect the agriculture of the Kona district of Hawaii: *Hawaii Agr. Exp. Sta., Bull.* **66**, 9-10, 16.
20. RAW, FRANK (1943), Some altered palagonite tuffs from Jamaica and the origin and history of their chlorites: *Jour. Geol.*, **51**, 215-243.

21. ROSS, C. S., AND SHANNON, E. V. (1925), The origin, occurrence, composition, and physical properties of the mineral iddingsite: *U. S. Nat. Mus., Proc.*, **67**, 16.
22. ROSS, C. S., AND SHANNON, E. V. (1926), Minerals of bentonite and related clays and their physical properties: *Am. Ceram. Soc. Jour.*, **9**, 77-96.
23. ROSS, C. S. (1927), Altered Paleozoic volcanic materials and their recognition: *Bull. Am. Assoc. Pet. Geol.*, **12**, No. 2, 143-164.
24. ROSS, C. S., AND KERR, P. F. (1931), The clay minerals and their identity: *Jour. Sed. Petrology*, **1**, 57-58.
25. ROSS, C. S. (1945), Minerals and mineral relationships of the clay minerals: *Jour. Am. Ceramic Soc.*, **28**, 178.
26. ROSS, C. S., AND HENDRICKS, S. B. (1945), Minerals of the montmorillonite group, their origin and relation to soils and clays: *U. S. Geol. Sur., Prof. Paper 205-B*, 70.
27. VON WALTERSCHAUSEN, W. SARTARIUS (1845), Ueber die submarinen Ausbrüche in der Tertiär-Formation des Val di Noto im Vergleich mit verwandten Erscheinungen am Aetna: *Gött. Stud.*, **I**, 371-431.  
——— (1847), *Physisch-Geographische Skizze von Island*, Göttingen.
28. WELLS, R. C. (1937), Analyses of rocks and minerals: *U. S. Geol. Survey, Bull.* **878**, 108.