# STATISTICAL RELATIONSHIPS OF MINOR CONSTITUENTS OF SOME NONTRONITES

# $B<sub>\gamma</sub>$

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## ABSTRACT

Replacement of alumina by ferric iron in the lattice structure features the nontronite member of the montmorillonite group. Chromium, in significant amounts, replaces ferric iron in the lattice structure of some nontronites.

Effect of migration of clay minerals under colloidal suspension and the transfer of true solutions complicate correlations of the chemical composition. Moreover, many nontronites are secondary and occur in fracture zones associated with kaolinitic and halloysitic clay. A tendency of certain nontronites to form lathlike crystals is well known.

Chemical composition of 15 selected nontronites from the United States of America, Germany, and Russia indicate a range of 30 to 60 percent SiO<sub>2</sub>, and a range of from 25 to 40 percent Fe<sub>2</sub>O<sub>3</sub>. Minor constituents are the oxides of magnesium, titanium, ferrous iron, and calcium, and the alkalis, potassium and sodium.

Magnesium percentages found in nontronites are proportional to the value of sigma for octahedral coordination. Ferrous iron is proportional to titanium in montmorillonite, and a similar relationship is observed in the nontronites.

A deficiency in alkalis typifies the composition of montmorillonite and this condition is likewise true in most nontronites. Potassium is limited to a narrow statistical range of between 0.5 to 0.6 ions of Al in tetrahedral coordination against an extreme deficiency of ferric iron and magnesium (combined) of less than 0.05 ion in octahedral coordination. Thus calcium occurs as the principal large cation and is present in nearly all the nontro· nites studied.

#### INTRODUCTION

Nontronite, a member of the montmorillonite group, was first proposed by Berthier (1827) for a mineral discovered by Lanoue and associated with manganese ore of Perigueux in the Arrondissement of Nontron near the village of Saint Pardoux, France.

In the montmorillonite group, nontronite is one of the three minerals, namely, montmorillonite, beidellite, and nontronite, that comprise a seemingly continuous series of solid solutions.

In the lattice structure, Fe<sup>3+</sup> and Al<sup>3+</sup> replace one another in octahedral coordination in all proportions; however,  $Al^{3*}$  can replace  $Si^{4*}$  apparently not to exceed one ion in four. The chemical formulas for this series and other members of the montmorillonite group are analysed in Figure 1 and Table 1 and in a table by Ross and Hendricks (1945, p. 47).

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# GEOLOGIC OCCURRENCE

# *Genesis of Nontronite*

In the Columbia River region of Washington, Oregon, and Idaho, nontronite was formed chiefly from basaltic glass. To a minor extent the mineral originated from augite and iddingsite.

TABLE 1. - IONIC COMPOSITION OF NONTRONITES AND CRYSTAL STRUCTURE<sup>1</sup>

Sample		Ions in Tetrahedral Coordination		Ions in Octahedral Coordination					Total Equiva- lence of External Ions and	
No.	Locality	Si	AI	$Al^{3+}$	$Fe3+$	$Fe2+$	$Mg^{2+}$	Sigma	Predomination	
55	Stary-Krym, Russia	3.77	0.23	0.69	1.26		0.03	1.98	0.34 Ca	
56	Woody, Calif.	3.76	0.24	0.06	1.86	0.07	0.01	2.00	0.40 Ca	
57	Petrovsk, Krivoirog, Russia	3.74	0.26	1.10	8.75		0.07	2.00	0.36 Ca	
58	Spokane, Washington	3.63	0.37	0.77	1.10	0.02	0.19	2.08	$0.28$ Ca	
59	Spokane, Washington	3.51	0.49	0.00	1.92	0.05	0.10	2.07	0.36 Ca	
60	Santa Rita, New Mexico	3.50	0.50	0.11	1.91	0.02	0.04	2.08	0.53 Ca	
	33a Garfield, Washington	3.50	0.50	0.05	1.93		0.12	2.10	0.46 Ca	
33b	Manito, Washington	3.50	0.50	0.03	2.02			0.005 2.055	0.35 Ca	
									$0.2$ Na	
61	Chevy Chase, Maryland	3.47	0.53	1.02	1.04			2.06	0.26 Ca	
62	Szekes-Fejevar, Hungary	3.45	0.55	0.07	2.00			2.07	0.07	
63	Stary-Krym, Russia	3.45	0.55	0.37	1.62		0.12	2.11	0.33 <sub>Ca</sub>	
64	Tachau, Germany	3.42	0.58	0.45	1.61	0.03	0.01	2.10	0.07	
65	Sandy Ridge, N. C.	3.42	0.58	0.39	1.70			2.09	$0.26$ acid	
66	Spruce Pine, N.C.	3.37	0.63	0.51	1.58		0.01	2.10	0.18	
67	Tachau, Germany	3.36	0.64	0.40	1.65	0.09		2.14		

1 Data from Ross and Hendricks (1945, p. 43) and Kerr, Kulp, and Hamilton (1950, p. 34).

Formation of palagonite is believed to be an intermediate step in the alteration that may be brought about through the action of steam in quenching of the lava. However, steam action is not always a prerequisite to the formation of nontronite, as shown by partial alteration of the glassy groundmass of basalts to nontronites.

Weathering, under conditions of poor drainage, is considered essential to the genesis of nontronite (AlIen and Scheid, 1946). The nontronite appears at the edges of pillows, within fissures and cracks, and at the surfaces of individual flows where the basaltic material is principally an unstable glass. This glassy condition is believed to be responsible for the rapid change of the basic material (with later migration of the altered product soon after formation, into cracks and fissures which it now occupies) .

## *Migration* 0/ *Clay Minerals*

The composition of a clay mineral is affected by migration. Migration of these minerals rarely takes place by transfer of their constituents as true solutions. Generally, the clay migrates as colloidal suspensions whose formation and movement are favored by the presence of dispersing agents as well as by conditions of good drainage.

Where poor drainage conditions exist, the clay minerals remain in the zone close to the surface in which they are developed by weathering, and form a plastic clay called gumbotil. Gumbotil commonly underlies broad, flat upland areas of poor drainage.

In contrast, in localities of rolling topography or hill slopes, the same position immediately below the surface is occupied instead by a silty zone from which significant amounts of clay minerals were carried to a lower zone.

The amount of ground water that circulates through a clay under conditions of good drainage determines whether the clay minerals remain in place or are carried to a new location. The presence of a dispersing agent which aids in furnishing minute mineral particles for colloidal suspensions is a factor (AlIen, 1945).

*Cenozoic* System.-Alkaline solutions are an important factor under conditions incident to drainage in the occurrence of nontronite in a deeply weathered basalt zone of the Spokane district. Here massive, waxy, green nontronite is found associated with kaolinite (Scheid, 1945). A high magnesium content which resulted from the alteration of the glassy groundmass and to a lesser extent of augite, played a part in the formation of nontronite.

At Garfield, Washington, large masses of nontronite occur at vein intersections surrounding quasi-polygonal blocks of weathered basalt, ranging from 6 to 18 inches in thickness. Semi vertical veins have been noted in lesser developed cross veins of basalt, but positions of the veins are dominantly vertical although a few thin stringers have been found in horizontal positions.

Paralleling the old erosion surface at Manito, Washington, many veins of yellow-green nontronite fill joint cracks and intersections between blocks of weathered basalt. The weathered basalt is a brown-gray, gray, and blue-gray

material overlain by 2 to 4 feet of poorly sorted clay and gravel sediments, in a road cut. Nontronite lenses range up to 8 inches in diameter.

*Mesozoic System.-Nontronite* occurs as a fracture filling in a zone in the sedimentary kaolin of the Tuscaloosa formation of the Cretaceous system at a locality in Irwinton, Georgia. Occurrence is secondary with migration having taken place downward from the clays of the Jackson group (of Tertiary Eocene age) which once overlay the Tuscaloosa formation in this region.

# MINERALOGY

## *Color*

The residual type of nontronite, occurring as dark-green grains, appears to be the first mineral formed from the decomposition of basalt at Spokane, Washington. The transported type, in contrast, is usually yellow. The ferric iron content affects the coloration.

Nontronite may be recognized generally by its yellow-green color in hand specimen plus its brown color (due to heating) in thin section. These features enable recognition of small localized areas of nontronite among other clay minerals. Nontronite is also characterized by relatively high indices of refraction which are due principally to its high ferric iron content (Table 2).

#### *Pleochroism*

Generally, minerals of the montmorillonite group are light colored and exhibit no pleochroism, but those examples that exhibit color show distinct pleochroism (Ross and Hendricks, 1945, p. 57). Thus, films of nontronite from Spokane, Washington, and Sandy Ridge, North Carolina, are bright green parallel to the elongation, and yellow perpendicular to that direction.

#### *Electron Micrographs*

Poor crystallization is characteristic of nontronite, a condition to be expected since this mineral is a member of the montmorillonite group. A

Sample Number	Locality	Ferric Iron Content Percent	Alpha	Beta	Gamma	Birefringence
33a	Garfield, Washington	29.46	1.567		1.605	.038
33 <sub>b</sub>	Manito, Washington	31.24	1.565		1.602	.037
58	Spokane, Washington	18.54	1.568	$\overline{\phantom{0}}$	1.606	.038
59	Spokane, Washington	29.57	1.570	1.590	1.600	.030
65	Sandy Ridge, N.C.	27.47	1.590		1.630	.040

TABLE 2. - EFFECT OF FERRIC IRON IN NONTRONITE ON INDICES OF REFRACTION AND BIREFRINGENCEl

1 Data from Ross and Hendricks (1945, p. 55) and Main (1950, p. 51).

tendency to form lathlike crystals is indicated, although a frayed appearance of the edges and ends is suggestive of montmorillonite. Faint striations parallel to the length are observed in the Garfield, Washington, sample (33a).

The micaceous cleavage of nontronite has been observed in thin sections (Ross and Hendricks, 1945, p. 58).

Presence of ferric iron in the lattice has been described as the principal cause of the ribbonlike habit of nontronite owing to the greater ionic radius of ferric iron. The produced strain, while restricting the width of a layer, permits elongational growth.

# *Thermal Analyses*

Differential thermal curves of four nontronites may be compared with curves from three montmorillonites in Kerr, Kulp, and Hamilton (1950, figs\_ 15, 18). Two of the nontronites shown (33a and 33b) exhibit considerable substitution of aluminum for silicon in tetrahedral coordination. Ferric ions dominate the octahedral position. The alkali content is low.

Calcium, the interlayer ion, is the cause of the initial pronounced endothermic peak, a feature common to both nontronites and montmorillonites. This peak temperature, however, is narrower in the nontronites studied (170° to 190 $^{\circ}$ C) than in the montmorillonites (140 $^{\circ}$  to 190 $^{\circ}$ C).

Two of the significant differences between the thermal curves of nontronites and montmorilIonites are: (1) the hydroxyl loss occurs at a considerably lower temperature than it does for montmorillonite, and (2) the hydroxyl loss is more rapid in nontronites than in montmorillonites.

**In** the nontronites studied, the hydroxyl loss is initiated at about 350°C and the peak occurs at 500° to 520°C. In contrast, the montmorillonites studied undergo initial decomposition at  $470^{\circ}$ C, and there is an average peak occurrence at 690°C.

Other significant differences discernible between the two minerals are related to (1) the lower final exothermic peak temperature in the nontronites, (2) the absence of an endothermic dip prior to the final exothermic dome, and (3) the presence of a smooth gradient in the final exothermic peak temperature in the nontronites; this anomaly is contrasted with the presence of extremely steep gradients in some montmorillonites (samples 20, 22, and 28).

In the nontronites, the final exothermic peak temperature occurs in a narrow range of from 870° to 875°C, whereas in the montmorillonites studied, this peak temperature may occur over a broad band of 130° ranging from 910° to 1,040°C (Table 3).

## *Base Exchange Curves*

Two principal factors are noted in a study of the chemical relationships of a group of selected montmorillonites in which the base-exchange capacities are determined by the isotherm method: (1) the magnitude of the calcium interlayer ion (and limited substitution by sodium) ; and (2) the value of sigma





2 Peak temperatures in degrees Centigrade.

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for ions in octahedral coordination. The base-exchange capacity is closely related to the size of the interlayer calcium ion, and the highest base-exchange capacities are found among those montmorillonites that exhibit the higher values of sigma.

Against this background study of the base-exchange capacities of montmorillonites, the writer has correlated the base-exchange curve for a selected nontronite, 33b, with those of two montmorillonites exhibiting very high baseexchange capacities (Figure 2).

It was found that the nontronite curve selected followed the curves from samples 23 and 24 despite a marked contrast in crystal structure. Yet the values of sigma, interlayer ion, and base-exchange capacity for the nontronite sample compare very closely with sample 23, as follows:



The complete study is summarized in Table 4.

#### *Infrared Absorption Analyses*

Additional proof of the correlations between these two clay minerals is afforded by infrared absorption spectra shown in Bray and Stevens (1950, pI. 13, fig. 3, and pI. 16, fig. 3) and summarized in Table 5. There is good agreement in the 6.06, 9.71, and 11.72 micron band centers. The strongest absorption band, which is common to nontronite and montmorillonite as well as hectorite, is the 9.71 micron band center, which is due to vibration of the Si-O layer. However, the nontronite sample exhibits a band center, i. e., the 12.20 micron zone, from the vibrations of the O-Fe-OH layer unique to the nontronite, which is absent from the montmorillonite.

# *Essential Constituents*

Chemical analyses of 15 selected nontronites from the United States of America, Germany, and Russia indicate a range of from 30 to 60 percent  $\rm SiO_2$ , and range of 25 to 40 percent  $\rm Fe_2O_3$ . The loci of these nontronites have been plotted on a ternary diagram plot of  $SiO<sub>2</sub>$ ,  $Fe<sub>2</sub>O<sub>3</sub>$ , and other constituents (Fig. 3).

*Silica.-The* highest percentage of silica among these samples was 49.75 percent in sample 55 from Stary-Krym in southern Russia. This locality is in the graphite mines 12 kilometers north of Mariupol in a region of the Priasov crystalline slates. Platy crusts characterize this nontronite, which exhibits a dark olive color; in local spots, however, a yellow color is evident.

The lowest percentage of silica (39.54) was found in sample 62 from Rac



FIGURE 2. - Correlation of the base-exchange curve of a nontronite (33b) with two select montmorillonites.

quarry, Szekes-Fejevar, Hungary. This nontronite is a "pinguite"-like decomposition product exhibiting a grass-green color (Erdelyi, 1927).

*Alumina.-The* highest percentage of alumina (17.65 percent) was found in sample 61 from Chevy Chase, Maryland, from a claylike zone in schist associated with a small quantity of mica. This nontronite is featured by a high silica, low ferric-iron content (Wells, 1937, p. 109).

The lowest percentage of alumina (2.94 percent) was observed in sample 56 from Woody, California. This clay mineral is found in veinlets in a garnetpyroxene rock that represents roof pendants of a metamorphosed limestone included in granodiorite (Larsen and Steiger, 1928).

*Ferric iron.*—The highest percentage occurrence of ferric iron (30.32) in the true nontronites is found in sample 62 described above. Only 13.08 percent of ferric iron is found in sample 57, representing the other extreme, from Petrovsk, Krivoi-Rog region, southern Russia. This clay mineral occurs: with graphite in veins from 1 to 5 mm thick and 1 to 2 cm long. It also occurs as single phenocrysts in crystalline rocks. The mineral is plastic when freshly sampled. Its color ranges from yellow green to dark green.



<sup>1</sup> Expressed as milliequivalents per 100 g of 105°C dry-weight clay.

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TABLE 4. -- CORRELATION OF BASE-EXCHANGE CAPACITY WITH CHEMICAL RELATIONSHIPS BETWEEN A NONTRONITE TABLE 4. -- CORRELATION OF BASE·ExCHANGE CAPACITY WITH CHEMICAL RELATIONSHIPS BETWEEN A NONTRONITE

AND SOME MONTMORILLONITES

MINOR CONSTITUENTS OF SOME NONTRONITES

Sample No.	Locality	(Frequency in cm <sup>-1</sup> shown in brackets) Wavelength in Microns								
		6	7	8	9	10	11	12		
Nontronite										
33 <sub>b</sub>	Manito, Washington	6.06 (1650)			9.71 (1030)		11.72 (853)	12.20 (820)		
	Montmorillonite									
23	Chambers, Arizona	6.06 (1650)		8.91 (1122)	9.62 (1040)	10.87 (920)	11.81 (847)			

TABLE 5. - CORRELATION OF INFRARED ABSORPTION BAND CENTERS BETWEEN A NONTRONITE AND A MONTMORILLONITEl

<sup>1</sup> Data from Bray and Stevens (1950).

Iron associated with clay minerals remains stable in the environment in which the minerals occur. However, alteration of both pH and Eh occurs during migration of clay minerals from a terrestrial to a marine environment; this results in (1) removal of iron by change from  $Fe^{3+}$  to  $Fe^{2+}$ , (2) ionexchange reactions, and (3) instability of the clay mineral lattice.

Adsorption of iron oxides on the surface is related to the ion-exchange capacity of kaolinite with which some nontronites are associated (Carroll, in press).

 $\hat{C}$ *hromium.*—In the lattice structure  $Cr^{2+}$  proxies for  $Fe^{3+}$ , occupying a position in octahedral coordination with respect to oxygen. The affinity of  $TiO<sub>2</sub>$ for chromic nontronites is shown in Figure 4.



FIGURE 3. - Ternary diagram of  $SiO<sub>2</sub>$ , Fe<sub>2</sub>O<sub>3</sub> and other constituents for nontronites.



FIGURE 4. - Occurrence of titanium oxide in chromic nontronites.

The normal composition of chromite has been written as simply  $FeCr<sub>2</sub>O<sub>4</sub>$ ; however, variable replacements of Fe<sup>2+</sup> by Mg<sup>2+</sup>, and of Cr<sup>2+</sup> by Al<sup>3+</sup> and Fe<sup>3+</sup> occur. Chromite is a common- accessory in peridotites and in the serpentines



FIGURE 5. -- Weight percentage graphs of some nontronites showing replacement of  $Cr^{2+}$ by  $Al^{3+}$  and  $Fe^{3+}$ .

derived from them. This mineral forms during solidification of the magma. Chemical composition of some chromic nontronite is shown in Figure 5.

#### *Minor Constituents*

*Titanium.-*Titanium is widely distributed throughout the crust of the earth as the oxide; it is relatively abundant, being ninth in order and next below magnesum. Of 800 igneous rocks analyzed by the United States Geological Survey, 784 were found to contain titanium. The three minerals composed essentially of titanium dioxide are rutile, brookite, and anatase.

The soluble salts of titanium are readily hydrolyzed and carried into the clay minerals. Titanium is commonly present in the layer-lattice silicates. Thus  $Ti^{4+}$  is considered to replace  $Mg^{2+}$  or  $Al^{3+}$ ; it exhibits octahedral coordination with respect to oxygen. However, titanium, as in the micas, mayor may not be present as part of the crystal structure (Ross and Hendricks, 1945) .

Titanium is a relatively rare minor constituent in the nontronites. The presence of titanium was reported in only 3 of the 15 nontronites studied. Where  $TiO<sub>2</sub>$  was present, an appreciable amount of MgO was reported, thus:



*Magnesium.-It* is well known that magnesium may replace aluminum in octahedral coordination with respect to oxygen, a substitution which causes deficiency in valence. This deficiency is balanced by the exchangeable ions lying between the sheets. In the nontronites, the magnitude of MgO is generally proportional to the value of sigma in octahedral coordination with respect to oxygen, as shown in Figure 6.

*Ferrous iron.*—Organic material in association with certain bacteria results in reducing conditions in the clay-forming system. This may be brought about, either by direct supply of  $Fe^{2+}$  or by means of its higher solubility, which would increase the amount of iron available to the clay-forming system (Ross and Hendricks, 1945).

In the nontronites, ferrous iron is present in amounts from a trace up to 1.37 percent. The latter amount was measured in sample 67 from Paulusbrunn near Tachau, Germany, where the nontronite is a light-green, compact alteration product of hornblende·rich gneiss (NolI, 1930).

The second highest occurrence of ferrous iron was 0.99 percent measured in sample 56 from Woody, California, where the nontronite was found in veinlets in a garnet-pyroxene rock.



#### *Interlayer Ions*

The principal factors affecting those ions which occupy interlayer positions are: (1) chemical environment, (2) concentration, and (3) preferential adsorption (Ross, personal communication, 1949).

A deficiency of alkalis typifies the chemical composition of montmorillonite and this condition is likewise true in most nontronites. But the occurrence of potassium in clays is unlike that of sodium.

*Potassium.-The* occurrence of potassium in nontronite is limited to a narrow statistical range of between 0.5 and 0.6 ions of Al in tetrahedral coordination vs. an extreme deficiency of ferric iron and magnesium (combined) of less than 0.05 ion in octahedral coordination. Note this limited occurrence in Figure 7.

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 $FIGURE 7. - Role of potassium in nontronites.$ 

Although potassium goes into solution first among the interlayer ions, it does not remain in solution and often is adsorbed and occasionally enriched among the clay minerals.

*Sodium.-In* contrast to the behavior of potassium in the clays, sodium, after extraction from rocks during weathering, is removed from the environment. The result is a net loss of sodium from the sediments.

*Calcium.-Calcium* occurs in nontronite as the principal interlayer cation and is present in nearly all the nontronites studied. The range of the magnitude of the Ca ion is from 0.26 to 0.53 ion, with predominance from 0.35 to 0.45 ion.

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