

Primary Nontronite From the Venezuelan Guayana

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Abstract

Nontronite, the iron-rich end member of Smectite Group clays, has previously been reported as a hydrothermal alteration product, as a constituent of soil clays formed by weathering of a variety of rock types, and as an alteration product of volcanic rocks. This paper describes the chemical, optical, and X-ray properties of a new occurrence of the mineral where its origin is apparently related to direct crystallization from high temperature waters. The mineral is further unique in that it contains only a very small percentage of alumina and thereby closely approaches the previously unreported wholly iron end-member.

Significant differences were found in the optical properties of the Venezuelan nontronite when compared with those of an earlier study, especially with regard to the variation in refractive index with Fe_2O_3 content. It now appears that this variation has been over-simplified and may not be as orderly as was previously believed. The various lines of evidence that argue against an origin by either hydrothermal alteration or chemical weathering are discussed, as well as those supporting an origin by direct crystallization from high temperature waters of probable magmatic or metamorphic origin.

Introduction

Nontronite is a Smectite Group clay mineral which occurs as the iron-rich end-member in the dioctahedral sub-group montmorillonite-beidellite-nontronite series. It has previously been reported as a constituent of sedimentary rocks, as the product of alteration of volcanic glasses and as a hydrothermal alteration product. This paper describes the chemical, optical, and X-ray properties of a specimen from a recently discovered new occurrence in southern Venezuela. Here the nontronite is apparently unrelated to weathering or alteration of previous minerals and has formed by crystallization from waters of hydrothermal or possibly metamorphic origin. The chemistry of the mineral from this location is also unusual in that it contains essentially no alumina and approaches the composition of the previously unreported theoretical end member.

Geological Occurrence

Ross and Hendricks (1945) in their detailed treatment of montmorillonite clays listed 13 locations where nontronite had previously been described. Of these, 7 were in the United States, 3 in the Soviet Union, 2 in Germany, and 1 in Hungary. At 8 of the 13 locations, the mineral was associated with metamorphic rocks and occurred as an alteration

product in gneisses and slates. At the other sites, nontronite was reported as forming narrow veinlets in both igneous and metamorphic rocks and was assumed to be an alteration product. At the type locality, Nontron, France, Berthier (1827) described the mineral as occurring as "onion-like" masses associated with manganese ore of Perigux, near the village of Saint Pardoux. Allen and Scheid (1946) identified nontronite in altered basalts of the Columbia River region and attributed it to the weathering of basaltic glass, palagonite, iddingsite, and augite under conditions of poor drainage. Similarly, Sherman *et al* (1962) described nontronite in weathered basalts and andesites from Australia, New Zealand, Fiji, and Hawaii where it was reported to have formed under a variety of climatic conditions, by chemical weathering.

Venezuelan Occurrence

The mineral described in this paper was found 2 km south of the Orinoco River on Federal Highway 19, 15 kilometers north of the turnoff to Guri Dam. Here it occurred as an intrusion within granitic rocks of the Precambrian Imataca Complex (see map, Fig. 1). The main intrusion, where exposed in a new road-cut, is approximately 2 meters thick and 3½ meters high. Numerous smaller veinlets could be seen extending outward into the surrounding granites. The

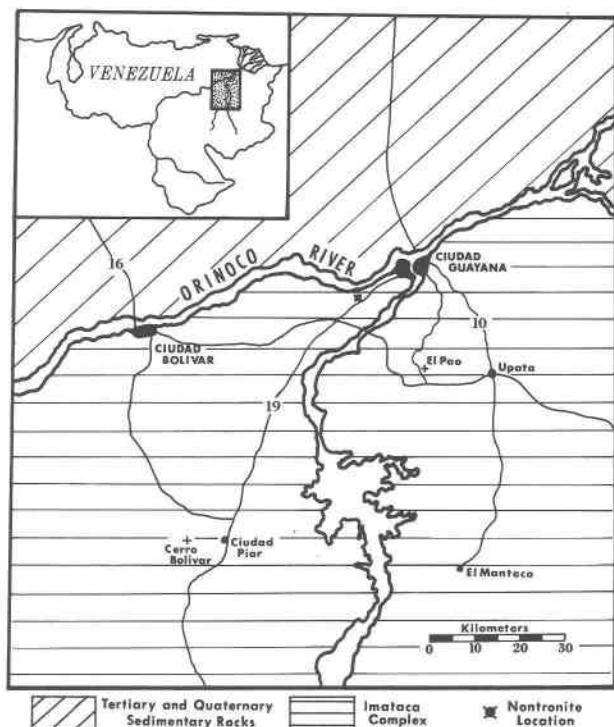


Fig. 1. Map showing Venezuelan nontronite locality and outcrop of Precambrian and younger rocks in study area.

nontronite was a uniform, yellow-green (10Y 6/6), dense mass containing occasional thin (2-5 mm) stringers of specular hematite. Though not chemically analyzed, a similar, but smaller, exposure of the same material was also seen 25 km to the southeast in the open pit iron mine of the Bethlehem Steel Corporation at El Pao.

Laboratory Analysis

Chemistry

Ross and Hendricks (1945) listed 13 reported analyses of samples considered to represent relatively pure nontronite (those containing down to two atoms of iron per unit cell layer). The composition of the

dioctahedral iron end-member of the beidellite-nontronite series was given as:



but analyses corresponding to this chemical formula had not been reported. The type mineral from Nontron, France, was included with analyses from an additional 13 samples that were judged to contain an "iron-bearing" impurity, based on the fact that the chemical analyses showed these to contain more iron than could be accommodated in the octahedral sites. The 13 "pure" samples are shown in Table 1 along with one analysis reported by Kerr and Pill (1950); sample #15 is the Venezuelan nontronite described in this paper. Analysis #16 is the "type" mineral from Nontron, France, and is included for comparative purposes.

The most striking difference between the Venezuelan nontronite and the others listed in Table 1 is that of alumina content. The other published analyses show a range in Al_2O_3 from 2.94 to 17.65 percent, with a mean value of 9.55 percent. The Venezuelan nontronite, with an alumina content of only 0.27 percent, contains one-tenth that of the lowest previously reported analysis. The significance of this low alumina content has bearing not only on the existence of a complete solid solution series extending from beidellite, $(\text{Si}_{7.33}\text{Al}_{0.67})(\text{Al}_4)\text{O}_{20}(\text{OH})_4$, to nontronite, but on the origin of this unique deposit as well.

The existence of a complete solid solution series including montmorillonite and beidellite was first proposed by Collins (1877) and has since been largely confirmed in several later reports (see Gruner, 1935; Ross and Hendricks, 1945). The existence of a solid solution series extending from beidellite to the iron-rich end member, nontronite, is a later development and was proposed by Ross and Shannon (1925) and Larsen and Steiger (1928) and, similarly, Ross and Hendricks did much to verify its existence. They dis-

TABLE 1. Chemical Analyses (in percent) of Nontronite¹

Sample Number:	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16
SiO ₂	49.75	43.51	49.50	46.06	40.72	40.48	46.05	39.54	42.74	40.42	41.38	41.88	40.02	40.54	49.90	48.82
Al ₂ O ₃	10.06	2.94	16.18	12.22	4.96	6.00	17.65	6.04	9.76	10.42	9.84	11.90	10.55	5.19	0.27	4.30
Fe ₂ O ₃	22.06	29.61	13.08	18.82	30.28	29.59	18.39	30.32	26.71	25.76	27.47	26.20	27.53	31.63	29.50	35.88
MgO	0.25	0.05	0.61	1.62	0.74	0.1	tr	tr	1.06	0.13	tr	0.10	0.06	1.75	0.35
CaO	2.68	2.22	2.57	1.66	1.98	2.90	1.21	0.04	1.94	0.38	tr	0.67	1.92	0.77
K ₂ O	0.55	0.32	tr	0.52	0.24	0.01
Na ₂ O	0.55	0.24	tr	0.52	0.14	0.12
H ₂ O	15.87	20.67	17.11	17.26	22.12	21.04	16.36	22.27	17.16	21.80	21.35	18.45	21.83	20.75	16.12	9.66

¹ Samples 1-13 from Ross and Hendricks (1945); Sample 14 from Kerr and Pill (1950); Sample 15 from Venezuelan locality; Sample 16 from Nontron, France.

cussed, at length, the then available information on the chemical variation among nontronites, but admitted that wider variation might exist. Evidence was present, they believed, to support their contention that a solid-solution series existed with limited-to-extensive substitution of aluminum for silicon in the tetrahedral sites, and of iron for aluminum in the octahedral sites. The chemical analyses carried out on the Venezuelan nontronite confirm this belief. Thus, unlike the wholly iron end-members of both the enstatite-ferrosilite and phlogopite-annite series, the iron-rich end-member of the beidellite-nontronite series is stable and can form during natural geologic processes. The extremely low aluminum substitution in the octahedral and tetrahedral sites results in an oxide chemical formula for this mineral of:



or, in terms of octahedral-tetrahedral site occupancy:



The very limited substitution of aluminum for silicon creates only a slightly unbalanced charge in the tetrahedral layer. Hence the presence of small amounts of sodium (0.02%) and calcium (0.77%) in the interlayer sites is largely due to excess charges arising in the octahedral layer caused by the undetermined amount of iron present as Fe^{2+} . The cation exchange capacity was predictably low, therefore, when compared with other Smectite Group clays, with a value of 48.9 m.e.q./100 grams soil obtained using the ammonia extraction procedure.

The information derived from the chemical analysis of the nontronite has also forced a re-examination of some generalizations made by Ross and Hendricks (1945) in their exhaustive study of the Smectite Group minerals. For example, a major contradiction was found to exist in the interpretation of optical data (discussed in the next section) and with regard to statements concerning the general chemistry of nontronites. Ross and Hendricks noted that (1945, p. 45) “. . . nontronites contain relatively small amounts of magnesium. This relationship is particularly true for the specimens having chiefly Fe^{+3} in octahedral coordination. . . . of the four samples containing less than 0.12 Al^{+3} in octahedral coordination, the highest was 0.04 Mg^{+2} .” Though this generalization does hold for the 13 nontronites considered by them as “pure” samples, it is not warranted if the MgO content of the 13 other samples included in their paper is considered (those containing an iron-bearing impurity). Ross and Hendricks

probably discounted these, believing that the higher MgO percentages (1.45 percent average versus 0.37 percent in the uncontaminated samples) could be attributed to MgO in mixed-layer clays. Based on the samples available for their analysis, they cannot be faulted for this logic. However, the Venezuelan nontronite does not support their conclusion. Though containing significantly lower octahedral and tetrahedral alumina than any of the samples used by Ross and Hendricks, the MgO content is nearly five times higher than that found in their analyses. X-ray diffraction studies on the Venezuelan material failed to disclose any reflections from mixed-layer clays; hence it is concluded that the magnesium is present in octahedral coordination in the nontronite and that the correlation of low alumina content with low magnesium was more apparent than real.

Optical Analysis

With regard to the optical properties of montmorillonites, Ross and Hendricks (1945) noted that these can be less definitely determined than those for, possibly, any other mineral group. This results from a number of factors, among which are: (1) the lack of observable crystals, (2) the tendency of these minerals to absorb immersion oils and, hence, undergo a change in refractive index, (3) the stacking order of the individual sheets, (4) their susceptibility to chemical weathering, and (5) the finely crystalline nature of these minerals in general coupled with their tendency to occur as micro-crystalline aggregates.

Using samples of the Venezuelan nontronite that had been crushed and then dis-aggregated in an ultrasonic separator, optical measurements were made on finely dispersed dried films, using the method described by Grim (1934), and on individual crystals in the 44-62 micro-size range. The nontronite proved to be biaxial (–) with $\alpha = 1.554$, $\beta = 1.590$, $\gamma = 1.594$, all ± 0.002 . The $2V$ angle was measured as 35° , using a micrometer ocular. Grains yielding centered biaxial (–) interference figures were non-pleochroic but varied in color from pale brown to yellowish brown.

The optical information obtained from the Venezuelan nontronite does not agree with certain observations made by Ross and Hendricks, especially with regard to variation of the α and γ indices with Fe_2O_3 content. Their chart (see Fig. 2), since reproduced in several standard references dealing with the optical properties of smectite clay minerals (see Heinrich, 1964; Deer, Howie, and Zussman, Vol. 3, 1962), predicts for the Venezuelan nontronite a

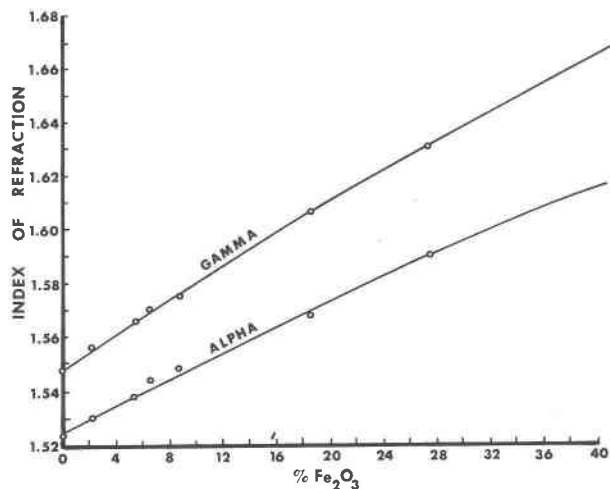


FIG. 2. Ross and Hendricks' (1945) chart showing variation in Fe_2O_3 content with α and γ indices of refraction.

value of approximately 15 percent Fe_2O_3 from its γ index and of 11.5 percent Fe_2O_3 using α . These differ significantly from the 29.5 percent obtained using the atomic absorption spectrophotometer. Because of this unexpected difference, an examination was made of the basis and rationale for the construction of Ross and Hendricks' chart. These are summarized below:

- (1) The curves are based on optical and chemical data from 7 samples whose ferric iron content ranged from 0.06 to 27.47 percent. Only 2 of the samples were true nontronites; the remainder were members of the montmorillonite-beidellite series.
- (2) The curves represent the "best fit" of the 7 analyses and were simply extended beyond the ferric iron content of the last analysis (27.47 percent) to 40 percent, based on the belief that the refractive index would continue to increase with Fe_2O_3 content.

Ross and Hendricks noted (p. 55) that, from the standpoint of variation in refractive index with iron content, those data points plotted show "... a very consistent relation." They further state, however, (p. 55) that "... a number of indices of low-iron members given in (their) Table 14 fail to fit this curve." They attributed this to several factors but believed that in high and moderately high iron members that the iron content was the dominant factor controlling refractive index, whereas in low iron members other factors did so (*e.g.*, aluminum:silicon ratio, water content, *etc.*). To determine the total actual amount of variation that exists in the beidellite-nontronite series, it was decided to plot

all the optical and chemical information listed in Ross and Hendricks' article, along with other, more recent, published data on nontronites. The data points shown in Figure 3 include the 7 analyses used by Ross and Hendricks to construct their curves but also included are 15 analyses omitted by them because either (1) the samples contained excess iron and were considered "impure" or (2) the data did not fit the α and γ curves because of low iron content. The writer has included data points from the "impure" samples because Ross and Hendricks noted that the amount of excess iron in these samples was generally very low and because several of the samples yielded refractive indices not greatly different from the Venezuelan nontronite. Seven of the 15 samples plotted are those excluded by Ross and Hendricks because of low iron content. They are included here because, since Ross and Hendricks used 5 such samples to derive their curves, it would seem reasonable to include all such samples available to determine the actual curve configuration.

Examination of Figure 3 immediately suggests that the use of refractive index to predict ferric iron content in nontronite will, at best, be hazardous and will frequently yield only a crude estimate of the actual percentage. Considerably more variation exists in iron content versus refractive index than is suggested by the smooth curves published by Ross and Hendricks. Their assumption that the ferric iron content increases with refractive index is, roughly, valid up to approximately 28 percent ferric iron. Past this value, there is a visible trend toward a *decrease* in index of refraction with increase in iron. In light of the large amount of scatter seen between iron contents of 0 to 10 percent and 28 to 32 percent, the writer questions whether any significant conclusions are warranted from refractive index data. Even in the central portion of the curves (between 10 and 28 percent iron), the curves are based on only three data points and future analyses could, conceivably, alter the smoothness of this portion of the α and γ curves. Until such additional data is forthcoming, the published curves of Ross and Hendricks should be used with advised caution.

X-ray Diffraction Analysis

Only a limited amount of data has been published dealing with the X-ray analysis of nontronite. Gruner (1935) determined the average dimensions of the nontronite unit cell as $a_0 = 5.23 \text{ \AA}$, $b_0 = 9.06 \text{ \AA}$ based on the analysis of six samples. Since the β crystallographic angle was unknown, the c_0 dimen-

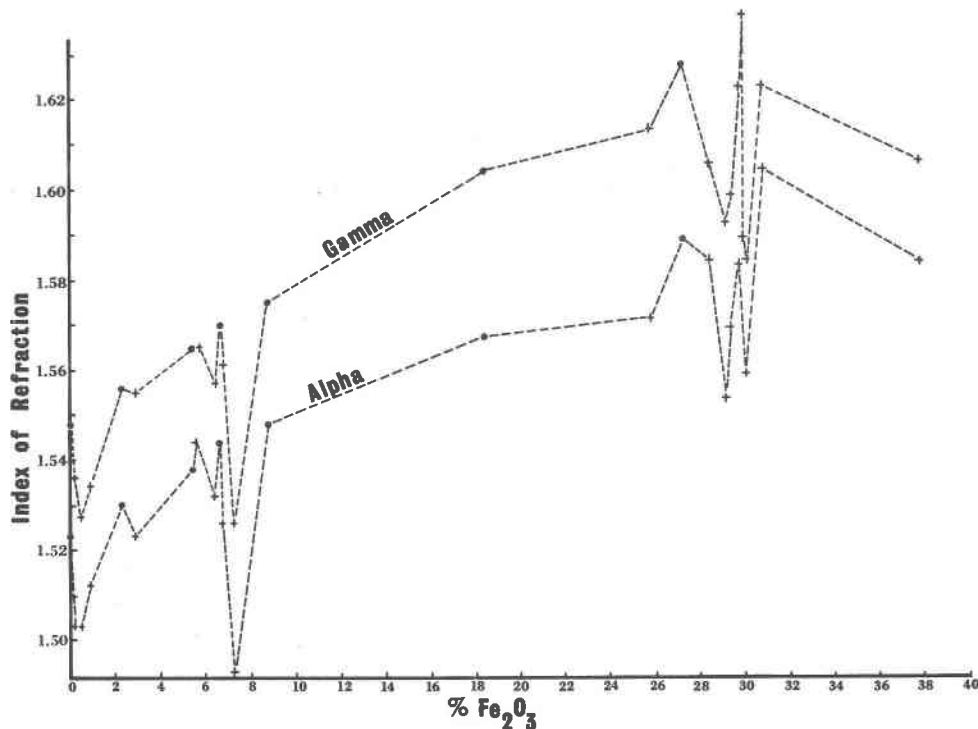


FIG. 3. Variation in α and γ indices of refraction with Fe_2O_3 content. Solid circles are samples used by Ross and Hendricks (1945); crosses are from other samples for which optical and chemical data was available.

sion was not calculated; Gruner did list the d_{02} dimension as 12.4 – 12.7 Å, however, depending on the amount of water present in the inter-layer positions. Nagelschmidt (1938) examined nontronite clays from the type location (Nontron, France) and from Behenjy, Madagascar, and calculated the a_0 and b_0 dimensions for both as 5.23 and 9.11 Å, respectively. The d_{02} dimension for these two samples was somewhat larger than that determined by Gruner and was given as 15.6 Å for the specimen from Madagascar and 15.4 Å for the sample from France. Since nontronite closely approximates an orthohexagonal lattice, the d_{02} can be considered as a very close approximation of the c_0 dimension. The sample from Venezuela produced results comparable to those of Nagelschmidt (1938) in that the b_0 dimension was found to be 9.117 Å. This dimension was determined using the equation of Brindley and MacEwan (1953) for dioctahedral clays for which $b(\text{Å}) = 8.92 + 0.06x + 0.09q + 0.18r + 0.27s$ (where p , q , r , and s are the numbers of Al^{3+} , Fe^{3+} , Mg^{2+} , and Fe^{2+} ions per half cell layer in octahedral coordination and x is the number Al^{3+} ions in tetrahedral coordination). Since the cell is essentially orthohexagonal, Brown (1961) states that the $a:b$ ratio is $1:\sqrt{3}$. Therefore

the a_0 dimension for the Venezuelan nontronite was calculated as $9.117\sqrt{3} = 5.264$ Å. The d_{02} was variable but averaged 14.80 Å. Treatment with glycerine caused the d_{02} peak to shift (expand) to approximately 19.4 Å (see Fig. 4). Heating to 300°C for 7 hours collapsed the peak to 14.3 Å; further collapse to 9.6 Å occurred when the sample was heated to 650°C for 10 hours. Total collapse of the lattice was effected by heating to 1,000°C for 4 hours and, as seen on Figure 4, only cristobalite peaks are visible on the diffractogram. Table 2 lists a comparison of powder camera data from Gruner (1935), Nagelschmidt (1938), and for the Venezuelan nontronite.

Origin

General Discussion

Montmorillonite clays, as a group, have been most frequently attributed to the weathering of volcanic detritus. They have also been described as the products of the alteration of muscovite, biotite, chlorite, serpentine, and hornblende in a variety of rocks and, as such, are often found as the principal constituents of some soil clays (see Weaver, 1958). More recently, Jeans (1968) has shown that many

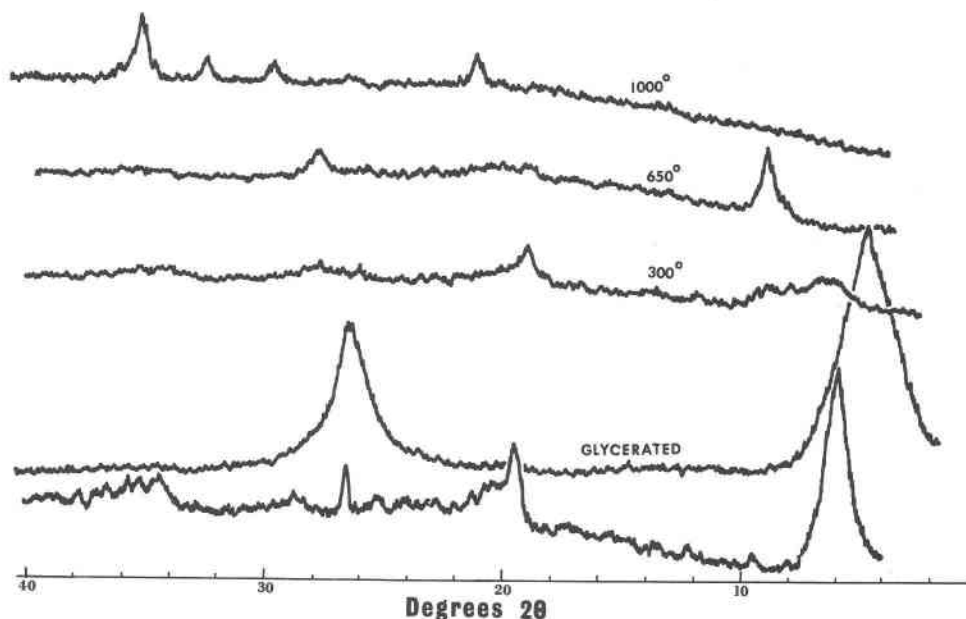


FIG. 4. X-ray diffractograms for untreated nontronite, glycerated sample, and samples heated to 300, 650 and 1,000°C (Copper $K\alpha$ radiation).

montmorillonites may actually be the products of direct crystallization in marine waters of normal salinity. Ross and Hendricks (1945) discussed the origin of vein and gouge clays of the montmorillonite-beidellite series and attributed them to the alteration of prior aluminous minerals (feldspar, tourmaline, spodumene, etc) by late stage hydrothermal fluids and by crystallization from low temperature waters. Nontronite clays were reported by Allen and Scheid (1946) to have formed as altera-

tion products of volcanic glass in the basalt flows of the Columbia River Plateau. Ross and Hendricks (1945) noted that a number of samples of nontronite have been reported as forming veins of unknown origin in the schists of the southern Piedmont.

Because the Venezuelan nontronite is exposed on the surface, an origin by chemical weathering was considered. Since it is also an obvious intrusion into the surrounding host-rock granites, an origin involving either hydrothermal alteration or direct crystallization from high temperature waters was also investigated.

Origin by Weathering

Genesis of the Venezuelan nontronite by surficial weathering can be quickly discounted for a number of reasons. First, the surrounding granitic rocks into which the nontronite is intruded show only slight evidence of chemical weathering, and this only in the upper half meter of the recently exposed highway cut. Even if selective chemical weathering is postulated for the primary vein minerals, the normally expected weathering product for this warm humid region would be kaolinite, accompanied by sesquioxides of alumina and iron. If the parent rock were presumed an iron-rich serpentine (rather than gabbro or diabase), other problems are encountered. Notwithstanding the fact that no such rocks have been previously reported in this area, the weathering

TABLE 2. Diffraction Data for Nontronite Samples

Venezuelan Nontronite		Behenuy, Madagascar*		Nontron, France		Faratsiho, Madagascar**	
Å	I	Å	I	Å	I	Å	I
14.80	vs	15.6	vs	15.4	vs	13.9	vs
4.50	s	4.55	vs	4.56	vs	7.1	w
4.27	w	3.11	w	3.11	w	4.44	vs
3.34	s	2.98	w	3.03	w	3.54	s
2.62	w	2.62	vs	2.64	vs	2.79	vw
2.61	vw	2.56	vs	2.56	vs	2.59	w-s
1.81	vw	1.72	s	2.43	s	2.51	w
1.73	vw	1.67	s	1.72	s	2.27	vw
1.69	vw	1.52	vs	1.67	s	1.72	w
1.53	s	1.32	s	1.52	vs	1.68	w
1.37	w	1.32	s	1.32	w	1.63	w
1.40	w	1.30	s	1.30	w	1.52	w
1.31	vw(?)	1.27	s	1.26	w	1.48	s
1.29	vw(?)	1.25	s			1.45	vw
1.25	vw(?)					1.31	vw

* Data from Nagelschmidt (1938)

** Data from Gruner (1935)

Venezuelan specimen analyzed using 57.3 millimeter diameter Debye-Scherrer camera, nickel-filtered, $CuK\alpha$ radiation.

chemistry of serpentine would present difficulties. Wildman, Whittig, and Jackson (1971) have shown that within the usual range of pH and low activities of Fe^{3+} , Al^{3+} , AlO_2^- , and Mg^{2+} encountered in soil matrix solutions, both $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ will be stable in the octahedral layers. If silica were present in sufficient concentration in the matrix solution, the formation of a layer silicate would provide a lower energy state for the iron and aluminum ions than is provided by their hydroxides. The result would be the formation of montmorillonite, rather than nontronite. This is caused by the fact that in the pH range of tropical soils, the percentage of alumina and iron remains essentially unchanged (in the pH range 4.5-9.0) because of their similar low solubilities (see Loughnan, 1969). If, in order to explain the low alumina content, a peridotite is assumed as the parent rock, then the end products of weathering, according to Loughnan (1969), would be iron oxides and saponite (the magnesium analog of nontronite). If an iron-rich peridotite or picritic diabase were the parent rock, then weathering could result in the formation of nontronite. Such an occurrence has been described by Sherman *et al* (1962) but only under conditions of low rainfall (15 inches per year). Even under such conditions, however, the mineral was reported to form only coatings surrounding unweathered olivine grains in picrite basalt. Again, it should be pointed out that although diabase, meta-gabbros, and amphibolites are present throughout the Imataca Complex; no serpentines, basalts, nor peridotites have been reported (see de Ratmiroff, 1964; Chase, 1963); hence, these are unlikely to have served as the parent rock.

An additional line of evidence that argues against an origin for the nontronite by the chemical alteration of any previous mineral is the high purity of the material. Optical and X-ray diffraction analyses disclose no "unaltered" minerals that could have served as a source for the nontronite, and electron photomicrographs at 1000 \times and 3000 \times similarly confirmed the material to be pure and essentially homogeneous (see Fig. 5). Further, crushed samples of the nontronite were placed in acetylene tetrabromide (sp. gr. = 2.96) to determine what heavy minerals, other than visually observed specular hematite, might be present, with the belief that these might give evidence as to the identity of some possible parent rock type. None were found to be present in any of the four crushed samples analyzed. If the nontronite were, in fact, the product of the alteration of either acid, intermediate, basic, or ultrabasic igneous rocks, it would be expected that small amounts

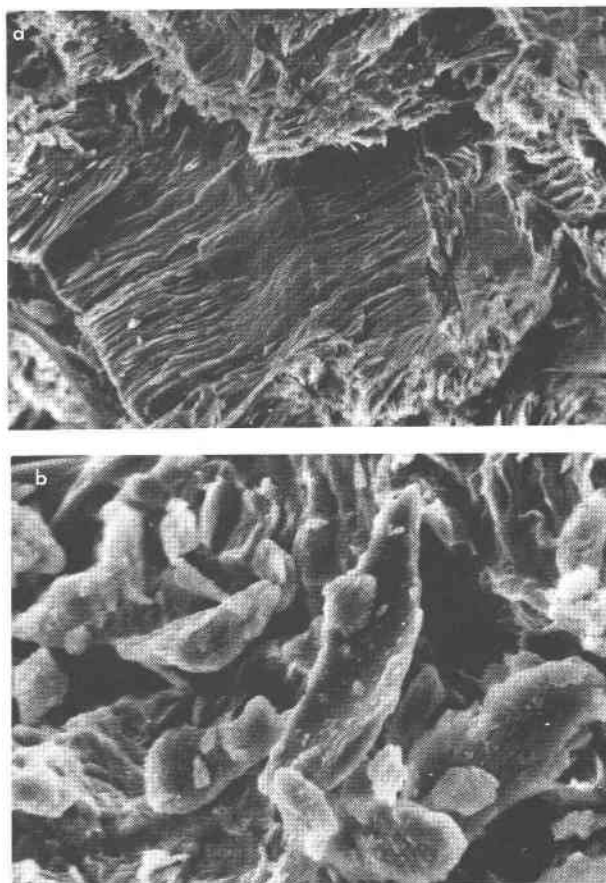


FIG. 5. Electron photomicrographs of Venezuelan nontronite samples. a. $\times 1000$; b. $\times 3000$.

of resistant minerals such as anatase, spinel, leucosene, ilmenite, apatite, sphene, zircon, garnet, *etc.*, should have survived the alteration process and be present. These have been reported (Chase, 1963) as common constituents of the igneous rocks of the Imataca Complex. Their complete absence is difficult to explain if the nontronite originated by simple chemical weathering. Finally, if the nontronite were the product of the weathering and alteration of previous rock-forming minerals of any type, at least a small quantity of either kaolinite or mixed-layer clays (or both) would be expected to appear on the diffractograms. Instead, these were found to be completely lacking. In an occurrence of nontronite reported by Hosking (1957), where the mineral was present as a weathering product of red-brown earths derived from hornblende granite, the sample was found to consist chiefly of halloysite, with nontronite present only in minor amounts. Allen and Scheid (1946), in their discussion of nontronite veins resulting from the weathering of basalt, presented photomicrographs that showed iddingsite, augite, plagioclase, volcanic

glass, and ilmenite *partially* altered to nontronite. In many cases the original minerals remained unaltered and were clearly discernible. Hence, the lack of any kaolinite, halloysite, or mixed layer clays in the Venezuelan nontronite, coupled with the complete lack of remnant minerals or residual heavy minerals, is strong evidence against its origin by chemical weathering.

Origin by Hydrothermal Alteration

Some of the arguments raised in opposition to an origin by chemical weathering apply also to one calling upon hydrothermal alteration of primary vein minerals. Again, the difficulty exists in finding a suitable parent rock that could give rise to the highly pure nontronite, even assuming an open thermodynamic system with addition and/or removal of mobile ions. Grim (1953) states that, in many or perhaps most instances, the hydrothermal alteration products consist of a mixture of several clay minerals, with mixed-layer clays invariably present. As mentioned under the discussion of chemical weathering, other clay minerals were conspicuously absent in diffractograms of the Venezuelan nontronite.

Another feature commonly exhibited by clays formed by hydrothermal alteration, which is also lacking in the Venezuelan occurrence, is the typical zonal arrangement of the constituent clays. Clays formed by hydrothermal alteration commonly display a central core of fine-grained white mica (sericite) which passes outward to kaolinite and/or montmorillonite, followed by an outer zone made up largely of chlorite. No zonal arrangement was found in the Venezuelan intrusion, and samples taken near the contact with the host rock were identical, mineralogically, to those in the center portions of the vein.

A further argument against an origin by hydrothermal alteration involves the extremely low alkali content of the nontronite. Krauskopf (1967) notes that, in addition to any metals and sulfur that might be present, hydrothermal waters would be expected to contain silica, the cations Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and anions such as Cl^- , SO_4^{2-} , HCO_3^- , etc. Because of their mobility in hydrothermal fluids, particularly those containing chlorides, Na^+ , K^+ , and Ca^{2+} ions commonly are found in the inter-layer exchange positions in hydrothermal montmorillonites. Their near complete absence in the Venezuelan nontronite is conspicuous and argues against its formation by hydrothermal alteration (see Table 1).

A final argument against hydrothermal alteration again concerns the lack of *any* remnant primary

minerals or residual heavy minerals, some of which should survive any alteration process. Regardless whether the parent rocks were acid, basic, or ultrabasic in composition, some remnant grains should be found. Partially altered grains were reported to be widespread in the nontronite clays found within basalts in the Columbia River region (see Allen and Scheid, 1946). Heavy minerals such as rutile, spinel, ilmenite, and zircon also are resistant to the attack of hydrothermal solutions and would be expected to remain essentially unaffected.

Primary Origin for the Venezuelan Nontronite

The unusually high iron, low alumina, low alkali composition of the Venezuelan nontronite, coupled with the lack of other associated clay minerals, remnant minerals, and resistant heavy minerals, suggests that it may be the product of direct crystallization from siliceous fluids rich in dissolved iron. Chase (1963) has noted that all the rocks in the Imataca Complex, except the diabase dikes, have been subjected to high grade regional metamorphism, ranging from low amphibolite to the granulite facies. The iron formations, trondhjemitites, gneisses, and amphibolites of the Imataca Complex underwent a major metamorphic event approximately 2,000 m.y. ago and were subsequently intruded by large granite plutons and later by diabase dikes. The diabase dikes are post-tectonic and have not been metamorphosed; the age of these post metamorphic intrusions is unknown; however, igneous events are known to have taken place in the area approximately 1,500 m.y. ago and during an interval from 800-1,070 m.y. ago, based on radiogenic ages from granites. Chase (1963) notes that these dates were obtained using only one method and are, therefore, not reliable indicators of either metamorphic or igneous events. Regardless, the presence of the ubiquitous siliceous iron formations throughout the Imataca Complex testifies to the availability of both a source of iron and silica. Though probably magmatic in origin, the waters needed to dissolve these ions may be related to Precambrian metamorphic events that occurred in the region. It has long been established that high temperature water with its high dielectric constant can react with and dissolve a wide range of ionic crystalline minerals. Following dissolution, a change in environmental conditions (reduction in temperature, change in pH, etc) may reprecipitate hydrated or hydroxyl-bearing minerals. Past studies have shown that montmorillonite can form, hydrothermally, and exist up to temperatures of 450°C (Ellis, 1967). Ewell and Insley (1935) synthesized nontronite by heating

$\text{Fe}_2\text{O}_3\text{-}2\text{SiO}_2$ gels for 6 days in a sealed bomb and noted that it was stable up to temperatures of 340°-350°C. Hence, the ability of various clay minerals to form by direct crystallization from high temperature waters has been clearly established. It is therefore postulated that high temperature waters, either of magmatic or metamorphic origin, locally dissolved iron and silica from the abundant iron formations and later, on cooling, directly deposited nontronite in their present host rocks. Such an origin explains the unusual chemistry of this mineral and the other anomalous features associated with its occurrence. Though the presence of most clay minerals found in veins has long been attributed to hydrothermal alteration (see Grim, 1953; Deer, Howie, and Zussman, 1962; *etc*), the fact that kaolinite, dickite, beidellite, and nontronite have been directly synthesized from high temperature waters indicates that, under appropriate circumstances, a primary origin for them in some geologic occurrence would not be entirely unexpected.

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