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## DEHYDRATION AND OPTICAL STUDIES OF ALUNOGEN, NONTRONITE AND GRIFFITHITE.

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### I. THE OPTICAL PROPERTIES AND DEHYDRATION OF ALUNOGEN.

*Introduction.* A specimen labelled "Mendozite, Pinto da Canon, New Mexico," kindly furnished the authors by Mr. Frederick A. Canfield, had optical properties that differed from those of any mineral known to the authors. An analysis showed the mineral to be alunogen and upon further study the optical properties of alunogen were found to vary considerably, probably due to a variable water content.

*Optical properties.* The alunogen from New Mexico is in the usual soft, white fibers, somewhat more coarsely crystalline than is common. The crystals are slender laths and the obtuse bisectrix (X) emerges sensibly normal to the flat face; the extinction on crystals lying on this flat face is  $Z_{\Lambda}$  elongation  $41^{\circ} \pm 2^{\circ}$ ; on edge, the laths give parallel extinction. The mineral is optically +,  $2E$  measured  $46^{\circ} \pm 5^{\circ}$ ,  $2V = 31^{\circ} \pm 3^{\circ}$ . The indices of refraction are given in the first column of Table I, and for comparison those as measured of specimens of alunogen from other localities; the measurements should not be in error more than  $\pm 0.003$ . All of the specimens are optically +, with small axial angle and large extinction angles. The differences in the values of the indices of refraction for the different specimens, as will be shown later, are probably due, in part at least, to a variable water content.

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Data described in this paper have been held for several years in the hope of an opportunity for further work and a more complete study. So far this opportunity has not materialized and having had several requests for the results the data are here presented.

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TABLE I. Indices of refraction of alunogen.

Locality	Pinta da Cañon, New Mex.	Erie Pa.	Utah	South Bolivia
$\alpha$ .....	1.460	1.470	1.473	1.475
$\beta$ .....	1.461	....	1.474	1.478
$\gamma$ .....	1.470	1.480	1.480	1.485

The flat faces of the crystals from New Mexico must be (010) and if the elongation is taken as the  $c$ -axis the optical orientation is  $X = b$ ,  $Z \wedge c = 41^\circ$ .

*Chemical analysis.* Material for an analysis was carefully selected and microscopic examination showed it to be homogeneous except for a few grains of sand. An analysis of the water-soluble portion is given in Table 2. The analysis agrees closely with the formula  $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 15\frac{1}{2}\text{H}_2\text{O}$ .

TABLE 2. Analysis and molecular ratios of alunogen from Pinto da Cañon, New Mexico. (Analyst, George Steiger.)

		Ratios
$\text{Al}_2\text{O}_3$ .....	16.59	$163 = 1.02 \times 160$
$\text{SO}_3$ .....	37.74	$472 = 2.95 \times 160$
$\text{H}_2\text{O}$ .....	44.64	$2480 = 15.50 \times 160$
Insol. ....	.94	....
	99.91	

*The dehydration of alunogen.* A one gram portion of the sample was heated at successively higher temperatures and the loss of water and the optical properties of the resulting product determined. The results are shown in Table 3 and in Fig. 1.

As shown in Table 3 there is a slight progressive change on heating until the material which had been heated to  $130^\circ$  was reached. This product showed a sharp and definite break, having gone over to the isotropic form, which form persisted in all preparations to complete dehydration, and as the water content decreased the index of refraction increased.

Referring to Fig. 1 a sharp break is observed in the dehydration curve in the neighborhood of  $90^\circ$ , this being within the region in which the material became isotropic.

Obviously the water in alunogen may vary considerably and can become as low as 39.38 per cent<sup>1</sup> which corresponds

<sup>1</sup> Per cent of water in product formed by heating to  $75^\circ$  C. after deducting impurities and recalculating to 100 per cent.

TABLE 3. The loss of H<sub>2</sub>O and corresponding change in optical properties of alunogen on heating.

Temperature C.	One gram		Indices of refraction			Remarks
	Loss of H <sub>2</sub> O	H <sub>2</sub> O retained	α	β	γ	
Before heating ..	Gms. .0000	Gms. .4464	1.460	1.461	1.470	Opt. +, 2V = 31° X = flat face, Z $\wedge$ elong. 44°
35° .....	.0061	.4403	1.474	1.475	1.486	Otherwise not appreciably changed.
75° .....	.0934	.3530	1.483	1.484	1.496	Opt. +, 2V small X = flat face, Z $\wedge$ elong. 41°
130° .....	.3172	.1292	....	1.502	....	Isotropic. Filled with gas pores.
160° .....	.3417	.1047	....	1.508	....	Do
Same after exposure to laboratory air over night	....	.1182	....	1.500	....	Do
210° .....	.3842	.0622	....	1.515	....	Do
Same after exposure to laboratory air over night	....	.0750	....	1.514	....	Do
290° .....	.4452	.0012	....	1.540	....	Isotropic. Much clouded.
Same after exposure to laboratory air over night	....	....	....	1.530	....	Do

approximately to the formula  $Al_2O_3 \cdot 3SO_3 \cdot 12\frac{1}{2}H_2O$ , the former contention as to whether alunogen contained 16 or 18 molecules of water being raised on the incorrect assumption that the water is present in a definite, fixed molecular proportion. The mineral from Pinto da Cañon, New Mexico, after being kept in a museum and laboratory in the eastern United States for years, contained about  $15\frac{1}{2}$  molecules of H<sub>2</sub>O, but it may have contained 18 molecules when first collected, especially if it came from a rather moist environment.

Dehydrated alunogen shows little tendency to rehydrate when exposed to air, this property being shown by the dotted line, Fig. 1; it is so slight as to be easily accounted for by the natural hygroscopic property of a fine powder due to surface coatings of water on the fine grains and capillarity.

## 2. NONTRONITE.

*Introduction.* During the spring of 1915 one of the authors (E. S. L.) visited a strip of garnet pyroxene rock, forming Iron Mountain and included in a great body of granodiorite near Woody postoffice, about 30 miles east of north of Bakersfield, California. This garnet-pyroxene rock represents a metamorphosed limestone inclusion of roof pendant in the granodiorite. Several prospect tunnels in the garnet-pyroxene

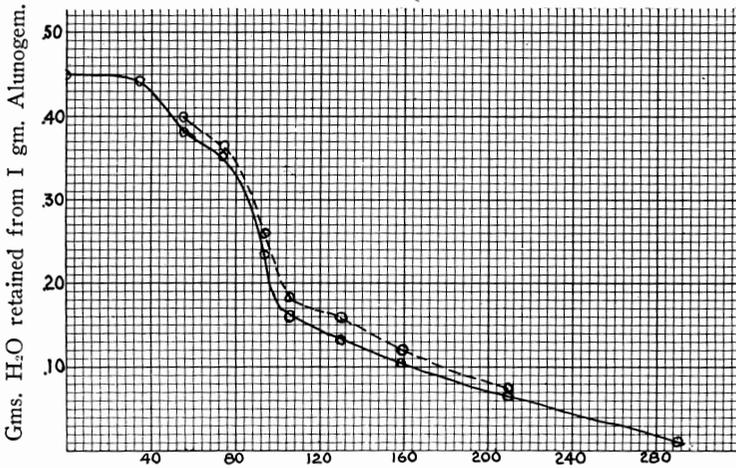


Fig. 1. Alunogen.

Temperature degrees Centigrade.

rock cut numerous veinlets, up to an inch or more across, of a dark olivine-green to bluish-green mineral which is soft and plastic when wet and is called "blue mud" by the prospectors. This "blue mud" is made up of scales of fibers arranged across the veinlets and is essentially homogeneous, except for a little pyrite. On drying and exposure to air it becomes harder. A microscopic and chemical examination of this material shows that its properties and composition agree closely with those of morencite described by Lindgren and Hillebrand<sup>2</sup> from Morenci, Arizona, and further study shows that both of these minerals belong to the species nontronite.

<sup>2</sup> Lindgren, W., and Hillebrand, W. F., this Journal, 18, 455, 1904.

*Physical properties.* The nontronite from Woody, California, was dark olive-green when first collected but after standing in the laboratory for some months became dark olive-buff (21''—of Ridgway's colors). The dry mineral has a silky luster, a hardness of about 2, and a specific gravity of 2.495.

*Optical properties.* The mineral analyzed consisted of rather coarse fibers and laths with Z parallel to the elongation and X normal to the flat face or cleavage. It is optically negative with a small axial angle and rather strong dispersion.

It is strongly pleochroic. The optical properties vary somewhat.

$$\begin{aligned} \alpha &= 1.56 \pm 0.01, \text{ pale-yellow} \\ \beta &= 1.585 \pm 0.01, \text{ olive-green} \\ \gamma &= 1.585 \pm 0.01, \text{ yellow-green} \end{aligned}$$

Another sample, probably with lower water content, has the following optical properties: Opt. —, 2V large, X emerges from a cleavage which is parallel to the fibers, Z parallel to length, pleochroic.

$$\begin{aligned} \alpha &= 1.58 \pm 0.01, \text{ orange to yellow-orange} \\ \beta &= 1.590 \pm 0.005, \text{ orange-yellow} \\ \gamma &= 1.600 \pm 0.005, \text{ yellowish green to bright green} \end{aligned}$$

Another specimen, altered to a yellowish-green mass, has somewhat variable properties: Opt. —, Z parallel to elongation, 2V large.

$$\begin{aligned} \alpha &= 1.610 \pm 0.01, \text{ yellow-brown} \\ \gamma &= 1.625 \pm 0.01, \text{ pale-yellow} \end{aligned}$$

The change in the optical properties on dehydration at various temperatures will be discussed in succeeding paragraphs.

A fragment from the original specimen of "morencite," described by Lindgren and Hillebrand from the Arizona Central mine, Arizona, kindly furnished by the U. S. National Museum, was examined optically and its optical properties agree well with those of the mineral from Woody, California, although it is too finely crystalline for satisfactory measurements. A microscopic examination showed it to be a mass of interwoven fibers, with positive elongation, small axial angle, and optically negative character. It is pleochroic in yellow-brown with absorption  $X > Z$ .

$\beta$  1.645  $\pm$  0.01, birefringence moderate. The optical properties vary somewhat.

*Chemical properties.* The nontronite from California is readily decomposed by HCl and shows some tendency to gelatinize. The material collected for the analysis was air dried by allowing to stand in a warm room for several months. Very little impurity was shown by a microscopic examination but the grains showed a small variation in their optical properties. The analyses and molecular ratios of nontronite from California are given in columns 2 and 3 of Table 4, and in column 1 the original analysis of morencite from Arizona is given for comparison.

TABLE 4. Analyses and ratios of nontronite and morencite.

	1	2	3	Molecular ratios
SiO <sub>2</sub> .....	45.74	47.51	788	= 78 × 10.102
TiO <sub>2</sub> .....	tr.	none		
Al <sub>2</sub> O <sub>3</sub> .....	1.98	0.37	4	} 224 = 78 × 2.872
Fe <sub>2</sub> O <sub>3</sub> .....	29.68	35.17	220	
FeO .....	0.83	none		
MnO .....	tr.			
CaO .....	1.61	2.50	45	} 82 = 78 × 1.051
MgO .....	3.99	1.40	35	
K <sub>2</sub> O .....	0.20	0.06	1	
Na <sub>2</sub> O .....	0.10	0.09	1	
H <sub>2</sub> O 105° .....	8.84	7.16	398	= 78 × 5.103
H <sub>2</sub> O 150° .....	0.12			
H <sub>2</sub> O below redness ...	4.27	5.90	328	= 78 × 4.205
H <sub>2</sub> O redness .....	0.69			
CuO .....	little			
FeS <sub>2</sub> .....	0.66			
P <sub>2</sub> O <sub>5</sub> .....	0.18			
SrO .....		none		
	<hr/> 98.89	<hr/> 100.16		

1. "Morencite" from Arizona. W. F. Hillebrand, analyst.

2. Nontronite from Woody, California. George Steiger, analyst.

The two analyses show sufficient similarity to indicate that the minerals belong to the same species. The H<sub>2</sub>O below 105° is no doubt variable, as it is in many other minerals. The formula derived from the California mineral is R''O<sub>3</sub>R'''<sub>2</sub>O<sub>3</sub>·10SiO<sub>2</sub>·9H<sub>2</sub>O, in which R'' is Ca and Mg and R''' is chiefly Fe with very little Al; the formula derived by Lindgren and Hillebrand from the Arizona mineral is 2R''O<sub>3</sub>R'''<sub>2</sub>O<sub>3</sub>·11SiO<sub>2</sub>·11H<sub>2</sub>O in which R'' is chiefly Mg with little Ca and Fe, and R''' is chiefly Fe with little Al.

Nontronite with a different appearance and somewhat different origin was found at the Woody locality and at many contact metamorphic garnet-hedenbergite zones studied by the author (E. S. L.). It is a platy to fibrous, citron green to light yellow-green aggregate, derived from the alteration (probably hydrothermal) of hedenbergite and is found in streaks and patches in the garnet-hedenbergite rock. Optical properties of different samples are somewhat variable—those of the material analyzed by Shannon are Opt. —,  $2V\ 66^\circ$  about. The indices of refraction are variable, probably due to colloidal material, the average values for the best fibers being  $\alpha = 1.57$ ,  $\beta = 1.59$ ,  $\gamma = 1.60$ . X is sensibly normal to a perfect cleavage or crystal face and Z is parallel to the elongation.

An analysis of this type of nontronite from Woody, California, was kindly made for the authors by Mr. Earl V. Shannon and is given in column 3 of Table 7. The mineral is difficultly soluble in  $H_2SO_4$  but is decomposed by HCl.

### 3. THE DEHYDRATION OF NONTRONITE.

A portion of the powder which was used in making the analysis (Table 4) of the nontronite from California was heated for several hours in an air bath at successively high temperatures, and the loss in  $H_2O$  and the optical properties of the dehydrated specimens determined. If the dehydrated samples are allowed to stand in a room exposed to the air they will take up a considerable part of the water lost. The results of these experiments are tabulated in Table 5 and plotted in Fig. 2.

In nontronite four molecules of water are retained after heating the material to  $105^\circ$ . Considering this portion of the water as part of the nontronite molecule leads to no simple ratio; if no water is included the metasilicate results  $R''R'''_6Si_{10}O_{30}$  while if all the water is retained the ratio is almost that of the orthosilicate  $R'_{18}R''R'''_6Si_{10}O_{39}$ .

On referring to the rehydration curve indicated by the dotted line, Fig. 2, it will be seen that the samples of nontronite which were dried out at temperatures from  $75^\circ$  to  $130^\circ$  rehydrated, when exposed to the air at ordinary temperatures, rather definitely to material containing .0952 gms. of the .1306 gms. of water in one gram of the original nontronite.

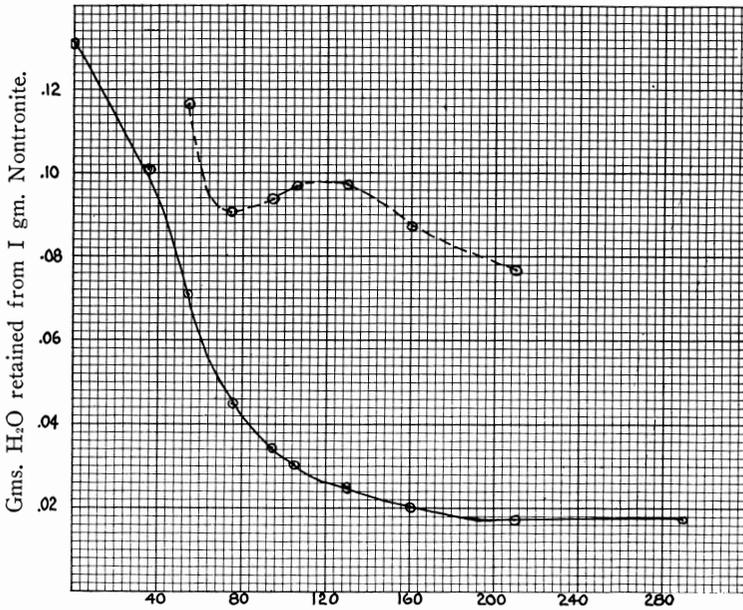


Fig. 2. Nontronite.

Temperature degrees Centigrade.

TABLE 5. The dehydration of nontronite from California.

Temperature	H <sub>2</sub> O retained per 1 gm. nontronite	$\beta$	Optical character	$2V$	Remarks
Original material ..	.1306	1.585	....	Small	Z = elongation X $\pm$ cleavage Pleochroic $\alpha$ = pale yellow Y = olive green Z = yellow
75° .....	.0440	1.615	....	....	Otherwise similar to <i>l</i>
105° .....	.0310	....	....	....	
130° .....	.0260	1.64	....	Very large	Faintly pleochroic, in brownish green. Otherwise as No. 1.
160° .....	.0200	1.655	....	....	Darker in color.
Same after standing in room over night.	.0980	1.645	....	....	
210° .....	.0180	1.67	....	....	
290° .....	.0180	1.69	....	....	Reddish brown in color and faintly pleochroic.
Same after standing in room over night.	....	1.69	....	....	

Assuming that only this portion of the water is constitutional gives a formula for nontronite having seven molecules of water,  $\text{RO} \cdot 3\text{R}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 7\text{H}_2\text{O}$ .

	Per gram of nontronite	Molecular ratios	
$\text{SiO}_2$ .....	.4751	788	$= 76 \times 10.36$
$\text{Al}_2\text{O}_3$ .....	.0037	4	} $224 = 76 \times 2.96$
$\text{Fe}_2\text{O}_3$ .....	.3517	220	
$\text{CaO}$ .....	.0250	45	} $82 = 76 \times 1.08$
$\text{MgO}$ .....	.0140	35	
$\text{K}_2\text{O}$ .....	.0006	1	} $= 76 \times 6.96$
$\text{Na}_2\text{O}$ .....	.0009	1	
$\text{H}_2\text{O}$ .....	.0952	529	

Whether completely dehydrated nontronite will rehydrate on exposure to the air to a definite point was not determined; the curve was completed to  $210^\circ$  only. However the experiments did show that nontronite dried at this ( $210^\circ$ ) temperature no longer retained the property of quickly rehydrating to the full seven molecules of water when exposed to air.

Referring again to Fig. 2 it will be seen that at about the same temperature at which the heated product fails to reabsorb the seven molecules of water, that the dehydration becomes a straight line and runs parallel to the base to  $290^\circ$ . Assuming that only water represented by the straight portion of the curve is water of constitution leads to an unsatisfactory ratio for the water molecule,  $(\text{SiO}_2)_{10.36} \cdot (\text{RO})_{1.08} \cdot (\text{R}_2\text{O}_3)_{2.96} \cdot (\text{H}_2\text{O})_{1.26}$ .

The low temperature at which nontronite and the related minerals, chloropal, pinguite, and morecite, lose a large part of their  $\text{H}_2\text{O}$  and their tendency to again take up this water on exposure to moist air has long been known. In 1877 Schauf<sup>3</sup> showed that the "chloropal" from Mugrau is "hygroscopic:" "an air-dried specimen contained 18.32 per cent of  $\text{H}_2\text{O}$ ; dried over  $\text{H}_2\text{SO}_4$  it has 13.59 per cent, and exposed to artificially moistened air it absorbed  $\text{H}_2\text{O}$  until it contained 22.02 per cent." At about the same time Collins<sup>4</sup> showed that nontronite from Smalacombe which originally contained 25.41 per cent  $\text{H}_2\text{O}$  "lost 11.58 per cent over  $\text{H}_2\text{SO}_4$  and a further

<sup>3</sup> Schauf, A., Neues Jahrb. Min., p. 255, 1877.

<sup>4</sup> Collins, J. H., Mineralog. Mag., 1, 67, 1876.

loss of 7.22 per cent at 250° C." Katzer<sup>5</sup> later showed that "pinguite" from Spaniow "lost 16.24 per cent H<sub>2</sub>O at 100° C., 16.53 per cent at 110°, 16.57 per cent at 120°, 16.87 per cent at 200°, 17.09 per cent at 250, and 22.77 per cent at red heat." Hillebrand<sup>6</sup> showed that the "morencite" from Morenci lost 8.84 per cent H<sub>2</sub>O at 105°, a further 0.12 per cent at 150°, an additional 4.27 per cent below redness, and a final 0.69 per cent was lost at redness. Weinschenk<sup>7</sup> found that nontronite from Passau "dried over CaCl<sub>2</sub> lost at 100° 10.62 per cent H<sub>2</sub>O, at 210° no additional loss, and at a red heat for 10 hours a final loss of 8.75 per cent H<sub>2</sub>O." A second specimen lost 7.93 per cent at 110°, and a further 7.97 per cent at red heat.

#### 4. THE IDENTITY OF NONTRONITE, MORENCITE, HOEFERITE, AND MULLERITE.

A large number of names have been proposed for the hydrous silicates of ferric iron; and of these nontronite, chloropal, pinguite, fettbol, and graminite are recognized by most mineralogists as belonging to the species nontronite, while müllerite (or zamboninite), hoeferite, morencite, and hisingerite, are commonly considered distinct species. Of these hisingerite is distinctly amorphous and isotropic or metacolloidal; it has a variable composition approximating  $m(\text{RO} \cdot \text{SiO}_2)$ ,  $n(\text{Fe}_2\text{O}_3 \cdot 2\text{SiO}_2) \cdot \text{XH}_2\text{O}$  and therefore differs considerably from the others which are all crystalline, and all except hoeferite are assigned a Fe<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> ratio of 1:3. The separation of the others is based largely on chemical analyses and for the most part on the difference in H<sub>2</sub>O content, although hoeferite is reported to have a different ratio Fe<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> and morencite is assigned RO in the formula. Slightly different blowpipe reactions and different results from treatment with acid have been assigned to the different minerals. The important diagnostic optical properties have not been described for most of the minerals, but new measurements by one of the authors (E. S. L.) have been made for chloropal and morencite. The principal properties assigned to the various minerals are summarized briefly in Table 6.

A careful study of the tables shows important differences between the minerals only for their chemical formulae, their

<sup>5</sup> Katzer, F., *Min. pet. Mitt.*, 14, 516, 1895.

<sup>6</sup> *Loc. cit.*

<sup>7</sup> Weinschenk, E., *Zeitschr. Kryst. Min.*, 28, 156, 1897.

TABLE 6. Principal properties of nontronite and related minerals.

Formula assigned	Nontronite or chloropal $Fe_2O_3 \cdot 3SiO_2 \cdot 5H_2O$	Morencite $2R''O_3 \cdot 3R_2''O_3 \cdot 11SiO_2 \cdot 11H_2O$	Zamboninite or müllerite $Fe_2O_3 \cdot 3SiO_2 \cdot 2H_2O$	Hoeferite $Fe_2O_3 \cdot 2SiO_2 \cdot 3H_2O$
Solubility in acid	Nontronite gelatinizes chloropal is partly decomposed. Pinguite, graminite, and fethbol are decomposed by $H_2SO_4$ with separation of $SiO_2$ .	Tends to gelatinize	Only slowly decomposed by concentrated HCl	Resists acids but slowly decomposed by hot $H_2SO_4$ with separation of pulverent $SiO_2$ .
Fusibility	Infusible to difficultly fusible	Infusible	Infusible	Infusible
Color	Yellow to green	Olive green to olive buff	Yellowish green	Apple to grass green
H	1 to 2	2	soft	1 to 3
g	1.727 (?) to 2.727	2.495	1.97	2.27 to 2.41
Crystallinity	Monoclinic, Metacolloidal to very fine lamellae or fibers.	Minute fibers		Amorphous (?)
Cleavage	(001) very per. Prismatic per.	Arizona		
Opt. character	Lacroix Bergéat Larsen	Woody (001) per.		
$\alpha$	—	—		
$\beta$	1.625	1.63	1.56 to 1.61	
$\gamma$	1.595	1.645	1.585 to 1.625	
$\gamma$	1.61	1.66	1.585 to 1.625	
$\gamma$	1.655	small	small	
2V	$30^\circ \pm$	66°		
Optical orientation	Z $\wedge$ elong. = 5-6° X $\perp$ plates	Z// fibers X $\perp$ plates	Z// elong.	
Pleochroism	X = yellow green Z = brown green to olive green	In yellow brown X = pale yellow Y = olive green Z = yellow green		

solubility in acids, and their specific gravities. The latter property, as commonly measured, is so variable and uncertain in porous, fibrous or platy, hydrous minerals as to give it little value. The difference in solubility in acids is no greater than might be expected from different specimens of the same species of a variable mineral, and might easily be due to the variable CaO, MgO, and FeO content and the highly valuable H<sub>2</sub>O content, together with the different states of aggregation of different specimens. The chemical composition, therefore, appears to be the only basis for recognizing more than one species.

A comparison of the formulae given in Table 6, and of the analyses given in Table 7, shows that there is a wide variation in the H<sub>2</sub>O content and considerable variation in the amount of R"O present. The R"O varies from almost zero in some nontronites to over  $\frac{2}{3}$  the amount of R<sub>2</sub>O<sub>3</sub> in morencite. Some of the low values are probably due to incomplete analyses and the high content in the morencite may have been partly due to chlorite, which was said to be mixed with the morencite. At any rate, the variation is considerable and probably most of the analyses carry about  $\frac{1}{3}$  as many molecules of R"O as of R<sub>2</sub>O<sub>3</sub>. The maximum amount of R"O is about 6.5 per cent which is high enough to be taken into account in assigning a formula. However, in such porous platy or fibrous minerals this is not excessive and it may be partly in solid solution, partly absorbed, and partly due to mechanical impurities. It seems possible to consider the formula of nontronite to be Fe<sub>2</sub>O<sub>3</sub>.3SiO<sub>2</sub>.3H<sub>2</sub>O or Fe<sub>2</sub>(SiO<sub>3</sub>)<sub>3</sub>.3H<sub>2</sub>O and that the R"O.SiO<sub>2</sub> is in solid solution in variable amounts. In the mineral from Morenci the R"O.SiO<sub>2</sub> may be wholly or in part contained in the chlorite or a related mineral with which the morencite was said to be mixed. The H<sub>2</sub>O varies from over 25 per cent in "graminite" to only 7.05 per cent in one specimen of "müllerite." Almost all values are represented except those between 14 per cent and 18 per cent. In the four analyses in which H<sub>2</sub>O was determined above and below 110°, all but from 3.79 per cent (at 120°) to 6.24 per cent was lost below 110°. These facts together with the dehydration experiments and the variable H<sub>2</sub>O content of a number of similar minerals, such as the members of the leverrierite group, show that there is no good reason for separating müllerite, morencite, and hoefelite from nontronite on account of their

TABLE 7. Analyses of nontronite and related hydrous ferric silicates.

Locality Name Analyst	Smallacombe Graminite Collins	Menzenberg Graminite Bergemann	Woody Yellow scales from hedenbergite Shannon	Ville-france Nontronite Dufrenoy	Pinguite Katzer	Mähren Nontronite Korar	Jamnitz Nontronite Johns	Theoretical Fe <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> ·5H <sub>2</sub> O	Nontron Nontronite Berthier	Montmars Nontronite Jacquelin	Mugrau Chloropal Schrauf	Kritz Hoeferite <sup>b</sup> Katzer	Morenci Morencite Hillebrand	Woody Nontronite Steiger	Nontron Müllerite Zambonine	Theoretical Fe <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> ·2H <sub>2</sub> O	Starbo Müllerite Weibull
SiO <sub>2</sub> .....	39.70	38.39	43.51	40.68	41.33	41.78	41.80	41.86	44.0	41.31	42.93	36.01	45.74	47.51	48.82	47.87	48.59
Al <sub>2</sub> O <sub>3</sub> .....	10.92	6.87	2.94	3.96	0.80	0.86	0.91	3.6	3.6	3.31	3.19	1.14	1.98	0.37	4.30	.....	9.09
Fe <sub>2</sub> O <sub>3</sub> .....	21.94	25.46	28.62	30.19	35.05 <sup>c</sup>	35.30	35.29	37.21	29.0	35.69	28.91	45.26 <sup>c</sup>	29.68	35.17	35.88	42.55	32.54
FeO .....	.....	2.80	0.99	.....	.....	.....	.....	.....	.....	.....	.....	.....	0.83	.....	.....	0.55	0.55
MnO .....	.....	0.67	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
MgO .....	.....	0.75	0.05	2.37	.....	0.40	0.92	.....	2.1	.....	2.84	.....	3.99	1.40	0.63	.....	trace
CaO .....	0.14	0.56	2.22	.....	1.01	0.92	1.04	.....	.....	0.19	3.35	.....	1.61	2.50	0.35	.....	2.09
Alk. ....	1.89	1.14 <sup>d</sup>	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
H <sub>2</sub> O+ .....	.....	23.36	{ 6.62	.....	{ 6.24	.....	.....	.....	.....	.....	.....	{ 3.79 <sup>e</sup>	5.08	5.90	.....	9.58	7.05
H <sub>2</sub> O- .....	.....	.....	{ 14.05	.....	{ 16.24	.....	.....	.....	.....	.....	.....	{ 14.39	8.84	7.16	.....	.....	.....
P <sub>2</sub> O <sub>5</sub> ·TiO <sub>2</sub> etc.	.....	.....	1.02 <sup>e</sup>	.....	.....	.....	.....	.....	1.2 <sup>f</sup>	0.90	.....	.....	1.14 <sup>f</sup>	1.15 <sup>g</sup>	.....	.....	.....
Sp. G. ....	100.00 1.89	100.00 1.87	100.02 .....	100.20 2.08	100.67 2.727	99.94 2.145	100.32 .....	100.00 .....	98.6 .....	100.03 .....	99.54 .....	100.59 2.27	98.89 .....	100.16 .....	99.64 1.97	100.00 .....	99.91 2.19
R <sub>2</sub> O <sub>3</sub> ·3SiO <sub>2</sub> ..	10.0	7.5	7.5	7.9	9.3	9.0	8.5	.....	8.1	9.8	7.2	.....	5.9	7.4	9.4	.....	8.6
RO <sub>2</sub> ·SiO <sub>2</sub> .....	0.0	2.5	2.5	2.1	0.7	1.0	1.5	.....	1.9	0.2	3.8	.....	4.1	2.6	0.6	.....	1.4
H <sub>2</sub> O .....	58.0	42.5	43.0	45.1	51.0	45.4	41.0	.....	38.7	40.0	30.2	.....	22.3	24.0	16.0	.....	11.6
Excess or Defi- ciency SiO <sub>2</sub>	-4.3	-7.2	+1.8	-3.7	-0.6	-1.0	-3.7	.....	+2.0	-4.9	-3.1	.....	+0.2	+2.3	+0.3	.....	-6.7

<sup>1</sup> K<sub>2</sub>O.  
<sup>2</sup> CaO.  
<sup>3</sup> Some FeO.  
<sup>4</sup> Clay.  
<sup>5</sup> Purified with dilute HCl before analyzing.  
<sup>6</sup> Loss at 120° C.  
<sup>7</sup> TiO<sub>2</sub> tr., K<sub>2</sub>O 0.29, Na<sub>2</sub>O 0.19, CaO little, Fe<sub>2</sub>S 0.66, P<sub>2</sub>O<sub>5</sub> 0.18.  
<sup>8</sup> TiO<sub>2</sub> tr., K<sub>2</sub>O 0.06, Na<sub>2</sub>O 0.09, SiO none

lower water content: indeed it is not at all unlikely that a specimen of normal nontronite with 20 per cent or more  $H_2O$  would dehydrate, without a break in its properties, to the composition of the type müllerite after long exposure to warm, dry air. Finally the ratio  $Fe_2O_3 \cdot SiO_2$  is 1 : 3 for all the analyses except that for hoeferrite, and as the analysis of hoeferrite was made on impure material after purification with dilute HCl, no great weight can be given to this ratio. The conclusion, therefore, seems justified that under ordinary conditions the water content of nontronite may vary widely from 7 to 25 per cent, and that until further evidence is presented müllerite (or zamboninite), morencite and hoeferrite should be considered varieties of nontronite that are low in  $H_2O$ . The formula for nontronite should be written  $Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O$  in which  $n$  may vary from less than 2 to 6 or over. More or less  $Al_2O_3$ ,  $CaO$ ,  $FeO$ , and  $MgO$  are commonly also present. The large amount of water that nontronite loses below  $100^\circ$  has been called hygroscopic water, but this is not justified and the water is more like the so-called "water of zeolitization." There is no distinction between the water below  $100^\circ$  and that above  $100^\circ$ .

The formula  $Fe_2O_3 \cdot 3SiO_2 \cdot nH_2O$ , here assigned to nontronite, is analogous to that of the corresponding aluminum silicate, the clay mineral beidellite. The aluminum mineral has been given the formula  $Al_2O_3 \cdot 3SiO_2 \cdot xH_2O$  by Larsen and Wherry,<sup>8</sup> while Ross and Shannon,<sup>9</sup> giving the same formula, determine the slightly variable water content to be about 4 parts. The percentages of water in beidellite, in the analyses given by Ross and Shannon, range from 17.26 to 22.64, which is about the same range as is found in nontronite.

These two silicates, nontronite and beidellite, form an isomorphous series with no important gaps as shown in Table 8. All beidellites analyzed contain some iron, varying from 0.80 per cent to 18.54 per cent. The latter value, found in a beidellite from Spokane, Washington, has as much iron as aluminum, molecularly.

<sup>8</sup> Larsen, E. S., and Wherry, E. T., Beidellite, a New Mineral Name, *Jour. Wash. Acad. Sci.*, **15**, No. 21, 1925.

<sup>9</sup> Ross, C. S., and Shannon, E. V., *Jour. Wash. Acad. Sci.*, **15**, No. 21, 1925; also *Jour. Amer. Ceramic Soc.*, **9**, 94, 1926.

TABLE 8. Representative analyses of nontronite and beidellite.

	1	2	3	4	5	6	7	8	9	10	11
SiO <sub>2</sub> .....	41.86	41.80	40.68	38.39	39.70	46.06	47.28	45.12	45.52	45.32	51.0
Ti <sub>2</sub> O <sub>3</sub> .....	.....	.....	.....	.....	.....	0.84	.....	.....	.....	.....	.....
Al <sub>2</sub> O <sub>3</sub> .....	.....	0.91	3.96	6.87	10.93	12.22	20.27	28.24	27.52	27.84	28.7
Fe <sub>2</sub> O <sub>3</sub> .....	37.21	35.29	30.19	25.46	21.94	18.54	8.68	4.12	2.80	0.80	.....
FeO .....	.....	.....	.....	2.80	.....	0.28	.....	.....	.....	.....	.....
CaO .....	.....	1.04	.....	0.56	0.14	1.66	2.75	0.88	0.52	2.76	.....
MgO .....	.....	0.92	2.37	0.75	.....	1.62	0.70	2.32	3.00	0.16	.....
K <sub>2</sub> O .....	.....	.....	.....	.....	.....	.....	trace	.....	.....	0.12	.....
Na <sub>2</sub> O .....	.....	.....	.....	.....	.....	.....	0.97	.....	.....	0.10	.....
H <sub>2</sub> O .....	20.93	20.36	23.0	23.36	25.41	17.26	19.72	18.72	19.60	22.64	20.3
H <sub>2</sub> O .....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
MnO .....	.....	.....	.....	0.67	.....	.....	.....	.....	.....	.....	.....
Alk. ....	.....	.....	.....	1.14 <sup>a</sup>	1.89	.....	.....	.....	.....	.....	.....
X .....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....
	100.00	100.32	100.20	100.00	100.00	98.48	100.37	99.40	98.96	99.64	

<sup>a</sup> K<sub>2</sub>O.<sup>1</sup> Analyses 1, 2, 3, 4 and 5 recopied from Table 7, this paper.<sup>2</sup> Analyses 6, 7, 8, 9, 10 and 11 taken from paper by Ross and Shannon: Jour. Wash. Acad. Sci., Vol. 15, No. 21, Dec. 19, 1925; also Jour. Amer. Ceramic Soc., Vol. 9, No. 2, Feb., 1926.

1. Ideal nontronite end member (Fe<sub>2</sub>O<sub>3</sub>·3SiO<sub>2</sub>·nH<sub>2</sub>O).
2. Jamnitz—nontronite—Johns.
3. Ville-france—Nontronite—Dufrenoy.
4. Menzenberg—Nontronite (Graminite)—Bergemann.
5. Smallacombe—Nontronite (Graminite)—Collins.
6. Iron-rich beidellite; Spokane, Washington, E. V. Shannon, analyst.
7. Beidellite, "leverrierite" gouge clay from Beidell, Saguache County, Colorado, E. S. Larsen and E. T. Wherry, Jour. Wash. Acad. Sci., 7: 208-217, 1917.
8. Bentonite, Maine Creek, near Nashville, Howard County, Arkansas. Coarser product than bentonite of analysis No. 9. E. V. Shannon, analyst.
9. Bentonite, same locality as No. 8, fine separation product.
10. Beidellite, "leverrierite" gouge clay, Black Jack vein, Carson dist. Owyhee County, Idaho. E. V. Shannon, Proc. U. S. Nat. Museum, 62, Art. 15, 1923.
11. Ideal beidellite end member (Al<sub>2</sub>O<sub>3</sub>·3SiO<sub>2</sub>·nH<sub>2</sub>O).

## 5. THE DEHYDRATION OF GRIFFITHITE.

Dehydration experiments on griffithite similar to those on nontronite were made and the results are shown in Table 9. Obviously the water content and indices of refraction of griffithite are variable and depend on the previous history of the particular sample in hand, temperature and degrees of saturation of the air to which it has been exposed, each having a substantial effect on the water content.

Heated at 55° C. griffithite lost 8.9 per cent or over half the original H<sub>2</sub>O; it regained all but 1.6 per cent of this on expo-

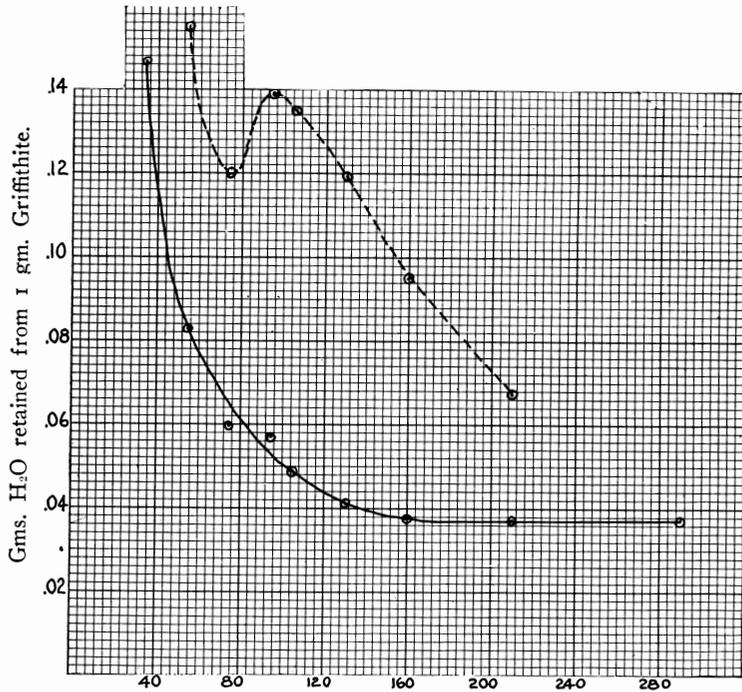


Fig. 3. Griffithite.

Temperature degrees Centigrade.

## Griffithite.

Cahuenga Pass, California.

SiO <sub>2</sub> .....	39.64
Al <sub>2</sub> O <sub>3</sub> .....	9.05
Fe <sub>2</sub> O <sub>3</sub> .....	7.32
FeO .....	7.83
MgO .....	15.80
CaO .....	2.93
Na <sub>2</sub> O .....	.71
K <sub>2</sub> O .....	none
H <sub>2</sub> O— .....	12.31
H <sub>2</sub> O+ .....	4.90

100.49

Analyst, George Steiger.

TABLE 9. The dehydration of griffithite.

Temperature	Gms. H <sub>2</sub> O retained from 1 gm. griffithite	$\alpha$	$\beta$	$\gamma$	
Original material	.172	1.485	1.569	1.572	Opt. —, 2V from 0-40° Pleochroic. X = pale yellowish Y = olive green Z = brownish green
75°	.060	1.50 ± 0.01	1.580	1.580	
130°	.041	1.52 ± 0.01	1.600 ± 0.005	1.600 ± 0.005	G = pale yellowish Y = olive green Z = brownish green
Same after exposure in room over night	.119				
160°	.037		1.611 ± 0.005		
After exposure in room over night	.096		1.601 ± 0.005		
110°	.036		1.623 ± 0.01		Opt. —, 2V very small
After exposure in room over night	.074		1.615 ± 0.01		X normal to plates
130°	.036	1.580 ± 0.01	1.640 ± 0.01 to 1.635 ± 0.01	1.640 ± 0.01	Strongly pleochroic. X = nearly colorless. Y & Z = olive green Opt. —, nearly uniaxial.

sure for a few days to the atmosphere, and it would probably continue to take up water until a condition of equilibrium was reached. From 55° to 130° the loss of water is more gradual and above 130° the water comes off still slower.

## CONCLUSION.

1. A study of alunogen from New Mexico shows that its water content may vary considerably without a breaking up of the crystal structure but with a progressive change in the optical properties: the mineral when analyzed had a composition near  $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 15\frac{1}{2}\text{H}_2\text{O}$ , on heating at 75° C. the composition approximated  $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 12\frac{1}{2}\text{H}_2\text{O}$ . Further dehydrating at a higher temperature destroyed the mineral and developed an isotropic form which persisted to complete desiccation. After partial dehydration alunogen shows only a slight tendency to again take up the H<sub>2</sub>O it has lost. These data account for the variable optical properties of alunogen and show that the long discussion as to the number of molecules

of  $\text{H}_2\text{O}$  in alunogen was based on the erroneous assumption that the water content is a fixed amount, corresponding to a definite molecular ratio. The water content, certainly that in excess of  $12\frac{1}{2}$  molecules of a given specimen of alunogen, will probably depend on its immediately preceding history and will vary from day to day. The optical properties of four specimens of alunogen, after long exposure to the atmosphere of museums, indicate a water content of from 15 to  $15\frac{1}{2}$  molecules.

2. Nontronite (including chloropal, pinguite, graminite, etc.), müllerite (or zamboninite), morencite, and hoferite, are shown with reasonable certainty to be the same species with variable water content which is probably due in some cases to loss of  $\text{H}_2\text{O}$  in the dry air of the museum. The partially dehydrated nontronite rather definitely rehydrates when exposed to air to the simplified nontronite formula  $(\text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O})$  containing two molecules of water. The name nontronite should be used for the species. Two varieties of nontronite from near Woody, California, are described and the optical properties and two analyses are given.

3. On heating nontronite and griffithite at successively higher temperatures they lose their water gradually and apparently without a break; at the same time their indices of refraction increase and their other optical properties change. Their crystal structure does not break down even when heated at about  $300^\circ\text{C}$ . at which temperatures nearly all their water is driven off. On exposure to the air of the laboratory they again take up a large portion of the water they had lost. Leverrierite<sup>10</sup> and beidellite have been shown to act similarly but their optical properties change only slightly on dehydrating. Obviously the water content of these minerals is variable and the water content of a specimen analyzed immediately after being collected from moist rocks with only ordinary drying will be very different from the water content of the same specimen after years exposure to the dry atmosphere of a museum.

The amorphous mineral halloysite from Colorado has been shown by Larsen and Wherry<sup>11</sup> to lose 8.55 per cent  $\text{H}_2\text{O}$  below  $100^\circ$ , most of it below  $30^\circ\text{C}$ ., only 2.15 per cent between  $100^\circ$  and  $400^\circ$ , and 12.85 per cent above  $400^\circ$ . After heating to  $100^\circ$  the mineral has very nearly the composi-

<sup>10</sup>Larsen, E. S., and Wherry, E. T., Leverrierite from Colorado, Jour. Wash. Acad. Sci., 7, 208-217, 1917.

<sup>11</sup>Larsen, E. S., and Wherry, E. T., Halloysite from Colorado, Jour. Wash. Acad. Sci., 7, 178-180, 1917.

tion of kaolinite. During the loss of water the index of refraction changes from 1.470 for halloysite with 25 per cent H<sub>2</sub>O to 1.555 for the mineral with 15 per cent H<sub>2</sub>O, which is about the amount in kaolinite. After ignition and complete desiccation the material appears to be still isotropic but the index of refraction decreases to 1.540. A number of specimens of halloysite from museum collections have the optical properties of the mineral with 16 per cent of H<sub>2</sub>O while many specimens sent in from the field indicate a much higher water content and it seems probable that the mineral dehydrates on exposure to the dry air of the museum.

The experiments on the dehydration of these three minerals were carried out simultaneously; the time of heating to determine the extent of dehydration was found to be 5 to 7 hours and was considered to be sufficient for good results. The samples were weighed in ordinary shaped platinum crucibles, heated to the desired temperature, cooled and weighed. The vapor tension, or humidity, in all experiments in which the temperature was 75° or over, was so low that its effect was negligible.

In the determination of the degree of rehydration in the various products, owing to lack of time, it was not possible to maintain all conditions necessary for the best work. These figures therefore are not so dependable as those for dehydration but will have to suffice until opportunity presents itself for better work. The work was carried out by taking the products of dehydration at the various temperatures and allowing them to stand exposed to the air, weigh and note the loss. Time allowed for dehydration at the various temperatures was as follows: 55°—89 hours; 75°—17 hours; 95°—43 hours; 105°—66 hours; 130°—165 hours; 160°—38 hours; 210°—161 hours.

The rehydration experiments were made in the middle of winter, the relative humidity varying between 20 and 50. Such degrees of humidity would almost certainly be vital in the extent to which rehydration takes place. The experiments should be repeated using carefully controlled and known humidities of different percentages, and possibly at various temperatures.

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