

# NOTES ON ALUNITE, PSILOMELANITE, AND TITANITE.

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## A PHOSPHATE-BEARING ALUNITE FROM TEXAS.

The material herein described was sent to the United States National Museum for examination and report by Mr. L. F. Christian, of Lockhart, Texas, the locality being given as "Gonzales County, Texas" (U.S.N.M. Cat. No. 88252). As preliminary examination showed it to possess somewhat unusual composition and properties, it was studied in detail. It has the following properties:

### PHYSICAL PROPERTIES.

Color: White with very slight yellowish hue; also shows superficial brown stains of iron rust.

Luster: Dull, like chalk.

Structure: Compact (cryptocrystalline); fracture subconchoidal.

Hardness:  $1\frac{1}{2}$ .

Density: 2.67.

Optical properties: Under the microscope seen to consist chiefly of a fine crystalline aggregate, with occasional grains up to .02 mm. in diameter; colorless; mean refractive index  $1.580 \pm .005$ ; double refraction .005.

### CRYSTALLOGRAPHIC PROPERTIES

Indeterminate.

### CHEMICAL PROPERTIES.

Qualitative tests: Before the blowpipe gives reactions for Al, K, Na,  $\text{SO}_3$ , and  $\text{H}_2\text{O}$ ; in HCl slightly soluble, the solution giving faint reactions for Al and  $\text{SO}_3$ ; after ignition,  $\text{H}_2\text{O}$  extracts  $\text{K}_2\text{SO}_4$ .

Quantitative composition: A sample was submitted to Dr. J. E. Whitfield, of Booth, Garrett, and Blair, of Philadelphia, who reported as follows (column 1):

Constituents.	1	2	3	4	5	6
	Analysis.	Kalio-alunite.	Natro-alunite.	Kalio-hitchcockite.	Natro-hitchcockite.	Clay (Cimolfitte.)
K <sub>2</sub> O.....	6.39	5.81		.43		.15
Na <sub>2</sub> O.....	2.81		2.56		.19	.06
H <sub>2</sub> O.....	15.20	6.63	4.43	.68	.44	3.02
Al <sub>2</sub> O <sub>3</sub> .....	36.31	18.87	12.62	1.45	.93	2.44
Fe <sub>2</sub> O <sub>3</sub> .....	.34					.34
SO <sub>3</sub> .....	32.89	19.70	13.19			
P <sub>2</sub> O <sub>5</sub> .....	2.20			1.34	.86	
SiO <sub>2</sub> .....	3.95					3.95
	100.09	51.01	32.80	3.90	2.42	9.96

The mineral composition, given in columns 2 to 6 inclusive, was obtained as follows: The sulphur trioxide found was first calculated to alunite,  $R_2O \cdot 6H_2O \cdot 3Al_2O_3 \cdot 4SO_3$ , or  $R_2 [Al(OH)_2]_6 (SO_4)_4$ , the  $R_2O$  comprising  $K_2O : Na_2O =$  approximately 3:2. (Columns 2 and 3.) The names for the end members are derived according to the standard rule advocated by the writer elsewhere, of assigning a group name (in this case *alunite*) to the isomorphous series as a whole and naming the (theoretical) end-members by chemical prefixes. The potassium (kalium) end-member thus becomes kalio-alunite, the sodium (natrium) one natro-alunite; the latter name is indeed already in use, having been proposed by Hillebrand and Penfield in 1902.<sup>1</sup>

The phosphoric oxide was then assigned in a corresponding way to a molecule with  $HPO_3$  replacing the  $SO_4$  of alunite,  $R_2O \cdot 8H_2O \cdot 3Al_2O_3 \cdot 2P_2O_5$ , or  $R_2H_4 [Al(OH)_2]_6 (PO_3)_4$ , the same ratio of K:Na being used. That this is the most probable form in which the phosphoric oxide found in alunite and related minerals is present was pointed out by Schaller.<sup>2</sup> Although the potassium and sodium salts of this radical are so far known only as isomorphous replacements in sulphates such as alunite, they may some day be discovered as independent minerals, and should be assigned names. As pointed out by Schaller, goyazite (hamlinite) is probably a strontium salt, gorceixite a barium salt, plumbogummite (hitchcockite) a lead salt, and florencite a cerium salt of the same radical. If these are all members of one isomorphous series, then all but one of the names are superfluous; one must be selected to apply to the series as a whole. Among them, plumbogummite has priority, having been introduced by De Laumont and Berzelius in 1819, which would make gummite

<sup>1</sup> Amer. Journ. Sci., ser. 4, vol. 14, 1902, p. 220.

<sup>2</sup> Journ. Wash. Acad. Sci., vol. 1, 1911, p. 112; Amer. Journ. Sci., ser. 4, vol. 32, 1911, p. 359; U. S. Geol. Surv. Bull. 509, 1912, p. 70.

the proper name for the series. Unfortunately, however, the name gummite (Dana, 1868), a contraction of uranogummite (Breithaupt, 1847), has been applied to a hydrous oxide of uranium of totally different composition and relationships. Furthermore, the members of the series under discussion are not characteristically gum like, so that the name gummite is not an appropriate one for it. Hitchcockite is next in point of date, having been proposed by Shepard in 1856. It is therefore recommended that the isomorphous series of the general formula  $R'_2O \cdot 0.8H_2O \cdot 3Al_2O_3 \cdot 2P_2O_5$ , or  $R'_2H_4[Al(OH)_2]_6(PO_3)_4$ , with  $R' = K, Na, \frac{1}{2}Ca, \frac{1}{2}Sr, \frac{1}{2}Ba, \frac{1}{2}Pb, \frac{1}{3}Ce$ , etc., be named the hitchcockite group. The names goyazite and hamlinite could then be discarded in favor of strontiohitchcockite, gorceixite or bariohitchcockite, and so on; the salts containing the phosphoric oxide in alunite would be kaliohitchcockite and natrohitchcockite.

After the constituents of the alunites and hitchcockites are subtracted, there remain all the  $Fe_2O_3$  and  $SiO_2$ , together with a little  $K_2O$ ,  $Na_2O$ ,  $H_2O$ , and  $Al_2O_3$  (Column 6). The first is undoubtedly present as a stain, and may be disregarded; the others are probably united in clay-like substances. The ratio of  $Al_2O_3 : SiO_2 = 1 : 3$  approximately, which would indicate a clay of the cimolite group.

It is therefore concluded that the alunite from Texas consists of about 51 per cent kalioalunite, 33 natroalunite, 4 of a potassium aluminium phosphate for which the name kaliohitchcockite is suggested, and 2 of the corresponding sodium compound, natrohitchcockite, admixed with some 10 per cent of a clay (cimolite).

#### SODIUM-BEARING ALUNITES FROM CALIFORNIA.

Another lot of alunite was received from Mr. Charles Muck of California, the locality being stated as a prospect pit in the Funeral Range Mountains, near Death Valley, California (U.S.N.M. Cat. No. 87529). It is similar to the preceding in certain respects, but differs in the presence of a considerable excess of sodium over potassium, as brought out in the description, which follows.

#### PHYSICAL PROPERTIES.

Color: White; specimens from near the surface stained red by iron oxides.

Luster: Dull, like chalk.

Structure: Compact (cryptocrystalline); fracture subconchoidal.

Hardness:  $2\frac{1}{2}$  (material from 60 feet beneath surface);  $3\frac{1}{2}$  (that from near the surface of the ground).

Density: 2.63.

Optical properties: Under the microscope, appears as confused minutely crystalline aggregates; colorless; mean refractive index  $1.585 \pm .005$ ; double refraction .01.

## CRYSTALLOGRAPHIC PROPERTIES.

Indeterminate.

## CHEMICAL PROPERTIES.

Qualitative tests: Before the blowpipe gives reactions for Al, Na,  $\text{SO}_3$ , and  $\text{H}_2\text{O}$ ; in HCl slightly soluble, the solution giving faint reactions for Al and  $\text{SO}_3$ ; after ignition,  $\text{H}_2\text{O}$  extracts  $\text{Na}_2\text{SO}_4$ .

Quantitative composition: Through the kindness of Prof. F. W. Clarke, chief chemist, two analyses of this material were made in the laboratory of the United States Geological Survey by R. K. Bailey. The material from near the surface gave the results in column 1, that from a depth of 60 feet those in column 5, below:

Constituents.	1	2	3	4	5	6	7	8
	Analysis (surface).	Natroalunite.	Kalioalunite.	Remainder.	Analysis (depth).	Natroalunite.	Kalioalunite.	Remainder.
$\text{Na}_2\text{O}$ .....	5.27	4.29	.....	.98	6.83	4.42	.....	2.41
$\text{K}_2\text{O}$ .....	3.05	.....	2.49	.56	1.04	.....	.67	.37
$\text{H}_2\text{O}$ .....	14.87	7.42	2.84	4.61	17.60	7.64	.77	9.19
$\text{Al}_2\text{O}_3$ .....	39.02	21.17	8.07	9.78	38.46	21.79	2.18	14.49
$\text{SO}_3$ .....	30.52	22.10	8.42	.....	25.03	22.75	2.28	.....
$\text{SiO}_2$ .....	7.46	.....	.....	7.46	10.27	.....	.....	10.27
Totals....	100.19	54.98	21.82	23.39	99.23	56.60	5.90	36.73

In the determination of the mineral compositions, the sulphur trioxide was first calculated to alunite, with Na:K in the first=approximately 5:2; in the second 9:1. The remainder contains in both cases  $\text{Al}_2\text{O}_3$ : $\text{SiO}_2$ =about 4:5, which indicates a clay belonging to the allophanite group; the alkalis left over may be adsorbed in this clay, or may be present in combination in a feldspar or other silicate, but the microscope fails to yield definite evidence on this point.

The specimens from California contain thus over 50 per cent of natroalunite, with small amounts of kalioalunite and a rather large amount of impurities.

## A LITHIUM-BEARING PSILOMELANITE FROM TENNESSEE.

A manganese dioxide, forming a coating on vein quartz, sent to the United States National Museum for examination and report by Mr. J. B. Lawson, of Sevierville, Tennessee (U.S.N.M. Cat. No. 87371), has proved to be so unusual in composition (approaching the variety which has been called lithiophorite), as to be worth special description. Mr. Lawson states that it occurs "loose in the soil in the vicinity of the proposed Appalachian Park." Its properties are as follows:

## PHYSICAL PROPERTIES.

Color: Black with slight bluish hue; streak brownish-black.  
 Luster: Dull-submetallic; more brilliant against surfaces of quartz;  
 opaque.  
 Structure: The several types exhibited by colloid minerals—botry-  
 oidal, globular, compact, and dendritic; fracture uneven.  
 Hardness: Varying from 3 to  $5\frac{1}{2}$ .  
 Density: Varying from 4.20 to 4.30.  
 Optical properties: Indeterminate.

## CRYSTALLOGRAPHIC PROPERTIES.

Indeterminate.

## CHEMICAL PROPERTIES.

Qualitative tests: Before the blowpipe gives reactions for Mn and Li  
 (flame red!). Soluble in HCl, with evolution of Cl; solution gives  
 reactions for Mn, Fe, Al, Co, and SiO<sub>2</sub> and traces of other elements.  
 Quantitative composition: The most homogeneous material obtain-  
 able from the specimens was submitted to Dr. J. E. Whitfield, of  
 Booth, Garrett, and Blair, who obtained the results given below  
 (with the exception of the Li<sub>2</sub>O, which was determined by the  
 writer, using the spectroscopic method):

Constituents.	Analysis.	Constituents.	Analysis.
H <sub>2</sub> O.....	11.40	Al <sub>2</sub> O <sub>3</sub> .....	7.83
Li <sub>2</sub> O.....	.35	Fe <sub>2</sub> O <sub>3</sub> .....	2.20
Na <sub>2</sub> O.....	1.20	MnO <sub>2</sub> .....	56.54
K <sub>2</sub> O.....	.44	SiO <sub>2</sub> .....	7.68
CaO.....	Trace.	P <sub>2</sub> O <sub>5</sub> .....	.49
BaO.....	3.12	SO <sub>3</sub> .....	.89
MnO.....	5.84		
CoO.....	1.76	Total.....	100.06
NiO.....	.32		

The results of analysis of psilomelanites (the termination *ite* is added for uniformity) have been previously interpreted in various ways. Rammelsberg<sup>1</sup> regarded the barium, manganous manganese, etc., as united with manganic manganese to form manganites, of the formula M'' (MnO<sub>3</sub>)''. Laspeyres<sup>2</sup> considered that these elements are present as basic manganates, M''<sub>2</sub>O (MnO<sub>4</sub>)'', and his view was adopted by Dana.<sup>3</sup> In the light of colloid-chemistry the mineral might be interpreted as colloidal manganese dioxide containing adsorbed substances.

<sup>1</sup> Handwörterbuch chem. Theils Mineralogie, 1841.

<sup>2</sup> Journ. prakt. Chem., vol. 13, 1876, pp. 1 and 215.

<sup>3</sup> System of Mineralogy, 1892, p. 257.

The bearing on this question of certain relations between constituents may be pointed out here. If the  $\text{SO}_3$  and  $\text{P}_2\text{O}_5$  found in the present specimen be regarded as united with  $\text{BaO}$ , the amount of the latter necessary would be 3.27 per cent, while 3.12 per cent was found. This essential agreement may be an accident, but the known stability of  $\text{BaSO}_4$  and  $\text{Ba}_3(\text{PO}_4)_2$  suggests the possibility that these compounds are actually present. The ratio of the  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  found is roughly 1:2, indicating that these constituents may be united as a clay of the halloysite group. The  $\text{Fe}_2\text{O}_3$  may well be combined with some of the  $\text{H}_2\text{O}$  to form limonite. But there remains about 10 per cent of oxides the condition of which is not so clear. Of these,  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$  should be soluble in water, yet water fails to extract them from the mineral, so they must be held in some peculiar way. They can not be in the form of manganates (Laspeyres-Dana theory), for their manganates prepared artificially are soluble in water to green solutions. No definite manganites of these elements have ever been obtained artificially. By exclusion, therefore, it would seem that the only form in which these oxides (and, correspondingly, the  $\text{MnO}$ ,  $\text{CoO}$ , and  $\text{NiO}$ ) can be present is as gels, united by adsorption to the  $\text{MnO}_2$  gel, which makes up the bulk of the material. Accordingly, no "mineral composition" is to be derived for psilomelanite, but it is to be regarded as composed essentially of adsorption products of the various oxides.

#### TITANITE OF UNUSUAL HABIT.

A yellowish-brown radiated-acicular mineral imbedded in datolite was discovered in 1913 in the northernmost quarry of the group situated on the east side of the Delaware River, 2 miles north of Lambertville, New Jersey, by Mr. Oscar Streland, of Philadelphia, and submitted to the writer for identification. Qualitative chemical and optical examination showed it to have the general features of titanite, but as this mineral had never before been observed in acicular form further investigation seemed desirable. Mr. Streland and Mr. Henry Munson, of Philadelphia, kindly presented several small specimens to the Museum (Cat. No. 59206), and of these all but one were broken up for examination. As the specific gravity of titanite ( $3.50 \pm .10$ ) is much higher than that of datolite ( $2.95 \pm .06$ ) mercuric potassium iodide solution of specific gravity 3.20 was used to separate them, and about 0.8 gram of the unknown mineral obtained, which proved to be quite homogeneous under the microscope, containing only minute amounts of datolite adhering to a few of the yellow grains, and of ilmenite, a mineral sparingly associated.

The mineral has the following properties:

## PHYSICAL PROPERTIES.

Color: Varying from cream (Ridgway's 19'f, yellowish orange yellow with 45 per cent white, broken with 32 per cent neutral gray) to Dresden brown (17'k, orange yellow with 70.5 per cent black, broken with 58 per cent gray).

Luster: Subadamantine; subtransparent.

Structure: Columnar to acicular, and radiated; maximum length of needles observed 2 cm.; diameter 0.1 to 1 mm. Needles somewhat fractured.

Hardness: 5.

Density: 3.52.

Optical properties: Under the microscope colorless; with crossed nicols shows large, variable extinction angle; in convergent light biaxial. Mean index of refraction 1.89.

## CRYSTALLOGRAPHIC PROPERTIES.

System: Indeterminate.

Habit: Long prismatic; no definite terminations observed; prism angle  $66^{\circ} 30'$ .

Cleavage: Prismatic, imperfect.

## CHEMICAL PROPERTIES.

Qualitative tests: Before the blowpipe gives reactions for Ca, Ti, Fe, and Si. Insoluble in HCl, but after fusion with  $\text{Na}_2\text{CO}_3$  dissolves, yielding reactions for Ca, Fe, Ti, and Si.

Analysis, made on 0.75 gram purified as above described; J. E. Whitfield, analyst:

Constituents.	1	2	3	4	5
$\text{CaO}$ .....	27.32	25.42	1.90	.3389	1.15
$\text{Fe}_2\text{O}_3$ .....	6.32	-----	6.32	.3958	1.35
$\text{TiO}_2$ .....	36.40	36.40	-----	-----	-----
$\text{SiO}_2$ .....	29.16	27.39	1.77	.2935	1.00
$\text{P}_2\text{O}_5$ .....	.42	-----	.42	-----	-----
	99.62	89.21	10.41	-----	-----

1. Results of analysis.

2. The percentages of the constituents corresponding to 36.40 per cent  $\text{TiO}_2$  in the form of titanite,  $\text{Ca}''(\text{TiO})''(\text{SiO}_4)''''$ ; amount of latter represented, 89.21 per cent.

3. Remainder left after subtracting 2 from 1.

4 and 5. Ratios of 3. (Disregarding the  $\text{P}_2\text{O}_5$ , the rôle of which is entirely unknown.)

The ratios of column 4 are as near a definite ratio (1:1:1) as could be expected considering the small amount of material used for analysis; and they indicate that in this occurrence, at least, the iron present in titanite is in the form  $\text{Ca}''(\text{Fe}'''\text{O})'_2(\text{SiO}_4)''''$ , or  $\text{CaFe}_2\text{SiO}_6$ , a compound presumably isomorphous with  $\text{Ca}(\text{TiO})\text{SiO}_4$ , as yet unknown in the pure state.

The mineral thus agrees in every essential respect with titanite, being unusual in containing a rather large percentage of ferric oxide, and in possessing an acicular form.