

ALLUAUDITE

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ABSTRACT

Alluaudite is described from a Black Hills pegmatite. Alluaudite is monoclinic, probably $C2/c$ (possibly Cc), with $a:b:c=12.004:12.533:6.404\text{\AA}$, $\beta=114^{\circ}22'$. The six stronger lines in a powder photo (Fig. 1) are: $2.73/10$, $6.27/8^-$, $3.07/7$, $2.51/7^-$, $5.47/6^-$, and $3.49/6^-$. Powder data appear in detail in Table 1. The optical orientation is $[b]\sim\gamma$, and $\beta\wedge[c]=+18^{\circ}.1$. The dispersion of the birefringence is given in Table 2. The chemical analysis of the Black Hills alluaudite appears in Table 3.

INTRODUCTION

Alluaudite from a pegmatite near Chanteloube in west-central France was described by Damour in 1848. While it is discussed in Dana's System (1892) as an alteration product of Fe-Mn phosphates, it later was neglected and so was not mentioned in Ford-Dana's Text or the Larsen-Berman tables. It was resurrected in 1937 by Quensel for the Varuträsk (Sweden) paragenesis, and has since been described from two Finnish, one Bavarian and one central African pegmatites. The writer now reports its first known occurrence in the United States.

At the Green pegmatite, 3 miles northeast of Pringle, South Dakota, near the south end of the Black Hills, on August 30, 1942, a nearly black phosphate nodule was found in the wall on the north side of the entrance to the tunnel. The material showing a faint greenish tinge, was hard, dense, fine-grained and apparently fresh and unaltered. The nodule was an irregular but smooth-surfaced ellipsoid with major axis horizontal and a foot long, minor axis vertical and half this amount. Its upper surface was in smooth curving contact with perthitic pink microcline; otherwise it was surrounded by albite-quartz-muscovite-tourmaline rock; columbite plates (as well as muscovite sheaves) in the latter rock extended into the phosphate nodule in typically-striking euhedral cross-cutting relationship. There was a hint of rectangular cleavages here and there in the phosphate; its other physical properties are as follows: Hard. 5-; Fus. 3-; streak, brownish; color, greenish-black. Its specific gravity is 3.52, whereas that from Chanteloube is 3.584.

The phosphate nodules of the Black Hills pegmatites, including lithiophilite and montebasite, apparently form as a rule at an early stage; they are often closely associated with cassiterite, and in many instances have suffered partial replacement by cleavelandite-columbite rock. Under the latter circumstances the Fe-Mn phosphates not uncommonly show evidence of some oxidation which apparently occurred through hydrothermal action. Mason and Quensel have demonstrated that the Fe''-Mn'' phosphates suffer oxidation in two stages, first the iron,

then the manganese. In many cases these nodules, which may be several feet across are composed in the main of single crystals, as is shown by their cleavages. Whether these crystals grew without the development of faces, or they later underwent partial solution, is a moot question. Rarely the smaller masses are subhedral, but in general these phosphates are low in the writer's morphogenetic series. It may seem unreasonable to think that essentially all of the larger crystals have suffered corrosion, but the Fe-Mn phosphates are very sensitive to oxidation.

X-RAY EXAMINATION

Precession pictures were taken of samples from La Vilate quarry near Chanteloube, Haute Vienne, France, and the Buranga pegmatite (lat. $1^{\circ}48'$ S., long. $29^{\circ}40'$ E.) in Ruanda, Central Africa (Thoreau, 1954). These were in good agreement, but the better results were obtained from the Buranga material. The crystals were monoclinic.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>B</i>
Buranga—	$12.004 \pm .002$	$12.533 \pm .004$	$6.404 \pm .001$	$114^{\circ}22' \pm 05'$
Chanteloube	$11.99 \pm .02$	$12.44 \pm .04$	$6.38 \pm .02$	$114^{\circ}20' \pm 10'$

The diffraction symbol is $1\ 2/m\ 1\ C \cdot c \cdot$; the conditions limiting the possible reflections are

$$hkl: h + k = 2n$$

$$h0l: l = 2n; (h = 2n)$$

$$0k0: (k = 2n)$$

The space group is thus $8-Cc=C_s^4$ or $15-C2/c=C_{2h}^6$, probably the latter.

Solely from the point of view of lattice geometry the elements could be $a:b:c=11.02:12.52:6.38$ with $\beta=97^{\circ}40'$. This is a less oblique cell, but yields systematic absent spectra which do not fit space group criteria. The transformation formula from this cell to the true one is $101/\bar{0}\bar{1}0/\bar{0}\bar{0}\bar{1}$.

Powder films were taken of alluaudite from several localities; the measurements are given in Table 1, and copies of four of them appear in Fig. 1. The Guinier-Wolff (Nonius) camera results, No. 4 in Table 1, are considered to be most accurate, since the dispersion of this instrument is equivalent to what would be obtained from an ordinary 229 mm. powder camera. Of course the number of lines shown in Table 1 depends on the dispersion of the camera. Using a standard 114 mm. camera, alluaudite is well characterized by the following six lines:

$$\frac{2.73/10}{12 \text{ (also } 13?)}, \quad \frac{6.27/8-}{2}, \quad \frac{3.07/7}{7-9}, \quad \frac{2.51/7-}{17}, \quad \frac{5.47/6-}{3}, \quad \frac{3.49/6-}{5}$$

The symbol is: (spacing/intensity)/(line number), where relative in-

TABLE 1. SPACINGS AND INTENSITIES FROM ALLUAUDITE POWDER FILMS

Line No.	Indices*	Computed spacings	1 Fringle		2 Sukula		3 Chanteloube			4		5 Burunga		6		7 Varutrask
1	110	8.19	3	8.241	1½	8.181†	3	8.181†	2+	8.3889	2	8.25	8.13	8.325		
2	020	6.266	8	6.296	8	6.279	8	6.261†	8	6.3650	7	6.25	6.271	6.246		
3	111	5.67	6	5.470	6	5.470	6	5.470†	4	5.5247	5	5.45	5.458	5.363		
—	200	5.468	6	5.470	6	5.470	6	4.880†	—	—	—	4.90	—	—		
—	021?	4.299	—	—	—	—	—	—	—	—	—	—	—	—		
4a, b	111, 220	4.182, 4.142	3	4.119†	1½	4.157†	2	4.119†	2	4.1522	1	4.65	4.33	—		
—	221, 130	3.99, 3.97	—	—	—	—	—	—	—	—	—	4.12	4.100	—		
—	311	3.708	—	—	—	—	—	—	—	—	—	—	—	—		
5	310, 131	3.49	5	3.493	5	3.509	6	3.482†	7	3.5145	5	3.49	3.471	3.471		
6a	202?	3.18	1	3.351	—	—	—	—	—	—	—	3.31	—	—		
6b	040	3.133	1	3.204	—	—	—	—	—	—	—	—	—	—		
7	112	3.072	5	3.053	5	3.081§	7	3.053†	5	3.0857	8	3.05	3.042	3.051		
8	131	3.047	—	—	—	—	—	—	—	—	—	—	—	—		
9	221	2.964	—	—	—	—	—	—	—	—	—	—	—	—		
10	002	2.9168	—	—	—	—	—	—	—	—	—	—	—	—		
11a	312	2.868	1	2.909	2	2.934	1	2.888	1	3.2049	—	—	—	—		
11b	331, 222	2.849, 2.836	3	2.860†	1	2.877	2+	2.860	2	3.1635	1½	2.90	2.851	2.871		
11c	041	2.760	3	2.819§	1	2.855§	1	2.819	1	2.7744	—	2.81	—	—		
12a	330, 400	2.745, 2.734	10	2.715	10	2.737†	10	2.715†	7	2.7431	10	2.71	2.706	2.706		
12b	240	2.696, 2.680	2	2.643†	1	2.667	1	2.643	10	2.7328§	—	—	—	—		
13	(421), 241	2.647	2	2.643†	1	2.614	1	2.643	10	2.7057	—	—	—	—		
14	402	2.600	2	2.586†	1	2.583	1	2.591	1	2.6124	—	2.63	2.617	—		
15	—	—	—	—	—	—	—	—	—	—	—	—	—	—		
16	311	2.583	2	2.586†	6	2.537	1	2.591	½	2.5941	—	2.578	2.58	—		
17a	132?	2.525	—	—	—	—	—	—	½	2.5344	—	—	—	—		
17b	112, 420	2.517, 2.500	4	2.510†	6	2.537	6	2.510†	2	2.5171	6	2.50	2.496	2.509		
18	150	2.443	1	2.396†	1	2.415	1	2.400	2	2.4183	—	2.39	—	—		
—	332?	2.408	1	2.396†	½	2.415	1	2.400	½	2.4183	—	—	—	—		
19	422, (511), 151	2.396-2.332	1	2.336	1	2.349	1	2.327	1	2.3495	—	2.32	2.3495	—		
20	(241), 331, (242)? (202)	2.290-2.225	1	2.246	1	2.246	1	2.226	1	2.2395	—	2.22	2.2395	—		
21	(512), (132), (151)	2.210-2.183	2	2.145	2	2.204	2	2.182	2	2.1938	—	2.18	2.1938	—		
22	(441), (510)	2.160, 2.151	2	2.145	2	2.169	2	2.148	2	2.1624	—	2.15	2.1624	—		
23	042?, (351), (222)	2.135-2.096	3	2.145	2	2.169	2	2.148	2	2.1361	—	2.15	2.1361	2.146		

Line No.	Indices*	Computed† spacings	1 Pringle		2 Sukula		3 Chanteloube		4		5 Buranga		7 Varutrisk	
			4	3	3	2	4	2	2	1	2	3		6
24a	060, 313, (531)	2.089-2.078	4	2.084	3	2.108	4	2.084	2	2.0759	3	2.08	2.085	
24b	350, 440, (421), (113)	2.064-2.033	3	2.063§	2	2.079§	3	2.06§	1	2.0481§		2.06		
—	223, 442?	2.015, 1.998												
—	532, (152)?, (061)	1.980-1.966	3	1.952	3	1.961†	1	1.982†	1	1.9432		1.975		
25a	260, 602	1.951, 1.944	3	1.931§	3	1.923	3	1.949	2	1.9432		1.94		
25b	(261), 530, 423	1.937-1.929	3	1.931§	1	1.923	1	1.934§	2	1.9432		1.93§	1.938	
26	352, (312)	1.908, 1.902	1	1.897†	1	1.897†	1	1.903†	3	1.9186		1.90		
—	621, 353	1.886												
27	(513), (023), 622	1.869-1.853	1	1.854	1	1.871	1	1.859	1	1.8702		1.8702		
28	(138), (600), 351	1.848-1.813	2	1.838§	2	1.833	2	1.833	1	1.8254		1.8254		
—	242?	1.818	2	1.818				2	2	1.818		1.818		
29	511, 152?	1.795, 1.793	2	1.793	2	1.808	2	1.793	1	1.8006				
—	113, 441, 261	1.775-1.773												
30a	(170), 243?	1.767, 1.761	2	1.744†	1	1.779	1	1.764	2	1.7686		1.745	1.743	
30b	332, (620), (262)?	1.748-1.746	2	1.744†	3	1.761§	2	1.744	1	1.7519				
31	(551), 171, (538)?	1.730-1.722	1	1.721	2	1.738	1	1.723	1	1.7317				
—	461, 443, 062?	1.711-1.700												
—	402, 712, 711	1.680-1.674												
32	641, 552, 623, 531, (171)	1.674-1.660	2	1.648	2	1.664†	2	1.656	2	1.6631		1.647	1.649	
—	133, 642, 460	1.649-1.647												
33	550, (462), (371), 422	1.646-1.622	1	1.624†	1	1.634	1	1.619	1	1.6226				
34a	(383), 370	1.616, 1.607	1	1.598§	2	1.594†	2	1.595	1	1.5996			1.611	
34b	314, 153?, 404	1.593-1.592	3	1.575†	3	1.575†	3	1.575†	5	1.579†	3	1.575	1.574	
35	203, 223, 640, 080	1.587-1.5667	1	1.546	2	1.545	2	1.549	2	1.5824†		1.575	1.574	
36														
37			2	1.529	2	1.526	2	1.533	2					
38			1	1.515	1	1.509	2	1.517	2					
39			1	1.492†	3	1.483	2	1.498	2					
40			2	1.468				1.471	2					
—								1.459	2					
41			1	1.450†	2	1.432†	2	1.448	2					
42			1	1.413†	2	1.409†	2	1.418	2					
—				1.384†										

* Indices in parentheses are regarded as unlikely ones.
 † Spacings (non-pinacondal) computed graphically, using Peacock-Bloss technique.
 ‡ Diffuse line.
 § Doublet (with the line immediately above).
 Nos. 1, 2, and 3 taken on Straumanns (Philips) 114 mm. camera with Fe/Al radiation; spacings and intensities by Leon Atlas; back-reflection lines (none very strong) omitted.
 No. 4 taken on Guinier-Wolf (Nonius) multiple camera with monochromatized cobalt radiation.
 No. 5 taken like numbers 1-3, but spacings by D. J. F. using a Nies scale; all intensities not given are <1; 10 weak lines between 1.90 and 1.575 omitted.
 Nos. 6 and 7 computed from results by Thoreau.

tensities are on a 10 unit scale. The indices of the lines involved can be obtained from the line number, using Table 1.

The relative intensities of the diffracted spots from all but 19 of the planes listed in the second column of Table 1 were observed on single crystal pictures. Those not seen include 021 , $22\bar{1}$, $13\bar{2}$, $33\bar{2}$, $24\bar{2}$, 132 , 042 and 12 others (all with $d < 2.0$) indicated by a question mark (?) in the table. There was good agreement between observed intensities on the single crystal photos and those on the powder films except as follows: $(20\bar{2})$ no. 6a is very weak on single crystal pictures; $(53\bar{2})$ just above No. 25a is very strong on single crystal pictures; $(33\bar{3})$ just above No. 27 has intensity 3 on single crystal pictures; while (133) and $(64\bar{2})$ just above No. 33 have intensities of 3 and 9 on single crystal pictures. It is possible that numbers should be assigned to the lines just above Nos. 25a and 33.

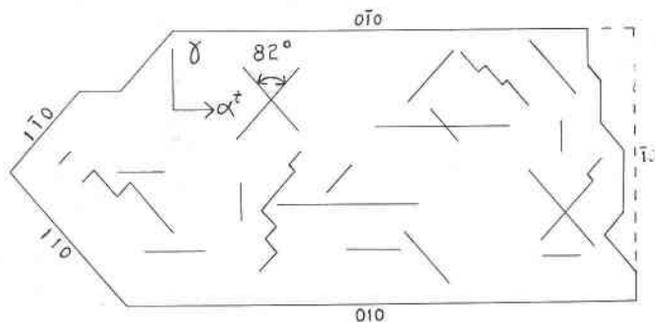


FIG. 2. Sketch of $(\bar{1}01)$ cleavage flake of alluaudite, modified slightly from J. Thoreau. α is $10^{\circ}.75$ off the plane of the section, dipping "down" in the direction of the arrow. The $(\bar{1}00)$ plane makes an angle of about $82\frac{1}{2}^{\circ}$ with the plane of the section; the angle is about $84\frac{1}{2}^{\circ}$ for the $\{110\}$ planes.

OPTICAL PROPERTIES

The $(\bar{1}01)$ cleavage flake of Buranga alluaudite, still on the same goniometer head with $[a^*]$ parallel its axis used for taking the x -ray precession pictures, was mounted on the universal microscope-goniometer (Fisher, 1952). Using the latter as a one-circle optical goniometer, it was determined that the S -arc had to be moved through $7^{\circ}.39$ to bring the $(\bar{1}01)$ cleavage (which was substantially parallel to the L -arc) parallel the dial axis. Using the instrument as a microscope with the crystal projecting into a cell containing methylene iodide, it was found that the S -arc had to be moved through an additional $10^{\circ}.75$ to bring an indicatrix axis (α) parallel to the dial axis. It was thus shown that $\alpha \wedge [a^*] = 18^{\circ}.14$; or that $\beta \wedge [c] = +18^{\circ}.14$ (with β lying in angle μ or "acute angle β ") since $[b] \sim \gamma$. Figure 2 shows J. Thoreau's sketch, slightly modified, with the addition of indices.

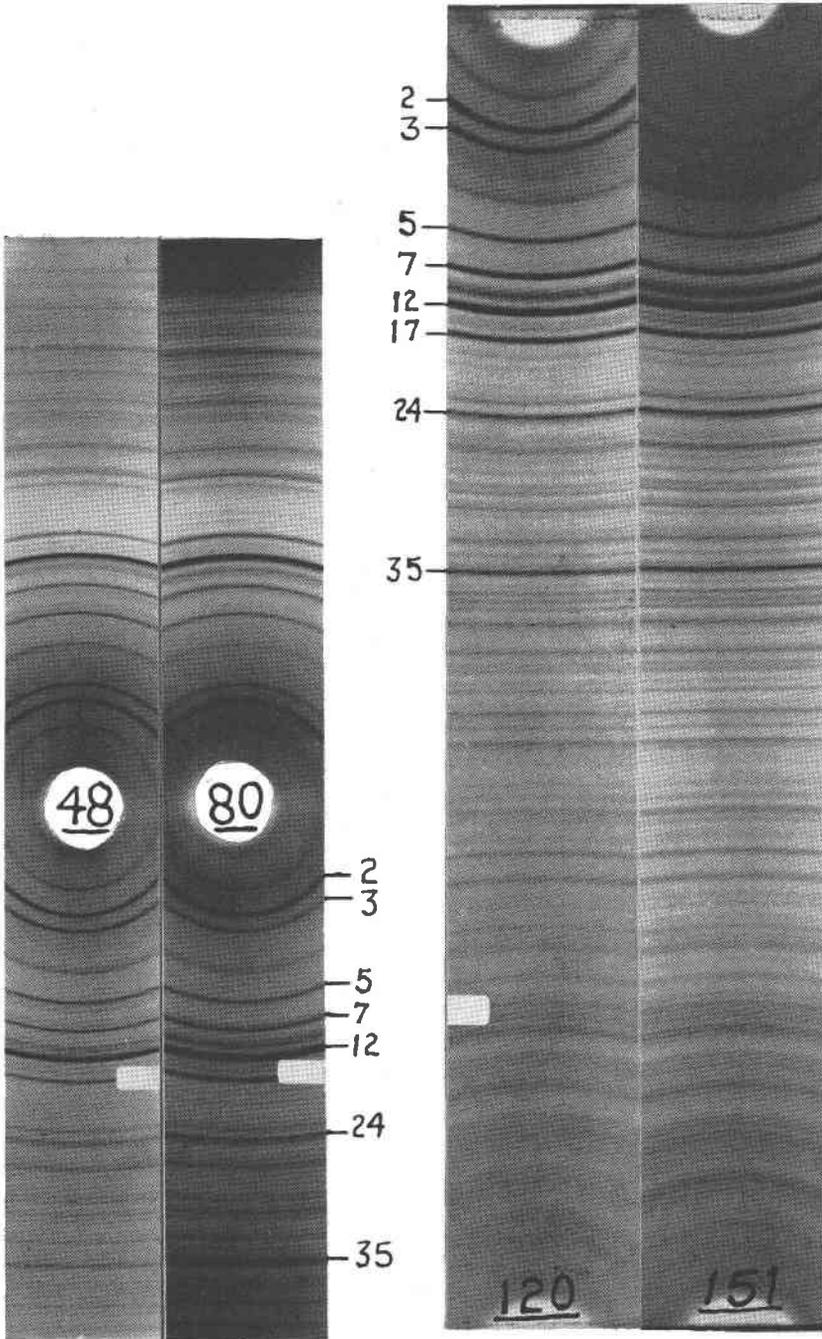


FIG. 1. Alluaudite powder films; left to right: Pringle, Sukula, Chanteloube, Buranga. All taken with Fe/Mn radiation in a 114 mm. Straumanis (Philips) camera. The two on the left are reduced; the others are approximately natural size. Some of the lines are numbered to correspond with what is given in the first column of Table 1.

The attempt to measure α was unsuccessful since its value appears to be above that of my 1.78 oil (*S* in methylene iodide) which at the temperature examined has indices 1.7887 (*E*-line) or 1.7747 (*D*-line). Even at $\lambda=500\text{m}\mu$ ($n=1.7966$) α of alluaudite seemed to be higher than the oil. I believe that the approximate value of α of 1.77 given by Thoreau is somewhat low. The higher $-n$ oils at my disposal contain phenyldiiodoarsine or arsenic tribromide; even the latter is not very transparent when used in the thinnest ($1/16''$) cell of my instrument, and the results obtained could not be interpreted satisfactorily.

In determining the birefringence $\gamma-\alpha$ of the crystal, the thickness of the cleavage flake was found to be 0.03340 mm. (in a direction $10\frac{3}{4}^\circ$ off the normal), and between crossed polars at 45° the retardations R observed are shown in Table 2. That is, for $\lambda=630$, the retardation was just 3λ ; for $\lambda=533$, it was just 4λ ; and in white light it was estimated that R

TABLE 2. BIREFRINGENCE ($\gamma-\alpha$) OF ALLUAUDITE

No.	λ	R	$R/t=\gamma-\alpha$
3	630	1890	0.0567
—	white	2000	0.0599
(3.454)	579	2000	0.0599
4	533	2132	0.0638

was 2000, using the Michel-Lévy birefringence chart; this corresponds to the data in line 3 of the table. It is considered that the birefringence values given for $\lambda=630$ and 533 are accurate within a few units in the fourth place. In short this technique leads to a quite accurate determination of the dispersion of the birefringence.

It was impossible to observe $\beta-\alpha$, since one is then looking nearly parallel the cleavage flake and the thickness is thus so great that the crystal is opaque. When looking at the $\gamma\alpha$ section the thin edges show the color for α as light brown, that for γ dark brown; i.e., $\text{Abs.}_\gamma \gg \text{Abs.}_\alpha$.

Working with crushed grains embedded in immersion media and using a sodium light Mrs. Phyllis Hull determined the indices of refraction of the Pringle alluaudite to be $\alpha=1.782 \pm .005$; $\beta=1.802 \pm .002$ and $\gamma=1.835 \pm .01$. Its color varies from pale olive (α) to medium olive (γ).

Study of a thin-section of the Buranga alluaudite on the universal stage (1.649 segments) using white, Na-vapor, and filtered Hg-vapor ($\lambda=546\text{ m}\mu$) light, yielded the following results. $\text{Abs.}_\gamma = \text{Abs.}_\beta > \text{Abs.}_\alpha$; the colors are: $\alpha \rightarrow$ straw to greenish-yellow straw; and $\beta = \gamma \rightarrow$ light yellow green to pale olive greenish to brownish-yellow. These observations were made on three different crystals using a micro-dichroscope; of course the

deeper shades refer to conditions where the thickness of the section was greater, due to higher tilt angles. The material is optically positive with $2V_{Na}=79.02$ and $2V_{Hg}=78.90$; i.e., crossed dispersion $r > v$, moderate. Thus since $\gamma - \alpha = 0.060$, it follows that $\gamma - \beta = .035$ and $\beta - \alpha = .025$. Crystals observed looking approximately along $[b] \rightarrow \gamma$ show thin polysynthetic twin lamellae with (101) the composition plane. The latter is a plane of symmetry between the two parts of the twin, since when it is set normal to the A_4 -axis (and parallel the vibration direction of the polarizer) the twin lamellae and the main part of the crystal show the same interference color, no matter what the A_4 reading. The absence of extinction between crossed polars when looking along an optic axis is very pronounced. This made orientation of the optic plane by standard extinction procedure quite difficult. This was remedied by using the isogyres for orientation purposes as follows: after getting approximate orientation by standard procedures and rotating on A_4 (conoscopic observation; polars at 45°) till a melatope is at the center of the field with an isogyre approximately parallel to A_4 , the stage is rotated 45° on A_5 making the isogyre about normal to A_4 ; it is brought normal to A_4 by rotation on A_1 and made to go through the center of the field by tilting on A_2 . Repetition of this procedure once or twice results in very perfect orientation of the optic plane. It should be noted that the absence of extinction along an optic axis is not due to dispersion (even in monochromatic light there is no extinction) but is caused by conical refraction (there is no evidence of rotary polarization); the conical angle for alluaudite is about $1^\circ 53'$.

CHEMICAL COMPOSITION

The results of recent analyses of alluaudites appear in Table 3. It will be noted that these samples are much closer to the iron-end of the Fe-Mn series than is true for any previously-described samples. Thus the Fe/Mn ratio is 1.07 (Sukula), 1.76 (Buranga), and 2.29 (Pringle); all other described samples are mangan-alluaudites. The original alluaudite carries slightly more manganese than iron (Fe/Mn=0.96). Nevertheless Dana's System (II, 674, 1951) has followed Quensel (1937) in using the terms alluaudite and mangan-alluaudite rather than alluaudite and ferri-alluaudite as would seem more logical. Spectrographic examination of the Green Mine alluaudite by Oiva Joensuu showed traces of Al, Ti, and Cu; and absence of Li, Co, Ni, Zr, Zn, Cd, Ag, Mo, V, Bi, Ge, Ga, W, Cr, and Pb. Recent work (Fisher, 1955) has stated that ferrodickinsonite (arrojadite) alters to alluaudite when heated between 485 and 555° C. It thus follows that the two must have related formulas, in which water is considered to play no essential role. This matter will be discussed

TABLE 3. RECENT ANALYSES OF ALLUAUDITES

	1	2
Li ₂ O	—	0.09
K ₂ O	0.02	—
Na ₂ O	4.4	3.90
CaO	4.04	1.40
MgO	0.40	0.47
FeO	1.61	—
MnO	12.9	15.34
Fe ₂ O ₃	30.9	31.48
Mn ₂ O ₃	—	0.88
P ₂ O ₅	43. ±	42.15
H ₂ O+	1.9	} 3.55
H ₂ O—	0.05	
Insol.	1.12	0.58
Total	100.34 ±	99.84

1. Green Mine near Pringle, S. Dak. Analysis by Brynjolf Bruun.
2. Buranga, Ruanda from Thoreau (1954). Other known analyses appear in Dana's System 2 (1951) 674.

in detail in a paper on dickinsonite now nearly ready for submission for publication.

THERMAL PROPERTIES

Heated in air for 24 hours Chanteloube alluaudite melts at about 1000°C.; the air-quenched sample failed to give an alluaudite powder diffraction pattern. Quenched from 990°, although the sample showed strong sintering, it yielded a perfect alluaudite diffraction film. The 960° sample showed only very slight sintering. Professor Thoreau* informs me that the 700° fusion figure given in his paper for the Buranga alluaudite was a typographical error; it should have been 850/860°. His statement regarding the absence of *D.T.A.* phenomena in alluaudite referred only to higher temperatures; he says there is a pronounced endothermal break at 215° C. due to loss of water (Thoreau and Bastien, 1954).

ACKNOWLEDGMENTS

Besides previous credits the writer thanks Dr. Brian Mason for samples from Sukula and Varuträsk, Dr. J. Thoreau for a fine Buranga sample, and Dr. F. A. Bannister for the Chanteloube specimen (British Museum 89941).

* Personal communication (11 Febr. 55).

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