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## VARIATION OF SOME RARE EARTHS IN ALLANITE<sup>1</sup>

JUDITH W. FRONDEL, *Harvard University, Cambridge, Mass.*

### ABSTRACT

Using *x*-ray spectrographic techniques, 64 specimens of allanite from 51 localities were analyzed for Ca, Ce, La, Nd and Y. Ce is the chief rare-earth in allanite, and makes up usually at least one-half of the total rare-earths. Ce almost always predominates over La in atomic per cent, with the ratio of Ce to La generally between 2:1 and 3:1. Nd, always present, is a significant member of the Ce group, and occurs in amounts greater than those of Y. Y is lacking in many allanites and rarely occurs in large amounts. Allanite—like minerals having  $Y_2O_3$  greater than 5.0 per cent may represent separate species, since *x*-ray diffraction patterns of such specimens are different from those of allanite. Except for these specimens of anomalous rare-earth composition, all heated specimens, in which order was restored, gave the allanite *x*-ray diffraction pattern. Heating increased the refractive indices of allanite.

### SPECIMENS STUDIED

In investigating the rare-earth variation in allanites, a total of 64 specimens were studied. All of these specimens, with the exception of two which came from the mineral collection of Bryn Mawr College, were selected from the Harvard University mineral collection, and represent 51 well-known allanite localities all over the world (Table I).

### X-RAY SPECTROGRAPHIC ANALYSIS

All specimens were analyzed with a Norelco broad-focus *x*-ray spectrograph, using a flow-counter with methane-argon gas mixture, a helium path and tungsten excitation. The unit was run at 50 KV and 45 ma. A chart-recorder was used and quantitative measurements were based on peak to background ratios. The samples were prepared for analysis in the following manner: A one-gram, powdered sample of each specimen was mixed with 15 grams of anhydrous borax [ $Na_2B_4O_7$ ] glass and fused in a platinum crucible at 1000° C. for 3 hours. The fusion was cast in a steel ring-mold held at 450° C., and then was annealed at 250° C. for 12 hours. This dilution method of sample preparation was used to minimize matrix absorption effects. The case buttons provide permanent and easily storable samples.

<sup>1</sup> Mineralogical Contribution No. 413, Harvard University.

TABLE I. LIST OF SPECIMENS STUDIED.

Specimen No.	Catalogue No.	Locality	Brief Description of Hand Specimen
(1)	Chaffee, C-1	Chaffee Co., Colorado	Prisms in red feldspar. Pegmatite veins in quartz monzonite.
(2)	Everard, SA-1	Everard Range, South Australia	Black vitreous large crystal, oxidized surface. Pegmatite veins in granite.
(3)	Nutarami, G-1	Nutarmint, Avigeit, West Greenland	Black, vitreous, in feldspar in granite rocks containing hornblende zircon crystals and allanite.
(4)	Pacoima, P-1	Pacoima Canyon, Los Angeles Co., California	Large platy crystals, dull greasy. Pegmatite intrusions in gabbro.
(5)	37111	Monroe, Orange Co., New York	Large crystal fragment, vitreous black. In gneiss.
(6)	37121	Buoe, near Arendal, Norway	Nearly pure mass, vitreous black, some feldspar and veinlike black greasy inclusions. Pegmatite veins in gneiss.
(7)	37144	Baringer Hill, Llano Co., Texas	Rounded pure mass, 5"×4"×1", vitreous black. Pegmatite in granite.
(8)	37211	Skepholm, Sweden	Small crystals in granitic veins and gneisses.
(9)	37231	Miask, Urals	Fragment of large platy (?) crystals. Inter-grown in miascitic granite.
(10)	80512	Avigeit, Greenland	Vitreous black small crystals in granite rocks containing hornblende, zircon crystals and allanite.
(11)	84632	Arendal, Norway	Large conchoidal vitreous black fragment. Pegmatite veins in gneiss.
(12)	86081	East Bradford, Chester Co., Pennsylvania	Weathered nodule. Pegmatite in granodiorite.
(13)	86089	Arendal, Norway	Large platy crystal. Pegmatite veins in gneiss.
(14)	86090	Modum, Norway	Columnar, in feldspar. In granite pegmatite.
(15)	91307	Friar Mountain, Lowesville, Virginia	"altered," dull greasy black. In granite pegmatite.
(16)	91985	Vaarala, Finland	Black vitreous, in feldspar. Pegmatite in granite gneiss.
(17)	92933	Woburn, Massachusetts	Black vitreous, massive, with pink feldspar. Pegmatite veins in gneiss.
(18)	96020	Hybla, Ontario, Canada	Black vitreous fragment. In granite pegmatite.
(19)	97399	Lake Baikal, Russia	Platy crystals, oxidized surface. In mica-pegmatite.
(20)	98965	Near Eau Clair, Nipissing District, Ontario, Canada	Large platy crystal. In granite pegmatite.

TABLE 1—(continued)

Specimen No.	Catalogue No.	Locality	Brief Description of Hand Specimen
(21)	99264	Franklin, Sussex Co., New Jersey	Platy crystals in green feldspar, with feldspar and magnetite.
(22)	99811	Consolidated Spar Mine, Kingman, Arizona	Black, vitreous, columnar. In granite pegmatite.
(23)	102385	Lac à Baude, Normand Twp., Laviolette Co., Quebec, Canada	Small fragment, vitreous, black. In granite pegmatite.
(24)	102406	Ytterby, Waxholm, Sweden	Columnar, vitreous, black. In granitic feldspar-rich differentiation of a black amphibolite.
(25)	102412	Lescombe property, Monmouth Twp., Haliburton Co., Ontario, Canada	From phlogopite mine, dull greasy type, very high Th (determined by qualitative run in x-ray spectrograph). From syenite pegmatite (?).
(26)	102414	White Face Mountain, Adirondacks, New York	Large fresh vitreous crystal (in anorthosit?)
(27)	102415	Midongy de l'Ouest, Madagascar	Fragment, vitreous black shiny. K-rich pegmatites in granites and schists.
(28)	102422	Bokspit, South Africa	Fragment of large crystal. Greasy. Dull; high Th (determined by qualitative run in x-ray spectrograph). Pegmatite in granite-gneiss.
(29)	102423	Frøyso 4, Iveland, Norway	Piece of large crystal, black vitreous. In granite pegmatite.
(30)	102429	Tvedestrand, Norway	Broken crystal. In granite pegmatite.
(31)	102449	Huddersfield Twp., V. 22, Pontiac Co., Quebec, Canada	Large bent platy crystals, with phlogopite, dull, greasy. In apatite-mica-pegmatite.
(32)	102470	Johnson Co., Wyoming	Greasy type, heavy. In granite pegmatite.
(33)	102471	Tataslawi, Randu, Dutria, Bihar, India	Large mass. Pegmatites in mica-schists and gneisses.
(34)	102480	1½ miles northeast of Jamestown, Colorado	Large irregular mass. In granite pegmatite.
(35)	102499	Gole Mine, Murchison Twp., Nipissing Dist., Ontario, IV, 14, Canada	Large altered columnar crystals. In granite pegmatite.
(36)	102505	Vaarala, Finland	Thick tabular crystals, sub-vitreous, black. Pegmatite in granite gneiss.
(37)	102506	Dickens Twp., Nipissing Dist., Ontario, Canada (from between Barry's Bay and Malawalka?)	Platy crystals, with feldspar, mica, quartz. In granite pegmatite.
(38)	102508	La Marche Mine, Kensington Twp., Gateneau Co., Quebec IV, 45, Canada	With sphene, calcite, feldspar, molybdenite. In apatite-mica-pegmatite.

TABLE 1—(continued)

Specimen No.	Catalogue No.	Locality	Brief Description of Hand Specimen
(39)	102512	Lyndoch Twp., V. 23, Renfrew Co., Ontario, Canada	Platy crystals. In granite pegmatite.
(40)	102516	La Marche Mine No. 2, Kensington Twp., Gateneau Co., Quebec IV, 45, Canada	Thin platy crystals (1 cm. X 1 mm.) and massive, with molybdenite, biotite, calcite. In apatite-mica-pegmatite.
(41)	102517	Lyndoch Twp., Renfrew Co., Ontario, Canada	Platy crystals in quartz, feldspar. In granite pegmatite.
(42)	102522	Macdonald Mine, Hybla, Ontario, Canada	Very large rough mass, shiny, subvitreous. In granite pegmatite.
(43)	102529	Twin Valley Mine, Huddersfield Twp., Pontiac Co., Quebec, Canada	With apatite, fluorite, phlogopite. In apatite-mica-pegmatite.
(44)	102534	Cardiff Twp., Ontario, Canada	Platy or lenticular small crystals in granite pegmatite.
(45)	102565	Argenteuil Co., Quebec, Canada "Old Sigelno property near Calumet," "Pleinville II, 27 (?)"	With ilmenite and micro-monazite. In granite pegmatite.
(46)	102573	Clapham Twp., IV, 28, Pontiac Co., Quebec, Canada	Large platy mass, vitreous, greasy, feldspar, mica, with diopside, scapolite, phlogopite. Vein in pyroxenite (?).
(47)	102585	Huddersfield Twp., Pontiac Co., Quebec, Canada	With fluorite, phlogopite, scapolite (?), massive, black. In apatite-mica-pegmatite.
(48)	102599	Macdonald Mine, Hybla, Ontario, Canada	1-foot mass, dull greasy, pyrite inclusions. In granite pegmatite.
(49)	102660	Cardiff Twp., Haliburton Co., Ontario XX, 7, Canada	Large platy crystals, with tengerite (?), red feldspar, calcite. In granite pegmatite.
(50)	102661	Gole Mine IV 14-15, Murchison Twp., Nipissing Dist., Ontario, Canada	Large altered columnar crystals. In granite pegmatite.
(51)	103886	Woburn, Massachusetts (A.C. Lane spec.)	In feldspar, with epidote. Pegmatite in gneiss.
(52)	105680	Aquarius Range, Mohave Co., Arizona	Black dull greasy fragment of large crystal, Ga, Pb, Be in spec. In granite pegmatite.
(53)	106172	Woodland Park, Colorado	Large crystal fragment, vitreous black. In granite pegmatite.
(54)	106180	Trout Creek Dist., Chaffee Co., Colorado	Columnar crystal, dull, greasy. Pegmatite in quartz monzonite.
(55)	106184	Amherst Co., Virginia	Large crystal, dull greasy, oxidized on surface. In altered feldspar in pegmatite.

TABLE 1—(continued)

Specimen No.	Catalogue No.	Locality	Brief Description of Hand Specimen
(56)	102875	Essexville, New York	Platy crystals in feldspar rock. In magnetite deposit.
(57)	No. 4, orthite?	Føne, Gjerstad, Norway	Grayish-black, fine-grained, possibly a mixture. In granite pegmatite.
(58)	No. 116, orthite	Flosta, Narestø, near Arendal, Norway	Black, vitreous, massive. Pegmatite in gneiss.
(59)	—	Eretveit, Iveland, Norway	Black, vitreous, massive. In granite pegmatite.
(60)	No. 1, Landsverk	Landsverk No. 1 pegmatite, Iveland, Norway	Black, columnar, sub-vitreous. In granite pegmatite.
(61)	—	Slobrekka pegmatite, Iveland, Norway	Very black, vitreous, marked conchoidal fracture. In mica-pegmatite.
(62)	—	Black Cloud mine, Divide, Teller Co., Colorado	Black, vitreous, conchoidal fracture. In granite pegmatite.
(63)	Vaux 5983 (from collection at Pennsylvania)	Near Pala, San Diego Co., California	Grayish-black, sub-vitreous. Pegmatite in gabbro.
(64)	Vaux 5985 (from collection at Bryn Mawr Coll., Pennsylvania)	E. Bradford, Chester Co., Pennsylvania	Grayish-black, weathered. Pegmatite in granodiorite.

*Method of analysis.* First, a standard "allanite mix" (Table II) was made from oxides weighed out in the proper molar proportions. The "average allanite" composition was computed from 61 representative analyses reported in the literature. The small content of alkalis, water, and of other accessory constituents was disregarded. Rare-earth standards were prepared by adding to this bulk mixture  $Ce_2O_3$ ,  $La_2O_3$ ,  $Nd_2O_3$  and  $Y_2O_3$  in varying molecular proportions and totaling 19.15 weight per cent. Each sample then was mixed with borax glass to give a weight ratio of 1:15 and was fused and cast. These buttons not only served as preliminary standards, but were used continually throughout the investigation to check the stability and response of the  $x$ -ray spectrograph.

The standard buttons were run in the  $x$ -ray spectrograph for Ce, La, Nd and Y, and the 55 specimens, prepared as buttons, also were run for these elements. Four of the 55 specimens were selected for conventional wet-method chemical analysis. Complete analyses were made on two specimens, one lacking Y and the other exceptionally high in Y. Partial analyses were made on two specimens representing the average Ce and La occurrence in allanite (Table III).

In the standard allanite buttons the per cent of CaO was constant, 9.96 weight per cent. Results for CaO in the two wet-method chemical analyses (42 and 35, Table III) were taken and, together with the standard buttons, formed the basis for a standard graph for Ca. The 55 allanite buttons were run then also for Ca. Comparisons of wet-method chemical analyses and *x*-ray fluorescence analyses on the same sample are made in Table IV. The results of all the *x*-ray spectrographic analyses are tabulated in Table V. Results were recalculated on the basis of the total rare-earths determined—100 per cent (Table VI).

TABLE II. STANDARD "ALLANITE MIX"

Oxide	Weight Per Cent
SiO <sub>2</sub>	31.81
Al <sub>2</sub> O <sub>3</sub>	15.84
Fe <sub>2</sub> O <sub>3</sub>	5.88
FeO	9.00
MnO	1.52
CaO	9.96
MgO	0.67
ThO <sub>2</sub>	1.18
UO <sub>2</sub>	0.30
TiO <sub>2</sub>	0.77
H <sub>2</sub> O	3.92
Total	80.85

Added to this standard mix were Ce<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>, in varying molecular proportions and totaling 19.15 weight per cent.

*Analysis on powders.* The four specimens analyzed by wet chemical methods were run also as powders in the *x*-ray spectrograph. Care was taken to have the samples uniformly ground and packed in the sample-holder. Graphs were plotted from the results and a comparison was made with the results on the same specimens run as buttons. The amount of error in the analyses on powder, due probably to element interference, was from less than 1 to 2.5 per cent for Y, from 6 to 20 per cent for Nd, from 3 to 5 per cent for Ce, and from less than 1 to 8 per cent for La. Though at first thought this may seem considerable, yet it would appear practical to run powders instead of borax fusions whenever only general orders of magnitude are needed or when time and apparatus for making the fusions are not available. With this consideration, nine specimens, for which borax fusions had not been made, were analyzed as powders only (Tables VII and VIII).

TABLE III. ANALYSES MADE BY CONVENTIONAL WET METHOD<sup>1</sup>

## A. Partial Analyses

Sample No.	(9)	(27)
Ce, La oxides	19.84	20.34
Y, Nd oxides	0.21	0.32
H <sub>2</sub> O (+)	3.45	2.79
H <sub>2</sub> O (-)	nil	nil

## B. Complete Analyses

Sample No.	(42)	(35)
SiO <sub>2</sub>	32.29	33.16
TiO <sub>2</sub>	0.06	0.24
Al <sub>2</sub> O <sub>3</sub>	18.19	18.69
Fe <sub>2</sub> O <sub>3</sub>	6.53	4.36
FeO	7.98	9.30
MgO	0.78	0.46
CaO+SrO	14.70	12.46
ThO <sub>2</sub>	0.41	0.33
Σ Ce, La oxides	15.00	7.60
Σ Y, Nd oxides	1.49	7.89
MnO	0.30	2.68
P <sub>2</sub> O <sub>5</sub>	0.21	0.13
H <sub>2</sub> O (+)	1.97	2.47
Na <sub>2</sub> O	.005	.022
K <sub>2</sub> O	nil	nil
SO <sub>3</sub>	tr.	nil
U <sub>3</sub> O <sub>8</sub>	n.d.	n.d.
PbO	tr.	tr.
Total	99.91	99.79
Ce <sub>2</sub> O <sub>3</sub>	6.72	1.54
Trace elements found spectrographically	Ga, Cu, Sn, Ni, Cr, Co, Mo, Zr, V, Bi, Be and Sc.	

<sup>1</sup> Analyst, Jun Ito.

*Results of x-ray spectrographic analysis.* In all but two samples, (35 and 50), Ce is the predominant rare-earth. In no sample is Ce<sub>2</sub>O<sub>3</sub> less than La<sub>2</sub>O<sub>3</sub> and the ratio of Ce<sub>2</sub>O<sub>3</sub> to La<sub>2</sub>O<sub>3</sub> almost always is between 2 to 1 and 3 to 1. In all except 5 of the samples Y<sub>2</sub>O<sub>3</sub> is less than Nd<sub>2</sub>O<sub>3</sub>. X-ray diffraction patterns<sup>1</sup> obtained on two (35 and 50) of these exceptional speci-

<sup>1</sup> See section on x-ray diffraction analysis.

TABLE IV. COMPARISON OF RARE EARTH DETERMINATIONS BY WET METHOD  
CHEMICAL ANALYSIS AND X-RAY SPECTROGRAPHY

Sample No.	Wet Method		X-Ray Spectrography	
	Oxides	Wt. Per Cent	Oxides	Wt. Per Cent
(9)	Ce+La Oxides	19.84	Ce+La Oxides Nd <sub>2</sub> O <sub>3</sub>	22.1 1.5
			Total	23.6
(9)	Y+Nd Oxides Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	.21 not determined separately not determined separately 20.05	Y <sub>2</sub> O <sub>3</sub> Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	— 14.1 8.0 23.6
(27)	Ce+La Oxides	20.34	Ce+La Oxides Nd <sub>2</sub> O <sub>3</sub>	20.3 3.2
			Total	23.5
(27)	Y+Nd Oxides Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	.32 not determined separately not determined separately 20.66	Y <sub>2</sub> O <sub>3</sub> Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	.4 15.3 5.0 23.9
(42)	Ce+La Oxides	15.00	Ce+La Oxides Nd <sub>2</sub> O <sub>3</sub>	12.8 3.3
			Total	16.1
(42)	Y+Nd Oxides Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	1.49 6.72 8.28 (by difference) 16.49	Y <sub>2</sub> O <sub>3</sub> Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	.2 9.7 3.1 16.3
(35)	Ce+La Oxides	7.60	Ce+La Oxides Nd <sub>2</sub> O <sub>3</sub>	5.6 2.0
			Total	7.6
(35)	Y+Nd Oxides Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	7.89 1.54 6.06 (by difference) 15.49	Y <sub>2</sub> O <sub>3</sub> Ce <sub>2</sub> O <sub>3</sub> La <sub>2</sub> O <sub>3</sub> ΣRE <sub>2</sub> O <sub>3</sub> determined	7.7 4.5 1.1 15.3

mens indicate that they are not allanite, though their chemistry (Table III; both 35 and 50 came from the same mine) is much like that of allanite. Hence it is suggested that where Y<sub>2</sub>O<sub>3</sub> is greater than 5.0 per cent, the material is not allanite, yet may be related closely to it.<sup>2</sup> Though Y<sub>2</sub>O<sub>3</sub> is not present or is less than one per cent of the total analysis in

<sup>2</sup> The relationship or identity of these specimens with lombardite of Neumann and Nilssen (1962) is the subject for a further investigation.

TABLE V. X-RAY SPECTROGRAPHIC ANALYSES  
(arranged in order of decreasing Ce<sub>2</sub>O<sub>3</sub>)

Specimen No.	(5)	(34)	(23)	(43)	(31)	(8)	(12)	(45)	(27)	(21)	(55)	(41)	(49)	(7)	(37)	(30)	(9)	(29)	(3)	(15)	(32)
CaO	9.7	8.9	9.7	12.1	11.3	11.8	10.7	10.2	8.3	9.7	10.7	10.5	10.5	8.1	10.5	10.0	11.3	10.0	12.1	11.3	12.5
Y <sub>2</sub> O <sub>3</sub>	.1	.15	.5	tr.	tr.	.2	.2	.5	.4	.1	.6	.15	.2	2.2	.1	.8	—	1.8	—	—	—
Nd <sub>2</sub> O <sub>3</sub>	3.9	3.3	4.0	2.1	2.1	3.3	4.7	3.4	3.2	3.6	4.1	3.6	2.3	6.4	3.3	4.3	1.5	5.4	2.2	4.2	2.3
Ce <sub>2</sub> O <sub>3</sub>	16.9	16.5	16.0	15.8	15.6	15.6	15.6	15.6	15.3	15.2	15.2	14.7	14.7	14.7	14.5	14.5	14.1	14.0	13.8	13.5	13.3
La <sub>2</sub> O <sub>3</sub>	6.5	6.7	6.8	7.9	7.3	6.0	5.6	5.6	5.0	6.0	5.6	5.8	7.1	8.9	5.8	5.8	8.0	3.7	6.3	4.9	6.3
ΣRE <sub>2</sub> O <sub>3</sub> det.	27.4	26.65	27.3	25.8	25.0	25.1	26.1	25.1	23.9	24.9	25.5	24.25	24.3	27.2	23.7	25.4	23.6	24.9	22.3	23.35	21.9
RE <sub>2</sub> O <sub>3</sub> +CaO	37.1	35.55	37.0	37.9	36.3	36.9	36.8	35.3	32.2	34.6	36.2	34.75	34.8	35.3	34.2	35.4	34.9	34.9	34.4	34.65	34.4

Specimen No.	(10)	(4)	(47)	(19)	(39)	(53)	(25)	(26)	(54)	(51)	(33)	(2)	(52)	(1)	(48)	(44)	(14)	(40)	(38)	(18)	(42)
CaO	12.5	11.3	14.3	11.3	11.8	8.0	7.0	14.3	9.7	12.5	14.7	12.5	8.3	11.3	13.7	11.3	12.8	10.5	11.3	14.3	14.7
Y <sub>2</sub> O <sub>3</sub>	tr.	.3	.15	.15	.35	2.0	3.1	3	.9	3	tr.	.5	2.6	2.3	.15	.15	1.4	—	.05	.15	.2
Nd <sub>2</sub> O <sub>3</sub>	1.8	2.0	2.1	2.6	1.4	5.4	6.2	2.8	5.0	1.8	2.9	2.6	5.5	5.9	2.8	1.0	2.9	1.3	.9	2.3	3.3
Ce <sub>2</sub> O <sub>3</sub>	13.3	13.1	12.9	12.9	12.9	12.9	12.9	12.2	12.2	12.0	11.6	11.6	11.6	10.5	10.4	10.4	10.0	9.7	9.7	9.7	9.7
La <sub>2</sub> O <sub>3</sub>	6.5	6.3	6.5	5.8	6.7	3.5	3.5	4.7	3.5	5.6	4.7	4.1	3.5	2.8	3.9	5.4	3.9	3.9	6.5	3.9	3.1
ΣRE <sub>2</sub> O <sub>3</sub> det.	21.6	21.7	21.65	21.45	21.35	23.8	25.7	20.0	21.6	19.7	19.2	18.8	23.2	21.5	17.25	16.95	18.2	14.9	17.15	16.05	16.3
RE <sub>2</sub> O <sub>3</sub> +CaO	34.1	33.0	35.95	32.75	33.15	31.8	32.7	34.3	31.3	32.2	33.9	31.3	31.5	32.8	30.95	28.25	31.0	25.2	28.45	30.35	31.0

Specimen No.	(17)	(11)	(36)	(28)	(22)	(13)	(20)	(16)	(24)	(46)	(6)	(35)	(50)
CaO	14.9	10.7	8.1	9.7	12.1	12.5	10.7	7.0	8.3	14.7	11.3	12.46	12.7
Y <sub>2</sub> O <sub>3</sub>	.3	2.8	4.3	.8	2.6	3.0	2.7	5.1	6.4	.15	5.6	7.7	7.5
Nd <sub>2</sub> O <sub>3</sub>	1.9	5.3	5.0	2.9	4.3	3.7	4.2	4.9	5.3	1.7	3.4	2.1	2.0
Ce <sub>2</sub> O <sub>3</sub>	9.7	9.7	9.7	9.5	9.2	9.2	9.0	9.0	9.0	7.5	7.3	4.5	4.4
La <sub>2</sub> O <sub>3</sub>	3.9	2.4	2.6	3.0	3.0	2.8	2.6	2.6	2.4	4.3	2.2	1.1	1.3
ΣRE <sub>2</sub> O <sub>3</sub> det.	15.8	20.2	21.6	16.2	19.1	18.7	18.5	21.6	23.1	13.65	18.5	15.4	15.2
RE <sub>2</sub> O <sub>3</sub> +CaO	30.7	30.9	29.7	25.9	31.2	31.2	29.2	28.6	31.4	28.35	29.8	27.86	27.9

TABLE VI. RARE-EARTH OXIDES CALCULATED AS PER CENT OF  $\Sigma$  RARE EARTHS DETERMINED  
(arranged in order of decreasing  $Ce_2O_3$ )

Specimen No.	(40)	(27)	(31)	(45)	(8)	(3)	(34)	(5)	(2)	(10)	(17)	(44)	(43)	(37)	(51)	(21)	(26)	(32)
$Y_2O_3$	---	1.7	---	2.0	.8	---	.6	.4	2.7	---	1.9	.9	---	.4	1.5	.4	1.5	---
$Nd_2O_3$	8.7	13.4	8.4	22.3	13.2	9.9	12.4	14.2	13.8	8.3	12.0	5.9	8.1	13.9	9.1	14.4	14.0	10.5
$Ce_2O_3$	65.1	64.0	62.4	62.2	62.1	61.9	61.8	61.7	61.7	61.5	61.4	61.3	61.3	61.2	61.0	61.0	61.0	60.7
$La_2O_3$	26.2	20.9	29.2	13.5	23.9	28.2	25.2	23.7	21.8	30.2	24.7	31.9	30.6	24.5	28.4	24.2	23.5	28.8

Specimen No.	(41)	(18)	(39)	(49)	(33)	(4)	(19)	(48)	(12)	(9)	(47)	(55)	(42)	(23)	(28)	(15)	(30)	(38)
$Y_2O_3$	.6	.9	1.6	.8	---	1.4	.7	.9	.8	---	.7	2.4	1.2	1.8	4.9	3.2	3.1	.3
$Nd_2O_3$	14.8	14.3	6.6	9.4	15.1	9.2	12.1	16.3	18.0	6.4	9.7	16.1	20.3	14.7	17.9	18.0	16.9	5.2
$Ce_2O_3$	60.6	60.5	60.4	60.4	60.4	60.3	60.2	60.2	59.8	59.7	59.6	59.6	59.5	58.6	58.6	57.8	57.1	56.6
$La_2O_3$	24.0	24.3	31.4	29.4	24.5	29.1	27.0	22.6	21.4	33.9	30.0	21.9	19.0	24.9	18.6	21.0	22.9	37.9

Specimen No.	(54)	(29)	(46)	(14)	(53)	(7)	(25)	(52)	(13)	(1)	(20)	(22)	(11)	(36)	(16)	(6)	(24)	(35)	(50)
$Y_2O_3$	4.2	7.2	1.1	7.7	8.4	8.1	12.0	11.2	16.0	10.7	14.6	13.6	13.9	19.9	23.6	30.2	27.6	50.0	49.3
$Nd_2O_3$	23.1	21.7	12.4	15.9	22.7	23.6	24.1	23.7	19.8	27.5	22.7	22.5	26.2	23.1	22.7	18.4	23.0	13.7	13.2
$Ce_2O_3$	56.6	56.2	55.0	55.0	54.2	54.0	50.3	50.0	49.2	48.8	48.7	48.2	48.0	45.0	41.7	39.5	39.0	29.2	29.0
$La_2O_3$	16.2	14.9	31.5	21.4	14.7	14.3	13.6	15.1	15.0	13.0	14.0	15.7	11.9	12.0	12.0	11.9	10.4	7.1	8.5

about three fourths of the specimens, no specimen was lacking in Nd, and  $\text{Nd}_2\text{O}_3$  virtually always is more than one per cent of the total analysis.

TABLE VII. ANALYSES MADE ON POWDER SAMPLES  
(arranged according to decreasing  $\text{Ce}_2\text{O}_3$ )

Specimen No.	(57)	(60)	(58)	(56)	(64)	(62)	(59)	(61)	(63)
CaO	9.5	9.8	11.3	9.8	7.8	5.8	9.5	9.8	7.8
$\text{Y}_2\text{O}_3$	—	.2	.2	.1	—	1.5	1.5	2.2	1.5
$\text{Nd}_2\text{O}_3$	2.0	6.0	4.3	2.6	4.1	4.6	5.7	5.9	4.3
$\text{Ce}_2\text{O}_3$	16.1	14.4	14.4	14.2	13.8	12.2	12.0	11.0	10.6
$\text{La}_2\text{O}_3$	6.6	3.6	4.6	5.0	4.0	3.0	3.2	2.9	2.9
$\Sigma\text{RE}_2\text{O}_3$ det.	24.7	24.2	23.5	21.9	21.9	21.3	22.4	22.0	19.3
$\text{RE}_2\text{O}_3 + \text{CaO}$	34.2	34.0	34.8	31.7	29.7	27.1	31.9	31.8	27.1

TABLE VIII. PER CENT OF RARE EARTHS IN  $\text{RE}_2\text{O}_3$  DETERMINED IN POWDER SAMPLES  
(arranged according to decreasing  $\text{Ce}_2\text{O}_3$ )

Specimen No.	(57)	(56)	(64)	(58)	(60)	(62)	(63)	(59)	(61)
$\text{Y}_2\text{O}_3$	—	.5	—	.9	.8	7.2	7.8	6.7	10.0
$\text{Nd}_2\text{O}_3$	8.1	11.8	18.7	18.3	24.8	21.6	22.2	25.5	26.8
$\text{Ce}_2\text{O}_3$	65.2	64.8	63.0	61.3	59.5	57.2	54.9	53.6	50.0
$\text{La}_2\text{O}_3$	26.7	22.9	18.3	19.5	14.9	14.0	15.1	14.2	13.2

SOME ANALYTICAL DATA FROM THE LITERATURE CONTRASTED WITH  
THE X-RAY SPECTROGRAPHIC DATA IN THE PRESENT STUDY

Hasegawa (1960) presented 19 new Japanese allanite analyses made by standard chemical methods and these were compiled together with 31 analyses found in the mineralogical literature. From these data Hasegawa drew histograms showing the weight per cent of various oxides versus the frequency of their occurrence. In Fig. 1, these histograms are contrasted with some drawn up from the x-ray spectrographic data in the present investigation. Discrepancy occurs mainly with the histograms for  $\text{La}_2\text{O}_3$  and  $\text{Ce}_2\text{O}_3$ . This is due, no doubt, to the fact that Hasegawa did not consider  $\text{Nd}_2\text{O}_3$  separately. Very probably, this oxide is included in the per cents for  $\text{La}_2\text{O}_3$ , and the values for  $\text{La}_2\text{O}_3$  appear greater than they actually are.

Though in the present investigation the limits of total rare-earths determined (Table V) are from 15.4 per cent to 27.4 per cent of the total analysis, allanites with as little as 2.44 per cent rare earths<sup>1</sup> or as much as

<sup>1</sup> From some data supplied by Michael Fleischer of the U. S. Geological Survey.



DIFFRACTION DATA

(to increasing *b*)

(29)		(13)		(57)				(56)		(27)		(61)		(34)		(4)		(40)		(55)			
Heated		Heated		Un-heated		Heated		Heated		Heated		Heated		Un-heated		Un-heated		Un-heated		Un-heated		Heated	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I
3.51	3	3.51	3	3.52	5	3.51	6	3.52	4	3.51	5	3.49	3	3.59	1	3.58	1					3.59	1
3.28	1	3.34	1	3.33	6	3.34	1			3.29	2			3.52	4	3.51	6	3.53	3	3.54	4	3.52	3
3.22	2	3.21	2	3.22	4	3.22	3			3.23	1			3.33	5	3.33	5	3.33	10	3.36	3	3.29	1
2.90	10	2.90	10	2.93	10	2.92	10	2.92	10	2.90	10	2.89	10	2.91	10	2.90	10	2.93	8	2.94	10	2.92	10
2.87	6	2.87	6	2.88	5	2.86	5	2.88	7	2.88	5	2.88	8	2.88	4	2.88	5	2.89	4	2.90	8	2.88	4
2.80	1			2.81	2	2.81	2	2.82	2	2.81	1			2.82	1	2.81	1			2.82	3	2.81	1
2.68	7	2.68	6	2.69	6	2.69	6	2.71	5	2.70	8	2.68	6	2.71	4	2.69	7	2.72	7	2.71	6	2.70	6
2.61	6	2.61	5	2.61	5	2.61	5	2.63	2	2.61	4	2.61	4	2.61	3	2.61	5	2.63	3	2.64	5	2.61	5
2.54	3	2.54	2	2.55	2	2.54	3			2.55	3			2.54	2	2.54	4	2.57	4	2.56	1	2.54	2
						2.49	1			2.49	1			2.50	1	2.49	1	2.50	2			2.49	2
														2.44	1					2.44	2		
2.40	2	2.40	2			2.42	2	2.42	2	2.40	1	2.40	2	2.40	1	2.40	1	2.42	1			2.41	2
2.32	2	2.32	1			2.31	2	2.33	2	2.32	1	2.32	2	2.33	1	2.33	1	2.34	1			2.33	2
2.29	1	2.29	1					2.18	2					2.29	1	2.29	1						
														2.18	2	2.17	2	2.19	3			2.17	5
2.17	4	2.16	2			2.17	5			2.17	3			2.16	2	2.15	4					2.15	4
2.13	2	2.13	2			2.13	3	2.14	3			2.12	3	2.13	1	2.14	3					2.14	4
														2.10	1							2.09	1
																						2.05	1
5.74	Å	5.74	Å	5.76	Å	5.72	Å	5.76	Å	5.76	Å	5.76	Å	5.76	Å	5.76	Å	5.78	Å	5.80	Å	5.76	Å

heated samples, 14 recrystallized and gave allanite x-ray diffraction patterns. Two other specimens (35 and 50, both from the same mine) recrystallized after heating for three days, but gave x-ray diffraction patterns somewhat different from allanite. (Though the patterns of these two specimens resemble each other and may represent a new species, the verification of this suggestion is left for a separate investigation).<sup>1</sup> All samples, heated and unheated, were ground to a very fine powder and run for an x-ray diffraction pattern. Subsequent regrinding of the samples was found, in general, to improve the quality of the patterns. Hence, each sample was reground and rerun until no further changes or improvement of the pattern could be obtained.

The results of this x-ray study are shown in Figures 2, 3 and 4, and Table IX. The patterns were indexed according to Ueda (1957) and measured. *b* was calculated from (020). Since no morphological measurements were obtained, the  $\beta$  angle could not be determined and, therefore *a* and *c* could not be calculated. No relationship was noted between the variation in rare earths and the variation in the *d* spacings. Moreover,

<sup>1</sup> See footnote *re: lombardite* of Neumann and Nilssen (1962).

such a relationship could be fortuitous, since variations in the rare earths probably are compensated for by variations in other elements (*e.g.* not only the rare earths substituting for Ca, but Al substituting for  $\text{Fe}^{3+}$ ) in the allanite structure.

Some difference in  $d$  spacings was noted between unheated and heated samples of the same specimen (Table IX and Fig. 4). Restoration of order, by heating, to the metamict allanite causes a decrease in the  $d$  spacings. This observation is in agreement with the results of Ueda and Kore-

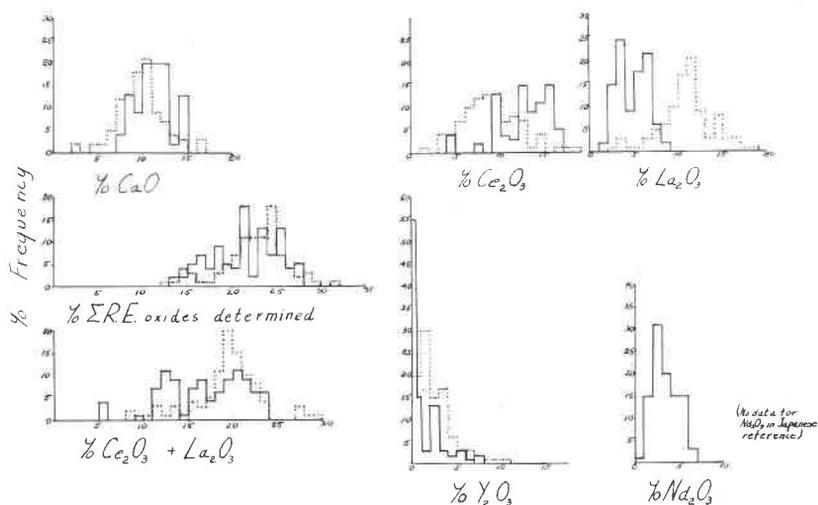


FIG. 1. Weight per cent of oxides *vs.* frequency of occurrence. Solid areas represent data from this study; dotted areas represent data from Hasegawa (1960).

kawa (1954) and Ueda (1957) who carried out detailed studies on the metamict state of allanite.

The degree of metamictization did not appear to be connected with any variation of the rare earths determined in the present study. It is more likely that the age of the allanite and the small amounts of U and Th generally present determine its metamict state.

#### SOME OPTICAL DATA

Optical measurements were made on only a few of the specimens. In view of the many varying and compensating elements in allanite, and the variable and often large content of non-essential water, a detailed optical study seemed futile. The effect of heating on the specimens was of chief interest. In all of the specimens studied optically, the indices of refraction were increased by heating (Table X).

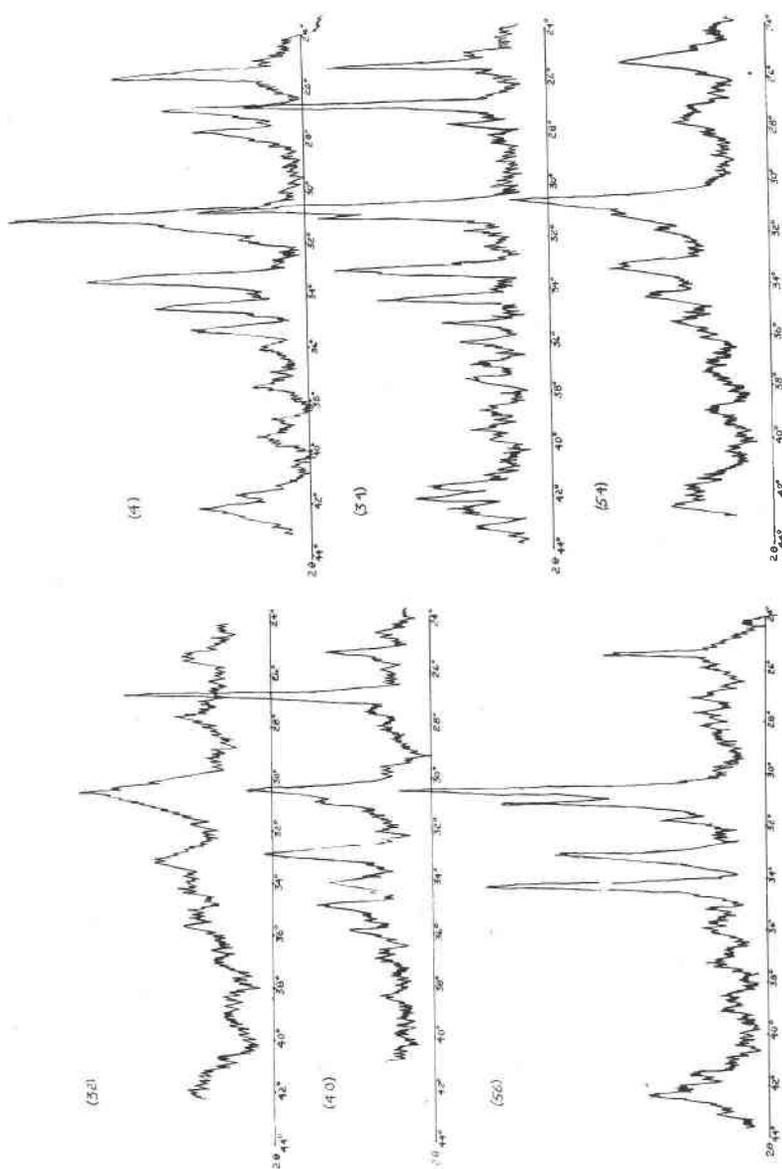


Fig. 2. X-ray diffraction patterns of some unheated allanites.

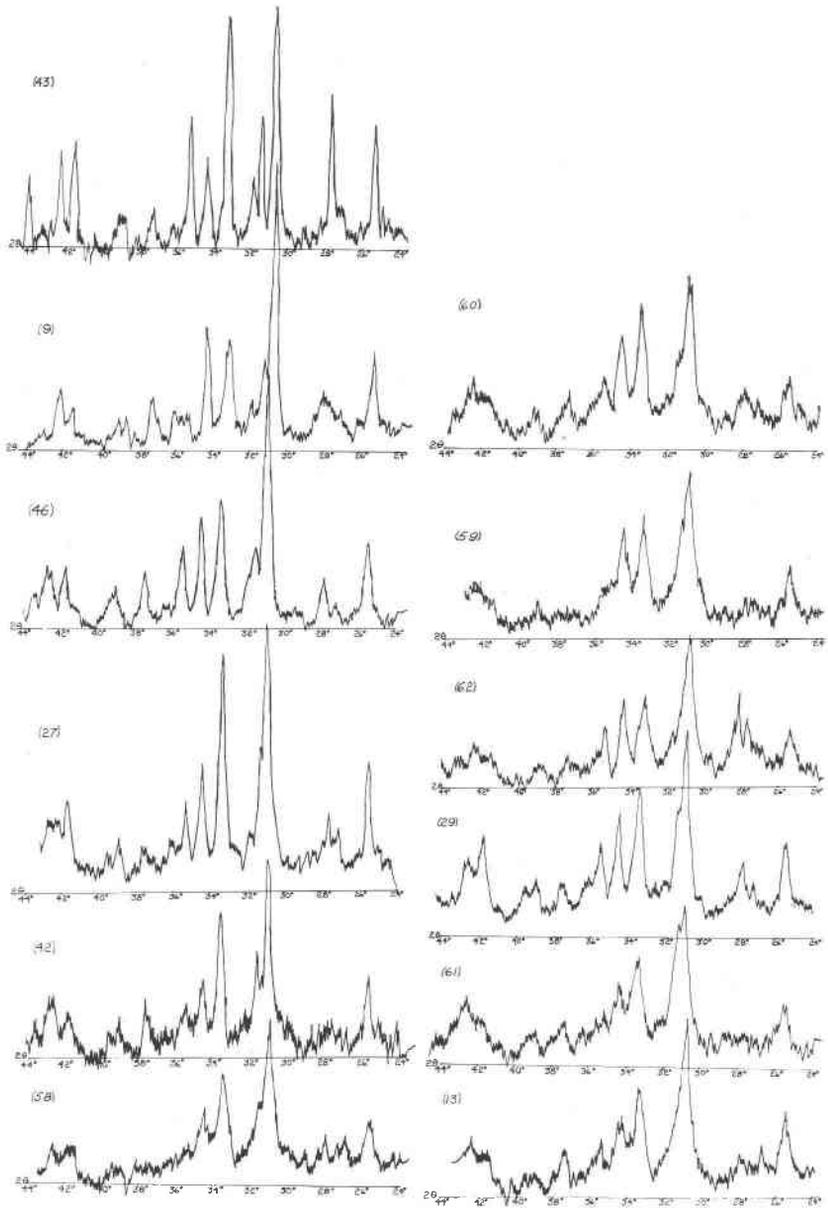


FIG. 3. X-ray diffraction patterns of some heated allanites.

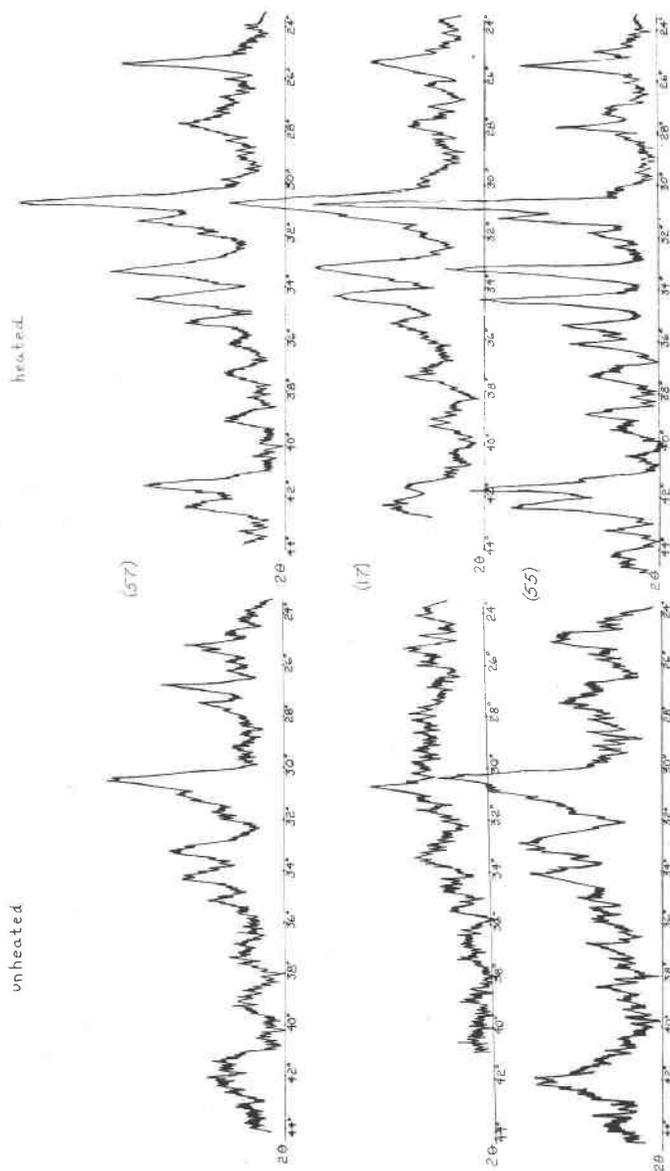


FIG. 4. Contrast of x-ray diffraction patterns of three allanite specimens before and after heating.

TABLE X. SOME OPTICAL DATA  
(all  $n$  values  $\pm .003$ )

Specimen No.	(35)	(43)	(46)	(42)	(9)	(17)	(55)	(27)
Remarks	Transparent, light olive-green, many grains have deep orange-brown inclusions	Faintly pleochroic, low birefringence	Low birefringence	Deep olive-green, transparent on thin edges	Dark brown to black, almost opaque except on thin edges which are olive-brown	Olive-brown	Low birefringence	Transparent on thin edges, olive-green, a few grains faintly anisotropic
Mean $n$	1.670		1.687		1.750	1.720		1.73
$\alpha$		1.710 pale yellow-green	1.710				1.750 almost colorless	
$\beta$		1.713 deeper yellow-green	1.715				1.755 yellow-green	
$\gamma$		1.720 yellow-green	1.723				1.760 olive-green	
2V	Isotropic	(+) Very large	(+) Large	Isotropic	Isotropic	Isotropic	(+) Moderate	(-) Moderate
Remarks	Transparent, olive-green, fine-grained inclusions gone	Pleochroic, low birefringence	Very fine-grained, low birefringence, pleochroic	Pleochroic	Strongly pleochroic	Faintly pleochroic	Increased birefringence	Faintly pleochroic
Mean $n$	1.695							
$\alpha$		1.740 almost colorless	1.745 almost colorless	1.745 pale yellow-green	1.785 light brown	1.765 almost colorless	?	?
$\beta$		1.745 yellow-green	1.753 yellow-brown	1.755 deep yellow-green	1.780 orange-brown	1.770 pale olive-brown	1.776 yellow-green	1.775 almost colorless
$\gamma$		1.752 deep yellow-green	1.755 olive-brown	1.760 olive-green	1.785 deep brown	1.775 orange-brown	1.782 brown-green	1.783 orange-brown
2V	Isotropic	(+) Very large	?	(-) Large	(-) Large	(-) Large	(+) Moderate	?

UNHEATED

HEATED

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