

# CELL SIZE, OPTICAL PROPERTIES AND CHEMICAL COMPOSITION OF LAUMONTITE AND LEONHARDITE

WITH A NOTE ON REGIONAL OCCURRENCES IN NEW ZEALAND  
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## ABSTRACT

Laumontite is found to be a large-scale replacement product of vitric tuffs in Southland, New Zealand, and a degradation product of plagioclase under incipiently metamorphic conditions. The well-known partial dehydration of laumontite to yield leonhardite is readily reversible, and optical and  $x$ -ray data are presented. Cell constants of leonhardite from Hungary are as follows:  $a=14.75\pm 0.03$  Å,  $b=13.10\pm 0.02$  Å,  $c=7.55\pm 0.01$  Å,  $\beta=112.0^\circ\pm 0.2^\circ$ . After soaking in water to convert to the laumontite form, the (100) lattice spacing of the same crystal increased from 13.68 to 13.86 Å and the (010) from 13.10 to 13.17 Å, all  $\pm 0.01$  to 0.02. There are corresponding changes in the intercleavage angle (110)^(110). Space group  $C2$  or  $Cm$ . 48 oxygen atoms per unit cell. Atomic ratios are calculated for numerous analyses including two new ones. It is shown that replacement of calcium by alkalies is both of the plagioclase and of the zeolite type. The composition of laumontite can be expressed by the formula:



where

$$x + y/2 \text{ does not exceed } 4$$

and

$$x + y \text{ is not less than } 4.$$

## INTRODUCTION

The calcium-rich zeolite, laumontite, was first found by Gillet Laumont at Huelgoat in Brittany in 1785. It has long excited interest on account of the extreme ease with which it loses water, often crumbling to a powder in the process. On this account some early descriptions referred to it as "efflorescent zeolite." The partially dehydrated form is known variously as leonhardite,  $\beta$ -leonhardite and caporcianite and has remarkably distinctive optical properties. The typical mode of occurrence of laumontite is as rather small and stout prismatic crystals in veins and cavities in crystalline rocks ranging from serpentines and gabbros to granites and schists, but it has rarely been reported in large amount.

During an investigation of the geology of part of the Taringatura Survey District, Southland, New Zealand (Coombs, 1950), laumontite was found to occur in a manner and on a scale which does not appear to have been recorded hitherto. It is one of the most important alteration products in the lower part of a thick series (nearly 30,000 feet) of Triassic

tuffs, graywackes, arkoses and siltstones, and many bedded masses are found to consist largely of the mineral. In the first part of the present paper, these and related occurrences of laumontite are described and the paragenesis is discussed. Further details of the chemical and mineralogical changes which have taken place in the series will be reported elsewhere. The major part of the paper describes a laboratory study of the mineral group.

The writer wishes to express his thanks to Professor C. E. Tilley for his unflinching interest and encouragement, to Dr. N. F. M. Henry for invaluable criticism and suggestions, and to Mr. K. Rickson who took the photomicrographs and powder photographs and gave technical assistance with the single-crystal  $x$ -ray work. The writer is indebted to Dr. M. Hey of the British Museum for providing one of the specimens referred to in this paper. Another specimen was collected during field work financed by a Research Grant of the University of New Zealand for which grateful acknowledgment is also made.

#### OCURRENCE IN SOUTHLAND, NEW ZEALAND

The lower part (North Range beds) of the Triassic succession in the Taringatura district of Southland consists very largely of altered lithic andesitic tuffs, but among these are many bands of originally glassy material, derived apparently from a slightly more acid magma than the rest. Some of these beds are only a few inches or a few feet thick, but one group, 450 feet thick, and traceable along the outcrop for many miles, consists almost entirely of water-sorted crystal-vitric tuffs. Nowhere in these rocks has glass been found to remain. Sometimes it is replaced by heulandite, but much more commonly by laumontite, and as a result numerous beds have a rather earthy appearance and a whitish or pale buff color. They are estimated to contain 30–80% laumontite. In thin section, groups of adjacent glass shards are seen to have been replaced by single laumontite crystals which together form an aggregate of interlocking grains 0.5–3 mm. across (Fig. 1). Cleavage faces are noticeable on freshly broken surfaces, but crystal outlines are rarely developed.

Plagioclase fragments in the laumontite rocks are invariably albitized (composition  $An_{0-4}$ ) and are often unattacked by the zeolite. Occasionally in the North Range beds, and very characteristically in graywackes from the near-by Roe Burn beds of probable late Palaeozoic age, albitized plagioclase may be partly or completely pseudomorphed by laumontite which spreads most readily along the (010) cleavage and twinning planes of the feldspar and thus sometimes gives an effect simulating twinning. The same type of alteration occurs in some Jurassic feldspathic sand-

stones from the Hokonui Hills to the south-east of Taringatura. In at least some of these cases it may be deduced from relict "islands" of little-altered material that the plagioclase originally had a composition in the range of acid labradorite to acid andesine.

In a similar fashion Hutton (1949) found laumontite to be an important product of the break-down of lime-bearing plagioclase in gray-



FIG. 1. Laumontitized tuff, no. 8795, North Range, Taringatura Survey District, Southland, New Zealand. A single crystal of laumontite (illuminated) extends right across the field of view, and incorporates many originally glassy ash fragments. These are delineated by dark chloritic films. The shaded region at the lower left and dark regions at the upper left and lower right of the field, represent similar laumontite crystals in near-extinction. Two fragments of twinned plagioclase are also visible. Crossed nicols.  $\times 60$ .

wackes of the Otama area of Southland. He attributed this to very low grade metamorphism. The Otama graywackes are part of a belt of almost unmetamorphosed late Palaeozoic rocks which separates the south flank of the Otago schists (Turner, 1938) from the Mesozoic sediments described above. The present writer has found that the mineral occurs abundantly along joint planes and shatter zones, replacing feldspar and as pools in the groundmass both in various igneous bodies and in the graywackes at many localities in this belt, and here also residual plagioclase is albitized in its presence. A crush-zone in albitic meta-gabbro  $1\frac{1}{4}$  miles  $15^\circ$  E of north from the Otama Hall may be taken as typical.

A sheet of pulverized and slickensided rock several inches thick has been almost completely replaced by laumontite (analysis no. 1, Table III) associated with a little prehnite and chloritic matter and containing broken fragments of augite, albitized feldspar and iron ore from the country rock. Cleavages and cross fractures in these minerals are penetrated by the laumontite.

Hutton (1944) has also described leonhardite replacing andesine in a porphyrite from Devon Well, Paritutu Survey District, New Zealand (analysis no. 12, Table III), and Petrov (1933) has described small apophyses consisting of an aggregate of laumontite (50%), opal, chlorite and zeolitized feldspar given off from a thin sill injected into bedded tuffs in the neighbourhood of Tiflis. It is also interesting to note that Park (1946) found laumontite to be locally abundant in the spilites and associated rocks of the Olympic Peninsula, Washington.

#### ORIGIN

It is significant that in the thick Triassic section of Taringatura, laumontite is rare or absent in the upper members in which plagioclase is generally unaltered and other mineralogical adjustments are slight. Towards the base of the series detrital plagioclase becomes progressively more commonly albitized, laumontite becomes widespread and other secondary minerals such as pumpellyite and prehnite appear. Laumontite, pumpellyite, calcite and sericite may all occur as inclusions in the albitized plagioclase, or the plagioclase may be entirely replaced by laumontite. In such cases laumontite appears to be a degradation product of lime-bearing plagioclase under incipiently metamorphic conditions (cf. Hutton, 1949). Sometimes the lime and alumina released during albitization of plagioclase are completely removed from the crystal and may contribute to the crystallization of laumontite in joint planes and crush zones as at Otama, and interstitially in porous beds. Under other conditions, perhaps at a slightly higher temperature, the formation is favoured of such minerals as prehnite, pumpellyite and epidote. In the laumontitized tuffs of the North Range, Taringatura, only a part of the lime and alumina were provided by the original glass and the andesine phenocrysts it contained. There is evidence that heulandite, and locally analcime, may have replaced the glass during diagenesis and before laumontitization, but these minerals also are relatively deficient in lime and, in the case of heulandite, in alumina. The lithic tuffs and tuffaceous graywackes with which the laumontite rocks are interbedded have been fairly uniformly albitized and lost appreciable amounts of lime in the process. It appears that interstitial solutions have carried some of this

lime to the beds of altering glassy tuff where it has been "fixed" as laumontite.

#### OPTICAL OBSERVATIONS ON THE LAUMONTITE-LEONHARDITE RELATIONSHIP

It has long been known that on exposure to the atmosphere, or on gentle heating, laumontite loses approximately one eighth of its water to form the sometimes powdery variety known variously as leonhardite,  $\beta$ -leonhardite or caporcianite (e.g. see Des Cloizeaux, 1862, p. 405;

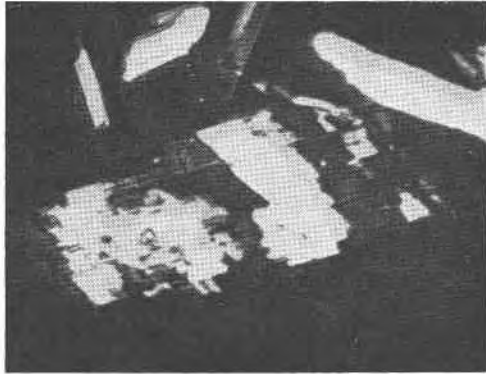


FIG. 2. Cleavage fragment of leonhardite (no. 192, Hungary) after immersion in water for two hours. Regions of rehydrated laumontite at the ends and in transverse fractures are in extinction. Residual leonhardite with its much larger extinction angle is still brightly illuminated. Crossed nicols. Length of grain=0.2 mm.

Walker and Parsons, 1922; Pagliani, 1948). Simultaneously the refractive indices drop, the extinction angle increases markedly and the optic axial angle changes. In most cases it decreases, but in one (no. 1, Table I) it appears to increase slightly. The ready reversibility of these changes does not appear to have been recorded. When crushed grains of leonhardite are placed in a drop of water between crossed nicols, a zone with the laumontite extinction angle is seen to form quickly at the broken ends of the grains and at any transverse cracks or cleavages (Fig. 2). The boundary between the two zones may be quite sharply defined. It migrates inwards, mainly in the direction parallel to the  $c$  axis, until after a period which in some specimens may be as brief as an hour or two, the whole grain has assumed the optic orientation of laumontite. Measurements of the optic axial angle and refractive indices show that these properties also return to values characteristic of fully saturated laumontite.

In some cases the formation of a leonhardite-type form from powdered laumontite may be watched microscopically in dry air, or more conveniently by immersion in a mild dehydrating agent such as glycerol. Thin sections heated in the usual way during preparation invariably show leonhardite optics. To make accurate measurements of optical properties of leonhardite it was found necessary to use very small cleavage fragments as larger grains frequently failed to extinguish properly, apparently due to distortion and to the superposition of regions of different hydration states. It was noticed that in each batch of crystals

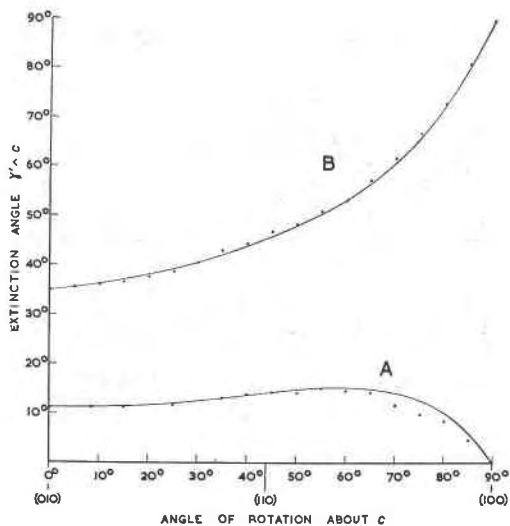


FIG. 3. Extinction angles  $\gamma' \wedge c$  in the prism zone of a crystal of laumontite (A), and of the corresponding leonhardite (B). B.M. 67213, Felső Certes, Transylvania. *Points* refer to angles measured with the help of the one-circle stage goniometer and the *full line* shows the variation as deduced from the Biot-Fresnel construction.

studied, the optic axial angle was distinctly variable. In general the maximum extinction angle in the prism zone is neither the angle  $\gamma \wedge c$  measured on (010), nor is it the angle often measured on (110) cleavage flakes, as can be shown both by the Biot-Fresnel construction and experimentally on the Universal Stage or stage goniometer. Recorded observations on fully hydrated laumontite indicate that it always has slow elongation, but it may be pointed out that in typical leonhardite the angle  $\gamma' \wedge c$  measured in the prism zone increases from a value of 30°–35° measured on (010) to 90° measured on (100). In the latter case the grain has fast elongation (Fig. 3). The leonhardite extinction angle of the Taringatura mineral appears to be unusually low.

Typical data follow (Table 1):

TABLE I. OPTICAL PROPERTIES OF LAUMONTITES AND THE CORRESPONDING LEONHARDITES

	1	2	3	4
Laumontite	$\alpha = 1.510 \pm .002$	$1.514 \pm .002$	$1.509 \pm .002$	$1.514 \pm .002$
	$\beta = 1.518 \pm .002$	$1.522 \pm .002$	$1.518 \pm .002$	$1.522 \pm .002$
	$\gamma = 1.522 \pm .002$	$1.524 \pm .002$	$1.521 \pm .002$	$1.525 \pm .002$
	(-)2V = $39^\circ \pm 5^\circ$	$33^\circ \pm 5^\circ$	$41^\circ \pm 3^\circ$	$47^\circ \pm 3^\circ$
	$\gamma \wedge c = 10^\circ \pm 2^\circ$	$8^\circ \pm 2^\circ$	$9^\circ \pm 2^\circ$	$11^\circ \pm 2^\circ$
	$\gamma' \wedge c$ on (110) = $13^\circ \pm 2^\circ$	$11^\circ \pm 2^\circ$	$11^\circ \pm 2^\circ$	$14^\circ \pm 2^\circ$
Leonhardite	$\alpha = 1.505 \pm .002$	$1.507 \pm .002$	$1.502 \pm .002$	$1.507 \pm .002$
modification	$\beta = 1.514 \pm .002$	$1.516 \pm .002$	$1.512 \pm .002$	$1.516 \pm .002$
	$\gamma = 1.517 \pm .002$	$1.518 \pm .002$	$1.514 \pm .002$	$1.518 \pm .002$
	(-)2V = $44^\circ \pm 3^\circ$	$26^\circ \pm 4^\circ$	$36^\circ \pm 4^\circ$	$38^\circ \pm 5^\circ$
	$\gamma \wedge c = 33^\circ \pm 2^\circ$	$32^\circ \pm 2^\circ$	8—19°	$35^\circ \pm 2^\circ$
	$\gamma' \wedge c$ on (110) = $39^\circ \pm 2^\circ$	$40^\circ \pm 2^\circ$	11—24°	$47^\circ \pm 2^\circ$

Marked dispersion  $r < v$  in all cases.

$\beta$  is parallel to  $b$ ,  $\gamma$  lies in the acute angle  $\beta$ .

1. Crush zone in meta-gabbro, Otama, Southland, New Zealand. Analysis no. 1, Table III.
2. "Laumontite on tuffa, Hungary, No. 192." Mineralogical Museum, Cambridge. The Museum specimen is leonhardite and the laumontite modification was derived from it by soaking in water. Analysis no. 2, Table III.
3. Laumontite from laumontitized vitric tuff, no. 8784, North Range, Taringatura Survey District, Southland, New Zealand. Another specimen from the same locality gave  $\alpha = 1.506 \pm .003$  for the laumontite form and  $\alpha = 1.502 \pm .003$  for the corresponding leonhardite form. Both of these Taringatura specimens were peculiarly resistant to the change and the low extinction angle of their "leonhardite" modification is unusual.
4. Felső Certes, Transylvania. B.M. 67213. The specimen has been kept continuously over water in the British Museum, but rapidly changes to the leonhardite form on exposure.

Pagliani (1948) considers from dehydration experiments and  $x$ -ray powder photographs that no essential change in crystal structure occurs when laumontite loses water to form leonhardite. The reversibility of the changes in optical properties tends to support this, although the apparent suddenness of the transition requires explanation. Pagliani reports that natural leonhardite and laumontite partially dehydrated at  $70^\circ$  C. both gave lines identical in position and relative intensity with those of fresh laumontite. This result is in conflict with observations on the laumontites in Table I as will be shown later. After an initial drop during conversion to leonhardite, both refractive indices and specific gravity were found

by Pagliani to remain fairly constant for a while and then to increase as the temperature of heating was raised progressively to 850° C. This is attributed by Pagliani to lattice shrinkage.

The general term "laumontite" is used in this paper except where it is wished to stress the water-poor nature and distinctive properties of a particular specimen. This procedure is normally advisable for records of field occurrences, as in some cases the variety collected from a particular outcrop may vary with the weather.

Gilbert (1951) in a short abstract has just recorded observations very similar to those of the present writer, based on laumontite occurring as cement in a sandstone from Anchor Bay, Mendocino County, California. He notes the ease of rehydration of leonhardite and records the accompanying changes in refractive indices and  $2V$  as follows: fully hydrated laumontite  $\alpha=1.515$ ,  $\gamma=1.525$ ,  $(-)2V=45^\circ \pm 5^\circ$ ,  $\gamma \wedge c=10^\circ$ ; variety leonhardite  $\alpha=1.506$ ,  $\gamma=1.517$ ,  $(-)2V=30-35^\circ$ ,  $\gamma' \wedge c$  on (110) = 39-41°.

#### RELATION OF OPTICAL PROPERTIES TO CHEMICAL COMPOSITION

The effect of dehydration on the refractive indices obscures the effect of alkalis and until more data are available on material of carefully defined hydration condition, the exact relationship will remain obscure. The data in Table III suggest that indices drop with increasing silica and alkali content in the usual way. Of the analyzed leonhardites which have been described optically, the most silica- and alkali-rich, no. 12, has the lowest indices,  $\alpha=1.502$ , whereas no. 14 with low alkali content has the higher value  $\alpha=1.508$ . A similar relationship probably holds for laumontite.

#### X-RAY STUDY

The Taringatura and Otama laumontites were not found to be suitable for single-crystal  $x$ -ray investigation. A specimen of leonhardite, no. 192, from Hungary, in the Mineralogical Museum, Cambridge, was therefore used. Optical properties and a chemical analysis are given in columns no. 2 of Tables I and III, respectively. Examination showed that most crystals have been distorted and opened along cleavage planes, presumably during loss of water from laumontite. Single-crystal oscillation and Weissenberg photographs were obtained from a small cleavage needle by giving long exposures. The same crystal was later placed and sealed in a capillary tube filled with water, and after two days was found by optical examination to have changed completely to the laumontite form. Oscillation and Weissenberg photographs were then taken about the  $c$  axis. The following cell constants were determined:



$$\begin{array}{l}
 \textit{Leonhardite form} \\
 a = 14.75 \pm 0.03 \text{ \AA} \\
 b = 13.10 \pm 0.02 \\
 c = 7.55 \pm 0.01 \\
 \beta = 112.0^\circ \pm 0.2^\circ
 \end{array}$$

$$\begin{array}{l}
 \textit{Laumontite form} \\
 a = 14.90 \pm 0.05 \text{ \AA} \\
 b = 13.17 \pm 0.02 \\
 c = 7.55 \pm 0.05 \\
 \beta = 111.5^\circ \pm 0.5^\circ
 \end{array}$$

In the case of leonhardite,  $a^*$ ,  $b^*$  and  $c^*$  reciprocal lattice dimensions were determined from high-angle reflections in the zero-layer Weissenberg photographs taken about the  $b$  and  $c$  axes, and had a reproducibility of better than 1 in 1,000. The photograph taken about  $b$  was used for the determination of  $\beta$  with the probable limits of error indicated. Since the determination of  $a$  and  $c$  from the reciprocal lattice depends on the function  $\sin \beta$ , errors in them are correspondingly greater than in  $a^*$  and  $c^*$ . The most accurate measurements on the laumontite form relate to the  $a^*$  and  $b^*$  reciprocal lattice dimensions. From these it is found that the (100) lattice spacing increased during the transition from 13.68 to 13.86 Å and the (010) from 13.10 to 13.17 Å, all  $\pm 0.01$ – $0.02$  Å. The value given above for the  $a$  cell edge is affected by the less accurately determined  $\beta$  angle and  $c$  is here based on layer-line spacings. The differential nature of the changes in ( $h00$ ) and ( $0k0$ ) spacings, produced simply by soaking in water, or conversely by air-drying, is striking and results in changed intercleavage angle and axial ratio. It is accompanied by the changes in optical properties described above and also explains why laumontite crystals fall to pieces along their prismatic cleavages during partial dehydration.

The axial ratio calculated from the  $x$ -ray data for the leonhardite modification is  $a:b:c = 1.12_6:1:0.57_6$  and that for the laumontite is  $a:b:c = 1.13_1:1:0.57_3$ . The corresponding calculated intercleavage angles  $(110) \wedge (\bar{1}\bar{1}0)$  are  $92.5^\circ$  and  $92.9^\circ$ , respectively. The leonhardite crystal gave poor cleavage reflections on the optical goniometer indicating an angle  $(110) \wedge (\bar{1}\bar{1}0)$  of  $92$ – $92\frac{1}{2}^\circ$ . Although apparently based on the same cell orientation, the  $x$ -ray figures, especially those for the leonhardite, differ somewhat from the classical data quoted for laumontite by Dana (1892):  $a:b:c = 1.1451:1:0.5906$ ,  $\beta = 68^\circ 46\frac{1}{4}'$ ,  $(110) \wedge (\bar{1}\bar{1}0) = 93^\circ 44'$ . Other published observations vary from a reported intercleavage angle of  $96^\circ 30'$  (Des Cloizeaux, 1862), which seems too high, to  $93^\circ 13'$  for the same modification (Reichert, 1924). The present study does not rule out the possibility of a modification with such figures, but mere prolonging of the immersion in water is unlikely to produce much further change, as the powder pattern of laumontite no. 192, produced from leonhardite by soaking in water for a few days, is indistinguishable from that of laumontite from Felsö Certes, Transylvania, B.M. 67213 (no. 4, Table I) which has always been kept over water at the British Museum. This

specimen was provided through the courtesy of Dr. M. Hey and has not been out of water since it left the Museum about a year before the powder photos were taken.

Powders of leonhardite 192 and of leonhardite produced by air-drying B.M. 67213 were rolled into thin rods with stiff gum tragacanth solution in the usual way for powder photos and allowed to dry. The resulting patterns were identical, but easily distinguished from those of the laumontite form of both minerals when taken in sealed capillary tubes filled with water. Data are given in Table II for specimen 192 after three modes of treatment: (a) leonhardite air-dried, (b) leonhardite sealed into a capillary tube after drying for three days over silica gel, and (c) laumontite produced by soaking in water for several days and sealed into a capillary tube filled with water. After correction for absorption, no significant differences are found between the first two. There is no difficulty in distinguishing the leonhardite and laumontite patterns side by side, but as a quick distinction the position of the two strong lines near 1.63 Å may be suggested. In leonhardite these are close together at approximately 1.623 and 1.635 Å, whereas in laumontite they are noticeably farther apart at 1.627 and 1.646 Å.

The analyzed Otama laumontite 979, air-dried, gave a predominantly laumontite-type pattern, but rather weak though distinctive leonhardite lines are present as well. It is significant that both types of lines should be present rather than continuous shading which would be expected for a gradual transition. This accords with the optical examination in which each grain of laumontite was seen to be coated with a zone having leonhardite optics. The Taringatura laumontite no. 8784, air-dried, gave a purely laumontite type of pattern. It is thus seen that of the four specimens examined by *x*-rays, the two with the lowest refractive indices, and in one case with proved relatively high alkali content, are relatively stable under normal atmospheric conditions as the laumontite modification, whereas the two specimens with higher indices and lower alkali content quickly change to leonhardite on exposure.

On the basis of the axial elements given above, all reflections of the type (*hkl*) are extinguished when  $(h+k) = 2n+1$ . There are no other systematic extinctions. The cell is therefore *C*-face centred in both modifications. Comparison of the Weissenberg photographs however, shows significant intensity changes in various reflections. Laumontite has usually been assumed to belong to the monoclinic holosymmetric class, *2/m*. Crystals of laumontite and leonhardite from three localities gave a negative result when tested with the Giebe and Scheibe tester for piezo-electric effect, but grains adhered firmly to aluminum foil when immersed in liquid air and removed again, thus indicating a strong pyro-

TABLE II. POWDER DATA FOR LEONHARDITE AND LAUMONTITE,  
(SPECIMEN No. 192, HUNGARY)

(Camera 19 cm. diameter, filtered Cu-K $\alpha$  radiation.  $\lambda = 1.542$ )

Indices	Leonhardite, air-dried		Leonhardite in sealed tube after drying over silica gel		Laumontite in sealed tube with water	
	$I/I_1$	$d$ in Å	$I/I_1$	* $d$ in Å	$I/I_1$	* $d$ in Å
200	6	6.88	6	6.88	6	6.97
201	2	6.21	2	6.21	1	6.16
111	2	5.07	2	5.07	1	5.14
220	1	4.75	1	4.75	2	4.77
221	3	4.51	3	4.51	1	4.50
130, 201	10	4.18	10	4.18	10	4.18
131	<1	3.77	<1	3.75	<1	3.76
401	4	3.67	3	3.67	4	3.67
221, 002	10	3.52	10	3.52	6	3.53
400, 131	<1	3.42	1	3.42	1	3.45
312	1	3.36	1	3.37	2	3.35
040	3	3.28	3	3.28	3	3.29
331 (311, 421)	2	3.21	2	3.21	3	3.21
330	1	3.16	<1	3.15	1	3.19
402	<1	3.09	1	3.10	4	3.08
420, 112	4	3.04	4	3.04		
240 (041)	<1	2.95	1	2.93	<1	2.97
511 (241)	3	2.88	3	2.88	3	2.89
	2	2.80	2	2.80	2	2.78
	<1	2.73	<1	2.73	3	2.61
	<1	2.64			1	2.60
	3	2.58	3	2.58	<1	2.51
	2	2.52	2	2.53	4	2.45
	1	2.46	1	2.47	2	2.383
	4	2.440	3	2.440	<1	2.347
	<1	2.394	<1	2.391	1	2.287
	2	2.361	2	2.360	1	2.212
	1	2.272	1	2.273	2	2.192
	2	2.216	2	2.218	1	2.180
	1	2.183	1	2.179	1	2.156
	3	2.155	3	2.153	<1	2.115
	1	2.090	1	2.090	<1	2.042
	<1	2.059	<1	2.048	1	2.023
	<1	2.041			<1	1.996
	1	1.994	1	1.997	2	1.968
	2	1.961	2	1.961	<1	1.932
	<1	1.910	<1	1.909	<1	1.908
	<1	1.888	<1	1.886	3	1.864
	1	1.869	2	1.871	<1	1.836
	1	1.852	1	1.850	1	1.785
	<1	1.826	<1	1.828	<1	1.766
	<1	1.796	1	1.798	<1	1.745
	1	1.762	2	1.761	1	1.724
	<1	1.733	<1	1.733	<1	1.688
	1	1.706	1	1.706	<1	1.667
	<1	1.677	<1	1.680	3	1.646

TABLE II (Continued)

Indices	Leonhardite, air-dried		Leonhardite in sealed tube after drying over silica gel		Laumontite in sealed tube with water	
	$I/I_1$	$d$ in Å	$I/I_1$	$*d$ in Å	$I/I_1$	$*d$ in Å
	2	1.635	2	1.635	3	1.627
	2	1.623	2	1.623	1	1.602
	<1	1.596	<1	1.598	1	1.586
	1	1.566	1	1.566	2	1.582
	<1	1.544	<1	1.544	<1	1.557
	2	1.523	2	1.521	4	1.535
	<1	1.497			<1	1.519
	<1	1.490	1	1.491	<1	1.502
	1	1.475	1	1.473	1	1.488
	1	1.445			<1	1.477
	2	1.437	2	1.440	2	1.451
	<1	1.423	<1	1.424	<1	1.428
	1	1.404	1	1.406	<1	1.413
	<1	1.387	<1	1.386	1	1.392
	<1	1.375	<1	1.373	1	1.375
	1	1.367	1	1.366	<1	1.359
			<1	1.350	2	1.347
	1	1.342	1	1.342	3	1.341
	1	1.329	1	1.328	2	1.316
	<1	1.315	<1	1.316	2	1.312
	1	1.305	1	1.305	<1	1.296
	<1	1.293	<1	1.293	2	1.278
	<1	1.279	<1	1.278	1	1.266
	2	1.265	2	1.264	<1	1.251
	1	1.256	1	1.256	2	1.236
	<1	1.245	<1	1.246	2	1.209
	1	1.230	1	1.231	<1	1.187
	1	1.191	1	1.190	1	1.177
	1	1.163	2	1.164	<1	1.167
	1	1.151	1	1.150	<1	1.156
	<1	1.132	<1	1.132	<1	1.145
	<1	1.119	<1	1.119	<1	1.108
	<1	1.088	<1	1.087	<1	1.101
	<1	1.046	1	1.046	1	1.092
	<1	1.024	1	1.024	<1	1.052
	<1	.984	<1	.984	<1	1.044
	<1	.975	<1	.975	<1	1.037
			<1	.967	<1	1.034
			<1	.958	<1	1.025
	<1	.952	1	.952	<1	.997
			<1	.942	<1	.989
			<1	.934	<1	.958

\* Owing to absorption caused by the glass capillary tubes and the rather thick columns of powder enclosed in them, lines with low and moderate values of  $\theta$  were displaced somewhat. The apparent spacings were corrected empirically on the basis of observed displacement of lines for the air-dried material when placed in a similar capillary tube.

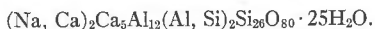
electric effect. Assuming no phase change in the temperature interval involved, it may be concluded that the structure lacks a centre of symmetry and the space group is either  $C2$  or  $Cm$ .

It may be noted that Fersman (1908) attempted a distinction based partly on physical grounds between "primary" or  $\alpha$ -leonhardite with high alkali content and no (010) cleavage and "secondary" or  $\beta$ -leonhardite formed by loss of water from laumontite and retaining the supposedly good (010) cleavage of the latter. These distinctions appear to be of doubtful validity. Gilbert (1951) did not find the (010) cleavage in his material, and no (010) cleavage is visible in the specimens described by the present writer. Another point of possible structural interest is the observation of Murata (1943) that laumontite is an exception to the general rule for silicates with a three-dimensional network that the ratio Al:Si must be greater than 2:3 for gelatinization with acids to occur.

#### CHEMICAL COMPOSITION

The chemical analysis, specific gravity and cell size for leonhardite 192 (no. 2, Table III) lead to the figure 48.3 oxygen atoms per unit cell, and assuming similar cell sizes for the other analyzed laumontites it may be shown that they also lead to figures approximating to 48 oxygen per unit cell.

Variants of the simple formula  $\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$  have long been quoted for laumontite, but the presence of alkalis has often been overlooked. Winchell in 1925 stressed the importance of isomorphic substitution in laumontite and other zeolites, but considered that it is confined to the mutual interchange of (NaSi) and (CaAl) as in plagioclase. On the basis of an arbitrarily assumed 80 oxygen per unit cell, he proposed the formula



Hey (1930, 1932) has shown for various zeolites that in addition to the above possibility, pairs of alkali atoms may proxy for Ca without affecting the Si:Al ratio. In 1935 Rossoni suggested for laumontite the formula  $(\text{Ca}, \text{K}_2, \text{Na}_2)_2\text{Al}_4(\text{SiO}_3)_8 \cdot 8\text{H}_2\text{O}$ , but unfortunately the analysis he published was made on very impure material and does not accord with fundamental zeolite requirements. As early as 1908, Fersman had proposed a similar formula with one molecule less water for " $\alpha$ -leonhardite."

To test the above possibilities, atomic ratios have been calculated for numerous analyses. An examination of published analyses of laumontite shows that wherever alkalis have been determined, they are present in appreciable amount. Analyses which contain no statement of alkali content are therefore not included in the accompanying Table III. As

some of the many analyses which do not include alkali determinations were probably made on material which was in fact alkali-poor, the overall picture set out in the Table may be distorted in this respect. Hey (1932, p. 57) showed that for a first class zeolite analysis  $(Al+Si) = 40 \pm 0.20$  as calculated for 80 oxygen atoms per unit cell, from which it follows that  $(Al+Si) = 24 \pm 0.12$  calculated for 48 oxygens. Furthermore, the summation must be between 99.70 and 100.80. Doelter (1922) listed 53 analyses of laumontite and leonhardite. Table III contains a selection of those taken from Doelter which satisfy the above requirements together with later analyses falling in Hey's classes "A" and "B." Five other analyses quoted in Doelter, and those published by Reichert (1924), Takats (1936) and Niggli, Koenigsberger and Parker (1940), although not included in Table III, are also compatible with the requirements here adopted. In calculating the formulas, small amounts of  $Fe_2O_3$ ,  $TiO_2$  and  $MgO$  were neglected except in the case of the Table Mountain analyses (no. 4 and no. 9) as Henderson and Glass (1933) give evidence that the  $Fe'''$  therein isomorphously replaces Al within the structure.

Starting from the ideal alkali-free end-member formula  $Ca_4Al_8Si_{16}O_{48} \cdot 16H_2O$  to which many of the analyses closely approximate, substitution purely of the plagioclase type suggested by Winchell would result in the sum  $Ca+Na+K$  remaining constant at 4, while Si would increase and Al decrease by an amount equal to the number of alkali atoms. This condition is approximated by only one analysis, a very old one, no. 6, which like many other analyses is unsupported by optical data. If substitution were purely of the type  $Ca = 2(Na, K)$ , the sum  $Ca + [(Na+K)/2]$  should remain at 4, and Si and Al should remain at 16 and 8, respectively. This condition is approached by analyses 1 and 3, although in both of these there is a slight deficiency in Si. Other analyses show the same effects less strongly. The work of Lemberg (1877, 1885) and others indicate that experimental replacement of Ca by alkali metals can readily be achieved in this way, but unfortunately Lemberg did not examine his products optically. Formulae calculated from his earlier analysis of leonhardite from Schemnitz (1877, no. 58) and of the soda-laumontite produced from it (*loc. cit.* no. 58a) are as follows:

58.  $(Ca_{3.03}Na_{0.13}K_{0.22})Al_{7.78}Si_{16.25} \cdot 13.37H_2O$ .

$$Ca + Na + K = 4.03; \quad Ca + \frac{Na + K}{2} = 3.83.$$

58a.  $(Ca_{1.38}Na_{4.86}K_{0.06})Al_{7.78}Si_{16.29} \cdot 13.00H_2O$ .

$$Ca + Na + K = 6.30; \quad Ca + \frac{Na + K}{2} = 3.84.$$

Several analyses show a combination of both types of isomorphic substitution. Hutton (1944) commented on the excess of lime and alkalis

TABLE III. CHEMICAL ANALYSES, OPTICAL PROPERTIES AND FORMULAE OF LAUMONTITE

	1	2	3	4	5	6	7
SiO <sub>2</sub>	50.63	52.04	50.94	51.43	52.07	53.67	50.96
TiO <sub>2</sub>	0.05	—	—	—	—	—	—
Al <sub>2</sub> O <sub>3</sub>	22.07	21.46	22.30	21.52	21.30	20.44	21.60
Fe <sub>2</sub> O <sub>3</sub>	0.73	0.12	0.12	0.94	—	0.59	0.03
MnO	tr.	—	—	—	—	—	—
MgO	0.40	tr.	—	—	—	—	—
CaO	10.72	11.41	7.65	11.88	11.24	9.79	11.27
Na <sub>2</sub> O	1.08	0.20	2.06	0.19	0.48	0.59	0.32
K <sub>2</sub> O	0.45	0.66	4.01	0.35	0.42	1.25	0.18
H <sub>2</sub> O	14.10	13.80	13.42	13.81	14.58	13.52	16.04
	100.23	99.69	100.50	100.12	100.09	99.85	100.40
Sp. Gr.	2.30 ± .02	2.29 ± .01	2.30–2.31	—	—	—	2.283
α	1.505	1.507	—	—	—	—	—
β	1.514	1.516	—	—	—	—	—
γ	1.517	1.518	—	—	—	—	—
2V <sub>α</sub>	44° ± 3°	26° ± 4°	—	—	—	—	—
γ∧c	33°	32°	—	—	—	—	small
γ'∧c on (110)	39°	40°	—	35–40°	—	—	—
Atomic formulae on basis of 48 Oxygen atoms							
	1	2	3	4	5	6	7
Ca	3.60	3.79	2.55	3.93	3.74	3.23	3.79
Na	0.65	0.12	1.24	0.12	0.28	0.35	0.19
K	0.18	0.26	1.59	0.14	0.17	0.49	0.07
Al	8.17	7.84	8.19	8.07	7.80	7.47	8.00
Si	15.87	16.13	15.87	15.92*	16.17	16.57	16.04
H <sub>2</sub> O	14.71	14.23	13.93	14.25	15.08	14.01	16.81
Ca+(Na+K)/2	4.02	3.98	3.97	4.06	3.97	3.65	3.92
Ca+Na+K	4.43	4.17	5.38	4.19	4.19	4.07	4.05
Al+Si	24.04	23.97	24.06	23.99	23.97	24.04	24.04

\* Includes 0.22 Fe'''.

† "B"—class analysis.

‡ Includes 0.52 Fe'''.

|| "Maximum extinction angle."

TABLE III. *Continued.*

	8†	9	10	11†	12	13†	14
SiO <sub>2</sub>	50.64	50.82	51.45	51.36	54.10	48.96	50.24
TiO <sub>2</sub>	—	—	—	—	0.11	—	—
Al <sub>2</sub> O <sub>3</sub>	21.86	20.06	22.74	22.55	20.44	22.24	23.64
Fe <sub>2</sub> O <sub>3</sub>	—	2.18	0.20	0.24	1.70	—	—
MnO	—	—	—	—	0.05	—	—
MgO	0.74	0.02	—	0.17	0.45	—	—
CaO	12.18	12.14	11.70	11.18	8.65	12.32	12.72
Na <sub>2</sub> O	0.42	0.31	0.14	0.12	2.60	0.63	0.35
K <sub>2</sub> O	1.34	0.22		0.28	0.55	0.31	0.15
H <sub>2</sub> O	13.59	14.87	13.77	14.56	11.45	16.41	13.36
	100.77	"99.97"	100.00	100.46	100.10	100.87	100.46
Sp. Gr.	2.23	—	2.2–2.3	2.281	2.38	2.265	2.241
$\alpha$	1.505	1.504	1.508	1.510	1.502	1.519	1.508
$\beta$	—	1.514	—	—	1.512	1.525	—
$\gamma$	1.513	1.516	1.524	1.520	1.514	1.527	1.516
2V $_{\alpha}$	—	—	—	—	35–38°	—	—
$\gamma \wedge c$	40°	30–36°	—	—	—	10–14°	35–36°
$\gamma' \wedge c$ on (110)	—	—	30°	—	40°	—	—
Atomic formulae on basis of 48 Oxygen atoms							
	8†	9	10	11†	12	13†	14
Ca	4.05	4.08	3.86	3.71	2.84	4.19	4.18
Na	0.25	0.19	0.07	0.07	1.54	0.38	0.21
K	0.53	0.09		0.11	0.21	0.13	0.06
Al	8.02	7.93†	8.24	8.24	7.39	8.32	8.55
Si	15.76	15.95	15.86	15.92	16.60	15.54	15.43
H <sub>2</sub> O	14.09	15.53	14.13	15.04	11.71	17.36	13.66
Ca+(Na+K)/2	4.44	4.22	3.90	3.80	3.72	4.45	4.32
Ca+Na+K	4.83	4.36	3.93	3.89	4.59	4.70	4.45
Al+Si	23.78	23.88	24.10	24.16	23.99	23.86	23.98

\* Includes 0.22 Fe'''.

† "B"—class analysis.

‡ Includes 0.52 Fe'''.

|| "Maximum extinction angle."



## EXPLANATION TO TABLE III

*Note: In all cases total water is listed.*

1. Laumontite partially dehydrated to leonhardite by exposure. Otama, Southland, New Zealand. The  $\text{Fe}_2\text{O}_3$  and  $\text{MgO}$  are due to a little finely intergrown ferruginous matter. Optical properties refer to the leonhardite form (cf. Table I). (D. S. Coombs, anal.)
2. Leonhardite, Hungary, no. 192. Mineralogical Museum, Cambridge. (D. S. Coombs, anal.)
3. "Primary leonhardite," Kurzow'schen, Russia. Fersman (1908).
4. Yellow crystals, Table Mountain, Colorado. Cross and Hillebrand (1885). (W. F. Hillebrand, anal.)
5. White crystals, Table Mountain, Colorado. Cross and Hillebrand (1885). (W. F. Hillebrand, anal.)
6. St. Johns, St. Bartholomew Is., West Indies. Cleve (1870). (Th. Nordström, anal.)
7. Laumontite, Margaretville, Nova Scotia. Walker and Parsons (1922). (E. W. Todd, anal.)
8. Leonhardite, Cascade Mountains, Southern Oregon. McClellan (1926). (E. V. Shannon, anal.)
9. Golden-brown crystals, Table Mountain, Colorado. Henderson and Glass (1933). (E. P. Henderson, anal.)
10. Enoggera, Queensland. Whitehouse (1937). (Queensland Govt. Analyst). Recalculated to exclude 0.36%  $\text{CO}_2$  as  $\text{CaCO}_3$ , but including  $\text{H}_2\text{O}$ - which was excluded in Whitehouse's recalculation.
11. Markovice, Bohemia. Kratochvíl (1941).
12. Devon Well, New Plymouth, New Zealand. Hutton (1944). (F. T. Seelye, anal.)
13. Fresh crystals of laumontite, Baveno. Pagliani (1948).
14. Leonhardite powder, Baveno. Pagliani (1948).

over the "theoretical" value in his Devon Well analysis (Table III no. 12). The formula for this could be derived by replacement of 0.61 CaAl by 0.60 NaSi and by further replacement of 0.55 Ca by 1.15 Na+K. The discrepancies are within the limit of analytical error. In such cases  $\text{Si} > 16$ ,  $\text{Ca} + \text{Na} + \text{K} > 4$ ,  $\text{Ca} + [(\text{Na} + \text{K})/2] < 4$ .

To summarize, introduction of alkalis into laumontite may be both of the plagioclase type in which Na and Si atoms simultaneously proxy for Ca and Al atoms, and of the zeolitic type in which two alkali atoms replace one of Ca. This latter type of base exchange may be carried out experimentally and no doubt can occur in nature if the mineral is exposed to alkaline solutions.

Most analyses appear to have been made on leonhardite or laumontite partially dehydrated by exposure. Assuming 16  $\text{H}_2\text{O}$  for 48 oxygen atoms in the structure of fully hydrated laumontite, we may express its composition by the formula



where  $x+y/2$  does not exceed 4 and  $x+y$  is not less than 4 or less precisely by the simple formula quoted above.

In conclusion it may be recalled that Henderson and Glass (1933) have indicated that Fe<sup>+++</sup> may proxy for Al to yield yellow and golden-brown crystals, and varieties rich in Be and V have been reported by the Italian workers Gallitelli (1928), Fagnani (1948) and Pagliani (1948, p. 179); and by Fersman (1922), respectively. Spectrographic analyses of two laumontite-rich rocks from Taringatura, kindly carried out by Dr. S. R. Nockolds, did not reveal significant quantities of either of these elements and showed that the content of Ba, Sr and Rb in the laumontite is very much less than in heulandite and adularia from the same area.

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