

NEW OCCURRENCE OF YUGAWARALITE FROM THE
CHENA HOT SPRINGS AREA, ALASKA¹G. DONALD EBERLEIN, R. C. ERD, FLORENCE WEBER,
AND L. B. BEATTY, *U. S. Geological Survey,*
Mentlo Park, California 94025.

ABSTRACT

Yugawaralite ($\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$), a relatively rare calcium zeolite, was found in a new locality near Chena Hot Springs, east-central Alaska in a geologic setting that differs from that described for occurrences in Japan and Iceland. It occurs as well-formed, quartz-encrusted crystals up to 8 mm long, elongate along the a axis and tabular parallel to $\{010\}$. Principal forms are $\{001\}$, $\{010\}$, $\{100\}$, $\{021\}$, and $\{11\bar{1}\}$.

The zeolite is monoclinic, space group Pa ; $a = 10.043 \pm 0.002$, $b = 13.997 \pm 0.003$, $c = 6.725 \pm 0.002$ Å; $\beta = 111^\circ 11' \pm 1'$; $a:b:c = 0.717_6:1:0.481_5$; volume = 881.5 ± 0.2 Å³; $Z = 2$. Strongest X-ray diffraction lines (in Å) are: 3.056 (100), 4.668 (73), 5.81 (64), 4.642 (64), 6.99 (60), and 4.293 (32). Optically it is biaxial (-); $\alpha = 1.492 \pm 0.002$, $\beta = 1.498 \pm 0.002$, $\gamma = 1.502 \pm 0.002$; $2V = 71^\circ \pm 2^\circ$; $r < v$ distinct; $Z = b$, $X \wedge c = -9^\circ$. The hardness is 5⁺; cleavage $\{100\}$ and $\{40\bar{1}\}$ distinct, $\{10\bar{1}\}$ imperfect; density = 2.22 ± 0.01 (measured), 2.22_6 g·cm⁻³ (calculated). These data agree with refined data obtained for yugawaralite from the type locality; however, none of the toptype material examined was optically positive, as reported by previous workers.

Chemical analysis shows SiO_2 61.47, Al_2O_3 17.38, $\text{Fe}_2\text{O}_3 < 0.04$, $\text{TiO}_2 < 0.01$, $\text{MgO} < 0.01$, CaO 8.51, SrO 0.21, Na_2O 0.06, K_2O 0.09, H_2O^+ 9.33, H_2O^- 2.79, total 99.90 wt. %. An apparent deficiency of cations [$\text{Al}_2\text{O}_3/(\text{R}_2\text{O} + \text{RO}) = 1.09$] disappears if H^+ , which is 0.3737 ions per formula in excess of that required by an ideal $8\text{H}_2\text{O}$ in the unit cell, is present as oxonium ion.

Thermogravimetric analysis gives good agreement with TGA curves from the type locality. Ion-exchange values determined show a low-exchange capacity as compared with most zeolites. Infrared absorption spectra obtained are distinctive but have similarities to those of the heulandite group.

INTRODUCTION

Yugawaralite, a relatively rare calcium zeolite, was first described by Sakurai and Hayashi (1952) from "Fudo-no-taki" Fall, near Yugawara Hot Spring, Kanagawa Prefecture, Japan. It has since been reported from Heinabergsjökull, southeastern Iceland (Barrer and Marshall, 1965; Walker, in press; See Kerr and Williams, 1969, p. 1190); the Onikobe geothermal area of northeast Japan (Seki and Okumura, 1968); Shimoda, Shizuoka Prefecture, central Japan (Sameshima, 1969); and the Tanzawa Mountains area of central Japan (Seki *et al.*, 1969). We here report on a new occurrence of yugawaralite in a geologic setting different from those earlier described. To facilitate comparison, this first complete description since that of Sakurai and Hayashi (1952) includes corrected and refined

¹ Publication authorized by the Director, U. S. Geological Survey.

crystallographic data obtained by restudying samples from the type locality.

Unless otherwise specified, all statements regarding yugawaralite refer to material from the vicinity of Chena Hot Springs, Alaska.

FIELD OCCURRENCE AND GEOLOGIC SETTING

The new occurrence of yugawaralite is in the Yukon-Tanana Upland on the north bank of the Chena River, approximately 40 miles east of Fairbanks, Alaska (NW1/4NW1/4, sec. 20, T. 1 N., R. 7 E., Fairbanks meridian). The upland is underlain by complexly folded and faulted schist, gneiss, quartzite, phyllite, slate, and metachert of Precambrian or early Paleozoic age which have been intruded by granitic rocks of Mesozoic and Tertiary age.

Yugawaralite, associated with quartz, laumontite, stellerite (Erd *et al.*, 1967), and stilbite, occurs mainly in a siliceous xenolith about 150 feet long and 60 feet wide near the edge of a small porphyritic quartz monzonite pluton 1-½ miles long and ½ mile wide (Fig. 1). The quartz monzonite pluton may be an apophysis of a much larger intrusive that is exposed across the Chena valley to the southeast. The host rock of the yugawaralite is brecciated, sugary-textured metachert, or very fine grained quartzite that is veined with quartz, chalcedony, and minor opal. At joint

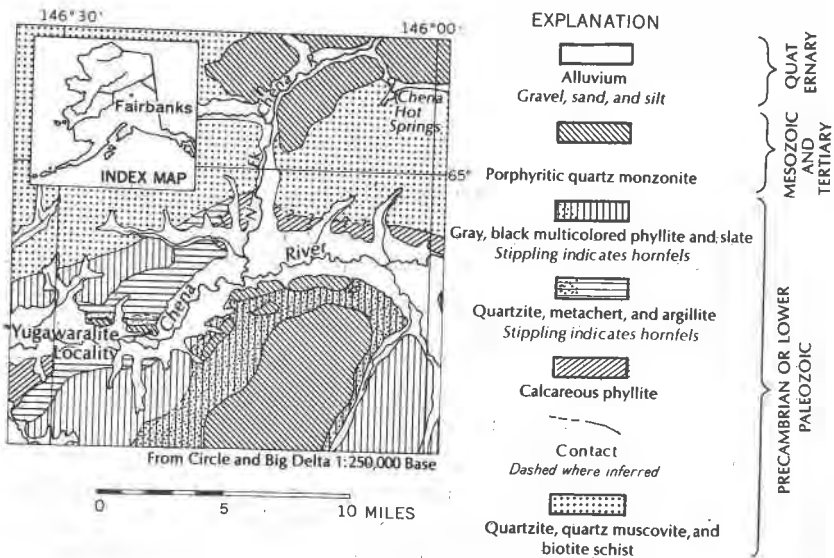


FIG. 1. Index and geologic sketch maps of yugawaralite locality, Chena River area, Alaska

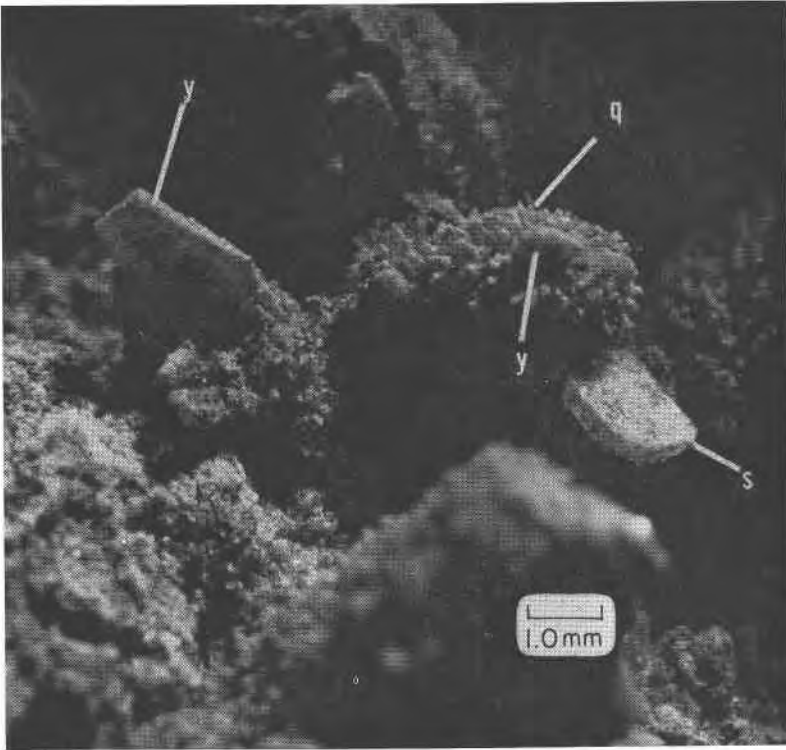


FIG. 2. Yugawaralite (y) and stibite (s) encased in quartz (q) scalenohedrons

intersections, quartz-encrusted yugawaralite crystals up to 8 mm long coat joint surfaces and vug-like enlargements. Locally, fractures are completely filled with yugawaralite, quartz, stellerite, stilbite, and laumontite. A film of hydrous iron oxide coats quartz and the surface of many yugawaralite crystals. Crystals of stellerite and stilbite are closely associated with the yugawaralite (Fig. 2). A soft white powdery coating of laumontite commonly occurs on crystals of yugawaralite, stellerite, stilbite, and quartz in the vugs.

The quartz monzonite contains 25–30 percent plagioclase (An_{40-45}), 35–40 percent quartz, 25–30 percent potassium feldspar, and about 5 percent biotite; accessory minerals are zircon, allanite, greenish-brown tourmaline, and cerite. Potassium feldspar occurs as xenomorphic phenocrysts, up to $1\frac{1}{2}$ cm in diameter, that enclose the other minerals. The pluton has many features in common with other intrusives in the Yukon-Tanana Upland that have yielded Late Cretaceous to early Tertiary isotopic dates.

At least three episodes of fracturing and late mineral deposition are indicated:

- (1) Early minor fracturing of the host rock and introduction of white vein quartz that probably was derived from the enclosing siliceous host rocks.
- (2) Brecciation and recementation by chalcedony and white quartz, probably at the time of intrusion by quartz monzonite.
- (3) Late fracturing and introduction of quartz, yugawaralite, stellerite and/or stilbite, laumontite, chalcedony and minor opal in the order given.

The association of yugawaralite with laumontite and quartz in an area of thermal-spring activity near Yugawara Hot Spring, Japan (Sakurai and Hayashi, 1952); the occurrence of yugawaralite with laumontite, analcime, and quartz in a drill-hole core at an active geothermal area at northeast Japan (Seki and Okumura, 1968); and the fact that the Alaska occurrence is only 14 miles from Chena Hot Springs suggest the possibility of a similar geothermal origin. There is, however, no evidence of past or present thermal spring activity at the yugawaralite locality. Furthermore, the Chena Hot Springs are dilute thermal waters of probable meteoric origin that contain considerable silica and sulfate ions, but little calcium and magnesium. Very little mineral deposition is now taking place at Chena Hot Springs.

GEOCHEMICAL IMPLICATIONS

The geochemistry of zeolites and their natural associations have been reviewed and brought into better perspective by Coombs *et al.* (1959), Senderov (1965), and Seki *et al.* (1969); and significant contributions to the understanding of high-silica calcium zeolite assemblages have been made by Harada (1969), Miyashiro and Shido (1970), Thompson (1970), and Liou and Ernst (1971). In the light of these discussions, the paragenetic relations outlined above suggest that yugawaralite, stellerite, stilbite, and laumontite were deposited under conditions of relatively low fluid pressure (probably of the order of 150–300 bars) and in the temperature range 200°–300°C. Deposition probably occurred from relatively alkaline aqueous solutions in which the activity of silica was equal to or exceeded that of quartz.

CRYSTALLOGRAPHY

X-ray data. The *hk0*, *0kl*, *h0l*, *hk1*, and *h1l* reciprocal nets were photographed using Zr-filtered Mo radiation. Systematic absences indicate the

space group to be either Pa or $P2/a$.¹ Yugawaralite from Alaska and Japan is piezoelectric at various frequency intervals between 1.3 and 3.6 MHz. Furthermore, pyroelectricity and etch-pit symmetry (described below) confirm the absence of centrosymmetry. These data agree with the findings of Barrer and Marshall (1965, p. 485), Kerr and Williams (1967, p. 222), and Leimer and Slaughter (1969, p. 94), all of whom, by statistical study of intensities, found yugawaralite to be non-centrosymmetric. Our data for the unit cells of yugawaralite from Alaska and from the type locality at Yugawara Hot Spring, Kanagawa Prefecture, Japan, are shown in Table 1.

Our X-ray powder data for yugawaralite from Chena, Alaska (Table 2) agree closely with such data for yugawaralite from Heinabergsjökull, Iceland (Barrer and Marshall, 1965, Table 3) and from the Onikobe and Tanzawa Mountains areas, Japan (Seki and Okumura, 1968, Table 2). Our data for yugawaralite from the type locality (Table 2) agree well with those given for yugawaralite from this locality by Neumann *et al.* (1957, Pl. VII, no. 49) and by Seki (written communication, 1965), but they are in poor agreement with the original X-ray powder data of Sakurai and Hayashi (1952). The later data of Sakurai (1953) and Harada *et al.* (1969a) for material from the type locality are in good accord with ours.

Morphology. Crystals of yugawaralite are tabular to lath-like, flattened parallel to the most prominent form $\{010\}$, and elongate on a . Some larger crystals occur in elongate tabular aggregates of as many as eight individuals oriented parallel to $\{010\}$. The central crystals of such aggregates tend to be thickest and longest with progressively thinner and shorter crystals developed outward along b . The crystals are euhedral; no twinning was observed. No doubly terminated crystals were found. The forms noted and the interfacial angles measures on 18 crystals are shown in Table 3. A typical crystal is sketched as Figure 3.

Morphological departures from centrosymmetry are slight; this is consistent with the presence of a pseudocenter for the yugawaralite framework reported by Kerr and Williams (1967, p. 223; 1969, p. 1188). Nonetheless, the absence of a center of symmetry is expressed by perceptible differences in the interfacial angles of $\{0k\bar{l}\}$ and $\{0k\bar{l}\}$ domes

¹ We have followed the recommendation of the Commission on Crystallographic Data, International Union of Crystallography (Kennard, Speakman, and Donnay, 1967) in taking $c < a$ in designating the space group. Transformation from the setting of previous workers (space group Pc) may be accomplished by use of the matrix $01\bar{1}/0\bar{1}0/\bar{1}00$. The setting of Sakurai and Hayashi (1952) may be transformed to our setting by using the matrix $00\bar{1}/0\bar{1}0/\frac{1}{2}00$.

TABLE 1. UNIT-CELL DATA FOR YUGAWARALITE

	Chena Hot Springs, Alaska ^a	Yugawara Hot Spring, Japan ^b
Crystal system	Monoclinic	Monoclinic
Space group	<i>Pa</i>	<i>Pa</i>
<i>a</i>	10.043±0.002Å	10.050±0.002Å
<i>b</i>	13.997±0.003Å	14.008±0.003Å
<i>c</i>	6.725±0.002Å	6.729±0.002Å
β	111°11'±1'	111°11'±1'
Cell volume	881.5±0.2Å ³	883.3±0.3Å ³
Cell content	2[CaAl ₂ Si ₆ O ₁₆ ·4H ₂ O]	2[CaAl ₂ Si ₆ O ₁₆ ·4H ₂ O]
Density (calculated)	2.22 ₅ gcm ⁻³	2.22 ₁ gcm ⁻³
Specific gravity (measured)	2.22±0.01 ^c	2.22±0.01 ^d
	2.22±0.01 ^d	

^a Initial parameters from X-ray single-crystal precession data. Final parameters from least-squares refinement of X-ray powder data (Table 2).

^b U.S. National Museum Specimen No. 10134.

^c Determined by the sink-float method and centrifuging using bromoform-acetone mixtures whose specific gravities were checked with a Westphal balance.

^d Determined in CCl₄ using a Berman balance (average value referred to distilled water at 4° C).

and by solution effects upon these domes, the $\{0kl\}$ domes being invariably more corroded than domes of the type $\{0k\bar{l}\}$. Furthermore, the pedion (00 $\bar{1}$) is normally less well developed than the pedion (001) and locally may be absent altogether.

Natural etch pits, produced by weathering, by late hydrothermal solutions, or perhaps by cold groundwater of appropriate pH, are present (Fig. 4), especially on $\{101\}$ and (001). The pits appear to be formed by centrosymmetric pairs which, if considered alone as evidence, would indicate higher symmetry. The pits are made up to $\{010\}$, $\{110\}$, and $\{021\}$ on $\{010\}$ and of (001) and $\{110\}$ on (001). Etching with dilute HF produces curved triangular (shield-shaped) pits (Fig. 5) whose bases are parallel to *c* and whose altitudes are parallel to *a*. The pedion (100) and domes $\{hk0\}$ show practically no effects of solution by natural weathering.

TABLE 2. X-RAY DIFFRACTION DATA FOR YUGAWARALITE

Calculated ^a				Observed			
hkl	$d_{hkl}(\text{\AA})$	I (calc.) ^b	I (calc.) ^c	Chena Hot Springs, Alaska ^d		Yugawara Hot Spring, Japan ^e	
				$d_{hkl}(\text{\AA})$	I	$d_{hkl}(\text{\AA})$	I
010	13.997	3.3	3.8	13.9	6	14.0	6
110	7.783	8.5	1.1	7.78	5	7.80	4
020	6.999	37.0	33.7	6.99	60	7.01	31
001	6.270	6.8	6.0	6.26	5	6.27	4
111	5.809	100.0	100.0	5.81	64	5.81	52
011	5.722	0.4	1.0				
120	5.606	2.8	4.1	5.62	3		
121	4.717	0.5	3.1				
200	4.682	29.4	33.6				
021	4.670	54.2	46.7	4.668	73	4.672	70
030	4.666	5.2	0.4				
201	4.641	83.1	75.8	4.642	64	4.652	67
210	4.440	5.6	6.7	4.439	8	4.442	8
211	4.405	13.9	15.5	4.402	13	4.410	10
111	4.293	36.0	32.7	4.293	32	4.295	26
130	4.176	19.3	11.7	4.177	20	4.179	14
220	3.892	7.8	5.7	3.890	8	3.897	4
221	3.868	0.7	2.0	3.867	4		
121	3.791	1.0	0.8				
311	3.767	8.7	10.3	3.768	10	3.770	7
031	3.743	3.5	3.8	3.740	3		
040	3.499	0.1	0.2				
230	3.305	4.7	4.0	3.301	6		
231	3.290	2.9	2.5	3.290	6		
140	3.278	1.5	3.1				
112	3.268	5.4	5.9	3.263	7		
131	3.243	7.3	7.9				
201	3.233	24.6	29.5	3.231	30	3.237	29
311	3.223	11.9	12.3				
202	3.192	2.8	2.0	3.191	5	3.193	6
211	3.150	2.7	2.6				
002	3.135	6.0	5.4	3.131	5	3.132	6
212	3.113	5.5	5.9	3.108	5	3.110	5
141	3.069	0.1	0.4				
012	3.059	1.1	2.1				
041	3.056	91.2	95.1	3.056	100	3.057	100
310	3.047	15.9	14.1				
122	3.030	2.0	0.7				
321	2.994	3.5	4.2	2.996	5	2.998	4
221	2.935	15.0	14.5	2.936	17	2.938	10
222	2.905	22.9	27.1	2.906	19	2.904	22
022	2.861	4.1	3.0	2.860	5		
320	2.851	0.8	1.3	2.846	2	2.856	3
240	2.803	0.6	1.0				
050	2.799	0.0	0.0				
241	2.794	0.4	0.9				
141	2.765	15.3	15.7	2.765	14	2.767	12
231	2.727	0.4	0.0				
213	2.715	13.8	15.6	2.715	12	2.718	11
133	2.701	4.5	3.6				
051	2.682	11.8	13.6	2.682	18	2.686	13
132	2.657	4.0	2.8	2.657	5		
211	2.646	9.4	9.3	2.644	9	2.648	9

Plus additional lines all with $I < 9$

^a All calculated spacings (Alaska material) listed for $d_{hkl} \geq 2.640 \text{ \AA}$. Indices from least-squares analysis of X-ray powder data using the digital computer program of Evans *et al.* (1963).

^b Values for the intensities of the diffraction maxima were calculated from the atomic parameters given by Kerr and Williams (1969) using the computer program of Borg and Smith (1969).

^c As for ^b, but calculated from the atomic parameters of Leimer and Slaughter (1969).

^d Split of analyzed (untreated) sample. X-ray diffractometer conditions are: Chart No. X-3084; Cu/Ni radiation $\lambda_{\text{CuK}\alpha} = 1.5418 \text{ \AA}$; silicon used as internal standard; scanned at $1/4^\circ 2\theta$ per minute.

^e U.S. National Museum Specimen No. 10134. Chart No. X-3094. Other X-ray diffractometer conditions as for ^d.

TABLE 3. ANGLE TABLE FOR YUCAWARALITE FROM ALASKA

Form ^a	φ (meas.) ^b	φ (calc.) ^c	P (meas.) ^b	P (calc.) ^c	A	B	C
c 001	90° 00'	90° 00'	21° 14'	21° 11'	68° 49'	90° 00'	---
r-c 001	89° 56'	90° 00'	159° 05'	158° 49'	111° 11'	90° 00'	180° 00'
b 010	0° 00'	0° 00'	90° 00'	90° 00'	90° 00'	0° 00'	90° 00'
a 100	90° 01'	90° 00'	90° 00'	90° 00'	---	90° 00'	68° 49'
k 110	56° 16'	56° 13'	90° 00'	90° 00'	33° 47'	56° 13'	72° 31'
w 011	38° 44'	38° 54'	31° 54'	31° 41'	70° 44'	65° 52'	24° 08'
v 021	22° 00'	21° 58'	46° 06'	46° 01'	74° 23'	48° 08'	41° 51'
x 041	11° 24'	11° 24'	63° 11'	62° 58'	79° 51'	29° 10'	60° 50'
-v 021	-21° 39'	-21° 58'	134° 17'	133° 59'	105° 37'	48° 08'	138° 09'
-x 041	-11° 02'	-11° 24'	117° 22'	117° 02'	100° 09'	29° 10'	119° 10'
h 111	34° 26'	34° 32'	149° 50'	149° 45'	73° 25'	65° 29'	134° 36'
h 443	41° 25'	41° 39'	138° 10'	138° 31'	64° 22'	60° 54'	123° 28'

^a Also noted but less common are $\ell\{210\}$, $\ell\{727\}$, and $u\{1-10-1\}$.

^b Averaged values of five best measurements.

^c Values calculated from refined unit-cell parameters shown in Table 1.

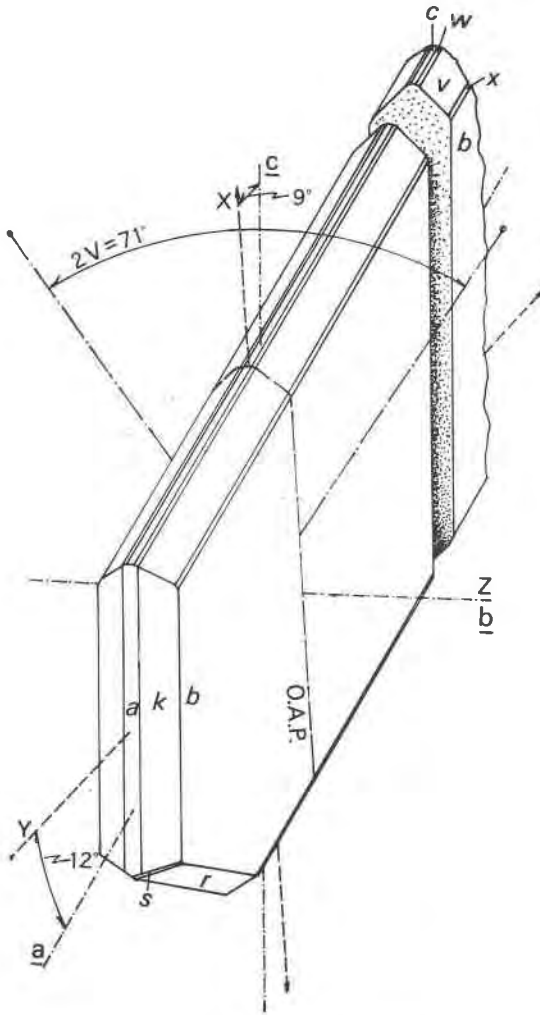


FIG. 3. Drawing showing optical orientation and typical habit of yugawaralite from Alaska

The yugawaralite crystals are commonly enclosed by a quartz "envelope" composed of clear massive quartz terminating in small (to 0.3 mm long), multiple, scalenohedral crystals (Fig. 2). The envelope has a maximum thickness of about 1.0 mm. The quartz forms on the $\{010\}$, $\{001\}$, and $\{0kl\}$ surfaces of yugawaralite, but breaks away at the interface, especially easily if immersed in water. The smooth inner surface of the quartz replicates the $\{010\}$ yugawaralite surface. Outlines of progressive zonal growth are best seen on this surface, marked by edges

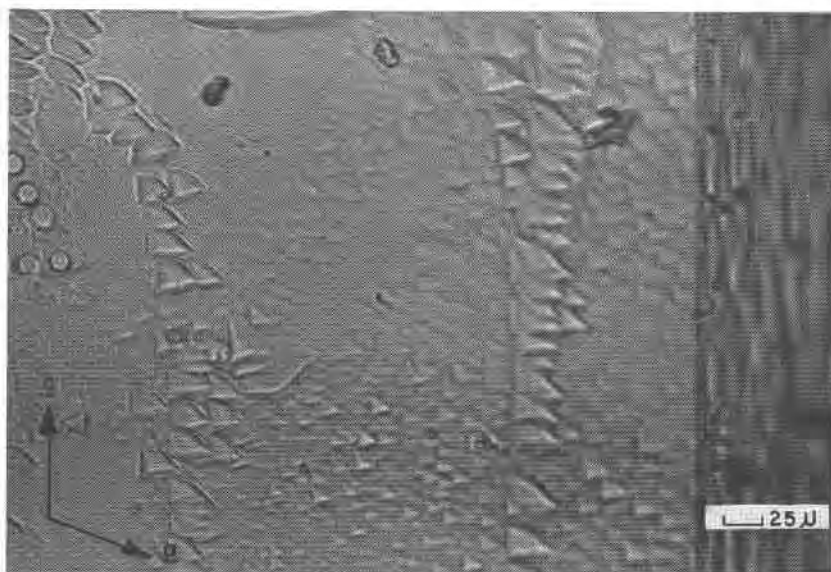


FIG. 4. Shield-shaped pits produced on (010) surface by etching with cold dilute HF. Note etch striae parallel to *c* near center of photograph. (In air).

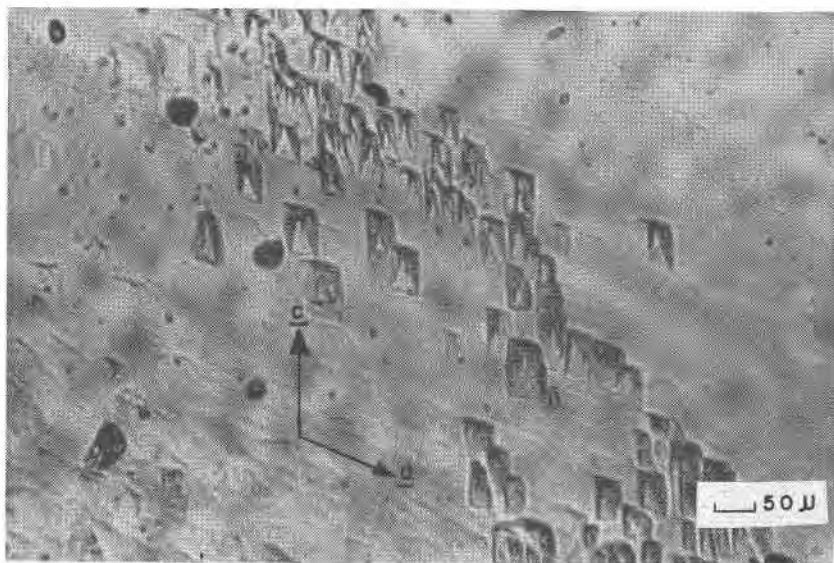


FIG. 5. Natural etch pits on (010) surface. (In air)

parallel to a and c . The comparative width of the zonal bands shows the growth rate to be fastest along the a axis. A few quartz scalenohedrons were found intergrown with $\{0kl\}$ and $\{001\}$ forms of yugawaralite, but quartz is rarely present on $\{100\}$ or $\{110\}$. Some yugawaralite crystals contain fluid inclusions aligned parallel to the a axis.

All the yugawaralite crystals that we examined were attached to the matrix surface by the antilogous end of the a axis. Many references to similar phenomena of attachment and unequal growth rates on polar axes are found in Grigor'ev (1965, p. 24).

PHYSICAL AND OPTICAL PROPERTIES

The physical and optical properties of yugawaralite are summarized in Table 4; the optical orientation is shown in Figure 3.

Indices of refraction for sodium light were determined with immersion liquids checked by means of an Abbé refractometer at the temperature of determination. Crystals were oriented for measurement by means of the spindle stage (Wilcox, 1959). The optical orientation data were measured with a 4-axis universal stage using small single crystals immersed in a liquid ($n = 1.500$) within a Waldmann sphere. When immersed in distilled water the orientation remains unchanged, but the observed optic axial angle ($2H_a$) is lowered (from 71°) to 48° . A similar change in optic axial angle of a stellerite crystal from the Alaskan locality was reported by Eberlein and Christ (1968), who demonstrated that the value of $2H_a$ was directly related to the chemical potential of water in the crystal. The dispersion remains $r < v$, distinct.

We find all crystals of yugawaralite examined from Alaska and from the type locality were optically negative rather than positive (Sakurai and Hayashi, 1952; Sakurai, 1953; Harada *et al.*, 1969a, and b and Leimer and Slaughter, 1969).

ZONING

An optical zoning was observed in crystals examined from both the new Alaska occurrence and near Yugawara Hot Spring, Japan. The zoning, which is displayed by differences in interference tint and extinction angle among transitional bands 10–125 μm wide parallel to crystal edges, is most obvious in sections parallel to the prominent $\{010\}$ form and is enhanced by heating. Etching heated or unheated crystals with dilute HF produces striae (Fig. 5) coincident with the zone boundaries. The cause of the observed zoning has not been determined, but such zoning may be the result of compositional variations. Although no compositional variation in Al, Si, or Ca could be detected in two independent electron microprobe studies of heated and unheated crystals, the possibility remains

TABLE 4. PHYSICAL AND OPTICAL PROPERTIES OF YUGAWARALITE

	Chena, Alaska	Yugawara Hot Spring, Japan	
		This study ^a	Harada <i>et al.</i> (1969a,b)
A. PHYSICAL			
Cleavage	{10 $\bar{1}$ } imperfect; {40 $\bar{1}$ }, {100} distinct	{10 $\bar{1}$ } imperfect; {40 $\bar{1}$ }, {100} distinct	{010} imperfect ^b
Fracture	conchoidal	conchoidal	---
Hardness	5 ⁺	5 ⁺	4-1/2
Fusibility	5	5	---
Electrical	piezoelectric; pyroelectric	piezoelectric; pyroelectric	---
Magnetic	nonmagnetic	nonmagnetic	---
Luminescence	nonfluorescent	nonfluorescent	---
Color	colorless	colorless	colorless to white
Streak	white	white	white
Luster	vitreous; pearly iridescence on {010}	vitreous; pearly iridescence on {010}	vitreous
Transparence	transparent to semi-transparent	transparent to semi-transparent	transparent
B. OPTICAL			
Color	colorless	colorless	colorless
Pleochroism	nonpleochroic	nonpleochroic	---
α ($n_D^{25^\circ C}$)	1.492±0.002	1.493±0.002	1.496
β ($n_D^{25^\circ C}$)	1.498±0.002	1.499±0.002	1.497
γ ($n_D^{25^\circ C}$)	1.502±0.002	1.503±0.002	1.504
$2V_\alpha$	71°±2°	72°±2°	$2V_\gamma = 78^\circ$
Character	biaxial (-)	biaxial (-)	biaxial (+)
Dispersion	$n < v$, distinct, horizontal	$n < v$, distinct, horizontal	$n < v$, weak
Orientation	$Y_A = -12^\circ$ $Z = b$ $X_{AC} = -9^\circ$	--- $Z = b$ ---	$X \doteq a$ $Z = b$ $Y \doteq c$ ($\gamma_{AC} = 6^\circ-7^\circ$)
Optic axial plane	\perp {010}	\perp {010}	\perp {010}

^a U.S. National Museum Specimen No. 10134.^b There is parting along {010}, a plane of parallel growth.

that the zoning is related either to differences in atomic Al-Si distribution below the detection limit of the probe or to trace-element distribution, especially of transition elements (Table 6).

CHEMICAL PROPERTIES

Analysis. A sample of yugawaralite was purified by centrifuging a nonmagnetic fraction in bromoform-alcohol mixtures. The resulting concentrate was split into two fractions, one of which was heated to 60°C in 1:1 HCl for 20 minutes to remove a thin film of hydrous iron oxide that adhered to some of the untreated grains. The purity and composition of the untreated and acid-treated fractions were checked by X-ray diffraction, optical methods, and infrared analysis. No distinction between the two fractions was made by these tests. The only identifiable impurity determined by X-ray and optical examination was less than 3 percent quartz.

The untreated fraction (3.63 g) and acid-treated fraction (4.37) g of sample 64AWr142 were submitted for analysis. Within the limit of the procedures used, no significant difference between the two fractions could be detected (Tables 5, 6). SiO_2 was determined colorimetrically using the molybdenum blue method adapted for silicate rock analysis by Shapiro and Brannock (1962). Al_2O_3 and CaO plus SrO were determined gravimetrically. Flame photometry was used for the determination of SrO and the alkalis. Fe_2O_3 , TiO_2 , MnO , and MgO were analyzed by various colorimetric methods. The values obtained were less than the accepted lower limits of detection for the procedures used. Total water was obtained by fusing the sample with a flux for 1 hour at 1000°C and calculating the weight loss.

The apparent deficiency of cations [$(\text{Al}_2\text{O}_3/(\text{R}_2\text{O}+\text{RO})=1.09)$] shown by the analysis (Table 5) disappears if H^+ , which is 0.3737 ions per formula in excess of that required by an ideal $8\text{H}_2\text{O}$ in the unit cell, is present as oxonium ion.

Solubility. Yugawaralite is insoluble or nearly so in hot concentrated HCl , HNO_3 , H_2SO_4 , aqua regia, and water. It is only slightly attacked by a hot concentrated solution of KOH but is soluble in HF and decomposes readily in KOH and Na_2CO_3 fusions. Etching with dilute HF produces, in addition to the etch pits mentioned above, striations on $\{010\}$ parallel to crystal edges, especially prominent parallel to c . (Fig. 5). The striations coincide with the zone boundaries, detected optically in heated material. The corroded rounded $\{001\}$ and $\{0kl\}$ forms, compared with the fresh or only slightly pitted (100) and $\{hkl\}$ forms, are evidence of differential solubility during hydrothermal or weathering processes.

Pyrognostics. When heated in a closed tube, small fragments give off water, turn opaque white, and develop prominent cracks at temperatures below red heat. Heated before a blowpipe, the grains first become white and opaque, then, with continued heating, colorless and transparent with rounded edges.

THERMAL DATA

Dehydration. Samples of yugawaralite were heated in covered platinum crucibles in an electric furnace at various temperatures and for various periods of time. The samples were weighed as soon as possible upon removal from the furnace and at various times thereafter to determine the rate of rehydration. One molecule of water is lost by 106° , the second by 350° , and the third and part of the fourth by 435°C . The final loss of a fraction of a molecule (about 0.5 percent weight loss) occurs at $900\text{--}1000^\circ\text{C}$.

The physical changes accompanying dehydration are of interest. There is a marked pyroelectric effect evidenced by grains clumping together when the first molecule of water is lost. The pyroelectric effect is noted up to 350°C , at which point the grains turn white and are opaque in air (but are transparent in immersion oils). At about 435°C , a phase change accompanies the loss of the third and partial fourth molecules of water. (This phase will be described in a later note.) Two intersecting sets of cracks develop at this temperature. One set is approximately perpendicular to $\{001\}$ or roughly parallel to $[401]$ and the other set is parallel to the a axis. Those parallel to $[401]$ are widely spaced, continuous, long (some 1.5 mm), and relatively broad (approximately $5\ \mu\text{m}$). Those parallel to a are numerous, closely spaced, interrupted, short (averaging about 0.1 mm), and narrow ($<1\text{--}2\ \mu\text{m}$).

At about 935°C yugawaralite melts to a translucent glass that becomes transparent at about 970°C . With continued heating to 1040°C , crystals of anorthite and β -cristobalite slowly develop in the clear glass.

Rehydration. Complete rehydration of yugawaralite is achieved in about 5 hours from 106°C , 13 hours from 350°C , and 3 days from 435°C (when heated for one-half hour at this

temperature). When heated at 435°C for a longer period of time (more than 5 hours), the new phase appears. No rehydration of the new phase to yugawaralite was detected by weight gain or by examination of the X-ray powder data after the new phase had been kept in a humidifier for 3 months.

TABLE 5. CHEMICAL ANALYSES OF YUGAWARALITE FROM ALASKA

Oxide	Weight percent		Ion	Ions/Formula ^a	
	Untreated	Acid treated			
SiO ₂	61.44	61.47	Si ⁴⁺	11.8420	} 15.9907
Al ₂ O ₃	17.43	17.38	Al ³⁺	4.1486	
Fe ₂ O ₃	<0.05	<0.04	Fe ³⁺	0.0046	
TiO ₂	<0.01	<0.01			
MgO	<0.05	<0.01	Mg ²⁺	0.0030	
CaO	8.51	8.51	Ca ²⁺	1.8467	
SrO	0.21	0.21	Sr ²⁺	0.0247	
Na ₂ O	0.07	0.06	Na ⁺	0.0236	
K ₂ O	0.06	0.09	K ⁺	0.0233	
H ₂ O ⁺	9.23	9.33	OH ⁻¹	12.6045	} 16.3737
H ₂ O ⁻	2.84	2.79	OH ⁻¹	3.7692	
Total	99.90	99.90		Oxygen remainder	23.6263
				Total charge	80.0000

Leonice B. Beatty, analyst.

^a Calculations based on analysis of acid-treated material after deducting 3% quartz (=58.47% SiO₂) and assigning weight percentages of Fe₂O₃ (=0.03) and MgO (=0.01) on the basis of quantitative spectrographic analyses (Table 6). Ions per formula were calculated following the anion-based hydrogen-equivalent method programmed in Extended Algol (Jackson *et al.*, 1967)

Normalizing factor = 12.1691.

Weight percentage of oxygen = 52.59.

Formula = (K_{0.02}Na_{0.02}Ca_{1.85}Sr_{0.02})(Al_{11.15}Si_{11.84})O₃₂·8H₂O .

Density = 2.221 gcm⁻³ (calculated for this composition and measured cell volume = 881.5 Å³).

TABLE 6. SPECTROGRAPHIC ANALYSIS OF YUGAWARALITE FROM ALASKA^a

	Untreated ^b Weight percent	Acid treated ^b Weight percent
Fe ^c	0.024	0.026
Mg ^c	0.010	0.0043
Ti ^c	0.0010	0.0008
Mn ^c	0.0002	0.0006
Ag	<.00007	<.00007
Ba ^c	0.0028	0.0024
Cr	0.005	0.007
Cu ^c	0.0003	0.0009
Ga	0.0005	0.0005
Ni	0.0015	0.003
Sr ^c	0.20	0.17

^a Amounts of major elements shown in Table 5.

^b Chris Heropoulos, analyst. Semiquantitative spectrographic analyses except as noted under ^c. Looked for but not found: K, P, As, Au, B, Ba, Bi, Cd, Ce, Co, Ge, Hf, Hg, In, La, Li, Mo, Nb, Pb, Pd, Pt, Re, Sb, Sc, Sn, Ta, Te, Th, Tl, U, V, W, Y, Yb, Zn, Zr. For limits of sensitivity see Bastron *et al.* (1960).

^c Robert E. Mays, analyst. Quantitative spectrographic analyses. The results have an overall accuracy of ± 15 weight percent except near the limits of detection where only one digit is reported.

Thermogravimetric analysis. A thermogravimetric analysis of a 117.2 mg sample of yugawaralite was carried out by F. O. Simond using a Chevenard thermobalance and a heating rate of 4°C/minute. The resulting curve is shown in Figure 6. The first molecule of water is lost between 110–175°C, the second from 350–440°, and the third and a fraction of the fourth from 440–500°; the final loss occurs by 1000°C. Because of the rate of heating, these temperatures are apparently higher than those determined by the isothermal method described above. The results are in good agreement with the TGA curves obtained by Sakurai and Hayashi (1952) Sakurai (1953), and Imai *et al.* (1964) for yugawaralite from the type

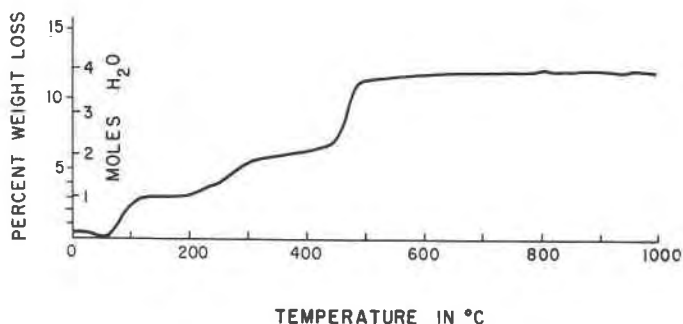


FIG. 6. Thermogravimetric curve for yugawaralite from Chena River area, Alaska

locality and with the data of Barrer and Marshall (1964, p. 492) for the synthetic strontium analog.

ION EXCHANGE

The ion-exchange values for yugawaralite were determined by Harry C. Starkey (written communication, 1967). The mineral has a total exchange capacity of 4.3 meq/100 g, which is attributable to Ca^{2+} , as no exchangeable Na^+ , K^+ , Mg^{2+} , or Sr^{2+} was detected. The determinations were made by leaching the sample for 16 hours in 1N neutral NH_4Cl . The samples were separated from the leachates by centrifuging and were washed with methyl alcohol; the washings were added to the leachates, which were retained for cation analysis. The exchange capacity was determined by ammonia distillation of the samples. Ca^{2+} and Mg^{2+} were determined by versene titration, Na^+ and K^+ by flame photometry, and Sr^{2+} by atomic absorption. Hawkins (1967), using a different ion-exchange method, obtained cation-exchange capacities ranging from 14.4 to 100 meq/100 g for the synthetic strontium analog of yugawaralite.

The exchange capacity of yugawaralite is very low compared with that of zeolites

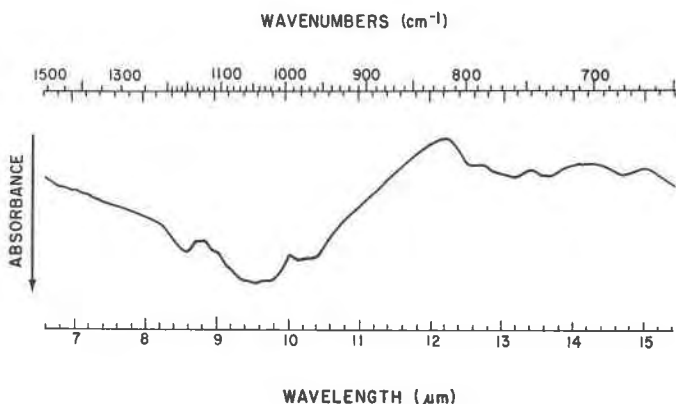


FIG. 7. Infrared spectra of Alaskan yugawaralite in the frequency region 650–1500 cm^{-1} . Irving Breger, analyst

(Carroll, 1959, p. 769-771); it compares more closely with the low exchange capacities reported for natural and synthetic wairakite (Ames, 1966, Table 1), bikitaite (Phinney and Stewart, 1961, p. D355), and buddingtonite (Erd *et al.*, 1964, p. 844-845). Ferrierite may also be included in this group, for Vaughan (1966, p. 987) noted that "... prolonged etching with hot acid does not remove a significant amount of Mg^{2+} from ferrierite."

INFRARED ABSORPTION ANALYSIS

The spectra of yugawaralite were obtained by I. Breger using both untreated and acid-treated samples. One mg of each sample was mixed with 300 mg KBr and pressed into a 25-mm disc. The spectra showed no change when the discs were run at room temperature and at 110°C against a 300-mg KBr reference pellet, and no difference could be detected between the curves of the untreated and acid-treated samples. The region 650-1500 cm^{-1} of the untreated samples is shown in Figure 7. In addition to the absorption maxima shown here, there are peaks at 1631 and 3436 cm^{-1} which may be assigned to H-O-H bending and to residual water ($\sim H_2O^-$) respectively. There is no indication of structural water ($\sim H_2O^+$) at temperatures to 110°C. The spectra are distinctive but compare most closely with spectra for stilbite and heulandite of the infrared spectra for zeolites obtained by Moenke (1962). This agrees with the findings of Kerr and Williams (1967, p. 224) who note that yugawaralite has similarities to the heulandite group but represents a unique structural group of zeolites.

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