THE AMERICAN MINERALOGIST, VOL. 56, MARCH-APRIL, 1971

WAKEFIELDITE, YTTRIUM VANADATE, A NEW MINERAL FROM QUEBEC[1]

NORMAN M. MILES, *Soil Research Institute, Department of Agriculture, Ottawa, Canada*, DONALD D. HOGARTH, *Department of Geology, University of Ottawa, Ottawa, Canada*, AND DOUGLAS S. RUSSELL, *National Research Council, Ottawa, Canada.*

ABSTRACT

Wakefieldite (YVO_4) occurs in a zoned granite pegmatite near Wakefield Lake, Quebec. Wakefieldite has been found in the quartz core, giant perthite-quartz zone, and on the mine dump. It is considered a secondary mineral, possibly derived by leaching of hellandite, and precipitated from warm alkaline solutions.

About 60 minerals, including compounds of Y, U, Th, Nb, and Bi occur in the pegmatite; 9 of these are unidentified. Pure wakefieldite could not be obtained for chemical analysis but Y and V are important constituents. YVO_4 is also found in solid solution (about 10 wt %) in thorogummite at this locality.

The X-ray pattern is similar to synthetic YVO_4. The mineral has the zircon structure, space group $I4_1/amd$, $a=7.105\pm0.003$ Å, $c=6.29\pm0.01$ Å, $Z=4$. Strongest lines are 4.74 (17), 3.56 (100), 2.66 (50), 2.51 (30), 2.21 (25), 1.824 (75), 1.774 (20).

The mineral is pulverulent and fills cavities in quartz. The color varies from pale tan to yellow. Synthetic YVO_4 is optically uniaxial, positive with $\omega=2.00$, $\epsilon=2.14$; ρ (calc) $=4.25$.

INTRODUCTION

Wakefieldite[2] is a new mineral which has been found at the Evans-Lou mine, about 25 miles north of Ottawa, Canada. The name is derived from Wakefield Lake which lies 1¼ miles to the south-southwest. It is probably the first vanadium-rich mineral, other than vanadian magnetite, found in the Grenville region.

The Evans-Lou mine, once a productive feldspar quarry, has been idle for many years; mine buildings have collapsed and the quarry is now partly water-filled. The following historical information of the mine was supplied by Mr. Leo MacDonnell, area manager of International Minerals and Chemical Corporation (Canada) Ltd. From 1938 to 1952 25,000 tons of feldspar and 10,000 tons of quartz were produced by Canada Flint and Spar Ltd., the latter as a source of silica for the Electric Reduction Company of Buckingham, Quebec. During the course of mining, a quartz mass 20×40 feet was encountered near the south end of the pit. Many of the rare element minerals now found on the dump apparently came from this quartz mass close to its contact with the giant perthite-quartz zone. This portion of the pit is now covered with about 30 feet of water.

The mine dumps were visited by staff and students of the University of Ottawa in mid-October 1968. At this time numerous specimens were collected and these were examined during the winter. It is from this collection that wakefieldite was first identified. Access to

---

[1] Contribution No. 350. Soil Research Institute, Canada Department of Agriculture, Ottawa, Ontario.

[2] The name wakefieldite has been approved by the Commission on New Mineral Names of the International Mineralogical Association.

the interior of the pit was by ski in early April, 1969. Wakefieldite was found in place in two locations on the quarry wall. The mine dumps and surrounding country were again visited several times later in the spring and during the summer and several new specimens of wakefieldite were collected during these excursions.

OCCURRENCE AND ASSOCIATED MINERALS

All consolidated rocks of the area are considered Precambrian. The only geological map of this area is the reconnaissance sheet of Wilson (1920) which shows the area underlain by sillimanite-garnet gneiss and quartzite, although we saw no sillimanite-garnet gneiss near the quarry.

Rocks of the area include foliated quartzites and, possibly metasedimentary, rather massive calc-silicate rock (Figure 1). The former contains considerable perthite and a little biotite and garnet; the latter is mainly made up of actinolite and diopside and lesser amounts of sphene, phlogopite, apatite, and plagioclase. A poor foliation is sometimes evident in the calc-silicate rock caused by a segregation of actinolite and diopside into layers. The calc-silicate rock is mineralogically similar to "pyroxenite" of the Ottawa Valley but its high tenor in Ni and Cr[1] suggests an affinity with periodotite. The pegmatite is in faulted contact with calc-silicate rock on the west but contains xenoliths of this rock on the east.

Granoblastic to gneissoid quartz-monzonite is also in sharp contact with the pegmatite and its foliation is clearly transected by pegmatite in the south. The rock is mainly composed of plagioclase (An 15–20 core of crystals, An 8–14 rim), microcline-perthite, and quartz with lesser amounts of biotite.

Quartz diorite and granodiorite, commonly cataclastically deformed or appearing as graphic granite, are in contact with the pegmatite although these contacts are poorly exposed. Quartz and oligoclase (An 18–24) are locally segregated into rude layers that parallel the regional foliation. Actinolite and diopside are the most common mafic constituents. These rocks contain a few xenoliths of calc-silicate rock.

The pegmatite can be traced along the crest of a ridge for 400 feet in a northerly direction and is up to 85 feet wide. It dips steeply to the west and appears to have normal but asymmetrical zoning with giant perthite-quartz at the centre and perthite-plagioclase (An 13–17)—quartz on the periphery of the dyke. Quartz and feldspar have been locally fractured and rehealed. Fergusonite and hellandite were deposited before this period of brecciation and sometimes appear as fragments surrounded by quartz. The spatial relationship of the quartz zone with re-

---

[1] X-ray fluorescence analyses of two specimens gave—320, 430 ppm Ni; 2000, 700 ppm Cr.

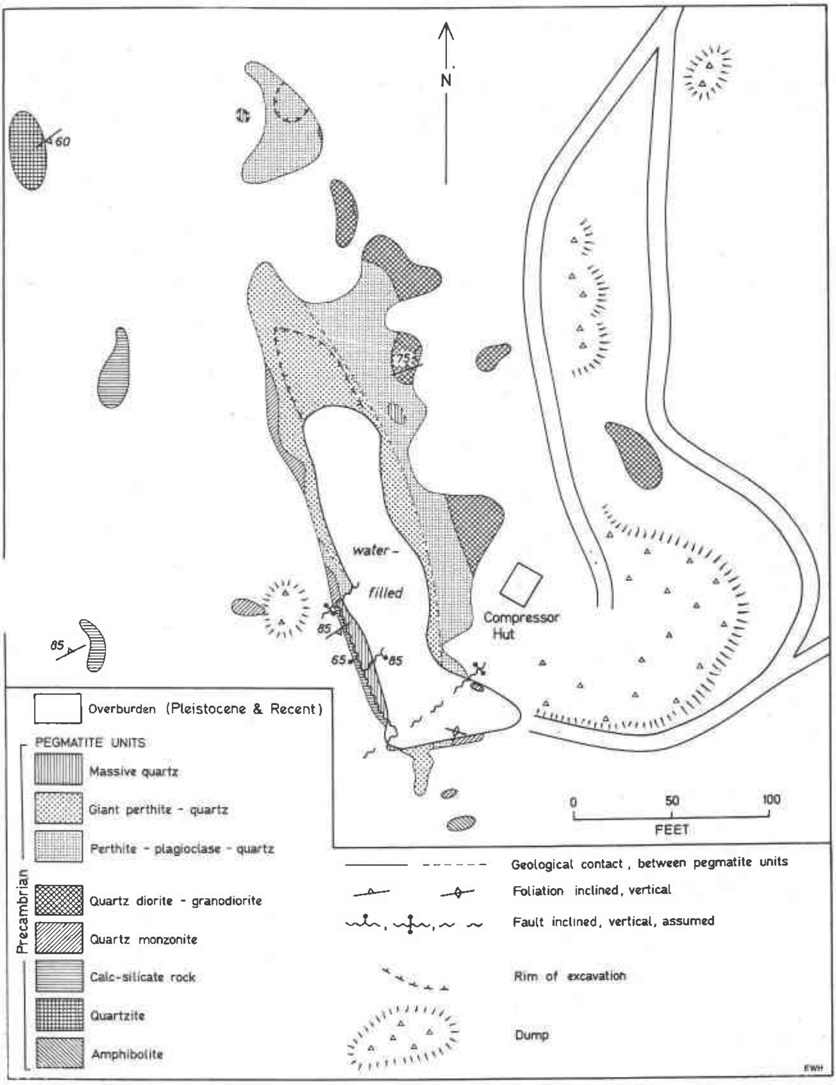

FIG. 1. Geology of the Evans-Lou Mine.

spect to the other two pegmatite zones varies although the main mass of quartz apparently is situated near the centre of the dyke at the south.

Large crystals of pink microcline (up to 5×2 feet) and weathered allanite (up to 4×2 feet) appear on the quarry wall in the giant perthite-quartz zone. Also noted in this zone is an abundance of vugs up to several feet across which contain large quartz crystals (up to 7 lbs) commonly coated with montmorillonite, goethite, or hematite.

Table 1 lists the minerals of the pegmatite. Of the accessory minerals on the dump, biotite, yttrian spessartite, allanite, hematite, goethite, and fergusonite are the most common, probably in that order of abundance. Minerals have been identified by X-ray diffraction and some by optical properties combined with X-ray data. Metamict minerals were X-rayed after ignition in nitrogen at 700°C for 3 hr. The paragenesis of the more common yttrium minerals is planned for a later paper.

The unidentified minerals have been found only on the dump; except for UN-4 (unknown number 4), they are rare (Table 2). An X-ray pattern of one of the unidentified minerals (UN-17) compares well with that of a synthetic compound listed in XRDF. Eighteen of the nineteen lines listed for $Mg_YTa_2O_{5+Y}$ ($Y<3$) in card 13-527 are present in UN-17, the missing line in UN-17 being weak in magnesium tantalate. In addition, there are two weak lines in UN-17 that do not appear in magnesium tantalate. Small differences in intensity in the X-ray pattern of the mineral may be due to niobium proxying for tantalum. This mineral occurred in very small amounts on a single specimen. The small quantity of material did not permit further work.

For a considerable time wakefieldite was known from a single specimen taken from the dump and it was from this specimen that nearly all the data were collected. A pale tan mixture of wakefieldite, intimately associated with quartz and hellandite, and lesser amounts of cenosite and montmorillonite, filled cavities in quartz in three sites on this specimen. Subsequently, canary yellow wakefieldite was discovered at two locations within the quarry. At one of these locations, near the southwest end of the pit (quartz zone), wakefieldite was associated with montmorillonite in vuggy quartz. Yttrian fluorapatite and thorogummite were found nearby. At the other location, in the northwest end of the pit (giant perthite-quartz zone), wakefieldite was mixed with montmorillonite in cavities in quartz near a cluster of fergusonite crystals. Fine-grained xenotime occurred a few inches away. Wakefieldite was found with montmorillonite in quartz in four additional specimens on the dump; in two of these specimens wakefieldite was intimately associated with hellandite.

After preliminary studies, in which the X-ray pattern of wakefieldite was found to correspond to the pattern of synthetic YVO_4 in ASTM cards, wakefieldite was scraped from the original specimen for further work. About ten mg of material from one site was centrifuged and cleaned with tetrabromethane. Seven mg were recovered.

TABLE 1. MINERALS IDENTIFIED AT THE EVANS-LOU MINE

Minerals	Description	Pegmatite zones[a]			Mine[a] dump
		Quartz	Giant perthite quartz	Perthite plagioclase quartz	
Native elements					
Native bismuth	Granular masses with bismutite				U
Graphite	Small flakes in feldspars			U	
Sulfides					
Chalcopyrite	Tiny anhedral grains and tetrahedra				U
Pyrite	Small cubes, commonly interleaved with biotite	C	C	U	C
Pyrrhotite	Anhedra with chalcopyrite				U
Oxides					
Anatase	Yellow leucoxene after sphene		C		U
Hematite	Specularite and "red hematite"	C	C		C
Goethite	Tiny prismatic crystals and "limonite"	C	C		C
Magnetite	Tiny octahedra			U	
Uraninite	Small cubes and sooty masses	U			U
Fergusonite (metamict)	Long tapering crystals	C	C		C
Euxenite (metamict)	Rounded tabular crystals		U		U
Pyrochlore	Chocolate-brown powder				U
Oxyhalides					
Zavaritskite	Yellowish gray powder				U
Carbonates					
Calcite	Prismatic crystals and rhombohedra	U	U		U
Malachite	Stain on quartz				U
Bismutite	Yellow-green and brown powder				C
Azurite	Stain on quartz				U
Tengerite (of Vorma *et al.*, 1966)	Microcrystals in vugs and fractures				C
Beyerite	Light greenish yellow powder				U
Doverite	Pink crystals on tengerite				U
Sulfates					
Gypsum	Incrustation on microcline near pyrite		U		
Phosphates					
Xenotime	Tiny yellow, green and pink dipyramids		C		C
Apatite (yttrian)	A single large blue crystal in quartz	U			
Vanadates					
Wakefieldite	Yellow powder on quartz	U	U		U
Orthosilicates					
Sphene (yttrian)	Brown crystals up to 1 foot across	U	C		U
Andradite	Black dodecahedra in quartz				U
Spessartite (yttrian)	Brown in biotite, black in quartz	U	U		C
Eulytine	White incrustation on quartz				U
Zircon	Tiny dipyramids			U	
Thorogummite (non-metamict)	Yellow, green and white powder	C	C		C
Uranothorite (partly metamict)	Black prismatic crystals		C		U
Uranophane	Yellow tufts of crystals	U	C		U
Betauranophane	Yellow radiating crystals		U		
Hellandite	Large broken yellow and black crystals in breccia				C

TABLE 1.—(*Continued*)

Minerals	Description	Pegmatite zones[a]			Mine[a] dump
		Quartz	Giant perthite quartz	Perthite plagioclase quartz	
Sorosilicates					
Epidote and clinozoisite	Microcrystals sealing fractures in feldspars			U	U
Allanite (metamict and nonmetamict)	Large anhedral masses, commonly highly altered	C	C	C	C
Ring silicates					
Tourmaline	Large black prisms		U	C	U
Cenosite	Prisms up to 2 mm long in quartz and hellandite				C
Chrysocolla	Nodules on quartz				U
Chain silicates					
Diopside	Partly uralitized prismatic crystals			U	U
Actinolite	Prismatic crystals			U	U
Hornblende	Large equant grains				U
Layer silicates					
Muscovite	Tiny greenish books	C	C	C	C
Biotite (partly chloritized)	Books to 2 feet across		C	C	C
Chlorite	Interleaved with biotite and as fine-grained masses		C		C
Montmorillonite	In cavities in quartz		C		C
Septachlorite	In cavities in quartz				U
Framework silicates					
Quartz	Irregular grains and crystals up to 7 lb	R	R	R	R
Microcline	Mainly pink, some amazonite	C	R	R	R
Plagioclase (albite and oligoclase)	White and Pink	C	R	R	R

[a] Key to symbols—R rock-forming mineral
C common accessory mineral
U uncommon accessory mineral

TABLE 2. UNIDENTIFIED MINERALS FROM THE EVANS-LOU MINE DUMP

No.	Description	Strongest X-ray diffraction lines (Spacing in ångströms and intensities in parentheses)				
UN-3	Yellow or pink powder	4.62 (5)	3.43 (10)	2.67 (6)	2.49 (6)	
UN-4	Ochre yellow powder	4.47 (10)	3.07 (1)	2.58 (6)	1.51 (7)	
UN-10	Light-yellow stain	4.19 (8)	3.31 (10)	3.07 (8)	1.82 (2)	
UN-11	White powder	6.85 (10)	4.85 (8)	3.31 (8)	2.58 (8b)	
UN-12	Canary-yellow stain	5.40 (3)	4.85 (10)	2.86 (5)	1.97 (1)	
UN-13	Yellowish-white powder	4.19 (1)	3.22 (5)	3.05 (10)	2.64 (2)	
UN-16	White crusts	6.81 (10)	3.30 (10)	2.08 (10)	1.87 (10)	
UN-17	Greenish yellow prismatic crystals	4.98 (5b)	3.63 (8b)	2.85 (10b)	2.51 (8b)	2.48 (5)
UN-18	Red-brown, waxy	3.21 (10)	2.71 (5)	2.64 (5)	2.52 (2)	

X-RAY STUDIES

X-ray patterns of wakefieldite from the original specimens were obtained with Debye-Scherrer cameras and a Norelco diffractometer. Systematic extinctions were in accord with the space group $I4_1/amd$. In addition there were a few, low angle, impurity lines in the natural material which matched hellandite, quartz, cenosite, and montmorillonite. Canary-yellow wakefieldite, from a location within the pit, gave only wakefieldite lines on X-ray photographs. However the amount of pure material was insufficient for further studies.

In order to conclusively establish wakefieldite as YVO_4 crystallizing with the zircon structure type it was necessary to compare the mineral with the synthetic product. The compound YVO_4 was synthesized after the manner suggested by Milligan *et al.* (1948) and Schwarz (1963a and b). Vanadium pentoxide was prepared by heating ammonium vanadate in a muffle furnace at 425°C for 45 min. This compound and commercial Y_2O_3 were tested by X-ray diffraction and then ignited together in a platinum crucible in equal molecular amounts at 975°C for $2\frac{1}{2}$ hr. The product YVO_4 was verified by X-ray diffraction and X-ray fluorescence; the diffraction data matching the published data of Schwarz (1963 a) for every line except (211) which was absent in Schwarz and very weak in our synthetic product.

The wakefieldite pattern compares well with synthetic YVO_4 (Table 3). The pattern was indexed by computer using a *d*-spacing program prepared by Dr. E. J. Gabe of the Department of Energy, Mines and Resources. The unit cell dimensions, $a = 7.105 \pm 0.003$ Å, $c = 6.20 \pm 0.01$ Å, were determined from diffractometer data with CoK α radiation, $\frac{1}{2}°$/min scanning speed, and quartz as standard. The (400) and (600) reflections were used to calculate a and the (512) reflection to calculate c. Intensities were determined from a diffractometer chart and visually from photographs using CuK α radiation.

CHEMICAL COMPOSITION

Seven mg of dried concentrate were analysed in powder form by X-ray fluorescence (LiF and EDDT crystals, W- and Cr-target tubes). Strong Y and V$K\alpha$ and $K\beta$ peaks were registered on the spectrogram. The sample yielded 35 percent Y_2O_3 and 27 percent V_2O_5 using synthetic YVO_4 as standard. The analysis also yielded significant Fe and Si; 1 or 2 percent of each of U, Dy, Yb, Er; lesser amounts of Ho and Ce; P, Mo, As, Th, Zr, and La were not detected.

The chemical compositions of the two other samples from the original hand specimen (samples B and C) were investigated with a 3.4 M direct-reading optical spectrograph. Results are presented in Table 5. All

TABLE 3. X-RAY POWDER DATA OF WAKEFIELDITE AND SYNTHETIC YVO_4

Wakefieldite: Tetragonal, $a=7.105$, $c=6.29$ Å CuKα=1.5418 Å				Synthetic YVO_4: Tetragonal, $a=7.1192$, $c=6.2898$ Å CuKα_1=1.5405 Å Swanson *et al.*, 1967	
I	*d*(obs.) Å	*d*(calc.) Å	*hkl*	*I*	*d*(obs.) Å
17	4.74	4.7132	101	8	4.711
100	3.56	3.5515	200	100	3.559
5	2.83	2.8364	211	2	2.831
50	2.66	2.6686	112	46	2.668
30	2.51	2.5113	220	12	2.518
5	2.35	2.3566	202	6	2.357
25	2.21	2.2163	301	12	2.220
10	2.01	2.0138	103	5	2.012
10	1.881	1.8802	321	6	1.884
75	1.824	1.8288	312	46	1.830
20	1.774	1.7757	400	13	1.780
<3	1.752	1.7518	213	1	1.751
<3	1.661	1.6617	411	1	1.666
15	1.585	1.5883	420	8	1.5915
5	1.573	1.5750	004	4	1.5722
		1.5711	303		
<3	1.547	1.5469	402	1	1.5485
15	1.477	1.4784	332	11	1.4805
15	1.435	1.4398	204	7	1.4381
		1.4368	323		
5	1.386	1.3858	501	3	1.3884
			431		
15	1.329	1.3343	224	7	1.334
		1.3319	143		
<3	1.290	1.2896	314	<1	1.2894
15	1.274	1.2740	512	7	1.2761
<3	1.251	1.2556	440	2	1.2586
5	1.185	1.1838	600	5	1.8165
5	1.176	1.1783	404		
		1.1767	503	3	1.1783
		1.1767	433		
—	—	1.1712	215	1	1.1699
<3	1.150	1.1482	611	1	1.1507
10	1.136	1.1362	532	7	1.1383
<3	1.122	1.1231	620	4	1.1255
10	1.117	1.1184	424	5	1.1189
		1.1169	523		
<3	1.094	1.0925	541	—	—
—	—	1.0615	325	1	1.0609
<3	1.044	1.0442	631	1	1.0466
		1.0434	514		
3	1.025	1.0278	116	2	1.0262
—	—	1.0206	613	2	1.0218
—	—	1.0170	415	1	1.0164
—	—	0.9850	640	2	0.9873
<3	0.9830	0.9818	444	2	0.9826
		0.9809	543		
—	—	0.9642	721	1	0.9662
—	—	0.9636	534	1	0.9643
5	0.9571	0.9570	712	5	0.9589
			552		
—	—	0.9512	316	2	0.9503
<3	0.9475	0.9463	604	3	0.9472
		0.9455	633		
—	—	0.9426	505	1	0.9427
3	0.9140	0.9144	624	3	0.9153
		0.9136	703		
3	0.8942	0.8944	732	4	0.8960
—	—	0.8881	800	2	0.8897
—	—	0.8886	336	2	0.8890
—	—	0.8728	811	1	0.8745
—	—	0.8647	217	2	0.8648
3	0.8621	0.8616	820	2	0.8633
5	0.8380 (Kα_1)	0.8377	516	6	0.8383
3	0.8349 (Kα_1)	0.8350	644	5	0.8362
		0.8346	653		

values are based on synthetic standards. The lanthanide oxides have been reduced to atomic percent metal and plotted on Figure 2. It can be seen that the specimen is strongly selective for the medium and heavy lanthanides with a maximum at dysprosium. The rare earth distribution conforms to the rule of Oddo and Harkins which states that any even-numbered element should be more abundant than its odd-numbered neighbours in the periodic system.

Wakefieldite specimens A and B contain considerable quartz and

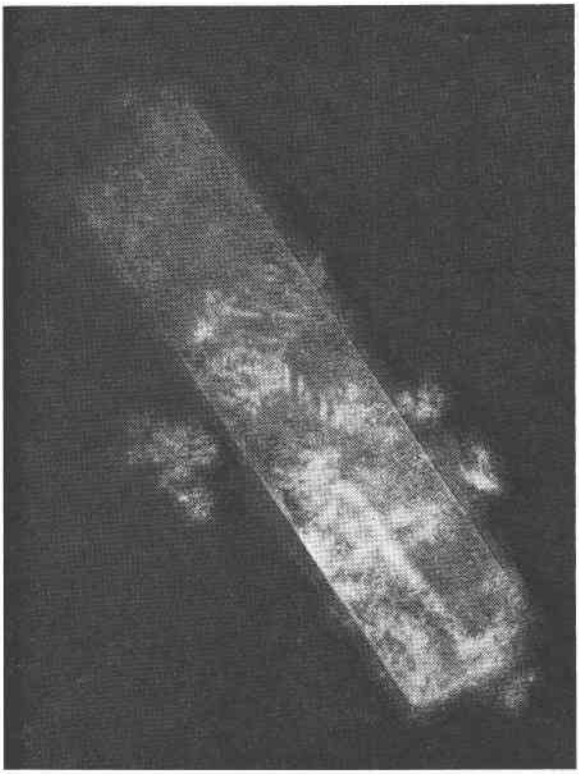

FIG. 2. Electron micrograph of a crystal of wakefieldite.
Length of crystal about 0.1μ.

hellandite as well as lesser amounts of cenosite and montmorillonite. This admixture accounts for the high percentage of Fe_2O_3, CaO, B_2O_3, BeO, SiO_2, and part of the yttrium and lanthanides. Vanadium does not enter into these minerals in large amounts and its presence must be essentially ascribed to wakefieldite. Judging by the vanadium content alone, YVO_4 would account for about 60 wt percent of the concentrate and 28 wt percent B and C. These figures may be little low for the wakefieldite component owing to substitution of Si for V. However, considering the small difference in cell volume between wakefieldite and synthetic YVO_4 (wakefieldite, $V = 317.5$ Å^3; YVO_4, data after Swanson *et al.*, 1967, $V = 318.8$ Å^3), one would not expect this substitution to be large.

One sample of thorogummite (EL-91), analysed by X-ray fluorescence contained 11 percent Y and 3 percent V suggesting thorite with about 10 weight percent solid solution of each of xenotime and wakefieldite. Other specimens showed X-ray diffraction line intensities midway between thorite and xenotime and cell sizes somewhat smaller than that of thorite. The extent of substitution among thorite, xenotime, coffinite, and wakefieldite is not known, but considering the ionic radii of the elements concerned ($Si_{IV}^{4+}=0.40$, $P_{IV}^{5+}=0.33$, $V_{IV}^{5+}=0.56$, $Th_{VIII}^{4+}=1.06$, $Y_{VIII}^{3+}=0.95$, $U_{VIII}^{4+}=1.01$ Å; values from Green, 1959), one might expect extensive substitution among thorite ($ThSiO_4$), xenotime (YPO_4), coffinite ($USiO_4$), and less substitution between these minerals and wakefieldite (YVO_4). The coupled substitution scheme, $Y^{3+}+(P^{5+}, V^{5+}) \rightleftharpoons (Th^{4+}, U^{4+})+Si^{4+}$, is inferred.

PROPERTIES OF WAKEFIELDITE

Wakefieldite from the original specimen was examined in some detail. The hardness, as determined by gritting a fine-grained but coherent mass on a glass slide, appeared to be approximately equal to that of apatite. Specific gravity could not be accurately determined on the small amount of sample but Schwarz (1963a) reports 4.21 for synthetic YVO_4, which is close to the value 4.25 calculated from their cell volume. Munsell color of the cleaned mineral is 10 YR 5.5/6 as compared with 10 YR 7/8 for synthetic YVO_4. The refractive indices were high but could not be resolved owing to submicroscopic grain size. Our synthetic YVO_4 is uniaxial positive, $\omega=2.00\pm0.01$, $\epsilon=2.14\pm0.01$; $2\omega+\epsilon/3=2.05$. The mean value agrees with the calculated mean refractive index of YVO_4 according to the rule of Gladstone and Dale with $d=4.25$ gm/cc, yielding $dk+1=2.05$. The ω value is identical with that reported by Popov *et al.*, (1968).

Crystallites were studied with a Siemens electron microscope set at 44,000× magnification. Some crystals showed prisms with pyramidal terminations, others appeared to have basal terminations (Figure 3), still others had a sawtooth habit. Because of similarities of these morphologies with those of zircon (see Milner, 1962, especially plate 44, figures 3A, 8A, 12A, 1C, 2C, 4C), they were assumed to belong to wakefieldite. The average particle size was 0.07 micron. There were also hexagons, possibly due to a few aggregated chlorite grains in formless masses of unknown identity. This work was carried out by Dr. I. L. Stevenson of the Canada Department of Agriculture.

Table 4 lists properties of wakefieldite and other minerals with the zircon structure. Although there are some differences in physical and optical properties among the various members coffinite, chernovite, xenotime, wakefieldite, and thorite, they are often too fine-grained for simple routine determination. However, wakefieldite is easily distinguished from the other species by X-ray examination: the cell constants

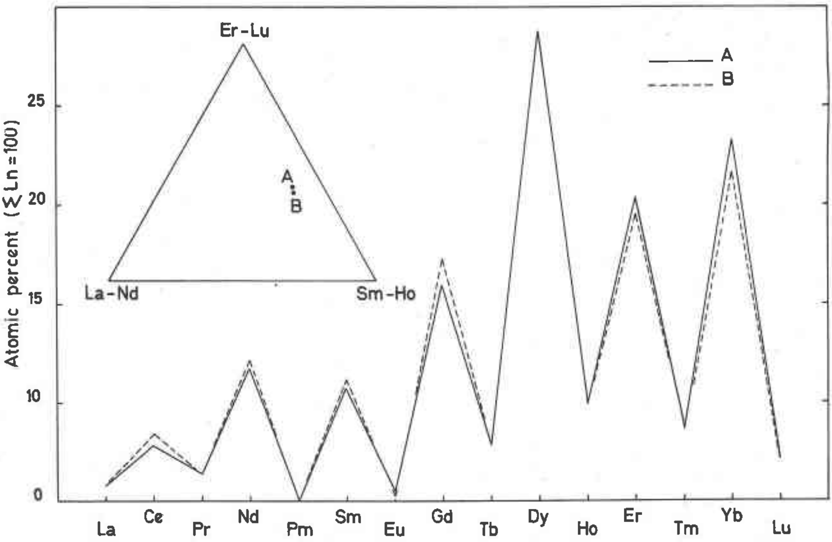

FIG. 3. Lanthanide composition of wakefieldite-rich rock.

of wakefieldite are larger than those of zircon, chernovite, and xenotime; from thorite and coffinite it is readily distinguished by diminished intensity of the low angle (101) reflection.

GENESIS

The presence of yttrium vanadate in the Evans-Lou pegmatite is difficult to explain. Yttrium becomes somewhat enriched towards the

TABLE 4. PROPERTIES OF MINERALS WITH THE ZIRCON STRUCTURE

	Zircon	Thorite	Coffinite	Chernovite	Xenotime	Wakefieldite
Formula	$ZrSiO_4$	$ThSiO_4$	$U(SiO_4)_{1-x}(OH)_x$	$YAsO_4$	YPO_4	YVO_4
a	6.60	7.142 (syn.)	6.99	7.053	6.904	7.105
c	5.88	6.327 (syn.)	6.26	6.285	6.033	6.29
$I_{101}:I_{200}$	0.45	0.83 (syn.)	0.97 (syn.)	~0	0.25	0.078 (syn.)
Hardness	7.5	4.5–5	5–6	4.2–4.7	4–5	~5
ρ	4.7	5.4	5.1	4.561 (syn.)	4.4–5.1	4.25 (calc., syn.)
ω	1.92–1.96	1.80	~1.74	1.783	1.721	2.00 (syn.)
ϵ	1.96–2.02	1.81		1.879	1.816	2.14 (syn.)
ϵ-ω	0.04–0.06	0.01	<0.01 (positive or negative optic sign)	0.096	0.095	0.14
Most common color in hand specimen	Pink, brown	Black, brown, yellow	Black	Colourless to pale yellow	Yellow, pink	Yellow

Data from A.S.T.M. cards, Hoekstra and Fuchs (1956), Fuchs and Gebert (1958), Moench (1962), and Goldin, Yushkin and Fishman (1967).

TABLE 5. SPECTROGRAPHIC ANALYSES OF TWO WAKEFIELDITE—RICH SAMPLES

	C	B	B, $\Sigma=100.0$
La_2O_3	0.09	0.09	0.1
CeO_2	0.38	0.45	0.5
Pr_2O_3	0.18[a]	0.18[a]	0.2
Nd_2O_3	0.85	0.9	0.9
Sm_2O_2	0.75	0.8	0.8
Eu_2O_3	0.07	0.06	0.1
Gd_2O_3	1.5	1.7	1.8
Tb_2O_3	0.4	0.4	0.4
Dy_2O_3	3.3	3.3	3.5
Ho_2O_3	0.7	0.7	0.7
Er_2O_3	2.2	2.1	2.2
Tm_2O_3	0.5	0.5	0.5
Yb_2O_3	2.7	2.5	2.6
Lu_2O_3	0.32	0.34	0.4
ThO_2	0.6	1.0	1.1
Sc_2O_3	0.02	0.025	
V_2O_5	12	12.0[b]	12.6
Y_2O_3		20.0	21.1
Fe_2O_3	8	5.6	5.9
CaO	2.5	3.8	4.0
MgO		0.7	0.7
SiO_2		21.0	22.1
CuO		0.3	0.3
TiO_2		0.4	0.4
BeO		0.8	0.9
ZrO_2		< 0.1	
B_2O_3		2.6	2.7
Al_2O_3	0.3	0.4	0.4
U_3O_8		2.5	2.6
P_2O_5		Tr.	
L.O.I. at 850°C		10.0	10.5
Total	37	95.1	100.0

[a] Pr_2O_3 determined by X-ray fluorescence analysis. Analyst: D. S. Russell.

[b] V_2O_5 later checked giving by atomic absorption 11.1 and 10.6, and colorimetric methods 10.97.

terminal stages of magmatic differentiation. Turekian and Wedepohl (1961) show that ultrabasic rocks contain less than 1 ppm Y compared with 21 ppm Y in basalts and 40 ppm Y in granites. Some granite pegmatities, such as the Evans-Lou pegmatite, are characterized by primary yttrium minerals and presumably contain much more yttrium than 40 ppm. On the other hand vanadium becomes enriched in the midstages of magmatic differentiation. Turekian and Wedepohl (1961) give 40 ppm V for ultrabasic rocks, 250 ppm V for basalts, and 44 ppm V for granites. Most of the vanadium is incorporated in magnetite (Rankama and Sahama, 1950, p. 594–597). Primary vanadium minerals do not seem to have been recognized from pegmatites although vanadium-bearing sphene (0.3 percent V) has been noted by Rose (1967, p. 14) in a pegmatite 50 miles west of the Evans-Lou mine. Pucherite ($BiVO_4$), apparently a secondary mineral, has been noted from pegmatities in Madagascar, Brazil and California (Palache *et al.*, 1951, p. 1051), but the primary vanadium mineral is not known.

At the Evans-Lou mine, it is possible that vanadium and yttrium were directly introduced and precipitated from late hydrothermal solutions connected with the pegmatite-forming process. However, the close association of wakefieldite, with coarse-grained yttrium minerals, such as fergusonite and hellandite, cannot be overlooked, and for this reason it is believed that wakefieldite might possibly be a secondary product derived from a primary vanadium-bearing yttrium mineral. Other possible sources of yttrium were also investigated (Table 6).

Besides wakefieldite, minerals with essential vanadium have not been found either in the Evans-Lou pegmatite or in the calc-silicate rock nearby. Vanadium contents of some minerals and rocks are presented in Table 6. The data are derived from X-ray fluorescence analyses of ground specimens using synthetic YVO_4 as an external standard and must be regarded as semiquantitative. Of the primary minerals at the Evans-Lou mine, hellandite alone appears to be a possible source of the vanadium in thorogummite and wakefieldite. In one specimen, hellandite gave 0.1 percent V; another specimen, analysed by optical spectrography, was estimated to contain vanadium in the range 0.1–0.5 percent (W. H. Champ, Geological Survey of Canada, personal communication). In this regard, it is interesting to note that a new spectrographic analysis of hellandite, from the Kalsbad-Lindvikskollen pegmatite in Norway, one of the two known occurrences of the mineral, showed "rather unusual concentrations of V, probably several thousand ppm" (Oftedal, 1964). At the Evans-Lou mine, hellandite is locally abundant, and in three specimens it is in direct contact with wakefieldite.

It is possible that vanadium may have been incorporated in such minerals as biotite, sphene, fergusonite, or allanite and later separated by solution. Although tests on these minerals failed to reveal any vanadium, it may be significant that they are all somewhat altered and the bulk of the element may have been leached out long ago.

The presence of wakefieldite, an orthovanadate, suggests precipitation from an alkaline solution. The orthovanadate is stable only at a pH

Table 6. Yttrium and Vanadium Contents[a] of Various Minerals and Rocks at the Evans-Lou Pegmatite

Mineral	Specimen Number	Occurrence	% Y[b]	% V[b]
Actinolite with some diopside	EL-14	Calc-silicate rock from about 50 feet west of the north end of the quarry.	<1	n.d.[c]
Allanite with included uranothorite	EL-45	Somewhat weathered allanite from the north end of the quarry in the giant perthite—quartz zone.	2	n.d.
Allanite with minor quartz	EL-1	North end pit in giant perthite-quartz zone.	1	n.d.
Andradite with minor quartz	EL-191	Black garnet. From dump.	<1	n.d.
Biotite and chlorite	EL-5	Mica occurring with allanite in giant perthite quartz zone. North end quarry.	n.d.	n.d.
Bismutite	EL-212	Alteration of native bismuth. From quartz fragment on dump.	n.d.	n.d.
Chlorite	EL-180	From rehealed breccia. Rough separation from hellandite, cenosite, and "tengerite". From dump.	2	n.d.
Chlorite and biotite	EL-46	From giant perthite-quartz zone, east side of quarry. Leaves of mica roughly separated from spessartite and microcline.	1	n.d.
Diopside. Minor phlogopite and brown hornblende	EL-3	Outcrop of calc-silicate rock about 70 feet west of pegmatite.	n.d.	n.d.
Fergusonite	EL-204	Fresh fergusonite. From rehealed brecciated quartz on dump.	22	n.d.
Fergusonite with minor thorogummite	EL-201	Somewhat weathered fergusonite from vuggy quartz on dump.	22	n.d.
Fluorapatite	EL-8	Two-inch crystal from quartz zone.	1	n.d.
Hellandite	EL-109	Yellow. Contains a little "tengerite". From quartz on dump.	26	<0.1
Hellandite	EL-60	Fresh black. Contains a little cenosite. From dump.	28	0.1
Montmorillonite	EL-7	From near fergusonite and wakefieldite in giant perthite —quartz zone. North end quarry.	1.5	0.1
Phlogopite	EL-3	Separation from calc-silicate rock. From 70 feet west of quarry.	n.d.	n.d.
Spessartite	EL-178	Black garnet. Separation from rehealed quartz on dump.	5.5	n.d.
Sphene	EL-36	Fragment from 1-foot crystal of Y-Nb-Sn sphene. From dump.	5.5	n.d.
Thorogummite	EL-91	White pulverulent from cavity in quartz. From dump.	11	3

[a] X-ray fluorescence analysis by B. C. Stone, Department of Agriculture of Canada.

[b] Approximate lower limit of detection 0.01% Y, 0.05% V.

[c] n.d. signifies not detected.

greater than 12.6, concentration of solution 0.112 mole/l (Evans and Garrels, 1958), but the natural environment ordinarily does not have a pH greater than 9.4 (Baas Becking *et al.*, 1960). Precipitation from an alkaline thermal solution is a more probable mode of origin. It should be noted that the boundary of precipitation of VO_4 compounds "moves to lower pH values with rising temperature" and normally in the vanadium-oxygen system "changes are in the order of 0.01 to 0.02 pH units/°C" (Evans and Garrels, 1958, p. 142). The extremely fine-grained nature of wakefieldite and its close association with montmorillonite suggest that the temperature of formation did not exceed a few hundred degrees centigrade. The vuggy and fractured nature of the quartz would provide an easy access for solutions.

Cenosite and tengerite are not inconsistent with a high pH environment. Rare earth carbonates dissolve with difficulty in pure water. However, when carbonates of sodium and potassium are present, double carbonates of the alkali metals and rare earths are formed and solubility increases markedly with rising pH (Shvey, 1962). This is an effective means of transfer and precipitation may result simply by lowering the pH.

ACKNOWLEDGEMENTS

The writers would like to thank B. Stone, of the Department of Agriculture, for X-ray fluorescent analyses and J. M. Stewart of the Mines Branch for indexing the powder pattern of wakefieldite.

We are grateful to Miss A. P. Sabina, of the Geological Survey of Canada, for drawing our attention to this quarry as a location of rare minerals. Azurite and native bismuth were identified by Miss Sabina but were not found by the writers. X-ray standards of zavaritskite and hellandite were provided by H. R. Steacy of the Geological Survey of Canada. We would also like to thank Mr. Leo MacDonnell, of International Minerals and Chemical Corporation (Canada) Ltd., for granting permission to visit the property and collect specimens.

The manuscript was read by D. C. Harris of the Mines Branch and D. S. Cronan and R. Kretz of the University of Ottawa. The authors gratefully acknowledge their helpful criticism.

Expenses were partly defrayed by a grant of the Geological Survey of Canada awarded to one of us (D.D.H.).

REFERENCES

BAAS BECKING, L. G. M., I. R. KAPLAN, AND D. MOORE (1960) Limits of the natural environment in terms of pH and oxidation-reduction potentials. *J. Geol.* **68,** 243–284.

EVANS, H. T., AND R. M. GARRELS (1958) Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits. *Geochim. Cosmochim. Acta,* **15,** 131–149.

FUCHS, L. H., AND GEBERT (1958) X-ray studies of synthetic coffinite, thorite and uranothorite. *Amer. Mineral.* **43,** 243–248.

GOLDIN, B. A., N. P. YUSHKIN, AND M. V. FISHMAN (1967) A new yttrium mineral, chernovite. *Zap. Vses. Mineral. Obshch.* **96,** 699–704. [in Russian, abstr. *Amer. Mineral.* (1968) **53,** 1777].

GREEN, J. (1959) Geochemical table of the elements for 1959. *Geol. Soc. Amer. Bull.* **70,** 1127–1184.

GRIM, R. E. (1968) *Clay Mineralogy, 3rd Ed.* McGraw-Hill Book Co., New York.

HOEKSTRA, H. R., AND L. H. FUCHS (1956) Synthesis of coffinite-$USiO_4$. *Science,* **123,** 105.

MILLIGAN, W. O., L. M. WATT, AND H. H. RACHFORD, JR. (1948) X-ray diffraction studies on heavy metal orthovanadates. *J. Phys. Coll. Chem.* **53,** 227–234.

MILNER, H. B., A. M. WARD, AND F. HIGHAM (1962) *Sedimentary Petrography. Vol. 2: Principles and Applications, 4th Ed.* George Allen and Unwin Ltd., London.

MOENCH, R. H. (1962) Properties and paragenesis of coffinite from the Woodrow Mine, New Mexico. *Amer. Mineral.* **47,** 26–33.

OFTEDAL, I. (1964) Contributions to the mineralogy of Norway, No. 24 On the chemical composition of hellandite. *Norsk. Geol. Tidsskr.* **44,** 35–37.

PALACHE, C., H. BERMAN, AND C. FRONDEL (1951) *The System of Mineralogy of . . . Dana, 2, 7th Ed.* John Wiley and Sons, New York.

POPOV, V. I., KH. S. BAGDASAROV, I. N. GUSEVA, AND M. V. MOKHOSOEV (1968) Crystallization of yttrium orthovanadate by the Verneuil method. *Kristallografiya* **13,** 1109–1110. [in Russian. transl., *Sov. Physics, Crystallogr.* **13,** 974–975 (1968)].

RANKAMA, K., AND TH. G. SAHAMA (1950) *Geochemistry.* University of Chicago Press, Chicago.

ROSE, E. R. (1967) Vanadium occurrences in Canada. *Geol. Surv. Canada, Pap.* **66–57.**

SCHWARZ, H. (1963a) Über die Chromat(V) der Seltenen Erden. IV. Yttriumchromat (V) $YCrO_4$. *Z. Anorg. Allgem. Chem.* **322,** 137–144.

——— (1963b) Die Phosphate, Arsenate und Vanadate der Seltenen Erden. *Z. Anorg. Allgem. Chem.* **323,** 44–45.

SHVEY, I. V. (1962) Main problems of the geochemistry of rare earth elements and yttrium in endogenous processes. *Geol. Mestorozhd. Redk. Elem. 15* [in Russian, transl. Geol. Surv. Can.].

STIEFF, L. R., T. W. STERN, AND A. M. SHERWOOD (1956) Coffinite a uranous silicate with hydroxyl substitution: A new mineral. *Amer. Mineral.* **41,** 675–688.

SWANSON, H. E., H. F. MCMURDIE, M. C. MORRIS, AND E. EVANS (1967) Yttrium vanadate, YVO_4 (tetragonal). *Nat. Bur. Stand.* [*U.S.*] *Monogr.* **25,** Sec. 5, 59.

TUREKIAN, K. K., AND K. H. WEDEPOHL (1961) Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Amer. Bull.* **72,** 175–191.

VORMA, A., P. OJANPERA, V. HOFFRÉN, J. SIIVOLA, AND A. LOFGREN (1966) On the rare earth minerals from the Pyörönmaa pegmatite in Kangasala, S.W.-Finland. *Bull. Comm. Géol. Finlande,* **222,** 241–274.

WILSON, M. E. (1920) The Buckingham sheet. *Geol. Surv. Canada Pub.* **1691.**

Manuscript received, June 11, 1970; accepted for publication, November 23, 1970.